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Organometallic molecular wires and other nanoscale-sized devices. An approach using the organoiron (dppe)Cp*Fe building block

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Abstract

In this paper, the potential that organometallic architectures consisting of two transition metal centers linked by an organic unsaturated spacer present for the study and development of new molecular wires is discussed. After a bibliographical survey of representative existing molecules, emphasis is set on the decisive role of the terminal organometallic capping groups. In this connection, the very rich redox chemistry of the (dppe)Cp*Fe unit in mononuclear complexes is subsequently developed. Finally, the syntheses and studies of diverse organometallic molecular wire models realized in our group and incorporating this fragment are presented and conclusions on the present state of the art are drawn. A review with 352 references.

Keywords: Organoiron; Molecular wires; Mixed valence; Nanoscopic devices; Polynuclear complexes; Electron transfer

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Abbreviations

Ar	aromatic group
bipy	2,2-bipyridine
COD	1,4-cyclooctadiene
Cp	cyclopentadienyl
Cp′	methyl-cyclopentadienyl
Cp*	pentamethyl-cyclopentadienyl
$Cp^{\#}$	pentaphenyl-cyclopentadienyl
CV	cyclic voltammetry
Cy	cyclohexyl
DBU	1,8-diazabicyclo-[5.4.0]-undec-7-ene
DCV	derivate cyclic voltammetry

DFC	density functional calculation(s)
dmg_2	1,2-dimethyl-glyoximate dimer
dppe	1,2-bis(diphenylphosphino)ethane
dppf	bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dpyp	2,5-bis(*ortho*-pyridyl)-1,4-phenylene
e	electron(s)
Fc	ferrocenyl
ICT	intervalence charge transfer
Kc	comproportionation constant (for symmetrical MV only)
MV	mixed-valence
OTf	trifluoromethyl sulfonate
o-Py	*ortho*-pyridyl
Py	pyridine
SCE	saturated calomel electrode
Tp′	hydridotris(3,5-dimethylpyrazolyl)borate
terpy	2,2′,5′,5″-terpyridine
tterpy	4′-*para*-tolyl-2,2′,5′,5″-terpyridine
Vab	electronic coupling parameter

1. Introduction

There is actually a great interest regarding the miniaturization of various electronic components. The current industrial approach driven by productivity requirements is to develop new materials with great processability and to scale down the electronic circuitry using new technologies like nanolithography. However, with the ultimate limit ever reachable for reduction being the molecular level, many research teams in the world have tackled the problem from the other side and attempted to build “wires” or other nanoscopic devices starting from molecular building blocks. For now, molecular electronics have had only a marginal industrial appeal, but the field of “molecular wires” certainly constitutes the cradle of big innovations in the future [1–4].

Even if very promising, the molecular approach also has its uncertainties. First, it constitutes a tremendous synthetic challenge to build molecular wires of increasing length, controlling the shape of the molecules at each stage of their synthesis and the chemical purity of the final material. Moreover, one should not forget that the synthesis of those molecules usually has to be optimized in order to facilitate their realization at an increased scale for study purposes. Then, once synthesized and characterized, the wire has to be connected or “addressed” in order to be evaluated, or even used when desired [5,6]. Here appears the fundamental question of the conduction properties of such connectors: will we observe similar physical laws to bulk conductors, or will they exhibit peculiarities related to their molecular nature? This question is still unanswered and, currently, experimental or theoretical studies allowing one to shed light on this point are strongly needed [7]. For now, the few studies reported are nevertheless quite encouraging [3,4,8,9].

Our present contribution in this field is related to the synthesis and study of organometallic molecular wires based on the organoiron synthon “(dppe)Cp*Fe” (dppe = 1,2-bis(diphenylphosphino)ethane; Cp* = pentamethyl-cyclopentadienyl) developed in our team. When we became involved in molecular electronics, we soon realized that such a fragment would allow the synthesis of very interesting model compounds of molecular wires. Thus, in parallel with the development of adapted synthetic protocols leading to the target molecules, we studied electron delocalization capabilities of these molecular wire models. Before describing our results in this review, we first recall some basic facts about molecular wires and emphasize the interest of organometallic molecules in this respect (Section 2). We then introduce the properties of the (dppe)Cp*Fe fragment in mononuclear complexes and its interest as a capping group for the realization of molecular wire models in Section 3. Finally, in Section 4 we describe the synthesis and the study of the various organoiron wire models realized in our group, before concluding on the potential that this fascinating organoiron fragment presents for molecular device elaboration (Section 5).

2. Organometallic σ-metallated molecular wires

2.1. General notions

From its definition, a molecular wire is a "one dimensional molecule allowing a through-bridge exchange of an electron/hole between its remote ends/terminal groups, themselves able to exchange electrons with the outside world" (see Scheme 1) [6]. Thus, such a compound must possess two redox-active termini. Also implied in this definition is the fact that the compound has to have a known and finite structure, emphasizing the importance of synthetic protocols allowing isolation of discrete molecules in a chemically pure state for such purposes.

Following the early report of Aviram and Ratner in 1974, stating that some organic molecules might be used as unidirectional molecular wires or molecular rectifiers [10], much effort has been devoted to the realization of such molecular devices. Thus, long molecules constituted by various unsaturated organic units and featuring a conjugated π-electron network spreading all over the molecule were realized. Such purely organic molecules were usually sufficiently soluble and stable to allow chromatographic purification and many molecules of impressive size were isolated. Organic chemistry was versatile enough, using protection–deprotection sequences, to allow selective and high yield activation of one or both ends of the molecule. As a consequence, high yield stepwise linear syntheses could be devised starting from a simple set of building blocks [11]. Thus, by the use of such recurrent approaches, discrete molecules up to 128 Å in length could be isolated [12]. Organic molecular wires were usually very diversified in shape owing to the large number of organic unsaturated elementary units available and presented either a flexible or a rigid core. An extensive overview of the synthetic achievements in this field can be obtained from a recent review [13].

Quite recently, organometallic chemists incorporated metal centers in similar compounds.[1] A priori, such organometallic metal-containing conductors were very appealing, owing to the possibility of fine-tuning the electronic properties of the wire, by variation of the ancillary ligands present on the metal centers or by change in their oxidation state. On the whole, the syntheses of those metal-containing molecules were much more diverse and exploited the peculiar reactivities of the metal centers incorporated in them. Nevertheless, synthetic problems, such as decreased stability of the compounds when labile metal complexes were present, often impeded their isolation in a pure state and precluded a rapid development of organometallic molecular wires. Accordingly, to date, the maximal lengths of discrete one-dimensional organometallic molecules able to transfer electrons from one end to the other are much smaller than the lengths of their purely organic homologues [2,14–16].[2]

We would like to point out here that, among all those realizations, actually very few of these potential molecular wires were experimentally tested and evaluated for their electron conduction capability. Many of those molecules were in fact often realized by analogy with other already existing compounds bearing conjugated unsaturated units, the ability of which to convey electrons was inferred from theoretical studies. It is important to realize that, for discrete compounds, only a few of them can be considered as molecular wires *based on experimental evidence.*

2.1.1. Evaluation of molecular wires

Before being considered as a molecular wire a given compound should have a proven ability to convey electrons. However, experimental evaluation of the electron conduction capability is not always a simple task and, to our knowledge, only three means have been devised so far.

(1) One possibility consists in direct measurement of the bulk conductivity of the material, either from amorphous solid, or better from a crystal. This approach is often used for polymers [18–20] and gives only statistical information about the molecular conductivity, since it is strongly dependent on the solid-state structure of the material [7,21].

(2) Then, in order to get information on the discrete species, with chemically pure and sufficiently soluble products, a convenient way is to look at the electronic interaction between the redox-active termini using electrochemistry (cyclic voltammetry (CV)). Moreover, when odd-electron states are stable, near-infrared (NIR) spectrometry and electroabsorption spectroscopy (Stark effect) can also bring deci-

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[1] Certain typical inorganic systems were known for a long time to constitute “molecular wires” as well. See type *I* compounds (Section 2.2) for leading references.

[2] Access to organic, organometallic or inorganic molecular wires can also be achieved using various polymerization reactions; however, the compounds isolated in this way are usually a mixture of different oligomers differing in length and very difficult to separate. Even if those molecular wires are often much longer than those isolated after stepwise syntheses, we will not consider this type of realization in the following discussion since only limited information about the properties of the single molecular components present is available from their study [17,18].

sive information (see Section 2.1.2) [22].[3] Alternatively, with photoswitchable redox groups, as in the case of "photonic" molecular wires, time-resolved UV–visible absorption, emission spectrometry and fluorimetry permits the study of electron transfer [23–26]. Additionally, when different (electron-donor and electron-acceptor) capping groups are present, a polarized wire or "rectifier" is obtained [6] and O.N.L. measurements might also bring some qualitative information on electronic delocalization within the wire. In this case, care has to be exercised when considering these data, since factors other than delocalization also come into play here [27].

(3) Finally, the direct measurement of the conductivity of a single molecule probably constitutes the optimal way of investigating this property with a discrete compound. Although not trivial, this might be achieved with molecules possessing sufficient length (around 10 nm for now) using the same types of instrument as those used for macroscopic connectors (voltmeter, amperometer and galvanometer) by positioning it across a nanojunction [7,9,28,29]. Until now, such a connection has been studied mainly on theoretical grounds. Electron conduction is believed to be highly dependent on the HOMO–LUMO gap of the molecule and should exhibit low distance dependence [30–32]. To our knowledge, such an innovative investigation was only seldom performed experimentally on real discrete molecules, well defined in size and shape [1,33,34].[4] Among these, the sole attempt involving a single one-dimensional rigid molecule gave rather inconclusive results regarding its conductivity [37].[5] Apart the theoretical problem of interpreting the data, there is also the delicate problem of properly interfacing molecule ends with macroscopic conductors, which raises here the choice of appropriate wire termini [3,4,9]. Nevertheless, such measurements are becoming increasingly feasible from a technological point of view and their routine realization will certainly constitute a major achievement in the field of molecular wires [6].

We do not intend to discuss further the problem of addressing the wire here, but one has to realize that for eventual applications concerned with incorporation of a molecular wire in macroscopic devices, both ends of the wire will have to be efficiently connected to a macroscopic interface. Thus, it should be kept in the mind of current investigators that any molecule realized for such applications will have to present adapted end-groups allowing efficient electron exchange between the wire termini and the different poles of the macroscopic junction. Interfacing will occur after coordination/adsorption on a surface or, alternatively, by incorporation in a membrane. Indeed, Lehn and coworkers have demonstrated that electrons could efficiently be transmitted by molecular wires through micellar membranes in liquid media [40].

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[3] As pointed out by one referee, for compounds presenting very long bridges the observation of the ICT band may sometimes prove to be difficult owing to its possible weakening with lengthening of the conduction path (especially with class-II MV complexes). Additionally, with extension of the bridge core, the stability of the mono-oxidized state may decrease as well for most of the compounds presenting highly delocalized electrons.

[4] For other recent representative examples of measurements effected on a single molecule see also Refs. [35,36].

[5] Related recent studies have been conducted on carbon nanotubes as well, although those molecule lie outside the scope of this review. See Refs. [38,39] and references cited therein.

Thus, a molecular wire presenting an adapted molecular topology for aggregation in membranes might equally constitute an interesting molecule for macroscopic interfacing.

2.1.2. *Wires with redox-active termini*

Redox molecular wires with simple electroactive termini present a simplified conduction mechanism compared with the photonic wires (see Fig. 1). When termini possessing different redox states are present at both ends of the spacer, an odd electron-containing species or mixed-valence (MV) compound can be generated electrochemically and a wealth of information about through-bridge electron transfer can be gained by the study of such a species [41,42]. Although purely organic mixed valence compounds are known now [43], most often the MV compounds are dinuclear transition metal complexes. Such compounds were initially characterized experimentally by Creutz and Taube in 1969 [44]. They present a weak intervalence charge transfer (ICT) band characteristic of the optically induced intramolecular electron transfer in the NIR spectral domain which is absent in the spectra of the reduced and oxidized states [45]. Even with certain photonic wires, such an ICT transition could be observed in the transient photoexcited triplet state [26]. Depending on the delocalization of the unpaired electron over both capping redox sites, a classification has been proposed by Robin and Day [46].[6] An MV compound belongs to class-I if the valence is totally localized i.e. no through-bridge electron exchange between metal centers occurs and no ICT band can be observed. It belongs to class-III if the electron is fully delocalized, i.e. no available spectroscopy is able to discriminate the metal centers (for such compounds $\Delta E > 200$ mV usually). In

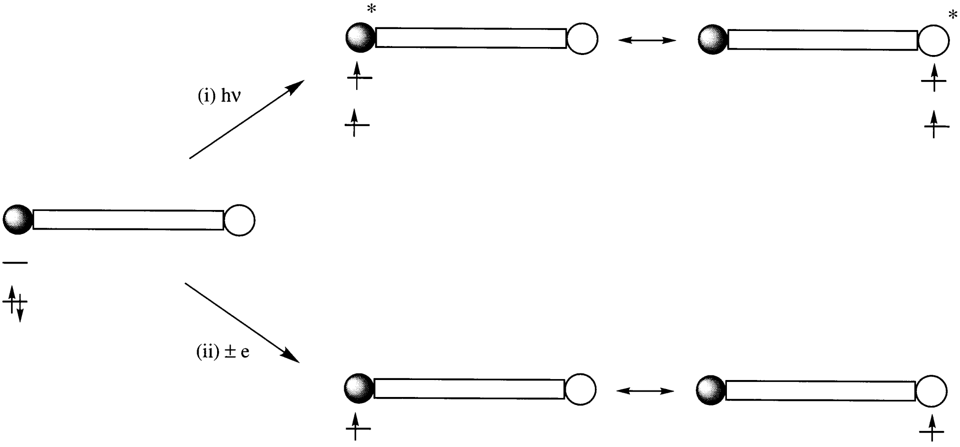

Fig. 1. Schematic representation of electron conduction in a photonic (i) and a redox (ii) molecular wire.

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[6] For weakly coupled systems, this thermal electron transfer is distinct from electron tunneling between the metallic termini (nuclear tunneling). The latter is a process which can become preponderant at very low temperatures, but is not expected to compete significantly at the usual temperatures where the thermal electron transfer occurs, see Refs. [45,47].

this case the ICT band is solvent independent and shows no solvatochromism. Finally, it belongs to class-II in other cases, i.e. at least one spectroscopy is able to distinguish one site from the other while an ICT band is present. In this case, the energy of ICT absorption is often solvent dependent.

CV with the most stable redox state usually constitutes the easiest way to look at the electronic interaction between the remote electroactive termini. With symmetrical compounds, in the case of a sufficiently strong interaction, two 1-e^- events should be observed. The potential difference ΔE between the two waves is representative of the thermodynamic stability of the corresponding MV state relative to the other redox states and its comproportionation constant K_c can be computed using Eq. (1). Alternatively, when there is no, or negligible, communication, only a single redox event is observed. In such cases, whenever possible, K_c has to be determined by other means, such as spectrometric titration [48,49].

$$\begin{gathered}\text{Ox–Ox} + \text{Red–Red} \overset{K_c}{\rightleftarrows} 2\text{Ox–Red} \\ -(RT/F)\log(K_c) = \varDelta E^0\end{gathered} \tag{1}$$

The potential difference ΔE^0 is often invoked as a measure of electronic interaction through a given organic bridge for symmetrical compounds [50]. As stated before, this quantity is in fact related to the thermodynamic stability of the MV for which other energetic terms than the one related to electronic interaction come into play. For instance, through-space electrostatic interaction [49,51], solvation or entropy [52] or more specific factors, like increased π-acidity in the MV state, steric interactions in the other redox states and structural distortion upon oxidation, influence its magnitude [53]. Therefore, this assumption is not always valid, and careful attention should be given regarding ΔE^0 significance for each case, especially for weakly delocalized ionic systems in polar solvents.

In non-symmetrically substituted compounds, CV can also be used to evaluate the amount of electronic interaction between metal centers. In this case, the metal centers being already differentiated in the parent complex, two separate redox processes are expected. In order to evaluate the through-bridge electronic interaction, comparison has to be made between those and the redox potentials measured in model compounds containing each metal center with comparable geometric and electronic environments [52]. Of course, no K_c value can be obtained by this means.

Moreover, for all complexes, the reversibility of the CV waves at a moderate scan rate constitutes a good indicator of the stability of the corresponding redox states. In the case of non-reversible oxidation waves, attention should be paid to the origin of each redox event, in order not to misinterpret signals due to fast consecutive chemical reactions or to subsequent electron transfer which would impede the observation of a second wave. In this respect derivate CV (DCV) is a particularly interesting complementary technique [54].

When the MV species are stable enough to be studied, spectroscopic investigations often allow the determination of the class of the various MV compounds. Indeed, averaging or differentiation of the two termini occurs depending on the acquisition time relative to the rate of electron transfer associated with a given spectrometry.

Additionally, solvent dependence of the ICT absorption following Eq. (2c) can establish its belonging to weakly coupled class-II compounds as well. This brings us now to the second and more definitive method of evaluating electronic delocalization in MV compounds, which is the experimental measure of V_{ab}, the electronic coupling parameter of the MV complex. The V_{ab} value depends on the overlap between the electronic wave function of the donor and the acceptor groups in the transition state [5,24,41]. V_{ab} is a very informative parameter on charge delocalization in the molecule which allows comparison between similar sets of compounds to be made. From the spectral characteristics of the ICT absorption, the calculation of V_{ab}/cm^{-1} can be performed depending on the class of the mixed valence compound in the classification of Robin and Day [46].

For class-II complexes presenting little delocalization between the metal centers, Eqs. (2a), (2b) and (2c) based on Hush theory can be used. Eq. (2a) is general, whereas Eqs. (2b) and (2c) are specific to symmetric compounds [24]. Eq. (2b) allows prediction of the experimental bandwidth $(\Delta\nu_{1/2})_{\mathrm{theo}}$ and Eq. (2c) relates the energy of the ICT to solvent parameters $(1/\epsilon_{\mathrm{op}}-1/\epsilon)$ [45].[7]

$$V_{ab}=2.05\times10^{-2}(\varepsilon_{\max}\bar{\nu}_{\max}\Delta\bar{\nu}_{1/2})^{1/2}/R_{\mathrm{MM}'} \tag{2a}$$

$$(\Delta\nu_{1/2})_{\mathrm{theo}}=(2310\bar{\nu}_{\max})^{1/2} \tag{2b}$$

$$\nu_{\max}(\mathrm{solvent})=1/\hbar[\lambda_{\mathrm{i}}+(e^2/2r)(1/\varepsilon_{\mathrm{op}}-1/\varepsilon)] \tag{2c}$$

where ε is the molar extinction coefficient, $\nu_{\max}/\mathrm{cm}^{-1}$ is the ICT band maximum, $\Delta\nu_{1/2}/\mathrm{cm}^{-1}$ is the half-height width of the ICT band, $R_{\mathrm{MM}'}/\mathrm{\AA}$ is the through-space intermetallic distance, e/eV is the electron charge, is Planck's constant, λ_{i} is the inner-sphere reorganization energy, ε is the solvent dielectric constant and $\varepsilon_{\mathrm{op}}$ is the squared solvent refractive index.

For class-II complexes, an α coefficient can often be found in the literature as well. This coefficient is related to the degree of mixing between the two limiting localized initial ($\Psi(\mathrm{M}^+\mathrm{M}')$) and final ($\Psi(\mathrm{MM}'^+)$) electronic states (see Eq. (2d)) and is indicative of the degree of mixing between the donor and acceptor orbitals of the metal termini through the bridge. This parameter was originally defined by Robin and Day to classify the MV complexes [46,58].[8] Subsequently, for weakly coupled class-II complexes, its expression was related to the ICT optical energy by Hush (see Eq. (2e)) and can be related to V_{ab} as well under the same assumptions

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[7] Hush theory relates the energy for the optical electron transfer to the activation energy for the thermal electron transfer. The assumptions made are twofold: (i) the temperature is high enough for $kT \gg h\nu$; (ii) the ITC absorption band has a Gaussian shape. This theory does not consider the coupling between electronic and vibronic energetic states; however, it constitutes a sufficiently sophisticated model for general needs. A more complete mathematical model for intramolecular electronic transfer was developed by Schatz and coworkers. For a detailed description cf. Refs. [55,56]. Moreover, when Hush assumptions are fulfilled, for any V_{ab} parameter experimentally measured, the electron transfer occurs from an excited state. In some unusual cases when the excited state geometry changes much, the V_{ab} parameter calculated using Hush theory is different from the actual V_{ab} corresponding to the thermal electron transfer in the fundamental state [57]. We also did not consider this possibility in the following.

[8] For class-I complexes, $\alpha=0$, for class-III complexes $\alpha>0.25$ and for class-II $0<\alpha<0.25$.

(Eq. (2f)) [22,24,45,58,59]. For non-symmetrically substituted complexes, α was also obtained by the measurement of the redox potentials in a family of analogous complexes differing in one of the end-groups [60]. The applicability of such an approach remains, however, a matter of debate [61].

$$\Upsilon_{\text{Ground State}} = (1-\alpha^2)^{-1/2}[\Psi(\mathrm{M}^+\mathrm{M}') + \alpha\Psi(\mathrm{MM}'^+)] \tag{2d}$$

$$\alpha^2 = 4.5\times10^{-4}\varepsilon_{\max}\Delta\bar{\nu}_{1/2}(\nu_{\max}R^2_{\mathrm{MM}'})^{-1} \tag{2e}$$

$$\alpha^2 = (V_{\mathrm{ab}}/E_{\mathrm{op}})^2 \tag{2f}$$

For class-III compounds, where electronic delocalization is optimal [62–65], Eq. (3) based on a simple potential energy diagram of the system [58] can be used to approximate V_{ab} with symmetrical compounds [59]. Among the few values of V_{ab} reported to date for class-III MV compounds, some were purposely calculated using the inappropriate Eq. (2a) [22,58,66], and this mainly for comparison sake with existing data for class-II complexes [67]. In fact, here we are reaching the limit of the V_{ab} model which makes use of only two wave functions centered on the donor and on the acceptor for describing the electron transfer. Indeed, in the ideal case of a class-III complex, the electron is delocalized in one molecular orbital (MO) that spreads over the whole molecule and such a situation may be described more accurately by the use of a more complete set of atomic orbitals. In this case the observed "ICT" does not involve directional charge transfer (unless the molecule is non-symmetrical) but corresponds to a low-energy molecular transition between delocalized levels [68].

$$V_{ab} = \bar{\nu}_{\max}/2 \tag{3}$$

When the geometry of the compounds is known, V_{ab} can also be computed from an *ab initio* or semi-empirical MO analysis of the MV state using various approaches. A complete overview of the various methods allowing the computation of V_{ab} from MO considerations was given by Launay and coworkers [32].

As expected, V_{ab} decays with increasing distance of the organic spacer length. For simple homogeneous bridges, this trend follows an exponential empirical law given in Eq. (4a) [22,69].[9] The constant term γ is dependent on the chemical nature of the bridge units and $R_{\mathrm{MM}'}$ is the distance between the two metal centers expressed in ångströms (see Table 1) [32]. This law is reminiscent of the more popular formula giving the exponential decay of the electron transfer rate in function of the length of the spacer (Eq. (4b)). Eq. (4a) can be related to Eq. (4b) by the assumption that the rate constant for electron transfer is proportional to the square of V_{ab}.[10] The

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[9] An inverse order law relative to intermolecular distance has also been proposed, but seems to be less subtantiated by experiment, at least with unsaturated bridges in type *III*-3 complexes [47].

[10] Using this equation, Ziessel and coworkers have established the attenuation factor for the rates of electron/hole transfer with increasing length in photonic wires; however, the mechanism of charge transport is different [73,75,76]. Indeed, in photonic wires the electron travels through the LUMO of the bridge concomitantly with the hole traveling through the HOMO, whereas in redox wires the electron/hole is unpaired and travels through one single path. Thus, comparisons between attenuation factors for electron transfer in photonic and redox molecular wires has to be made with caution. Attenuation for the energy transfer rate was also estimated using this law by Sauvage and coworkers [72].

Table 1
Selected attenuation factors for various organic bridges

Compounds	β (Å^{-1})[a]	Refs.
Alkyl bridge	~1.00[b]	[32]
Fc–OC(O)$(CH_2)_{2n}$–SH[Surf.]	0.90[b]/1.00[c]	[70]
[Ru]–Py–(*trans*-CH=CH)$_n$–Py–[Ru]		[32,48,57]
	0.16[d]/0.16–0.31[c]	
Fc–(*trans*-CH=CH)$_n$–Fc	0.11–0.22	[71]
[Ru]–terpy–(*p*-C_6H_4)$_n$–terpy–[Ru]	0.16[d]	[67]
[Ru]–dpyp–(*p*-C_6H_4)$_n$–dpyp–[Ru]	0.26[d]	[67]
[Ru]–dpyp–(*p*-C_6H_4)$_n$–dpyp–[Os]		[72]
	0.33(energy)[b]	
[Ru]–terpy–$(C_2)_n$–terpy–[Os]	0.04(hole)[b]	[73,74]
	0.18(e^-)[b]	
	0.17(energy)	
Fc–[C≡C–*p*-(C_6H_4)]$_n$–SH[Surf.]	0.57[b]/0.54[c]	[70]

Fc = ferrocenyl; Py = pyridine; terpy = 2,2′,5′,5″-terpyridine; dpyp = 2,5-bis(*ortho*-pyridyl)–1,4-phenylene.
[a] See Eq. (4b).
[b] Experimental value computed for photochemical electron/hole or energy transfer-rate attenuation, not really e^--transfer in a redox molecular wire.
[c] Computed value reported.
[d] Computed by us from published experimental data.

constant term β in Eq. (4b) is then simply the double of γ in Eq. (4a) [77].

$$V_{ab} = V^0_{ab} \exp(-\gamma R_{M/M}) \tag{4a}$$

$$k = k^0 \exp(-\beta R_{M/M}) \tag{4b}$$

In some cases many ICT bands were observed in the NIR region, and many coupling parameters could be calculated for a given MV [62,78]. This happens either when different compounds are present in solution (isomers or conformers), or when several distinct orbital paths favoring an electron transfer from the donor metal complex toward the acceptor are possible, each of them being characterized by a single V_{ab} parameter and giving rise to a distinct ICT band. This is typically what happens in the case of third-row transition metals like osmium, where strong spin–-orbit coupling takes place, lifting the degeneracy between otherwise orbital degenerate sets of valence metal-based atomic orbitals, and thus increasing the number of potent donor and acceptor orthogonal atomic orbital sets available for electron transfer [79,80].[11] Most often in the latter case, the various ICT bands are too broad to be resolved and the V_{ab} measured experimentally from their envelope actually corresponds to a mean value of the various V_{ab} parameters [80]. Finally, it should be pointed out that transitions other than ICT bands can sometimes be

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[11] This is not to be confused with the case where several paths are possible within the bridging ligand but involving the same set of metal-based donor and acceptor atomic orbitals. In this case, usually a single ICT band is observed, its intensity depending on the way the different "channels" interact. In the case of a strong interference the ITC band can weaken and even vanish in some extreme cases [81].

observed in the NIR domain [82], especially for organometallic radicals [83], and in the case of many absorptions observed in this spectral region one has to make sure that all really correspond to ICT transitions.

2.2. Organometallic compounds with carbon-based σ-metallated bridges

Considering only the metal-containing compounds, we can distinguish many types of one-dimensional architectures that might constitute interesting organometallic molecular wires (see Fig. 2). Four main "types" (*I–IV*) can be distinguished depending on the number and location of metal sites present in those compounds. An additional distinction can then be made depending on whether the metal centers are linked by a σ-bond or by a dative/π-bond to the organic core, giving all types depicted in Fig. 2. Many examples belonging to type *I* and presenting a fully metallic conduction-path are known to constitute efficient wires. They are usually solids with a polymeric structure [84–87]. Compounds belonging to type *II* are also known. Many such complexes where an electron-acceptor (-donor) metal center was linked to a strong organic electron-donor (-acceptor) via an unsaturated spacer have aroused much interest as NLO-active molecules during the last decade [27]. Although these compounds constitute prototypes of polarized molecular wires or rectifying devices as well, they were seldom studied as such. Type *III* comprises the largest set of molecules and especially type *III-1* to which most of the MV complexes studied so far belong. A lot of experimental data on intramolecular electron transfer are available from these molecules (see Section 2.2.2). Examples belonging to types *III-2* and *III-3* are far less numerous and, accordingly, less data are available as well regarding electronic delocalization in those complexes (see Section 2.3 for type *III-3*) [88–91]. Compounds of type *IV* studied for electronic conduction properties were

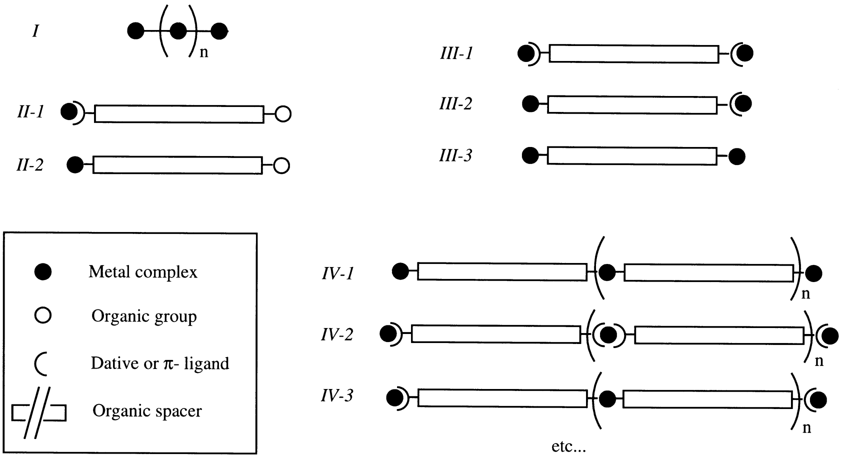

Fig. 2. Schematic representation of various architectural types of metal-containing one-dimensional molecule.

mostly of polymeric nature [92–96]. Nevertheless, several interesting studies on discrete molecules have been recently reported [72,97–102].

2.2.1. Properties and synthetic approaches

In our mind, compounds of type *III-3* with two metal–carbon σ-bonds to the bridge deserve special attention regarding molecular wire elaboration (Fig. 2).[12] Indeed they present very attractive architectures where metal centers with "tunable" electron exchange capabilities can be associated with the most efficient organic spacers. Moreover, it appears from various recent studies that direct metal-carbon σ-linkage of the organic bridge to the metal center usually results in increased electronic delocalization in comparison with connections made through a dative or a π-bond (type *III-1*) [23,24,72]. Non-symmetric compounds constitute polarized wires and might even undergo spontaneous electron transfer from one end to the other. Additionally, with high-energy polarizable d electrons or low-energy empty d orbitals present on the metal centers, an electron vacancy/occupancy might be generated on one terminal group and lead to electron exchange with the other. This can be achieved either by irradiation (photonic wires), when the terminal complexes exhibit strong charge transfer upon photochemical excitation, or by stoichiometric or non-stoichiometric (doping) redox reactions, when metal complexes possess many stable redox states (see Fig. 1). As a consequence, such compounds should allow external switching of the electron transfer capability by irradiation or by 1-e^- redox processes respectively. In the latter case, compounds will give rise to MV complexes that might be easily amenable to study. Finally, convenient addressing or interfacing of these types of molecule should be possible by a simple chemical complexation reaction between the terminal metal centers and functionalized electrodes.

The syntheses of type *III-3* compounds have usually been realized using the basic strategies outlined in Fig. 3. Symmetrical compounds were obtained by four synthetic routes: (i) simultaneous bis-coupling of a symmetrical unsaturated bridge with two equivalents of metal complex (*S0*); (ii) coupling of a pre-synthesized monometallic synthon already containing the bridge as a ligand (*S1*); (iii) homocoupling of a pre-synthesized monometallic synthon containing half of the bridge as an unsaturated ligand (*S2*) or bis-coupling on a di-functional third spacer (*S2*-bis); (iv) transformation of a metallated symmetric bridged precursor, itself synthesized following one of the previous routes (*S3*). Access to non-symmetric complexes can analogously be achieved by reproducing *S0–S2* with different partners, paying attention to the use of a chemoselective coupling reaction if no mixture of compounds is desired (i.e. *S0′–S2′*) or by effecting a transformation which "disymmetrizes" the complex, starting from a symmetric precursor in *S0* or *S3* (i.e. *S0′* and *S3′* respectively). Alternatively, specific one-pot reactions (not schematized in Fig. 3 but denoted *S4* or *S4′* in Tables 2–7) sometimes allow selective isolation of symmetric or non-symmetric compounds from an initial mixture of complex and bridge precursors.

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[12] Complexes belonging to this type with heteroatoms σ-bonded to the metal are also known and some were even studied as molecular wire models, e.g. see Refs. [103,104,105] and references cited therein. Although interesting results were reported, we do not discuss this sub-type of compound in this paper.

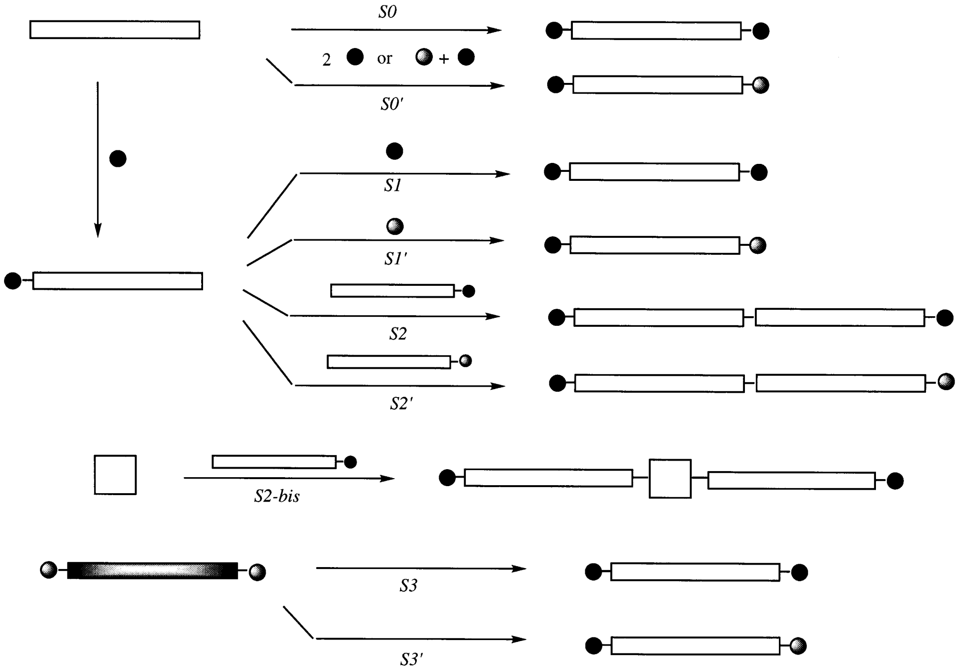

Fig. 3. Schematic representation of various strategies used for synthesis of type *III-3* (see Fig. 2) organometallic architectures.

Such syntheses have no general character owing to the high degree of self-organization needed in this type of reaction rendering it unpredictable. Relevant examples of all types of synthesis (*S0–S4* and *S0'–S4'*) can be found in Tables 2–7.

2.2.2. *Influence of the organic spacer in related compounds*

Depending on the nature of the bridge, a plethora of compounds with various organic spacers belonging to type *III-1* organometallics have been studied [106]. From those studies, useful information can be gained on the effectiveness of a given type of organic spacer regarding electronic delocalization. It has been shown that electron transfer could be achieved intramolecularly through alkyl spacers [107–109]. Such organic bridges are usually far less suited for electron transfer than ones possessing a π-network conjugated all over the molecule [30,76,72]. In that respect, much experimental evidence indicates that alkyne or polyyne units can convey an electron from one end to the other much more efficiently. Recently, Ziessel and coworkers have found a very low attenuation factor for the rate of electron/hole transfer with increasing length in photonic wires featuring such spacers (Table 1) [73,74]. In accordance with independent results [72], they established qualitatively that the rate attenuation was roughly the same for polyalkynyl as for polyalkenyl bridges and much better than for single alkyl bridges [76]. This is a good indication that alkynes or alkenes constitute interesting carriers for long-range electron transfer (typically >20 Å). An advantage of polyynes over polyenes is a stricter control of the geometry within the molecule, imparted by the relative rigidity of such spacers [76].

Alkenyl and polyalkenyl units were already known for a long time to constitute good electronic conductors [40]. They appeared to be even better molecular conductors than polyynes since the electronic coupling factor V_{ab} calculated for various MV was usually higher for polyalkene- than for polyalkyne-type bridges of comparable length. Moreover, a very low attenuation factor has been found by Launay and coworkers for polyalkene bridges in di-ruthenium complexes (Table 1) [48,71]. Independent data confirm that quite long-range electron transfer can be expected before complete attenuation of such a spacer comes in play [26,110]. Additionally, polyene bridges are also able to convey magnetic coupling over quite a long range [76,110]. A theoretical study conducted by Joachim *et al.* indicated the increased resistance with length could be attributed to a Peierls distortion taking place and disrupting the alternant character of polyene. Unfortunately, the realization of wires with highest possible V_{ab} and lowest β is not an easy task since it seems that these two parameters cannot be simultaneously optimized[13] and that a good compromise would be to build rigid (fused) bridges, less prone to undergo the Peierls deformation [32]. Accordingly, a heterocyclic spacer such as 2,5-thiene-diyl, which can be viewed as a rigid dienyl unit, although weakly aromatic, usually gives superior V_{ab} values than its butadiene-diyl counterpart in analogous mixed valence complexes [48]. Such heterocycles are known to constitute good conducting units in polymers upon doping [111,112], and various electrochemical studies indicate that they might even be superior to alkynes or alkenes [50,103]. Incorporation of a cationic methylene unit in the polyethenyl spacer gives a new spacer which is also particularly efficient for electron transfer and which presents a low attenuation coefficient. Such bridges with an odd number of carbon atoms were studied recently in type *III-1* di-ferrocenyl compounds [113].

Among simple spacers, the para-substituted (poly)phenylene units are also conjugated linkers of fixed geometry composed of sp^2 carbon atoms. Whereas some conductivity data on discrete poly-heteroaryls can be found [112,114], data on discrete polyphenylene units are rather scarce, possibly due to the low solubility of such compounds. The decreased solubility often observed for such compounds with increasing number of phenylene units was tentatively attributed to π-stacking between chains. On theoretical grounds, the conductivity of such a unit has been discussed by various authors [107,115,116]. Effective electron delocalization in this spacer implies loss of aromaticity (see Fig. 4). Thus, a polyphenylene bridge should present an increasing energetic activation barrier with length for intramolecular electron transfer. This has been predicted theoretically and can explain a decreased efficiency in comparison with other unsaturated spacers composed of simple units such as ethyne or ethene [21]. Moreover, rotation of any 1,4-phenylene unit in such a bridge will also diminish the electronic interaction, since a decreased π-orbital overlap is expected for perpendicular conformation of two successive *para*-substituted units. Such thermal-switching has been discussed in a theoretical fashion for

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[13] An experimental illustration of this behavior can be found in Ref. [67] with (poly)phenylene spacers.

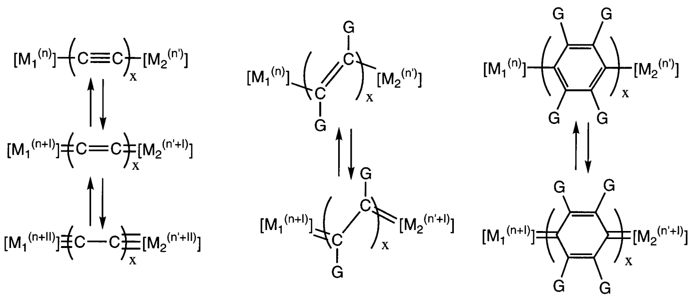

Fig. 4. Possible mesomeric structures for polyethyne-diyl-, polyethene-diyl- and *para*-polyphenylene-based bridges in dinuclear type *III-3* organometallic complexes.

compounds with related bridges [21,117]. Experimentally, it has recently been confirmed that the 1,4-phenylene unit was less efficient than the alkynyl or alkenyl units for simple energy transfer [74] and for transmission of an electronic interaction [24,118,119]. For energy transfer, its attenuation factor has been found to be superior to those of enes or ynes (see Table 1) [72]. Curiously however, regarding electron transfer, published data allow calculation of a comparable attenuation factor [67]. Nonetheless, the electronic coupling through polyphenylene spacers relative to polyene or polyyne spacers remains smaller, even for spacers up to 20 Å, which can be attributed to a much lower V^0_{ab} relative to the other spacers (see Eqs. (4a) and (4b)). This, coupled with the solubility problem, has usually made the *para*-phenylene spacer less attractive than the previous ones for electron transfer, and although constituting a typical sp^2 carbon bridge, by no means can it be considered to be a rigid substitute for a 1,4-butadiene unit. Despite its disadvantages, the 1,4-phenylene unit is nevertheless attractive regarding its stability and synthetic potential. Incorporated in bridges composed of several different spacers, it imparts stability, rigidifies the wire core, and allows geometric modifications or multibranching to be achieved. Such properties have recently been used by Launay and coworkers for the isolation of stable ferrocenyl-based polyenyl wires expanding over more than 40 Å [15].

2.3. *Bibliographic survey of σ-metallated organometallics*

We will now give some representative synthetic type *III-3* (see Fig. 2) realizations, where two transition metals are linked by an unsaturated organic spacer through M–C(sp) or M–C(sp^2) bonds, as well as their reported potential as organometallic wires. Polyyne-, polyene- and phenylene-type σ-metallated bridges will be examined first (see Fig. 5), before looking at more elaborate bridges containing such units (see Fig. 6).

2.3.1. *All-carbon sp bridges [120,121]*

The stability of purely organic polyynes has proven to be highly dependent on their size and on the nature of the terminal capping groups. The maximum length

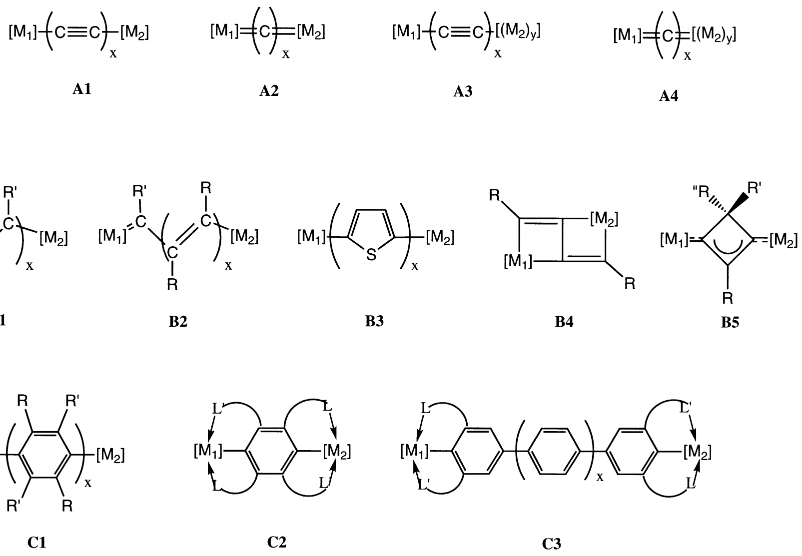

Fig. 5. Known type *III-3*-bridged dinuclear organometallics with polyethyne-diyl-, polyethene-diyl- and *para*-polyphenylene-based regular bridges.

for stable and isolable polyynes obtained by stepwise controlled synthesis is around six acetylenic units. However, longer organic polyynes were generated *in situ* and could be observed transiently in solution [122–124]. The origin of the instability seems essentially kinetic and intermolecular in origin, since polyynes with up to 150 triple bonds appear to be accessible using trifluoromethyl or cyano end-groups [125].

When we started our work in the early 1990s, the kinetic stability of metallated analogues (**A1**–**A4**) with increasing elemental carbon chains was questionable (see Fig. 5). Among the C_x-bridged organometallic dinuclear complexes known, most contained a C_2 bridge.[14] For an exhaustive list of symmetrical and disymmetrically substituted complexes of this type, see Refs. [106,121,126–128] and references cited therein. Examples with C_4 or longer bridges were much rarer until the early 1990s and only few examples had been reported without [129–131] or with minimum [132] characterization (see Table 2). Interest in these types of compound arose after the realization of new types of metal-containing polymers by Hagihara et al. and was motivated by the need to model their repeating units [159]. Initial work was mainly focused on the development of new synthetic methods to access such compounds, symmetrically or disymmetrically substituted [139], and only in very few realizations was the interaction between metals challenged experimentally [140]. These compounds were made following the reaction strategies described in Fig. 3 (*S0–S4* or *S0′–S4′*). Grafting of the capping transition metal complexes was achieved mostly by transmetallation from Group I–IV organometallics on electrophilic transition

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[14] Owing to the shortness of the spacer, we were not further interested in such compounds as model complexes for molecular wires (see Table 18 in Appendix B for a more extensive list).

Table 2
Bridged polyyne-diyl dinuclear complexes (see Fig. 5 for structural types and corresponding labels)

Entry	Structural type	[M_1]	[M_2]	x	RX (x): global charge of the complex	Obs./isol. redox. st.[a]	Synthesis type	Refs.
1	**A1**	$(CO)_2Tp'Mo^{IV}$	$(CO)_2Tp'Mo^{IV}$	2	no	2/1	*S3*	[133]
2	**A1**	$(CO)_2Tp'W^{IV}$	$(CO)_2Tp'W^{IV}$	2	no	2/1	*S3*	[133]
3	**A1**	$(CO)_3CpW^{II}$	$(CO)_3CpW^{II}$	2,4	no	1/1	*S2*	[100]
4	**A1**	$(NO)(PPh_3)Cp^*Re^{II}$	$(NO)(PPh_3)Cp^*Re^{II}$	2–10	yes(2): 0 yes(2): +2	3/1–3	*S2*	[62,134–137]
5	**A1**	$(CO)_3(bipy)Re^{I}$	$(CO)_3(bipy)Re^{I}$	2	yes(2): 0	1/1	*S2*	[138]
6	**A1**	$(CO)_2CpFe^{II}$	$(CO)_2CpFe^{II}$	2,4	yes(2): 0	1/1	*S0,S2*	[131,139–141]
7	**A1**	$[(CN)_5Fe^{II}]^{4-}$	$[(CN)_5Fe^{II}]^{4-}$	2	no	1/1	*S1*	[132]
8	**A1**	$(dppe)Cp^*Fe^{II}$	$(dppe)Cp^*Fe^{II}$	2,4	yes(2): +1	3/3	*S2*	[142,143]
9	**A1**	$(CO)_2CpFe^{II}$	$(CO)(PPh_3)CpFe^{II}$	2	no	1/1	*S1′*	[140]
10	**A1**	$(dppe)Cp^*Fe^{II}$	$(CO)_2Cp^*Fe^{II}$	2	yes(2): 0	3/2	*S1′*	[144]
11	**A1**	$(dppe)Cp^*Fe^{II}$	$(CO)_2Cp^{\#}Fe^{II}$	2	no	3/2	*S1′*	[144]
12	**A1**	$(PPh_3)_2CpRu^{II}$	$(PPh_3)_2CpRu^{II}$	2	yes(2): 0	1/1	*S0*	[145]
13	**A1**	$(PMe_3)_2CpRu^{II}$	$(PPh_3)_2CpRu^{II}$	2	no	4/3	*S0*	[146]
14	**A1**	$(PPh_3)(PMe_3)CpRu^{II}$	$(PPh_3)(PMe_3)CpRu^{II}$	2	no	4/3	*S3*	[146]
15	**A1**	$[(Py)H(PMe_3)_2Rh^{III}]^+$	$[(Py)H(PMe_3)_2Rh^{III}]^+$	2	no	1/1	*S0*	[147]
16	**A1**	$Cl(H)(P^iPr_3)_2Rh^{III}$	$Cl(H)(P^iPr_3)_2Rh^{III}$	2	no	1/1	*S0*	[148]
17	**A1**	$[(Py)H(P^iPr_3)_2Rh^{III}]^+$	$[(Py)H(P^iPr_3)_2Rh^{III}]^+$	2	no	1/1	*S3*	[148]
18	**A1**	$(CO)(P^iPr_3)_2Rh^{I}$	$(CO)(P^iPr_3)_2Rh^{I}$	2	yes(2): 0	1/1	*S0*	[149]
19	**A1**	$[(MeCN)(CO)(PPh_3)_2Ir^{II}]^+$	$[(MeCN)(CO)(PPh_3)_2Ir^{II}]^+$	2	no	1/1	*S0*	[150]
20	**A1**	$Cl(H)(P^iPr_3)_2Ir^{III}$	$Cl(H)(P^iPr_3)Ir^{III}$	2	no	1/1	*S0*	[151]
21	**A1**	$[(Py)H(P^iPr_3)_2Ir^{III}]^+$	$[(Py)H(P^iPr_3)_2Ir^{III}]^+$	2	no	1/1	*S3*	[151]

22	**A1**	$(PPh_3)CpNi^{II}$	$(PPh_3)CpNi^{II}$	2–4	no	1/1	*S1,S2*	[131]
23	**A1**	$(CN)(NH_3)_3Ni^{II}$	$(CN)(NH_3)_3Ni^{II}$	2	no	1/1	*S1*	[132]
24	**A1**	$Cl(P^nBu_3)_2Pd^{II}$	$Cl(P^nBu_3)_2Pd^{II}$	2	no	1/1	*S0*	[130]
25	**A1**	$Cl(P^nBu_3)_2Pt^{II}$	$Cl(P^nBu_3)_2Pt^{II}$	2,4	no	1/1	*S0*	[129,152]
26	**A1**	$(CO)_3CpMo^{II}$	$(CO)_3CpW^{II}$	2	no	1/1	*S1′*	[100]
27	**A1**	$(CO)_3CpMo^{II}$	$(CO)_2CpFe^{II}$	2	no	1/1	*S1′*	[140]
28	**A1**	$(CO)_3CpMo^{II}$	$(CO)(PPh_3)CpFe^{II}$	2	no	1/1	*S1′*	[140]
29	**A1**	$(CO)_3CpW^{II}$	$(CO)_5Mn^{I}$	2	no	1/1	*S1′*	[100]
30	**A1**	$(CO)_3CpW^{II}$	$(CO)(PPh_3)CpFe^{II}$	2	no	1/1	*S1′*	[140]
31	**A1**	$(CO)_3CpW^{II}$	$(CO)_2CpFe^{II}$	2	no	1/1	*S1′*	[100,140]
32	**A1**	$(NO)(PPh_3)Cp^*Re^{II}$	$(CO)(PPh_3)_2Rh^{I}$	2	no	1/1	*S1′*	[135]
33	**A1**	$(NO)(PPh_3)Cp^*Re^{II}$	$Cl(PEt_3)_2Pd^{II}$	2	no	1/1	*S1′*	[135]
34	**A2**	$(CO)_2Tp'Mo^{IV}$	$(CO)_2Tp'W^{IV}$	3	no	1/1	*S3*	[153]
35	**A2**	$(O)_2Tp'Mo^{IV}$	$(CO)_2Tp'W^{IV}$	3	no	1/1	*S3*	[153]
36	**A2**	$(CO)_2Tp'Mo^{IV}$	$(O)_2Tp'W^{IV}$	3	no	1/1	*S3*	[153]
37	**A2**	$(NO)(PPh_3)Cp^*Re^{II}$	$[(CO)_2CpMn^{I}]^+$	3	yes(3): +1	1/1	*S2′*	[154]
38	**A2**	$(NO)(PPh_3)Cp^*Re^{II}$	$[(CO)_2(C_5Cl_5)Mn^{I}]^+$	5	no	1/1	*S2′*	[155]
39	**A3**	$(NO)(PPh_3)Cp^*Re^{II}$	μ_3-η_1-$[Re_2(CO)_9]^+$	3	yes(3): +1	1/1	*S2′*	[156]
40	**A3**	$(NO)(PPh_3)Cp^*Re^{II}$	η_1-$Os_3(CO)_{11}$	3	yes(3): 0	1/1	*S2′*	[156]
41	**A4**	$Cp(CO)_3W^{II}$	μ_2-η_3-$[HRu_3(CO)_9]$	2	no	1/1	*S1′*	[157]
42	**A4**	$[(NO)(PPh_3)Cp^*Re^{II}]$	μ_2-$[HOs_3(CO)_9]$	2–4	yes(2): 0	1/1	*S1′*	[158]
43	**A4**	$Cp(CO)_3W^{II}$	μ_2-η_2-$[HCo_2(CO)_6]$	2	no	1/1	*S1′*	[100]

Tp′ = hydrotris(3,5-dimethylpyrazolyl) borate; bipy = 2,2-bipyridine; $Cp^{\#}$ = pentaphenyl-cyclopentadienyl.

[a] Observed and isolated redox states of the compound (without skeletal changes).

metal centers. Thus, mainly stoichiometric reactions of Group I–II alkynides with transition metal halogenides were used (Eq. (5)) [140,145], but also copper-promoted coupling with palladium or platinum halides (Eq. (6a)) [96,129,130] or palladium/copper cocatalyzed coupling with other metal halides (Eq. (6b)) [139]. Alternatively, using electron-rich complexes of rhodium, the direct activation of a terminal alkyne unit with or without base assistance, following Eq. (6a) or Eq. (7) respectively, was reported, rhodium-hydrides being formed in the latter case [149,148,147]. Nucleophilic iridium complexes could also be grafted on such spacers by the use of difunctional iodonium (poly)alkyne salts (Eq. (8)) [150]. Whenever possible, another interesting access to butadiyne-diyl **A1** compounds was the deprotonation of bis-vinylidene precursors (**D2**) [133,142].

$$(\text{Bridge})\text{–}[\text{M}']+\text{X–}[\text{M}]\rightarrow(\text{Bridge})\text{–}[\text{M}]+\text{X–}[\text{M}'] \tag{5}$$

$$(\text{Bridge})\text{–H}+\text{X–}[\text{M}]+\text{NR}_3 \xrightarrow{\text{CuX (Cat.)}} (\text{Bridge})\text{–}[\text{M}]+(\text{X}^-,\text{HNR}_3^+) \tag{6a}$$

$$(\text{Bridge})\text{–SnR}_3+\text{X–}[\text{M}] \xrightarrow{(\text{Ph}_3\text{P})_2\text{-PdX}_2\text{ (Cat.)}} (\text{Bridge})\text{–}[\text{M}]+\text{X–}[\text{M}'] \tag{6b}$$

$$(\text{Bridge})\text{–H}+[\text{M}]\rightarrow(\text{Bridge})\text{–}[\text{M}]\text{–H} \tag{7}$$

$$[(\text{Bridge})\text{–I(O)Ph(CN)}]+[\text{M}]\rightarrow(\text{Bridge})\text{–}[\text{M}]^+ +\text{PhI(O)CN} \tag{8}$$

where [M′] = Li, Na, K, Mg, SnR_3,; X = Cl, Br, I; [M] = terminal metal group.

Starting from monometallic synthons, a copper-based acetylene coupling reaction was often used to synthesize the final dinuclear complexes or to increase the bridge size in the complex. The Eglinton coupling reaction (Eq. (9)) was suited for the former case [62,100,134,138,135,160,136], whereas the Cadiot–Chodkiewicz coupling (Eq. (10)) was effective for the latter [134,135,161].

$$2[\text{M}]\text{–(Bridge)–H} \xrightarrow[\text{Oxidant O}_2]{\text{CuX (Cat.)}} [\text{M}]\text{–(Bridge)–(Bridge)–}[\text{M}] \tag{9}$$

$$[\text{M}_2]\text{–(Bridge 1)–Cu}+[\text{M}_2]\text{–(Bridge 2)–Br}\rightarrow[\text{M}_2]\text{–(Bridge 1)} \\ \text{–(Bridge 2)–}[\text{M}_2]+\text{CuBr} \tag{10}$$

Thus, from 1990, many additional symmetrical and non-symmetrical polyynediyl compounds from C_6 to C_{20} were synthesized [62,100,138,135,160,136,143,162,137]. These constitute most of the complexes reported in Table 2.

Owing to the structural versatility of all-carbon bridges, many electronic structures can be envisioned (see Fig. 4). The X-ray data obtained for **A1** complexes indicates that the bridge usually has an alternant and polyynic structure rather than a non-alternant and cumulenic one, only one example being firmly identified in the latter case [62]. In this context, the butadiyne-diyl complexes reported recently by Templeton and coworkers constitute possibly the first example of the third category with a C_4 bis-carbyne structure [133]. This illustrates the fundamental influence exerted by the metal termini on the bridge structure, as expected from theoretical studies.[15] Calculations have demonstrated that the HOMO of such systems are mainly metal-based [62], due to the occurrence of destabilizing d-π/4-e^- two orbital interactions [163–166]. Whereas this influence appears determining for short bridges, properties are, however, expected to tend toward those of a pure carbon chain or "carbyne" for longer chains [167,168].

Compounds possessing an odd number of carbon atoms in the bridge (**A2**–**A4**) were much rarer, and only non-symmetrical examples are currently known for obvious reasons related to the introduction of the "C_1" unit of the chain as a carbene (Eq. (11a)) [155,154] or carbyne moiety (Eq. (11b)) [153,169,170]. The bridge structure of such **A2** compounds is now cumulene-like [154].

$$(\text{Bridge})\text{–}[M']+(OC)\text{–}[M]^{+} \xrightarrow[\substack{(2)\ \text{“R}^{+}\text{”}\\ (3)\ BF_3}]{(1)} (\text{Bridge}){=}C{=}[M]+ +[M']^{+}+ROBF_3 \tag{11a}$$

$$(\text{Bridge–}[M']+X\text{–}C{\equiv}[M]\rightarrow(\text{Bridge})\text{–}C{\equiv}[M]+[M']\text{–}X \tag{11b}$$

Regardless the nature of the bridge, replacement of the second metal center by an electroactive cluster which could function as an electron reservoir [169] or permit specific bridge extension reactions [171] was also a very attractive project (**A3** and **A4**). Such molecules were synthesized recently by Bruce et al. [100,157] and Gladysz et al. [156,158] for even and odd carbon-containing bridges. Thus, **A3** compounds were obtained by terminal hydrogen activation on di-cobalt, tri-ruthenium or tri-osmium compounds for Eq. (7) [100,157,156], whereas **A4** compounds were made by nucleophilic coupling on a carbonyl ligand (Eq. (11a)) [158].

Experimental evidence for through-bridge electronic interaction between metal termini in all these compounds (**A1**–**A4**) was rather scant (mainly IR) before the work of Gladysz and coworkers in 1993. They reported the first complexes with an odd number of carbon atoms (>1) in the bridge (**A2**) and observed a charge transfer band in the visible range, indicative of the electron transfer along the all-carbon chain from rhenium to the manganese [155,154]. Then, studying the MV state in symmetric C_4 di-rhenium complexes, they could establish the potential of such molecules as molecular wires [62,136,137], concomitantly and in accordance with our own work on symmetric di-iron complexes [162]. The need to synthesize and study analogues with longer chains was thereby emphasized [160]. The synthesis of the longer iron and rhenium homologues was only realized lately and their study indicates an interesting modification of their properties upon lengthening of the bridge (see Section 4.3.1) [135,160,143]. In this context, Gladysz and coworkers' successful isolation of a C_{20} complex indicates that metallic termini can exert a stabilizing effect on polyyne chains as important as typical organic protective groups did [134,161]. Study of a non-symmetric rhenium–rhodium heterobimetallic complex was disappointing. No clear electronic interaction between metal centers was evident [135]. More interesting compounds are, however, expected upon replacement of the

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[15] A MO-based discussion on the effect of the metal on the C_n bridge can be found for C_2 compounds in Ref. [127] and references cited therein.

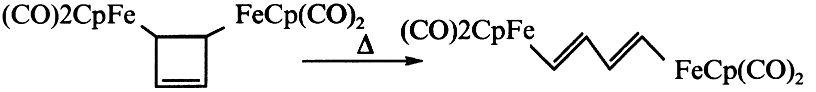
rhodium center by an electroactive metal complex possessing stable redox states in a more accessible potential range [172]. Regarding the cluster-containing molecules (**A3**, **A4**) only preliminary data were communicated for most of them, and further study of these new compounds is eagerly awaited. Apparently, only one redox process is observed in CV [156,158].

2.3.2. Carbon-based sp^2 *bridges*

As with polyynes, the stability of organic polyenes decreases with length [6], but the stability of the shorter representatives is superior in the polyene series. However, with such bridges, organometallic **B1** compounds (see Fig. 5) are scarce (see Table 3) [106]. The syntheses reported for several **B1**–**B3** complexes have no general character [189,174,197,181], whereas the syntheses of the others are based on reactions like transmetallations (Eq. (5)) [184,180,300] or deprotonation from saturated bridge precursors, themselves obtained by oxidative coupling (see Eq. (12)) [173,175]. Some **B1** complexes were also accessed by photochemical ligand substitution on a known **B1** precursor [63,178].

$$2[M]{=}C(OR){-}CH_2^- \xrightarrow[\text{(2) Base}]{\text{(1) Oxidant (Cu}^{I}\text{, Ag}^{I}\text{)}} [M]{=}C(OR){-}CH{=}CH{-}(OR)C{=}[M] \qquad (12)$$

The first **B1** compound to be reported was a di-iron compound with a butadiene-diyl bridge which was simultaneously structurally characterized by Churchill and coworkers [198,176] and Davies [177] in 1968. It was obtained by cycloreversion (Eq. (13)).[199]



(13)

The **B1** complex with the longest chain reported to date is di-molybdenum complex isolated by Schrock and coworkers in 1993 during olefin metathesis reactions [174], whereas the shortest bridge is found in symmetrical [200,201] or non-symmetrical [202,203] ethene-diyl complexes synthesized years before.[16]

Most of all these complexes were isolated in a context different from the present one and considered regarding their synthetic or catalytic potential [181,180]. To the best of our knowledge, the only studies investigating electronic interaction between metal centers in such complexes were reported by Sponsler and coworkers, on di-iron butadienyl complexes [63,164,178]. Accordingly, with our subsequent own work, they suggest that such compounds are also quite promising for elaboration of efficient molecular wires upon oxidation (see Section 4.3.5) [179,204]. Lugan and coworkers reported that a delocalized class-III (according to Robin and Day) MV compound was formed upon 1-e^- reduction of their di-manganese butadiene-diyl complex, but no characterization was communicated for it apart from ESR [175]. A general theoretical investigation reported by Sponsler on di-iron complexes with

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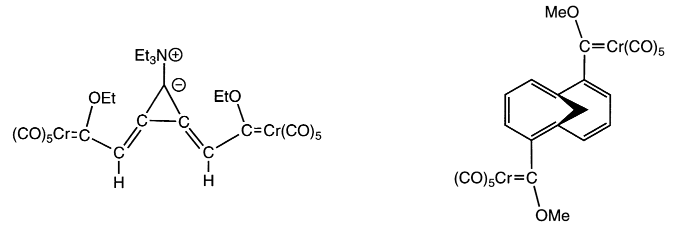
[16] See Table 19 in Appendix B for a more extensive list.

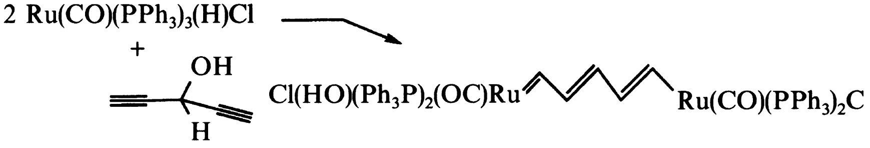


Scheme 1.

various types of bridge indicated that the butadiene-diyl spacer may even be more efficient than other types of spacer discussed in this paper for promoting electron delocalization in MV complexes. Theoretical V_{ab} values found in this study were in accordance with various independent experimental determinations (see Table 17) [164].

Polyheterocyclic compounds of type **B3** [184,183] or dimetalla-bicycles as **B4** [188,187,185,186] which could be seen as "conformationally blocked" butadiene-diyl or polyene-diyl complexes were also reported. Alternatively, complexes such as those depicted in Scheme 1 [205,206] can also be viewed as such. Unfortunately, knowledge of the amount of interaction between metal centers is lacking for all these complexes.

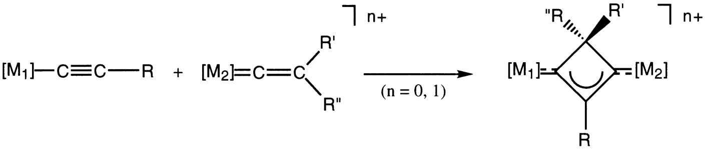
To the best of our knowledge, no sp^2 polyenyl-bridged compounds with an odd number of methylene units in the bridge (**B2**) have been made apart from the two examples reported recently by Jia and coworkers and obtained from diethynylpropargylic alcohol (Eq. (14)) [182]. The electronic interaction between ruthenium centers was not investigated.



(14)

In that context, complexes of type **B5** can also be considered as a particular type of odd-carbon-numbered polyene-diyl-bridged complex where the C_3 polyene chain is maintained rigidly in a C_4 frame [189,196,195,194,193,190–192]. In these compounds the occurrence of electronic delocalization is obvious from X-ray solid state structures (see Scheme 2) [189,196,195,190].

These compounds are formed by cycloaddition between a vinylidene complex and an alkynyl complex (Eq. (15)). Recently, they were even isolated with different metal centers [196,195].



(15)

Table 3
Bridged polyene-diyl dinuclear complexes (see Section 5 for structural types and corresponding labels)

Entry	Structural type	$[M_1]$	$[M_2]$	*x*	R/R′/R″	RX (*x*): global charge of the complex	Obs./isol. redox. st.[a]	Synthesis type	Refs.
1	**B1**	$(CO)_5Cr^I$	$(CO)_5Cr^I$	2	OMe/H	no	1/1	*S3*	[173]
2	**B1**	$(OR_F)_2(NAr)(dme)Mo^V$ [b]	$(OR_F)_2(NAr)(dme)Mo^V$ [b]	4	H/H	yes(4): 0	1/1	*S4*	[174]
3	**B1**	$(CO)_2Cp'Mn^I$	$(CO)_2Cp'Mn^I$	2	OEt/H	yes(2): 0	3/1	*S3*	[175]
4	**B1**	$Cp(CO)_2Fe^{II}$	$Cp(CO)_2Fe^{II}$	2	H/H	yes(2): 0	1/1	*S0*	[176,177]
5	**B1**	$(CO)(PPh_3)CpFe^{II}$	$(CO)(PPh_3)CpFe^{II}$	2	H/H	yes(2): 2^+	3/3	*S0*	[63,178]
6	**B1**	$(dppe)Cp^*Fe^{II}$	$(dppe)Cp^*Fe^{II}$	2	OMe/H	no	3/3	*S3*	[179]
7	**B1**	$(CO)(PMe_3)CpFe^{II}$	$(CO)(PMe_3)CpFe^{II}$	2	OMe/H	yes(2): 2^+	3/3	*S3*	[179]
8	**B1**	$Br(PEt_3)_2Ni^{II}$	$Br(PEt_3)_2Ni^{II}$	2	Ph/H	no	1/1	*S0*	[180]
9	**B1**	$Br(dppe)Ni^{II}$	$Br(dppe)Ni^{II}$	2	Ph/H	no	1/1	*S3*	[330]
10	**B1**	$(C\text{–}N)Pd^{II}$ [c]	$(C\text{–}N)'Pd^{II}$ [d]	2	CF_3/CF_3	yes(2): 0	1/1	*S4*	[181]
11	**B2**	$Cl(OH)(CO)(PPh_3)_2Ru^{IV}$	$Cl(CO)(PPh_3)_2Ru^{II}$	2	H	no	1/1	*S3′*	[182]
12	**B2**	$Cl(OH)(CO)(dppe)Ru^{IV}$	$Cl(CO)(dppe)Ru^{II}$	2	H	no	1/1	*S3*	[182]
13	**B3**	$(dppe)Cp^*Fe^{II}$	$(dppe)Cp^*Fe^{II}$	1	/	no	3/1	*S3*	[183]
14	**B3**	$Cl(COD)Pt^{II}$	$Cl(COD)Pt^{II}$	1–2	/	no	1/1	*S0*	[184]
15	**B3**	$Cl(P^nBu_3)_2Pt^{II}$	$Cl(P^nBu_3)_2Pt^{II}$	1–2	/	no	1/1	*S3*	[184]
16	**B4**	$(Cp')_2Ti^{II}$	$(Cp')_2Ti^{II}$	/	Ph	yes: 0	1/1	*S2*	[185,186]
17	**B4**	$(Me_2SiCp)_2Ti^{II}$	$(Me_2SiCp)_2Ti^{II}$	/	Ph	no	1/1	*S2*	[187]
18	**B4**	Cp_2Ti^{II}	Cp_2Ti^{II}	/	^tBu	yes: 0	1/1	*S2*	[188]
19	**B5**	$(NO)(PPh_3)Cp^*Re^{II}$	$[(NO)(PPh_3)Cp^*Re^{II}]^+$	/	H/H/H	yes: +1	1/1	*S2*,*S2′*	[189]
20	**B5**	$(CO)_2CpFe^{II}$	$[(CO)_2CpFe^{II}]^+$	/	Ph/Ph/H	yes: 0	1/1	*S2′*	[190–192]
21	**B5**	$(CO)_2CpFe^{II}$	$[(CO)_2CpFe^{II}]^+$	/	Ph/Ph/Me	no	1/1	*D2*	[192]

22	**B5**	$(CO)(PPh_3)CpFe^{II}$	$[(CO)(PPh_3)CpFe^{II}]^+$	/	H/H/H	yes: +1	1/1	*S2′*	[193]
23	**B5**	$(CO)(PCy_3)CpFe^{II}$	$[(CO)(PCy_3)CpFe^{II}]^+$	/	H/H/H	yes: +1	1/1	*S2′*	[193]
24	**B5**	$(PMe_3)_2CpRu^{II}$	$[(PMe_3)_2CpRu^{II}]^+$	/	Me/H/Me	no	1/1	*S2′*	[194]
25	**B5**	$(CO)_5Cr^0$	$(CO)_2CpFe^{II}$	/	R/Me/Me (R = ^{n}Bu, Me, Ph, $C_6H_4NO_2$-*p*, CO_2Me)	yes for 4: 0	1/1	*S2′*	[195]
26	**B5**	$(CO)_5Cr^0$	$(CO)_2CpFe^{II}$	/	^{n}Bu/$(CH_2)_2$	no	1/1	*S2′*	[195]
27	**B5**	$(CO)_5Cr^0$	$(CO)_2CpFe^{II}$	/	^{n}Bu/Ph/Ph	no	1/1	*S2′*	[195]
28	**B5**	$(CO)_5Cr^0$	$(CO)(P(OMe)_3)CpFe^{II}$	/	^{n}Bu/Me/Me	no	1/1	*S2′*	[195]
29	**B5**	$(CO)_5Cr^0$	$(CO)(P(OMe)_3)CpFe^{II}$	/	^{n}Bu/$(CH_2)_5$	no	1/1	*S2′*	[195]
30	**B5**	$(CO)_5Cr^0$	$(CO)(PPh_3)CpFe^{II}$	/	^{n}Bu/Me/Me	no	1/1	*S2′*	[195]
31	**B5**	$(CO)_5Cr^0$	$(CO)_2CpFe^{II}$	/	^{n}Bu/$=CR_2$ (R = $C_6H_4OCH_3$-*p*, $C_6H_4CH_3$-*p*)	yes: 0	1/1	*S2′*	[196]
32	**B5**	$(CO)_5Cr^0$	$(CO)_2CpFe^{II}$	/	Ph/$=C(C_6H_4OCH_3$-*p*$)_2$	no	1/1	*S2′*	[196]
33	**B5**	$(CO)_5Cr^0$	$(CO)_2Cp^*Fe^{II}$	/	Ph/$=C(C_6H_4CH_3$-*p*$)_2$	no	1/1	*S2′*	[196]
34	**B5**	$(CO)_5Cr^0$	$(CO)[P(OMe)_3]CpFe^{II}$	/	^{n}Bu/$=CR_2$ (R = $C_6H_4CH_3$-*p*, $C_6H_4OCH_3$-*p*)	yes: 0	1/1	*S2′*	[196]
35	**B5**	$(CO)_5Cr^0$	$(PEt_3)CpNi^{II}$	/	^{n}Bu/Me/Me	no	1/1	*S2′*	[195]
36	**B5**	$(CO)_5Cr^0$	$(PEt_3)CpNi^{II}$	/	^{n}Bu/$=CR_2$ (R = $C_6H_4CH_3$-*p*, $C_6H_4OCH_3$-*p*)	no	1/1	*S2′*	[196]
37	**B5**	$(CO)_5W^0$	$(CO)_2CpFe^{II}$	/	^{n}Bu/$=C(C_6H_4CH_3$-*p*$)_2$	no	1/1	*S2′*	[196]
38	**B5**	$(CO)_5W^0$	$(CO)[P(OMe)_3]CpFe^{II}$	/	^{n}Bu/$=C(C_6H_4CH_3$-*p*$)_2$	no	1/1	*S2′*	[196]
39	**B5**	$(CO)_5W^0$	$(PEt_3)CpNi^{II}$	/	^{n}Bu/$=C(C_6H_4CH_3$-*p*$)_2$	yes: 0	1/1	*S2′*	[196]

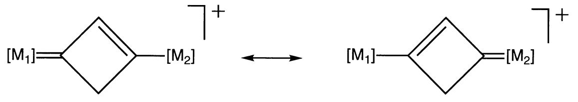
Cp′ = methyl-cyclopentadienyl; Ar = aromatic group.

[a] Observed and isolated redox states of the compound (without skeletal changes).

[b] $R_F = (CH_3)C(O)(CF_3)_2$ and Ar = 2,6-^{i}Pr–(C_6H_3).

[c] (C–N) = NMe_2CH_2-*o*–C_6H_4.

[d] (C–N)′ = $NMe_2CH(SiMe_3)$-*o*–yC_6H_4.

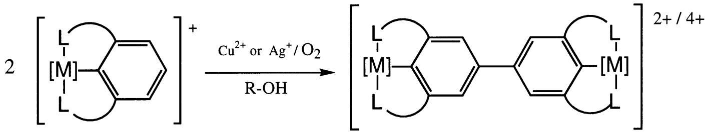


B5

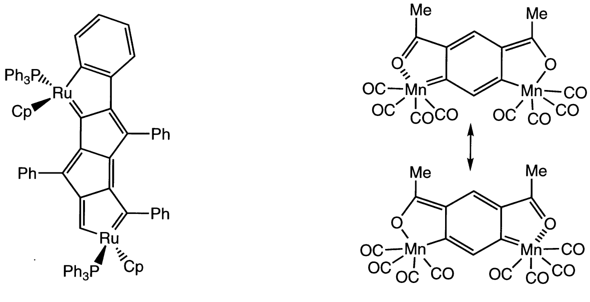
Scheme 2.

Finally, particular complexes such as those depicted in Scheme 3 constitute additional peculiar examples of sp^2 polyenyl-bridged complexes with an odd number of carbon atoms in the bridge. They were structurally characterized by Robinson et al. in 1992 [207] or Bruce et al. in 1991 [197].

Complexes with the para-substituted (poly-)phenylene spacer **C1** constitute another important family of rigid and conjugated sp^2 carbon-based bridges (see Table 4).[17] Despite increased stability and easier synthetic access to the precursors of these organic spacers in comparison with the polyenes or polyynes linkers, most of the **C1**–**C3** compounds were also reported recently, especially for longer bridges ($n > 1$) [214–216,209–211].[18] On the whole, they are symmetrical compounds. Apart for some **C2** complexes, where an original access was found using an oxidative *para*-coupling of the metallated phenylene unit in mononuclear complexes (Eq. (16)) [228,229,227], these compounds were usually synthesized by a one-step bis-metallation of the bridge precursor.



(16)



Bruce *et al.*, 1991

Robinson *et al.*, 1992

Scheme 3.

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[17] We will not consider here such 1,2- or 1,3-substituted spacers; however, some representatives of this type were also isolated and studied, 1,2-complexes being much rarer for obvious steric reasons. See for instance Refs. [207,233,234,235,214,215,236,216].

[18] Some other types of bridging aromatic unit are also known; see for instance Ref. [215] or Ref. [221].

Three reactions, depicted in Eqs. (5), (17a) and (17b), were used. Compounds **C1** and **C2** can been made by addition of di-lithium or di-magnesium aryl salts to halogeno–metal precursors following Eq. (5) [209,219,220,208]. Alternatively, with electron-rich metals like ruthenium, osmium, nickel or palladium, they can be made by double oxidative addition of the corresponding dibromo- of diodoaryl precursor (Eq. (17a)) [221–223,218]. The presence of complexing arms (**C2**, **C3**) on the aromatic core facilitate the complexation reaction and even allow C–H activation to take place by orthometallation with non-halogenated aryls [207,237,225,224]. Using the metallation reaction in a stepwise manner, Sauvage and coworkers [230] and van Koten and coworkers [226] could isolate the few disymmetrically metallated compounds known in this series. Finally, with metals able to form nucleophilic anions like iron, rhenium or manganese carbonyls, **C1** complexes can be formed by nucleophilic addition to the corresponding dihalogeno-acyl aromatic precursor, followed by decarbonylation (Eq. (17b)) [210–213]. Direct addition of such metal anions on a dihalogenoaryl is also possible but gives lower yields [215,215,216], excepted perhaps with bis-diazo precursors [217].

$$\text{(Bridge)–X} + [\text{M}] \rightarrow \text{(Bridge)–[M]–X} \tag{17a}$$

$$\text{(Bridge)–C(O)X} + [\text{M}]^- \underset{(2)\ \Delta(-\text{CO})}{\overset{(1)}{\rightarrow}} \text{(Bridge)–[M]} + \text{X}^- \tag{17b}$$

Initial work on the through-bridge electronic communication was initiated by Hunter and coworkers with symmetric **C1** complexes containing only one bridging phenylene unit. They established by electrochemistry, IR and NMR spectroscopies that this bridge allowed an electronic interaction from one metal to the other to take place and suggested that this might occur via a quinonic resonance form (see Fig. 3) [219,212,213]. Moreover, with 4,4′-diphenylene complexes they stated that the interaction diminished strongly upon increase in the spacer length and proposed that twisting of two successive phenylene units might be responsible for diminished interaction [220]. In addition, Stang and coworkers, from a recent NMR study on similar platinum and palladium complexes, confirmed the occurrence of a strong electronic communication between the metal centers and the bridge [222]. It was also stated independently that magnetic interaction through such a ligand was weak [209]. The participation of a quinonic form for the description of the electronic interaction in the neutral complex was seriously questioned later on by Richardson and Hall on the basis of a theoretical study [238]. Hunter and coworkers' proposal was also in contradiction with the theoretical study conducted recently by Sponsler [164]. The later stated, however, that in the oxidized states, π-delocalization might be much more significant than in the neutral state. Also of particular importance is the work of Sauvage and coworkers with longer representatives of this group (**C3**) [67,228,227,230,231]. They studied the MV states of these complexes and found an increased coupling parameter V_{ab} relative to their analogues presenting a dative M–N bond in place of the Ru–carbon bond. They established that the attenuation coefficient for the (poly)phenylene bridge was lower for electron transfer [24,67,229,227] than for energy transfer [230,231] (see Table 1). When used as

Table 4
Bridged *para*-polyphenylene dinuclear complexes (see Fig. 5 for structural types and corresponding labels)

Entry	Structural type	[M_1]	[M_2]	x	R/R′ or L/L′	RX (x): global charge of the complex	Obs./isol. redox. st.[a]	Synthesis type	Refs.
1	**C1**	$(Me)Cp_2Zr^{II}$	$(Me)Cp_2Zr^{II}$	1	H/H	no	1/1	*S0*	[208]
2	**C1**	Cp_2V^{III}	Cp_2V^{III}	1	H/H	yes(1): 0	1/1	*S0*	[209]
3	**C1**	$(CO)_5Mn^{I}$	$(CO)_5Mn^{I}$	1	H/H	no	1/1	*S3*	[210–213]
4	**C1**	$(CO)_5Mn^{I}$	$(CO)_5Mn^{I}$	1	F/F	no	3/1	*S1*	[212,213]
5	**C1**	$(PPh_3)(CO)_4Mn^{I}$	$(PPh_3)(CO)_4Mn^{I}$	1	Cl/Cl	no	3/1	*S1*	[212,213]
6	**C1**	$(CO)_5Re^{I}$	$(CO)_5Re^{I}$	1	H/H	no	1/1	*S3*	[210]
7	**C1**	$(CO)_2CpFe^{II}$	$(CO)_2CpFe^{II}$	1	F/F	yes(1): 0	1/1	*S0*	[214–216,212,213]
8	**C1**	$(CO)_2CpFe^{II}$	$(CO)_2CpFe^{II}$	2	F/F	no	1/1	*S0*,*S1*	[215]
9	**C1**	$(CO)_2CpFe^{II}$	$(CO)_2CpFe^{II}$	1	H/H	no	3/1	*S1*	[212,213]
10	**C1**	$(CO)_2Cp^*Fe^{II}$	$(CO)_2Cp^*Fe^{II}$	1	H/H	no	3/1	*S1*	[212,213]
11	**C1**	$(CO)_2Cp^*Fe^{II}$	$(CO)_2Cp^*Fe^{II}$	1	F/F	no	3/1	*S1*	[212,213]
12	**C1**	$(PPh_3)(dmg_2)Co^{III}$	$(PPh_3)(dmg_2)Co^{III}$	1–2	H/H	no	1/1	*S0*	[217]
13	**C1**	$Br(PPh_3)_2Ni^{II}$	$Br(PPh_3)_2Ni^{II}$	1	H/H	no	1/1	*S0*	[218]
14	**C1**	$Cl(PMePh_2)_2Ni^{II}$	$Cl(PMePh_2)_2Ni^{II}$	1–2	H/H	no	1/1	*S0*	[219]
15	**C1**	$(C_{12}F_8H)(PMePh_2)_2Ni^{II}$	$(C_{12}F_8H)(PMePh_2)_2Ni^{II}$	1–2	H/H	no	1/1	*S3*	[220]
16	**C1**	$Cl(COD)Pt^{II}$	$Cl(COD)Pt^{II}$	1	H/H	no	1/1	*S0*	[221]
17	**C1**	$Cl(P^nBu_3)_2Pt^{II}$	$Cl(P^nBu_3)_2Pt^{II}$	1	H/H	no	1/1	*S3*	[221]
18	**C1**	$Ph(P^nBu_3)_2Pt^{II}$	$Ph(P^nBu_3)_2Pt^{II}$	1	H/H	no	1/1	*S3*	[221]
19	**C1**	$I(PPh_3)_2Pt^{II}$	$I(PPh_3)_2Pt^{II}$	2–3	H/H	yes(2): 0	1/1	*S0*	[222,223]
20	**C1**	$(OTf)(PPh_3)_2Pt^{II}$	$(OTf)(PPh_3)_2Pd^{II}$	2	H/H	no	1/1	*S3*	[223]

21	**C1**	$[\mathrm{Py(PPh_3)_2Pt^{II}}]^+$	$[\mathrm{Py(PPh_3)_2Pt^{II}}]^+$	2	H/H	no	1/1	*S3*	[223]
22	**C1**	$\mathrm{I(PPh_3)_2Pd^{II}}$	$\mathrm{I(PPh_3)_2Pd^{II}}$	2	H/H	no	1/1	*S0*	[222]
23	**C1**	$\mathrm{I(PEt_3)_2Pt^{II}}$	$\mathrm{I(PEt_3)_2Pt^{II}}$	1–2	H/H	no	1/1	*S0*	[222]
24	**C2**	$\mathrm{(CO)_4Mn^{I}}$	$\mathrm{(CO)_4Mn^{I}}$	/	C(O)Me/H	no	1/1	*S0*	[207]
25	**C2**	$[\mathrm{Cl_2Pd^{II}}]^-$	$[\mathrm{Cl_2Pd^{II}}]^-$	1	$\mathrm{CH_2NEt_2/H}$	no	1/1	*S0*	[224]
26	**C2**	$[\mathrm{(CH_3CN)Pd^{II}}]^+$	$[\mathrm{(CH_3CN)Pd^{II}}]^+$	/	CSPh/CSPh	no	1/1	*S0*	[225]
27	**C2**	$[\mathrm{(Py)Pd^{II}}]^+$	$[\mathrm{(Py)Pd^{II}}]^+$	/	CSPh/CSPh	yes: +2	1/1	*S3*	[225]
28	**C2**	$\mathrm{ClPd^{II}}$	$\mathrm{ClPd^{II}}$	/	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S3*	[226]
29	**C2**	$[\mathrm{(CH_3CN)Pd^{II}}]^+$	$[\mathrm{(CH_3CN)Pd^{II}}]^+$	/	$\mathrm{CNMe_2/CNMe_2}$	yes: +2	1/1	*S3*	[226]
30	**C2**	$\mathrm{ClPd^{II}}$	$\mathrm{ClPt^{II}}$	1	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S1′*	[226]
31	**C2**	$[\mathrm{(CH_3CN)Pd^{II}}]^+$	$[\mathrm{(CH_3CN)Pt^{II}}]^+$	1	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S3*	[226]
32	**C3**	$[\mathrm{(tterpy)Ru^{II}}]^+$	$[\mathrm{(tterpy)Ru^{II}}]^+$	0	$\mathrm{Me_2N/Me_2N}$	yes(0): +4	3/1	*S2*	[227]
33	**C3**	$[\mathrm{(tterpy)Ru^{II}}]^+$	$[\mathrm{(tterpy)Ru^{II}}]^+$	0–2	*o*-Py/*o*-Py	yes(0): +2	3/3	*S2*	[67,228,229]
34	**C3**	$[\mathrm{(tterpy)Os^{II}}]^+$	$[\mathrm{(tterpy)Os^{II}}]^+$	0	*o*-Py/*o*-Py	no	3/1	*S2*	[229]
35	**C3**	$[\mathrm{(tterpy)Os^{II}}]^+$	$[\mathrm{(tterpy)Ru^{II}}]^+$	0–2	*o*-Py/*o*-Py	no	3/1	*S1′*	[230,231]
36	**C3**	$[\mathrm{ClPd^{II}}]$	$[\mathrm{ClPd^{II}}]$	0	$\mathrm{CNMe_2/CNMe_2}$	yes: 0	1/1	*S1*	[232]
37	**C3**	$[\mathrm{ClPt^{II}}]$	$[\mathrm{ClPt^{II}}]$	0	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S1*	[232]
38	**C3**	$[\mathrm{(CH_3CN)Pt^{II}}]^+$	$[\mathrm{(CH_3CN)Pt^{II}}]^+$	0	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S3*	[232]
39	**C3**	$[\mathrm{Cl_3Pt^{IV}}]^+$	$[\mathrm{Cl_3Pt^{IV}}]^+$	0	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S3*	[232]
40	**C3**	$[\mathrm{(CH_3CN)Pt^{IV}}]^+$	$[\mathrm{Cl(OH)_2Pt^{IV}}]^+$	0	$\mathrm{CNMe_2/CNMe_2}$	no	1/1	*S3*	[232]

$\mathrm{dmg_2}$ = 1,2-dimethyl-glyoximate dimer; COD = 1,4-cyclooctadiene; OTf = trifluoromethyl sulfonate; tterpy = 4′-*para*-tolyl-2,2′,5′,5″-terpyridine; o-Py = *ortho*-pyridyl

[a] Observed and isolated redox states of the compound (without skeletal changes).

photonic wires, those complexes with covalently linked bridges were far less efficient than their dative homologues [72]. Finally, they also managed to characterize crystallographically a biphenylene Ru(III)/Ru(III) **C3** complex. In line with Sponsler's statement about possible extended electronic delocalization in oxidized states, the bridge presented structural features in accordance with a dominant bis-quinonic mesomeric form (see Fig. 3) [227].

Another interest in the phenylene unit as an unsaturated linker is to allow trimetallation by branching in the 1,3,5-positions. Accordingly many σ-bonded trimetallated complexes were reported, and some examples are given in Table 5 [233,213,245,244,242,243,239,240]. No in-depth investigation was conducted on the interaction between metal centers in those molecules, but our own work on a slightly different bridge indicate that the 1,3,5-phenylene unit can constitute an interesting spacer for poly-branching of molecular wires (see Section 4.3.4) [241,246].

2.3.3. Other carbon-based sp/sp^2 bridges

Dinuclear compounds containing bridges composed of different units previously described have also been reported (see Fig. 6 and Tables 6 and 7). It is not possible to give an exhaustive list of all those compounds, given the huge number of variations in the bridge composition that can be imagined, but we will focus on certain types often encountered (**D1**–**D7**).

Among all possible organometallics containing non-symmetric bridges resulting from the side-by-side association of two types of spacer previously described, only the **D1** compounds have been reported. They result formally from the association of a (poly)ynyl spacer with a cumulenic one and have a bridge structure close to the polyyne-diyl compounds (**A1**). Few representatives of this type are known and present various bridge compositions [97,155,154,153,156,182,248,247]. Such complexes were made following diverse synthetic strategies. Nucleophilic attack of a lithiated metalla-(poly)alkynyl precursor on an electrophilic carbonyl ligand as depicted in Eq. (11a) without the dealkoxylation step [155,154,156] or transmetallation from a functionalized (poly)alkynyl carbene (Eqs. (5) and (6b)) were most

Table 5
Selected 1,3,5-phenylene-based trimetallic σ-metallated complexes $\{[M]\text{–}(C{\equiv}C)\}_3\text{–}1,3,5\text{-}(C_6R_3)$

Entry	[M]	x	R	RX (x): charge of the complex	Obs./isol. redox. st.[a]	Refs.
1	$(Me)Cp_2Zr^{II}$	0	H	no	1/1	[233]
2	$(CO)_5Mo^0$	0	H	no	1/1	[213,239,240]
3	$(CO)_2CpFe^{II}$	0	H	yes(0): 0	1/1	[213,239,240]
4	$(dppe)Cp^*Fe^{II}$	1	H	yes(1): 0	4/4	[241]
5	$Cl(PPh_3)_2(CO)(CH_3CN)Ir^{II}$	1	H	no	1/1	[242]
6	$Cl(PMe_3)_2Pt^{II}$	1	H	no	1/1	[243]
7	$Cl(PMe_3)_2Pt^{II}$	1	Me	yes(1): 0	1/1	[244]
8	$(Ph_3P)Au^I$	1	H	yes(1): 0	1/1	[245]

[a] Observed and isolated redox states of the compound (without skeletal changes).

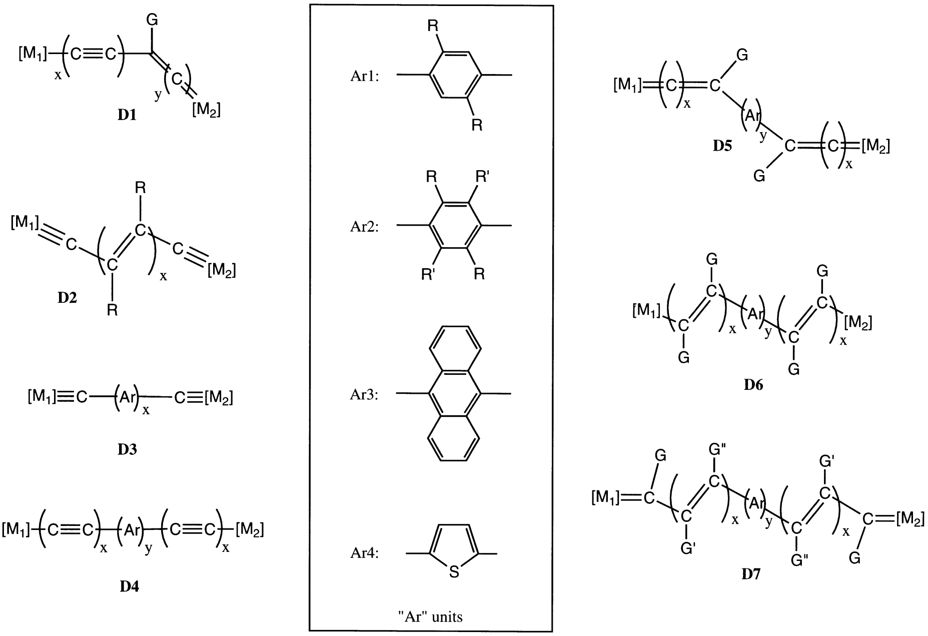


Fig. 6. Known type *III-3*-bridged dinuclear organometallics with mixed sp or sp^2 carbon-based units in the bridge.

often used [97,248]. Deprotonation of a suitable bridged precursor was used as well, but this is a much more specific reaction which depends on the metal centers present [153,247]. No firm data are available regarding the electronic metal–metal interaction in these compounds [248].

More common are compounds with bridges resulting from the incorporation of one type of spacer between units of the second. Families **D2**, **D3** and **D4**, where either a (poly)ethylene or an (hetero)aromatic moiety is bracketed by two sp-carbon-based linkers have been reported (see Fig. 6). Whereas **D2** [133,251,250,249] and **D3** [251–253] compounds are really scarce, symmetric **D4** compounds are much more numerous [94,98,129,147,150,209,242,267,254,257–259,266,256,255,260, 262,261,263,264]. This is possibly related to the easy synthetic access to such spacer precursors [282,283].

Complexes **D2** were isolated after olefin metathesis reactions [251,250], after deprotonation and in situ oxidation of corresponding alkyl-bridged precursors [133], or by oxidative coupling of in situ generated metal–alkynyl anions [249]. The few **D3** bis-carbyne compounds were made from the corresponding bis-carbenes (**D5**) using a route similar to that described in Eq. (11a) [252,253] or by alkyne metathesis reactions [251]. Electronic interaction was not studied in the **D2** complexes reported, whereas for the **D3** complexes an IR investigation indicates the occurrence of a substantial interaction between the carbyne moieties and the arene [253].

For now, all **D4** compounds were synthesized by simultaneous or stepwise metalla-

Table 6
Selected dinuclear complexes with mixed sp/sp^2 carbon bridges (see Fig. 6 for structural types and corresponding labels)

Entry	Structural type	[M_1]	[M_2]	*x*	*y*	R/R′	G/G′/G″	RX (*xy*): global charge of complex	Obs./isol. redox. st.[a]	Synthesis type	Refs.
1	**D1**	$(PPh_3)_2CpRu$	$[(PPh_3)_2CpRu]^+$	1	2		H	yes(1,2): +1	1/1	*S3*	[247]
2	**D1**	(dppe)Cp*Ru	[(dppe)Cp*Ru]$^+$	1	2		H	no	1/1	*S3*	[247]
3	**D1**	$(CO)_2Tp'W^{IV}$	$[(CO)_2Tp'W^{IV}]^-$	0.5[b]	1	/	H	no	1/0	*S3*	[153]
4	**D1**	$(CO)_5Mn^I$	$(CO)_5Cr^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
5	**D1**	$(CO)_5Re^I$	$(CO)_5Cr^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
6	**D1**	$(PPh_3)(NO)$Cp*Re	$(CO)_5W^0$	1	0	/	OMe	no	1/1	*S2′*	[154]
7	**D1**	$(PPh_3)(NO)$Cp*Re	$(CO)_2CpMn^{II}$	1	0	/	OMe	no	1/1	*S2′*	[154]
8	**D1**	$(PPh_3)(NO)$Cp*Re	$(CO)_2(C_5Cl_5)Mn^{II}$	2	0	/	OMe	no	1/1	*S2′*	[155]
9	**D1**	$(PPh_3)(NO)$Cp*Re	η^1-$[Re_2(CO)_9]$	1	0	/	OMe	no	1/1	*S2′*	[156]
10	**D1**	$(PPh_3)(NO)$Cp*Re	$(CO)_4Fe^0$	1	0	/	OMe	no	1/1	*S2′*	[154]
11	**D1**	$(PPh_3)(NO)$Cp*Re	η^1-$[Os_3(CO)_{11}]$	1	0	/	OMe	yes(1,0): 0	1/1	*S2′*	[156]
12	**D1**	$(CO)_2(Cp)Fe^{II}$	$(CO)_5Cr^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
13	**D1**	$(CO)_2(Cp)Fe^{II}$	$(CO)_5W^0$	1	0	/	NMe_2	yes(1,0): 0	1/1	*S2′*	[248]
14	**D1**	$(CO)_2(Cp)Fe^{II}$	$(CO)_5W^0$	2	0	/	NMe_2	no	1/1	*S2′*	[97]
15	**D1**	$(CO)(PPh_3)(Cp)Ru^{II}$	$(CO)_5Cr^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
16	**D1**	$(CO)_2(Cp)Ru^{II}$	$(CO)_5Cr^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
17	**D1**	$(CO)_2(Cp)Ru^{II}$	$(CO)_5W^0$	1	0	/	NMe_2	yes(1,0): 0	1/1	*S2′*	[248]
18	**D1**	$(CO)_2(Cp)Ru^{II}$	$(CO)_5W^0$	2	0	/	NMe_2	no	1/1	*S2′*	[97]
19	**D1**	$(PPh_3)_2(CO)Rh^I$	$(CO)_5W^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
20	**D1**	$(PPh_3)(Cp)Ni^{II}$	$(CO)_5Cr^0$	1	0	/	NMe_2	no	1/1	*S2′*	[248]
21	**D1**	$(PPh_3)(Cp)Ni^{II}$	$(CO)_5W^0$	1	0	/	NMe_2	yes(1,0): 0	1/1	*S2′*	[248]
22	**D1**	$(PMe_3Ph)(Mes)Ni^{II}$	$(CO)_5W^0$	1	0	/	NMe_2	yes(1,0): 0	1/1	*S2′*	[248]
23	**D2**	$(CO)_2CpCr^{IV}$	$(CO)_2CpCr^{IV}$	1	/	Ph	/	yes(1,/): 0	1/1	*S2*	[249]
24	**D2**	$(R_3SiNCH_2CH_2)_3NMo^{IV}$	$(R_3SiNCH_2CH_2)_3NMo^{IV}$	1	/	H	/	yes(1,/): 0	1/1	*S0*	[250]
25	**D2**	$(CO)_2Tp'Mo^{IV}$	$(CO)_2Tp'Mo^{IV}$	1	/	H	/	no	1/1	*S3*	[133]
26	**D2**	$(CO)_2Tp'W^{IV}$	$(CO)_2Tp'W^{IV}$	1	/	H	/	yes(1,/): 0	1/1	*S3*	[133]
27	**D2**	$(^tBuO)_3W^{IV}$	$(^tBuO)_3W^{IV}$	1	/	H	/	no	1/1	*S0*	[251]
28	**D2**	$[Me_2(CF_3)CO]_3W^{IV}$	$[Me_2(CF_3)CO]_3W^{IV}$	1	/	H	/	no	1/1	*S0*	[251]
29	**D2**	$[Me_2(CF_3)CO]_3(bipy)W^{IV}$	$[Me_2(CF_3)CO]_3(bipy)W^{IV}$	1	/	H	/	no	1/1	*S0*	[251]
30	**D3**$_{Ar1}$	$Br(CO)_4Cr^{III}$	$Br(CO)_4Cr^{III}$	1	/	/	/	no	1/1	*S3*	[252]
31	**D3**$_{Ar1}$	$Br(CO)_4W^{III}$	$Br(CO)_4W^{III}$	1	/	/	/	yes(1,/): 0	1/1	*S3*	[252,253]
32	**D3**$_{Ar1}$	$(^tBuO)_3W^{IV}$	$(^tBuO)_3W^{IV}$	1	/	/	/	no	1/1	*S0*	[251]

33	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cp_2V^{III}}$	$\mathrm{Cp_2V^{III}}$	1	1	H	/	no	1/1	*S0*	[209]
34	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{(CO)_2CpMo^{II}}$	$\mathrm{(CO)_2CpMo^{II}}$	1	1	/	/	no	1/1	*S0*	[254]
35	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{(CO)_2CpW^{II}}$	$\mathrm{(CO)_2CpW^{II}}$	1	1	/	/	no	1/1	*S0*	[254]
36	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(CO)_5Mn^{I}}$	$\mathrm{(CO)_5Mn^{I}}$	1	2	H	/	no	1/1	*S1′*	[255]
37	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(dmpe)_2Fe^{II}}$	$\mathrm{Cl(dmpe)_2Fe^{II}}$	1	1	H	/	no	3/1	*S0*	[256]
38	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(dppe)Cp^{*}Fe^{II}}$	$\mathrm{(dppe)Cp^{*}Fe^{II}}$	1	1	H	/	no	3/3	*S0*	[257]
39	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{(CO)_2CpFe^{II}}$	$\mathrm{(CO)_2CpFe^{II}}$	1	1	/	/	no	1/1	*S0*	[254]
40	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(CO)_2(PBu_3)_2Ru^{II}}$	$\mathrm{(CO)_2(PBu_3)_2Ru^{II}}$	1	2	H	/	no	1/1	*S0*	[258]
41	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(CO)(PPh_3)(dppf)Ru^{II}}$	$\mathrm{Cl(CO)(PPh_3)(dppf)Ru^{II}}$	1	1	H	/	no	1/1	*S0*	[259]
42	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(dppe)_2Ru^{II}}$	$\mathrm{Cl(dppe)_2Ru^{II}}$	1	1	H	/	no	3/1	*S0*	[98]
43	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{(CO)_2CpRu^{II}}$	$\mathrm{(CO)_2CpRu^{II}}$	1	1	/	/	no	1/1	*S0*	[254]
44	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(PMe_3)_4Rh^{I}}$	$\mathrm{(PMe_3)_4Rh^{I}}$	1	1–2	H	/	yes(1,1): 0	1/1	*S0*	[147]
45	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(P^{i}Pr_3)_2PyHRh^{III}}$	$\mathrm{Cl(P^{i}Pr_3)_2PyHRh^{III}}$	1	1	H	/	no	1/1	*S3*	[260]
46	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{[(PMe_3)_4HRh^{III}]^{+}}$	$\mathrm{[(PMe_3)_4HRh^{III}]^{+}}$	1	1–2	H	/	no	1/1	*S0*	[147]
47	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{[(PMe_3)_4HRh^{III}]^{+}}$	$\mathrm{[(PMe_3)_4HRh^{III}]^{+}}$	1	1	F	/	no	1/1	*S0*	[147]
48	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Rh^{III}]^{+}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Rh^{III}]^{+}}$	1	1	Me	/	no	1/1	*S0*	[242]
49	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Rh^{III}]^{+}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Rh^{III}]^{+}}$	1–2	1	H	/	no	1/1	*S0*	[150,242]
50	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Ir^{III}]^{+}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Ir^{III}]^{+}}$	1–2	1	H	/	no	1/1	*S0*	[150,242]
51	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(PPh_3)_2(CO)(OTf)Ir^{III}}$	$\mathrm{Cl(PPh_3)_2(CO)(OTf)Ir^{III}}$	1	1	H	/	no	1/1	*S0*	[242]
52	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Ir^{III}]^{+}}$	$\mathrm{[Cl(PPh_3)_2(CO)(CH_3CN)Ir^{III}]^{+}}$	1	1	Me	/	no	1/1	*S0*	[242]
53	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(PEt_3)_2Pd^{II}}$	$\mathrm{Cl(PEt_3)_2Pd^{II}}$	1	1	H	/	no	1/1	*S0*	[261]
54	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(NCS)(PEt_3)_2Pd^{II}}$	$\mathrm{(NCS)(PEt_3)_2Pd^{II}}$	1	1	H	/	no	1/1	*S3*	[261]
55	$\mathbf{D4}_{\mathrm{Ar2}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pd^{II}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pd^{II}}$	1	1	H/H H/Me H/Et	/	no	1/1	*S0*	[94,262]
56	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(PEt_3)_2Pt^{II}}$	$\mathrm{Cl(PEt_3)_2Pt^{II}}$	1	1	H	/	no	1/1	*S0*	[263,264]
57	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(NCS)(PEt_3)_2Pt^{II}}$	$\mathrm{(NCS)(PEt_3)_2Pt^{II}}$	1	1	H	/	yes(1,1): 0	1/1	*S3*	[263,264]
58	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pt^{II}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pt^{II}}$	1	1–2	H	/	no	1/1	*S0*	[94,129]
59	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{Cl(As^{n}Bu_3)_2Pt^{II}}$	$\mathrm{Cl(As^{n}Bu_3)_2Pt^{II}}$	1	1–2	H	/	no	1/1	*S0*	[94]
60	$\mathbf{D4}_{\mathrm{Ar2}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pt^{II}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pt^{II}}$	1	1	H/Me	/	no	1/1	*S0*	[94]
61	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{Ph(P^{n}Et_3)_2Pt^{II}}$	$\mathrm{Ph(P^{n}Et_3)_2Pt^{II}}$	1	1–3	/	/	(1,1–2): 0	1/1	*S0*	[265]
62	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{Ph(P^{n}Bu_3)_2Pt^{II}}$	$\mathrm{Ph(P^{n}Bu_3)_2Pt^{II}}$	1	2	/	/	no	1/1	*S0*	[265]
63	$\mathbf{D4}_{\mathrm{Ar2}}$	$\mathrm{Au^{I}}$	$\mathrm{Au^{I}}$	1	1–2	H/H H/Me^{c}	/	no	1/1	*S0*	[266]
64	$\mathbf{D4}_{\mathrm{Ar2}}$	$\mathrm{(PMe_3)Au^{I}}$	$\mathrm{(PMe_3)Au^{I}}$	1	1–2	H/H H/Me^{c}	/	no	1/1	*S0*	[266]
65	$\mathbf{D4}_{\mathrm{Ar1}}$	$\mathrm{(CO)_5Mn^{I}}$	$\mathrm{Cl(P^{n}Bu_3)_2Pd^{II}}$	1	2	H	/	no	1/1	*S1′*	[255]
66	$\mathbf{D4}_{\mathrm{Ar4}}$	$\mathrm{(CO)_2CpFe^{II}}$	$\mathrm{(CO)_3CpMo^{II}}$	1	1	/	/	no	1/1	*D1*	[267]

Table 7
Selected dinuclear complexes with mixed sp/sp^2 carbon bridges (see Fig. 6 for structural types and corresponding labels)

Entry	Structural type	[M$_1$]	[M$_2$]	*x*	*y*	R/R′	G/G′/G″	RX (*xy*): global charge of complex	Obs./isol. redox. st.[a]	Synthesis type	Refs.
67	**D5**	$(CO)(CpSiMe_3)Nb^{III}$	$(CO)(CpSiMe_3)Nb^{II}$	1	0	/	Me	yes(1,0): +2	1/1	*S2*	[352]
67	**D5**	$(dppm)(\eta^7\text{-}C_7H_7)Mo^{II}$	$(dppm)(\eta^7\text{-}C_7H_7)Mo^{II}$	1	0	/	Ph, ^{n}Bu	yes(1,0): +2	1/1	*S2*	[268]
68	**D5**	$(CO)_2Tp'Mo^{IV}$	$(CO)_2Tp'Mo^{IV}$	1	0	/	H	no	1/0	*S3*	[133]
69	**D5**	$[(CO)_2Tp'Mo^{IV}]^-$	$[(CO)_2Tp'Mo^{IV}]^-$	1	0	/	H	no	1/0	*S3*	[133]
70	**D5**	$[(CO)_2Tp'W^{IV}]^-$	$[(CO)_2Tp'W^{IV}]^-$	1	0	/	Me	no	1/0	*S3*	[133]
71	**D5**	$[(CO)_2Tp'W^{IV}]^-$	$[(CO)_2Tp'W^{IV}]^-$	1	0	/	CH_2Ph	no	1/0	*S3*	[133]
72	**D5**	$[(dppe)_2CpFe^{II}]^+$	$[(dppe)_2CpFe^{II}]^+$	1	0	/	Me	yes(1,0): +2	1/1	*S2*	[269]
73	**D5**	$[P(OMe)_3]_2(CO)_2Fe^0$	$[P(OMe)_3]_2(CO)_2Fe^0$	1	0	/	$CH[O_2C_2H_6]$	yes(1,0): +2	1/1	*S4*	[270]
74	**D5**	$[(dppe)Cp^*Fe^{II}]^+$	$[(dppe)Cp^*Fe^{II}]^+$	1	0	/	H	no	1/1	*S2*	[142]
75	**D5**	$[(PPh_3)_2CpRu^{II}]^+$	$[(PPh_3)_2CpRu^{II}]^+$	1	0	/	Ph	no	1/1	*S2*	[197]
76	**D5**	$[(PPh_3)_2CpRu]^+$	$[(PPh_3)_2CpRu]^+$	1/2[d]	0	/	H	no	1/1	*S1′*	[247]
77	**D5**	$[(dppe)Cp^*Ru]^+$	$[(dppe)Cp^*Ru]^+$	1/2[d]	0	/	H	no	1/1	*S1′*	[247]
78	**D5**	$Cl(P^iPr_3)_2Rh^{II}$	$Cl(P^iPr_3)_2Rh^{II}$	1	0	/	H	no	1/1	*S3*	[148]
79	**D5**$_{Ar1}$	$(CO)_5Cr^0$	$(CO)_5Cr^0$	0	1–2	H	OEt	yes(0,2): 0	1/1	*S0*	[252,271]
80	**D5**$_{Ar1}$	$(CO)_5Cr^0$	$(CO)_5Cr^0$	0	2	H	NEt_2	no	1/1	*S2-bis*	[271]
81	**D5**$_{Ar1}$	$(OR_F)_2(NAr)(dme)$ Mo^{V} [e,f]	$(OR_F)_2(NAr)(dme)$ Mo^{V} [e,f]	0	1	H	H	no	1/1	*S4*	[174]
82	**D5**$_{Ar1}$	$(CO)_5W^0$	$(CO)_5W^0$	0	1–2	H	OEt	no	1/1	*S0*	[252,271]
83	**D5**$_{Ar1}$	$(CO)_5W^0$	$(CO)_5W^0$	0	2	H	NEt_2	0	1/1	*S2-bis*	[271]
84	**D5**$_{Ar3}$	$(CO)_5W^0$	$(CO)_5W^0$	0	1	/	OMe	yes(0,1): 0	1/1	*S2-bis*	[272]
85	**D5**$_{Ar1}$	$(CO)_2CpMn^I$	$(CO)_2CpMn^I$	0	1	H	Ph	no	1/1	*S0*	[273]
86	**D5**$_{Ar1}$	$(CO)_2CpMn^I$	$(CO)_2CpMn^I$	1	1	H	H	no	1/1	*S3*	[274,275]
87	**D5**$_{Ar1}$	$(CO)_2Cp^*Fe^{II}$	$(CO)_2Cp^*Fe^{II}$	0	2	H	OMe	no	1/1	*S2-bis*	[183]
88	**D5**$_{Ar1}$	$(dppe)Cp^*Fe^{II}$	$(dppe)Cp^*Fe^{II}$	1	1	H	H	no	1/1	*S0*	[257]
89	**D5**$_{Ar1}$	$Cl(dppe)_2Ru^{II}$	$Cl(dppe)_2Ru^{II}$	1	1	H	H	no	2/1	*S0,S1*	[276]
90	**D5**$_{Ar1}$	$(p\text{-}NO_2C_6H_4C_2)(dppe)_2$ Ru^{II}	$(p\text{-}NO_2C_6H_4C_2)(dppe)_2$ Ru^{II}	1	1	H	H	no	2/1	*S0,S1*	[276]

91	**D5**$_{Ar4}$	Cl(dppe)$_2$Ru^{II}	Cl(dppe)$_2$Ru^{II}	1	1	/	H	no	2/1	*S0,S1*	[276]
92	**D5**$_{Ar4}$	(p-NO$_2$C$_6$H$_4$C$_2$)(dppe)$_2$ Ru^{II}	(p-NO$_2$C$_6$H$_4$C$_2$)(dppe)$_2$ Ru^{II}	1	1	/	H	no	2/1	*S0,S1*	[276]
93	**D5**$_{Ar1}$	(P^{i}Pr$_3$)CpRh^I	(P^{i}Pr$_3$)CpRh^I	1	1	H	H	no	1/1	*S3*	[260]
94	**D5**$_{Ar1}$	Cl(P^{i}Pr$_3$)$_2$Rh^I	Cl(P^{i}Pr$_3$)$_2$Rh^I	1	1	H	H	no	1/1	*S3*	[260]
95	**D5**$^g_{Ar1}$	(CO)$_5$Cr^0	(CO)$_4$Fe^0	0	1	H	NMe$_2$	yes(0,1): 0	1/1	*S0*	[277]
96	**D6**$_{Ar1}$	ClCp$_2$Zr^{II}	ClCp$_2$Zr^{II}	1	1	H	H	no	1/1	*S0*	[278]
97	**D6**$_{Ar1}$	Cl(CO)(PPh$_3$)(dppf) Ru^{II}	Cl(CO)(PPh$_3$)(dppf) Ru^{II}	1	1	H	/	no	1/1	*S0*	[259]
98	**D6**$_{Ar1}$	Cl(CO)(PPh$_3$)$_2$Ru^{II}	Cl(CO)(PPh$_3$)$_2$Ru^{II}	1	1–2	H	/	no	1/1	*S0*	[259,279]
99	**D6**$_{Ar1}$	(ArCN)Cl(CO)(PPh$_3$)$_2$ Ru$^{II\ f}$	(ArCN)Cl(CO)(PPh$_3$)$_2$ Ru$^{II\ f}$	1	1–2	H	/	no	1/1	*S3*	[279]
100	**D6**$_{Ar1}$	(p-Ph–Py)Cl(CO)(PPh$_3$)$_2$ Ru^{II}	(p-Ph–Py)Cl(CO)(PPh$_3$)$_2$ Ru^{II}	1	1–2	H	/	no	1/1	*S3*	[279]
101	**D6**$_{Ar1}$	Cl(CO)(PCy$_3$)$_2$Ru^{II}	Cl(CO)(PCy$_3$)$_2$Ru^{II}	1	1	H	/	no	1/1	*S0*	[279]
102	**D6**$_{Ar1}$	(ArCN)Cl(CO)(PCy$_3$)$_2$ Ru$^{II\ f}$	(ArCN)Cl(CO)(PCy$_3$)$_2$ Ru$^{II\ f}$	1	1	H	/	no	1/1	*S3*	[279]
103	**D6**$_{Ar1}$	(CF$_3$CO$_2$)(P^{i}Pr$_3$)CpRh^{III}	(CF$_3$CO$_2$)(P^{i}Pr$_3$)CpRh^{III}	1	1	H	H	no	1/1	*S3*	[260]
104	**D6**$_{Ar1}$	I(P^{i}Pr$_3$)CpRh^{III}	I(P^{i}Pr$_3$)CpRh^{III}	1	1	H	H	no	1/1	*S3*	[260]
105	**D7**$_{Ar1}$	(CO)$_5$Cr^0	(CO)$_5$Cr^0	1	1	H	OEt/H/H	no	1/1	*S2-bis*	[280]
106	**D7**$_{Ar1}$	(CO)$_5$Cr^0	(CO)$_5$Cr^0	1	2	H	OEt/NEt$_2$/Me	no	1/1	*S3*	[271]
107	**D7**$_{Ar1}$	(CO)$_5$W^0	(CO)$_5$W^0	1	1	H	OMe/H/H	no	1/1	*S0*	[281]
108	**D7**$_{Ar4}$	(CO)$_5$W^0	(CO)$_5$W^0	1	1	/	OMe/H/H	no	1/1	*S0*	[281]

[a] Observed and isolated redox states of the compound (without skeletal changes).

[b] Carbyne complex.

[c] Substitution in 1,5-positions: asymmetric compound.

[d] Non-symmetric compound with two different “*n*” values.

[e] $R_F = (CH_3)C(O)(CF_3)_2$.

[f] Ar = 2,6-alkyl disubstituted phenyl.

[g] meta-substituted compound.

tion of a bridge precursor, and not by carbon–carbon coupling of metallated mononuclear synthons. Thus, symmetric di-metallation was achieved by transmetallation from a di-potassium [264], di-lithium [209], di-sodium [256], or di-stannous [94,147,258] salt of *para*-ethynyl arenes on a suitable halogenated metal-precursor (Eq. (5)). In the case of copper salts, such transmetallations could even be rendered catalytic by addition of an amine (Eq. (6a)) [129,262]. Very recently, a palladium-catalyzed approach based on stannous mono-protected diethynyl derivatives of 2,5-thiophene also led to isolation of symmetric [254] or non-symmetric [267] **D4** compounds with fair yields. Non-symmetric complexes could be isolated as well by a stepwise transmetallation from stannous salts [255]. Alternatively, symmetric **D4** compounds were made in two steps by transition-metal-assisted activation of a *para*-diethynyl-arene and deprotonation by a base [98,257,266,260,261], or in one step by ligand metathins using two equivalents of a suitable metalla-ethenyl precursor [259]. They were also accessed from electrophilic iodonium salt of *para*-diethynyl-arene using nucleophilic metal centers (Eq. (8)) [150,242]. Few of all these **D4** complexes were examined regarding their metal–metal electronic interaction. In addition to our work on symmetric di-iron complexes [241,246,257], Field *et al.* [256] and Dixneuf and coworkers [98] reported the existence of electronic interactions between the metal centers for quite similar symmetric di-iron and di-ruthenium compounds respectively (see Section 4.3.4).

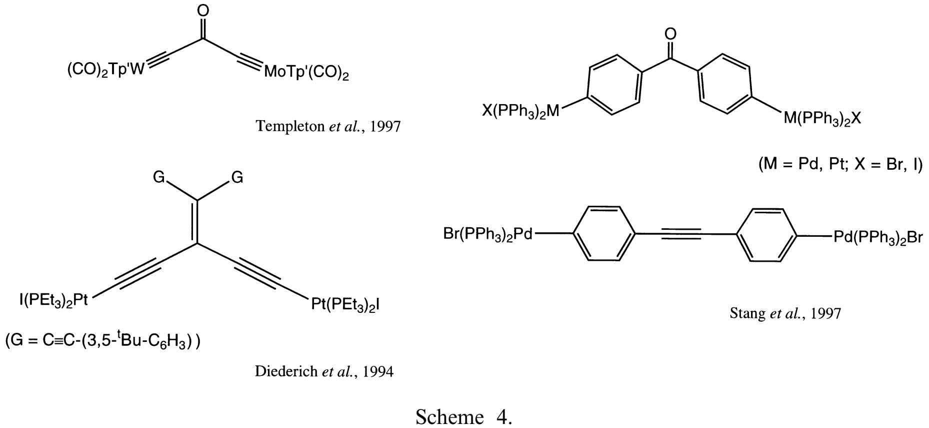
The last compounds reviewed in this section are the **D5**, **D6** and **D7** families (see Fig. 6), where sp^2-carbon atoms are the linkers between the different units of the bridge. For **D5** compounds another additional distinction has to be made between compounds having ($y \geqslant 0$) or not having ($y = 0$) an aromatic ring incorporated in the bridge. Examples of both **D5** compounds are known. In the latter series, nearly all compounds present long bridges, and only a few bis-carbenes featuring a C_2 spacer were reported [284,285]. The complex reported by Fischer *et al.* was structurally characterized. Such a complex presents an electronic structure of the C_2 bridge which is a possible mesomeric form of the bridge structure for a **B1** compound with a C_2 spacer (see Figs. 4 and 5); however, its solid state structure is strikingly different from the **B1** C_2-analogues previously mentioned (see Section 2.3.2) [284].

Various synthetic routes were followed for the synthesis of **D5** complexes without an aromatic unit in the bridge. Bis-vinylidenes were obtained by oxidative coupling of mononuclear alkynyl precursors (see Section 4.1.1) [148,142,197,284,268–270,352], or generated *in situ* by deprotonation of a precursor compound containing a saturated bridge [133]. Non-symmetric examples could be isolated from diethynyl-propargyl alcohols [247]. **D5** compounds with an arene in the bridge were accessed differently, depending on the bis-carbene or bis-cumulene structure of the bridge. Bis-carbene **D5** complexes were usually made by condensation of a dilithiated 1,4-phenylene unit on carbonyl ligands (Eq. (11a)) [183,252,272,271]. Alternatively, such compounds can also be accessed by complexation of a symmetric bis-diazo precursor of the bis-carbene bridge [273]. More recently, for *meta*- or *ortho*-substituted phenylenes, an approach based on Eqs. (17a) and (17b) with bis-tertiary amides was reported and allowed isolation of symmetric bis-carbenes. The first non-symmetric examples of this type could be isolated as well using this reaction in a stepwise manner [277]. Finally, although very specific to molybdenum- or tungsten-containing complexes, mention should be made of the possibility of using alkene metathesis reactions to make such compounds [174]. Bis-vinylidene **D5** complexes with an arene in the bridge were isolated after complexation of *para*-diethynylbenzene in one or two steps [257,260,274,275], or from propargyl alcohols in one step [276]. Only a few examples of **D6** compound are known; one was obtained by α-protonation of the corresponding bis-vinylidene precursor [260], the other by double hydrogenation of a bis-ethynyl ligand in the coordination sphere of the metal [259,278,279]. The **D7** complexes were synthesized either by insertion of amino-alkyne in a suitable **D5** precursor [271], or by bis-coupling of activated chromium carbenes with *para*-terephthalaldehyde [280]. For **D7** complexes, an approach based on coupling with bis-propargylic alcohols and allowing non-symmetrical substitution was recently reported as well [281]. Regarding the metal–metal interaction in all those complexes (**D5**–**D7**), no clear picture emerges. For **D5** compounds having an aromatic group incorporated in the bridge the solid state structure of a bis-carbene chromium complex was taken as evidence against any delocalization [271], whereas in the recently reported ruthenium bis-vinylidene complexes the electrochemical data are indicative of quite a strong electronic interaction [276].

As already stated, many other complexes with various mixed sp/sp^2 conjugated bridges have also been reported and might also constitute interesting molecules regarding molecular electronics. The examples given in Scheme 4 further illustrate the variety of type *III-3* organometallic architectures accessible; unfortunately, definitive data about the electronic metal–metal interaction are missing in most cases [153,222,286,287].

2.4. Conclusions

After this overview, one can easily realize the huge variety of compounds available that contain an organic unsaturated conjugated bridge linking two metal centers by σ metal–carbon bonds. Regarding energy transfer by photonic conduction, the few



Scheme 4.

studies with such architectures containing photoactive end-groups suggested that the σ-mode of ligation of the capping group to the bridge was less effective than dative bonds. However, with redox-active end-groups, those complexes were much more promising for electron conduction after reduction or oxidation. Few in-depth experimental studies have been performed on the electronic delocalization in those complexes relative to the large number of realizations, especially considering all redox states. In fact, a close examination of the data indicate that only a minor part of the reported complexes might be stable and isolable under at least two different redox states. The lack of stability of different oxidation states for such compounds precludes isolation or study of the corresponding MV complexes. Thus, few systematic investigations using the same terminal capping complexes and allowing direct structural comparison between different bridge structures to be made have been conducted. To date, theoretical studies indicate that not only the nature of the bridge [164,165], but also the nature of the complexes connected to it, have a strong influence on its conduction properties [62,163,165,166,258]. Additional experimental studies with compounds possessing diversified bridges in shape and structure are now needed in order to delineate more precisely the role exerted by the metals on the properties of the bridge in such a given molecule. Finally, since the few compounds studied to date presented quite short bridges, the study of homologues with longer bridges is also highly desirable in order to model long-range electron transfer.

3. Mononuclear complexes containing the "(dppe)Cp*Fe" electroactive unit

From Section 2, it is obvious that the ability of a given complex to constitute a valuable end-group for elaboration of type *III-3* organometallic molecular wires will depend strongly on its redox properties. It should possess at least two distinct and stable redox states and present a synthetic chemistry allowing its insertion in dinuclear models easily amenable to study. The (dppe)Cp*Fe fragment has very attractive features in this respect. The following overview on the rich redox chemistry of this fragment in mononuclear complexes will be illustrative for the reader.

3.1. Synthesis of the iron(II) mononuclear parent complexes

A large choice of iron(II) compounds bearing diverse ancillary ligands bound to the metal could be isolated with good yields and extensively characterized. All those complexes were low-spin, diamagnetic and usually thermally stable solids.

*3.1.1. The (dppe)Cp*Fe^{II} halide and hydride complexes*

The iron(II) chloro complex **1** [288,289] was conveniently accessed on large gram-scales from Cp*Li and $FeCl_2(dppe)(THF)_{1.5}$ according to

$$\mathrm{Cp^*Li} + \mathrm{FeCl_2(dppe)(THF)_{1.5}} \longrightarrow \underset{\mathbf{1}}{\mathrm{(dppe)Cp^*FeCl}} \qquad (18)$$

In this complex the iron–chlorine bond is rather weak and a partial dissociation occurs in polar media. As a consequence, compound **1** constitutes a convenient synthon for numerous compounds bearing different ligands coordinated at the iron. Thus reaction with 1 equiv. of potassium iodide quantitatively yields the iodo compound (dppe)Cp*FeI (**2**). Moreover, the 16-e$^-$ intermediate complex [(dppe)Cp*Fe][PF$_6$] (**3**) could even be isolated as a stable compound with potassium hexafluorophosphate (see Scheme 5) [290]. The substitution of the chloride can also be effected as well with LiAlH$_4$ and gives the hydride **4** in good yields (Eq. (19)) [289]. The major limitation to its use as starting material comes from its reluctance to undergo a transmetallation with alkyl lithium or Grignard reagents (Eq. (20)).

$$\underset{\mathbf{1}}{\text{(dppe)Cp*FeCl}} + \text{LiAlH}_4 \longrightarrow \underset{\mathbf{4}}{\text{(dppe)Cp*FeH}} \tag{19}$$

$$\underset{\mathbf{1}}{\text{(dppe)Cp*FeCl}} + \text{RLi} \not\longrightarrow \text{(dppe)Cp*FeR} + \text{LiCl} \tag{20}$$

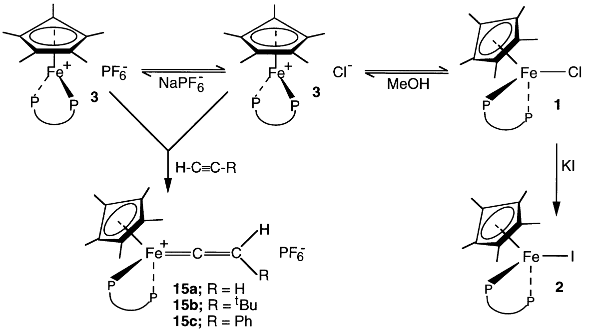
3.1.2. The (dppe)Cp*Fe^{II} alkyl and carbene complexes

An alternative route starting from the easily available dicarbonyl precursor complex **5** could be devised to synthesize the (dppe)Cp*Fe–R alkyl complexes (Eqs. (21) and (22)) [291]. Photochemical displacement of the CO groups by the dppe was, however, not possible when the alkyl ligand possessed hydrogen atoms on the β-carbon atom, since β-elimination was the kinetically favored process.

$$\underset{\mathbf{5}}{\text{(CO)}_2\text{Cp*FeBr}} + \text{RM} \longrightarrow \text{(CO)}_2\text{Cp*FeR} + \text{MBr} \tag{21}$$

$$\text{(CO)}_2\text{Cp*FeR} + \text{dppe} \xrightarrow[\text{toluene/CH}_3\text{CN: 95/5}]{\text{dppe, } h\nu} \text{(dppe)Cp*FeR} + 2\text{CO} \tag{22}$$

This procedure could, however, be extended successfully to the preparation of the



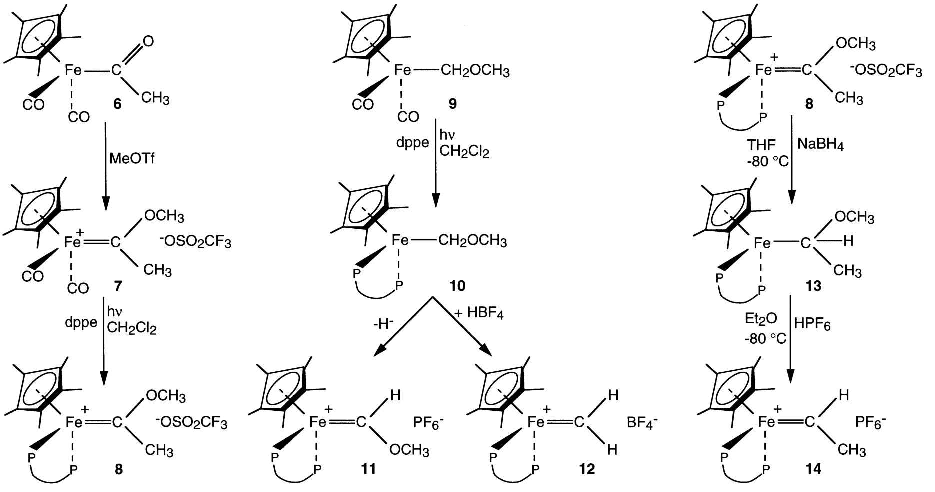
Scheme 5.

alkynyl complexes and subsequently to the σ-butadiynyl derivatives (Eqs. (23) and (24)) [143,144].

$$\underset{\mathbf{5}}{(CO)_2Cp^*FeBr} + RC\equiv C\text{-}C\equiv CLi \longrightarrow (CO)_2Cp^*Fe\text{-}C\equiv C\text{-}C\equiv CR \qquad (23)$$

$$(CO)_2Cp^*Fe\text{-}C\equiv C\text{-}C\equiv CR \xrightarrow[\text{toluene/CH}_3\text{CN: 95/5}]{\text{dppe, h}\nu} \underset{(R = H;\ \mathbf{32})}{(dppe)Cp^*Fe\text{-}C\equiv C\text{-}C\equiv CR} \qquad (24)$$

The electron-rich and bulky (dppe)Cp*Fe fragment was also perfectly suited for stabilization of various carbene ligands in comparison with other first-row transition metals. Carbene complexes could be obtained from various routes involving acyl, alkyl, or other carbene precursors (see Scheme 6) [292–295]. As expected, the Fisher-type carbene compounds **8** and **11** were stable at ambient temperature. The thermal stability of the non-heteroatom stabilized methylidene and ethylidene complexes **12** and **14** under similar conditions was, however, in marked contrast with that reported for all their first- and second-row transition metal analogues [293,296]. The latter readily disproportionated or decomposed even below room temperature [297]. Only for third-row transition metal analogues, such as tantalum [298] or rhenium [299], were similar stability trends observed. Compounds **12** and **14** represent a remarkable example of first-row transition metal methylidene and ethylidene complexes where synthesis, isolation, and X-ray characterization could be achieved at room temperature. Moreover, none of these carbene complexes reacted with electrophilic reagents like phosphines or alkenes. This indicates that the powerful stabilization provided by the (dppe)Cp*Fe moiety is both kinetic and thermodynamic in origin and also

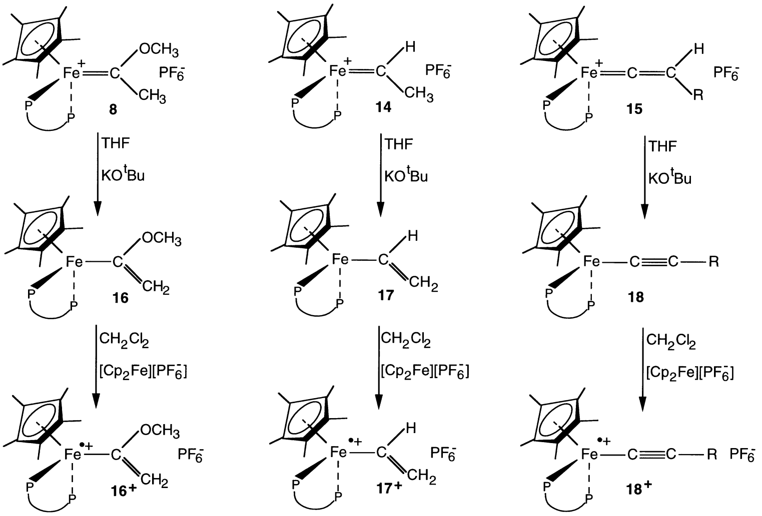


Scheme 6.

illustrates the ability of this fragment to form double bonds with carbon-based ligands.

Another access to derivatives possessing iron–carbon double bonds was revealed by attempts to achieve η^2-coordination of alkenes or alkynes on iron using the 16-e$^-$ complex [(dppe)Cp*Fe][PF$_6$] (**3**). Compound **3** stood unchanged under ethylene pressure but with the terminal alkynes (HC≡CR) a reaction took place and the corresponding stable vinylidene complexes [(dppe)Cp*Fe=C=C(H)R][PF$_6$] (**17**) were isolated. Although putative, a sensible mechanism could involve a transient η^2-alkynyl intermediate followed by fast 1,2-hydrogen shift [300], even if such an intermediate could never be observed in our (dppe)Cp*Fe series. Subsequently, a more direct route to the vinylidene complexes **5** was developed from the (dppe)Cp*FeCl complex in the presence of an hexafluorophosphate salt and a terminal alkyne in a one-pot reaction (see Scheme 5) [162,257,301,302].

Some of those carbene or vinylidene compounds possessing a double Fe=C bond then allowed, in turn, access to alkyl compounds, sometimes otherwise inaccessible. For instance, deprotonation with a strong base of the carbene complexes **8** and **14** afforded the vinyl derivatives **16** and **17** (see Scheme 7) [293], whereas deprotonation of the vinylidene complexes **15** yielded the alkynyl complexes **18** [301]. In the case of the carbenes, such reactions were very interesting since there was no previous synthetic route available to access (dppe)Cp*Fe–alkyl complexes possessing β-hydrogen atoms, as were the vinyl derivatives **16** and **18** (see Scheme 7). Moreover, **8** became a very interesting starting material to prepare 1-methoxyalkyl-iron complexes like (dppe)Cp*FeCH(OCH$_3$)CH$_3$ (**13**, Scheme 5) [295]. This alternative synthetic access often proved to be more convenient than the former one based on lithium alkynides (Eqs. (23) and (24)) in the case of the alkynyl complexes as well (see Section 4.1.1.) [142].



Scheme 7.

Consequently, a broad range of new (dppe)Cp*Fe complexes with hydrocarbon ligands having sp^3-, sp^2- and sp-carbon atoms bonded to the iron could be isolated by various routes. Such compounds exhibited an increased stability and a chemical reactivity often quite different from their structurally close (P_2)CpFeR homologues [303].

3.2. Synthesis and study of the corresponding iron(III) complexes

As indicated by their negative oxidation potentials *vs* SCE (see Table 9), all iron(III) derivatives can be obtained by simple chemical oxidation of their iron(II) homologues using ferricenium salts. All oxidations proceed quantitatively and give usually the corresponding d^5 low-spin thermally stable compounds. The stability of these 17-e^- complexes can be attributed to the strong steric shielding of the metal center by the Cp* and dppe ancillary ligands. Crystal structures solved for different iron(II) or iron(III) compounds indicate that the classical pseudo-octahedral geometry invariably observed for piano-stool complexes is maintained regardless of the oxidation state. The Cp* ring occupies three coordination sites, whereas the diphosphine and the ligand occupy the three remaining sites.

3.2.1. The (dppe)CpFe^{III} halide and hydride complexes*

Oxidation of the iron(II) hydride or chloro complexes yields the corresponding stable [(dppe)Cp*FeH][PF_6] (**4**$^+$) and [(dppe)Cp*FeCl][PF_6] complexes [289,304]. For the chloro complexes, X-ray crystal structures were obtained for both the 18- and 17-e^- derivatives. The data confirmed that the structural reorganization associated with the electron transfer was rather small (see Fig. 7 and Table 8). The bond distances and bond angles are not very different in these two compounds. On 1-e^- oxidation, a shortening of the Fe–Cl bond of *ca* 0.03 Å was observed concomitantly with a small elongation of the Fe–Cp* centroid distance and of the Fe–P bond

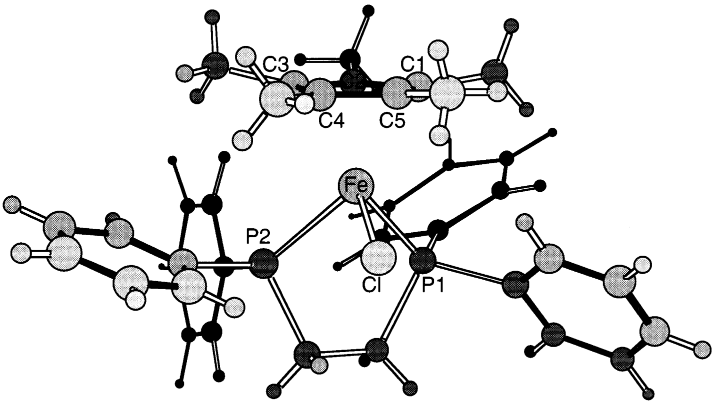


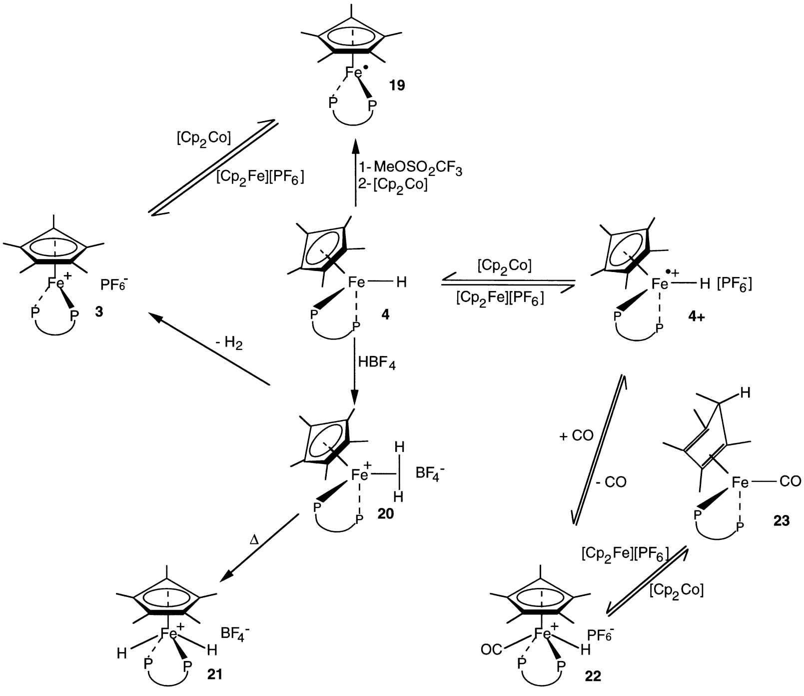
Fig. 7. Crystal structure of the iron(III) chloro complex [353].

Table 8
Significant bond lengths (Å) and bond angles (deg) for the (dppe)Cp*FeCl (**1**) [259] and [(dppe)Cp*FeCl][PF_6] (**1^+**) [353] complexes

Bonds/angles	Fe^{II} metal center	Fe^{III} metal center
FeP(1)	2.197(1)	2.2(1)
FeP(2)	2.210(1)	2.31(1)
FeCl	2.346(1)	2.23(1)
$FeCp^*_{centroid}$	1.768(4)	1.78(1)
P(1)FeP(2)	84.98(5)	81.5(3)
P(1)FeCl	86.03(4)	90.3(2)
P(2)FeCl	87.23(4)	90.9(2)

length of *ca* 0.1 Å. A similar trend was also reported in the case of the related $(dmpe)_2FeCl_2$ Fe^{II}/Fe^{III} series [256].

The isolation of the hydride radical cation [(dppe)Cp*FeH][PF_6] is more surprising (**4^+**, Scheme 8). Cation radicals of transition metal hydrides are usually very unstable, since these compounds are very acidic and a very fast proton transfer occurs between the radical cation and their 18-e^- parents. Thus, the closely related 17-e^- complex [(dppe)Cp*RuH][PF_6] cannot even be spectroscopically characterized [305]. The iron hydride complex (**4^+**) is stable in the solid state and in CH_2Cl_2 or



Scheme 8.

THF solutions for several hours and it does not react with its neutral analogue **4**, indicating that spontaneous proton transfer is not a kinetically favored process. The increased stability found for the organoiron hydrides comes certainly from the smaller atomic radius of the iron(II) which results in an increased steric protection of the hydrogen ligand.

3.2.2. *The (dppe)Cp*Fe^{III} alkyl complexes*

A large number of d^5-Fe^{III} 17-e$^-$ radical piano-stool organoiron derivatives have been prepared via oxidation of the 18-e$^-$ corresponding precursors [5], but only a small number of corresponding 17-e$^-$ iron complexes $[(C_5R'_5)Fe(L)(L')R]^+$ (L, L′=CO or tertiary phosphines, R=alkyl, R′=H, Me) were actually isolated [306]. Most of these 17-e$^-$ radicals were used to mimic intermediates in related oxidative processes and were studied *in situ* by electrochemical and spectroscopic methods [307].

In our group, we synthesized and studied $[(dppe)Cp^*Fe–R]^{+\cdot}X^-$ complexes bearing various carbon-based ligands (R) as alkyl, vinyl, vinyl ether, alkynyl, or butadiynyl by chemical oxidation of their iron(II) electron-rich precursors. The corresponding oxidation potentials were typically in the 0.0/−0.5 V *vs* SCE range (see Table 9). Thermally stable radicals were usually isolated ($i_a/i_c=1$) except for complexes with α-unsaturated hydrocarbon ligands without sufficient steric protection (no bulky substituents). These proved too reactive for isolation at 20 °C ($i_a/i_c<1$); thus, the vinyl, vinyl ether, butadiynyl, and terminal alkynyl complexes were unstable above −60 °C. Once oxidized, the 17-e$^-$ complexes abstracted a hydrogen atom from the medium to form the corresponding iron(II) vinylidene or carbene salts (see Scheme 8). At −80 °C, however, 17-e$^-$ radical cations were stable and could be isolated in the solid state and stored at this temperature. They were

Table 9
Electrochemical data[a] for (dppe)Cp*FeR complexes in CH_2Cl_2

R	E_0 (V)	i_a/i_c	Refs.	Compound
Me	−0.515	1.0	[289]	
CH_2OMe	−0.485	1.0	[289]	
H	−0.375	1.0	[289]	**4**
$C(OMe)=CH_2$	−0.35	0.6	[293]	**16**
$C(H)=CH–C(H)=CH_2$	−0.34	0.6	[308]	**42**
$C(H)=CH_2$	−0.32	0.8	[293]	**17**
$C\equiv C-{}^tBu$	−0.26	1.0	[301]	**18b**
Cl	−0.22	1.0	[289]	**1**
I	−0.13	1.0	[289]	**2**
$C\equiv C–H$	−0.11	0.8	[162]	**18a**
$C\equiv C–Ph$	−0.11	1.0	[301]	**18c**
$C\equiv C–C\equiv C–H$	+0.02	0.5	[309]	**32**

[a] Conditions: CH_2Cl_2, $[^nBu_4N][PF_6]$, 0.1 M, 20 °C relative to SCE calibrated with ferrocene at 0.460 V, Pt electrode, sweep rate 0.100 V s^{-1}.

subsequently studied by variable-temperature ESR spectroscopy, paramagnetic NMR and cyclic voltammetry.

3.2.3. *General properties of the d^5-Fe^{III} 17-e^- radicals*

The Mössbauer spectrum recorded at zero field constitutes a very useful means to determine the oxidation state of the iron center in crystalline samples [310]. Moreover, the purity of the sample can easily be checked by the observation of a single Mössbauer doublet [289]. As previously observed inter alia for the ferrocene/ferricinium systems [311–313], the parameters of the iron(III) compounds are well differentiated from those of the iron(II) parent compounds and the quadrupole splitting values ΔE_Q are diagnostic for the iron(II) and iron(III) states. In the (dppe)Cp*Fe series, these values are close to 2.0 for the Fe^{II} complexes with σ-linked R groups and below 1.0 for the related Fe^{III} derivatives. Thus, the isomeric shift δ constitutes a rough indication of the electronic density at the iron centers and two opposite tendencies can be drawn from the δ values (see Table 10). When the R groups become less electron releasing, as indicated by more positive E_0 values (Table 9), the isomeric shift for the iron(III) compounds decreases concomitantly with its increase in the iron(II) parents [309,317]. The major conclusion drawn from the Mössbauer spectra concerns the d^5-low spin character of all these organoiron radical cations. Consequently, the unpaired electron and the electronic hole are mainly located on the metal, even with vinyl or alkynyl ligands [289].

ESR spectroscopy corroborated this important conclusion. In the spectra recorded in low temperature glasses of CH_2Cl_2–$C_2H_4Cl_2$, three well-separated signals were usually observed (see Table 11). The three g-tensor components are characteristic of the low-spin iron(III) complexes in an octahedral symmetry. In some cases, as for the closely related $[Cp(dppm)Fe(C{\equiv}CR)]^{\cdot +}$ series (dppm = bis(diphenylphosphino-)methane), the two high-field features are split into 1:2:1 triplets by hyperfine coupling with the two equivalent ^{31}P nuclei [301]. The g tensors and ^{31}P coupling are similar to those reported for isoelectronic chromium(I), manganese(II), iron(III), and ruthenium(III) piano-stool complexes [315]. Accordingly, the g_1 and g_2 values are close to the free-electron g value ($g = 2.0023$), whereas the g_3 components are much larger, as expected for low spin iron(III) compounds having a singly

Table 10
Mössbauer parameters of iron(II) and iron(III) complexes in the $[(dppe)Cp^*FeR]^{n+}n[X^-]$ series

R	T (K)	δ (mm s^{-1})		ΔE_Q (mm s^{-1})		Refs.	Compound
		Fe^{II}	Fe^{III}	Fe^{II}	Fe^{III}		
CH_3	77.0	0.15	0.35	1.95	0.76	[289]	
CH_2OCH_3	77.0	0.13	0.25	1.97	0.95	[289]	
H	4.2	0.20	0.26	2.08	0.84	[289]	**4**
--C≡C−ᵗBu	77.0	0.28	0.26	2.00	0.85	[301]	**18b**
–C≡C–(C_6H_5)	77.0	0.27	0.25	2.02	0.90	[301]	**18c**
$(H)_2$	4.2	0.125(Fe^{IV})		1.516 (Fe^{IV})		[304]	**21**
(CO)(H)	4.2	0.30		0.71		[314]	**22**

Table 11

ESR spectroscopic data[a] for the mononuclear iron(III) complexes: $[(dppe)Cp^*FeR]^+[X^-]$

R	g_1	g_2	g_3	A_1 (cm^{-1})	A_2 (cm^{-1})	Refs.	
CH_3	1.9946	2.0441	2.3901			[289]	
CH_2OCH_3	2.0679	2.1193	2.3981	18.8		[289]	
H	1.9944	2.0430	2.4487	26.0	27.4	[304]	$\mathbf{4}^+$
$C(OMe){=}CH_2$	1.9922	2.0289	2.4056	17.0	17.0	[293]	$\mathbf{16}^+$
$-C{\equiv}C{-}^tBu$	1.980	2.036	2.442			[301]	$\mathbf{18b}^+$
$-C{\equiv}C{-}(C_6H_5)$	1.975	2.033	2.464			[301]	$\mathbf{18c}^+$
$-C{\equiv}C{-}H$	1.9719	2.0325	2.4857			[162]	$\mathbf{18a}^+$
$-C{\equiv}C{-}C{\equiv}C{-}SiMe_3$	1.9719	2.0325	2.4857			[309]	$\mathbf{32}^+$
(CO)(H)	2.0019	2.0367	2.0777	17.7 (^{31}P) 18.0 (^{31}P)	12.0 (^1H) 6.2 (^1H)	[314]	**22**
$Cp^*(dppe)Fe^I$	1.9934	2.1911	2.197	126.0 (^{31}P)		[290]	**19**

[a] At 77 or 80 K in CH_2Cl_2–$C_2H_4Cl_2$ (1:1) glass.

occupied HOMO with predominant $d_{x^2-y^2}$ character. Moreover, for the complexes having a σ-coordinated hydrocarbon ligand R, an increase in the g_3 values is observed with diminution of the hybridization of the metal-ligated carbon center. This tendency may be taken as an indication of the participation of the conjugated π-systems in delocalization of the odd electron. MO calculations for the simplified compound $[Cp(PH_3)_2Fe(CH_2OH)]^+$ (Cp = cyclopentadienyl) with imposed C_s symmetry have shown that three MOs can be identified with the t_{2g} set. These calculations indicated that the presumed singly occupied MO, 3a′, is the one that is the more delocalized on the ligands. Thus, the spin delocalization was mainly expected on the Cp ligand and on the (CH_2OH) group. This was in full agreement with the spectroscopic findings [289].

The presence of odd electrons adversely affects the line width and give rise to a paramagnetic shift in the NMR spectra of these complexes. In extreme cases of broadening, the resolution of a given peak can be below the threshold of detection of the spectrometer. Fortunately, this is usually not the case with our iron(III) $[(dppe)Cp^*Fe{-}R]^{+\cdot}X^-$ complexes and valuable information on the 17-e^- complexes can be gained from ^1H, ^{31}P and ^{13}C NMR [316]. Typical line widths observed (20 °C) were 100–300 Hz for the proton resonances in these complexes. Variable-temperature ^1H NMR showed that the isotropic chemical shifts δ_{iso} of all peaks exhibited a linear shielding *vs* $1/T$, except for the meta resonance of the aromatic rings, for which a weak deshielding was observed. The isotropic shift is larger for the methyl groups of the Cp* ligands than for the hydrocarbon ligand R and the less pronounced values are observed for the resonances of the phenyl rings of the dppe ligands. In these d^5-iron(III) cations, it was assumed that the chemical shifts reflected primarily the spin densities on the ligands and thereby it was concluded that the ligand contribution to the spin delocalization was predominant for the Cp* ring and to a lower extent for the R group. These conclusions gave further support to the preceding studies.

3.3. Electronic and geometric flexibility of the (dppe) Cp*Fe framework

As shown previously, the sterically crowded and electron-rich (dppe)Cp*Fe unit is stable as five-coordinated iron complexes, but also accommodates six- and seven-coordinated complexes in a wide variety of oxidation states.

3.3.1. Chemistry of the hydride complexes

The flexibility of the (dppe)Cp*Fe fragment is very nicely illustrated by the rich chemistry of the iron hydride **4** (see Scheme 8) [314]. Protonation at the hydride allows the isolation of the η^2-dihydrogen complex **20** at low temperature. This non-classical dihydride changes upon warming at room temperature to the seven-coordinate iron(IV) classical dihydride **21**. For the examples reported in the literature, the conversion of non-classical to classical transition metal hydride is always reversible. The gradual, complete and irreversible conversion of **20** to **21** observed here makes an exception to this rule. Again this particular behavior could result from the exceptional steric bulk around the (dppe)Cp*Fe unit rendering any structural interconversion more energetic.

The previously mentioned 17-e^- d^5 iron hydride $\mathbf{4}^+$ reacts with CO reversibly at -80 °C to give the unusual 19-e^- seven-coordinate d^7-Fe^{III} adduct **22** quantitatively isolated as a powder. Upon warming, complex **22** released CO to give back $\mathbf{4}^+$ at -80 °C. The reactivity of the hydride **22** upon 1-e^- reduction is consistent with its 19-e^- structure. This reaction provides the 18-e^- iron(0) complex (dppe)(η^4-Cp*H)Fe(CO) (**23**) via a 20-e^- iron(II) intermediate and reductive elimination of Cp* and hydride. The equilibrium between $\mathbf{4}^+$ and its CO adduct **22** is unique, involving isolated 17-e^- and 19-e^- species, and is of considerable relevance to ligand substitution reactions at 17-e^- metal complexes via an associative mechanism [314].

Upon treatment of the hydride **4** with methyl triflate, the stable triflate complex (dppe)Cp*Fe(OSO_2CF_3) is formed with methane evolution. In agreement with its X-ray crystal structure indicating a rather long Fe–O bond distance of 2.007(3) Å, the Fe–O bond is weak and the complex partially dissociates in THF. The 16-e^- species generated *in situ* was reduced by cobaltocene and the resulting iron(I) 17-e^- [(dppe)Cp*Fe]$^{\cdot}$ complex (**19**) was isolated and crystallized from a pentane solution (see Scheme 8) [290]. The 1-e^- oxidation of the very reactive but thermally stable compound **19** with ferricenium hexaflurophosphate gave the iron(II) 16-e^- species (**3**) isolated as an orange powder. It is noteworthy that, in this compound, the shortest distance between the iron center and the *ortho*-carbon atoms of the phenyl groups of the dppe is longer than 3.5 Å, definitely excluding any agostic interaction between the electron-deficient metal center and a C–H bond in the solid state. The X-ray crystal structures of compounds **3** and **19** show that the major structural difference between these two five-coordinated iron complexes concerns the pyramidalization of the iron atom. The structure of the 16-e^- cation **3** has close to C_{2v} symmetry. In the neutral complex **19**, the presence of the seventh d-electron causes a lowering of the symmetry and the geometry of the coordination sphere becomes intermediate between a typical C_{2v} structure with no vacant site and a distorted D_{4h} coordination geometry, assuming that the Cp* ligand occupies three ligand sites and the dppe the other two. The electron transfer process between **3** and **19** illustrates the flexibility of the (dppe)Cp*Fe framework, which generally stabilizes six-coordinated compounds but can also be adapted for five-coordinated complexes. As a consequence of its unusual geometry, the complex **3** exhibits a magnetic moment in solution ($\mu = 3.3\ \mu_B$, 310 K) corresponding to a high spin configuration with two unpaired electrons [290].

Thus, the basic chemistry around the iron hydride **4** involving electron, proton, hydride and CO transfer allowed the preparation, isolation and characterization of a series of compounds with five-, six-, or seven-coordinated iron(0), iron(I), iron(II), iron(III), and iron(IV) complexes with the same (dppe)Cp*Fe framework.

*3.3.2. The (dppe)Cp*Fe^{II} unit in molecular devices*

Thus, our studies on mononuclear complexes indicated that the (dppe)Cp*Fe core could display an exceptional electronic and structural flexibility in organometallic chemistry. This behavior allowed the isolation and the characterization of a family of 19-, 18-, 17-, and 16-e^- compounds with different oxidation states ranging from iron(0) to iron(IV) complexes [290,314]. Apart its potential as a Mössbauer probe, the widest interest of the (dppe)Cp*Fe organometallic building block is, however, its ability to stabilize the d^5 iron(III) species. This is very well illustrated by the isolation of the radical cation hydride $\mathbf{4}^+$. Couples of Fe^{II}/Fe^{III} complexes with the (dppe)Cp*Fe framework and various types of saturated or unsaturated organic ligand are readily accessible. Most of these compounds are stable, and the few non-stable iron(III) exceptions present generally conjugated electron-rich π-organic ligands without steric protection. Moreover, the iron(III) radical cations $[(dppe)Cp^*Fe^{III}X]^{\cdot +}$ carry a single unpaired electron, and thus are ESR-active at liquid nitrogen temperature and NMR-active in the liquid solvent temperature range as well.

Among the mononuclear compounds studied, stable iron(III) complexes with alkynyl or polyynyl ligands are promising synthons [142,301]. Meanwhile, the high unsaturated character of these ligands, the spin density and the electronic vacancy are mainly located on the iron center [144,317]. Moreover, the (dppe)Cp*Fe unit in the mononuclear compounds unit exhibits oxidation potentials that are among the lowest known to date for neutral complexes of highly unsaturated ligands [241,318]. In light of these data, we surmised that the construction of molecular devices possessing several such Fe^{II} and Fe^{III} units interacting through similar conjugated ligands could be of great interest for elaboration of nanoscopic devices such as molecular wire models. In such molecular architectures the delocalization of odd electron(s) and their magnetic coupling with iron(III) sites may give rise to new properties different from those of their mononuclear constituents. Moreover, regarding our experience with mononuclear species, we were able to gather decisive information about the electron distribution in polynuclear molecules by spectroscopy. Finally, the ability of this unit to undergo easy outer-sphere electron transfer in an accessible potential range made it a convenient wire terminus for eventual addressing/interfacing purposes.

4. Polynuclear complexes containing the "(dppe)Cp*Fe" electroactive unit

4.1. *Synthesis of the iron(II) dinuclear parent complexes*

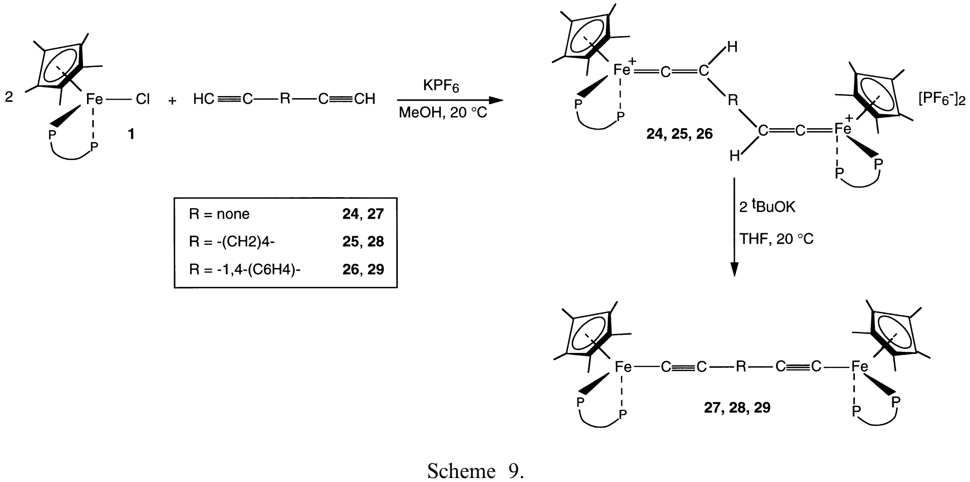
For describing the synthesis of our compounds, we will follow an organization similar to that depicted in Fig. 3. First we will describe the realization of compounds isolated by symmetrical grafting on preformed bridges. Then we will come to the synthesis of dinuclear complexes obtained from mono-metallated synthons such as those previously described. This approach will allow access to either symmetrical or non-symmetrical compounds.

4.1.1. *Alkynyl-based complexes*

Using the alkyne complexation reaction on [(dppe)Cp*Fe]$^+$ (**3**) previously described (see Schemes 6 and 7), we could access many different bridged complexes by use of bis-acetylenic moieties with good yields (see Scheme 9). Compounds such as **27**, **28** or **29** were isolated by this way [257,302]. Other complexes similar to **28** are known with other metals [148,242,319].

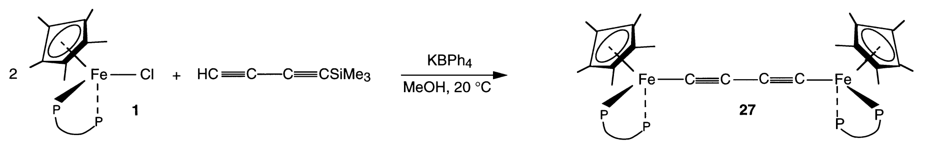
In principle, access to the butadiynyl-bridged complex **27** is possible using this reaction; however, owing to the well-known instability of butadiyne, we preferred to use an alternative high-yielding synthetic approach, i.e. oxidative radical coupling (see Scheme 12) [142]. Alternatively, access to these compounds is feasible from the mono-protected trimethylsilyl diyne precursor, using *in situ* deprotection (see Scheme 10) [309].

A similar approach with *in situ* deprotection was also used for the isolation of **30** and even for the trimetallic complex **31** as well (see Scheme 11). This route was more direct and safer than the complexation reaction used for **29** (see Scheme 9), when unstable terminal polyethynyl aromatics are used, and allowed isolation of

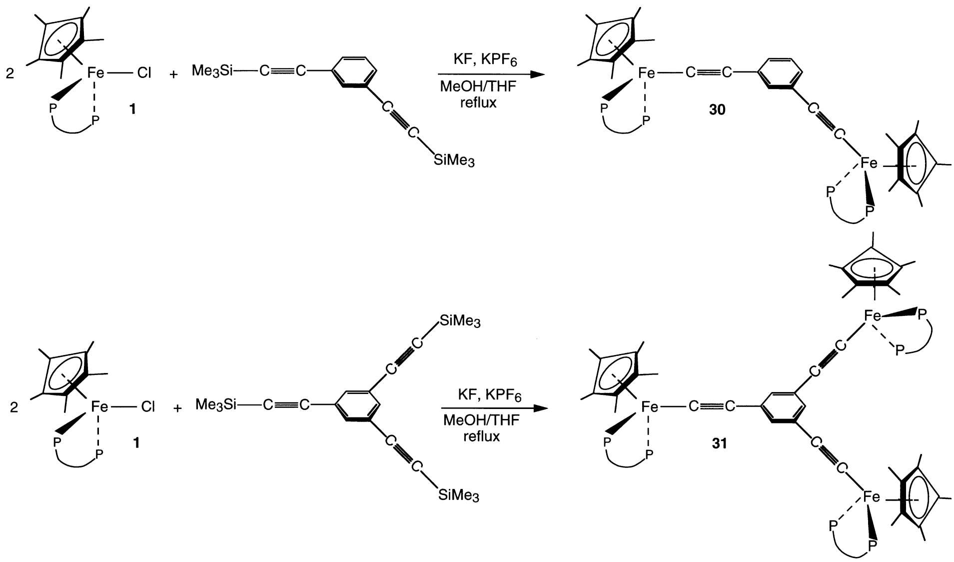


R = none	**24, 27**
R = -(CH2)4-	**25, 28**
R = -1,4-(C6H4)-	**26, 29**

Scheme 9.



Scheme 10.

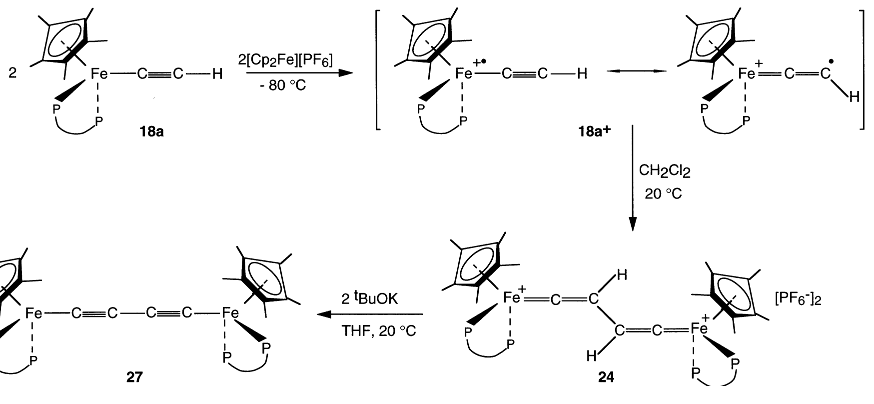


Scheme 11.

meta-substituted analogues of **29**. In these reactions, the de-silylating agent KF is introduced in the medium at the beginning of the reaction [241].

As mentioned previously, in order to gain access to **27** with fair yields using non-dangerous reactants, we used the coupling reaction of the alkynyl (dppe)Cp*Fe^{III} complex that we discovered serendipitously (see Scheme 12) [142]. Similar couplings for related, but non-H-terminal, iron or molybdenum alkynyls were reported by Iyer and Selegue [269] and Whiteley and coworkers [268, 352] respectively. Such an extension of this coupling reaction is very interesting, since quantitative yields of the desired bridged complex **27** are isolated after deprotonation of the bis-vinylidene **24**, itself obtained from the stable and easily available precursor **18a**. An analogous oxidative coupling reaction may be responsible for the formation of the first butadiynyl complex during the synthesis of terminal iron alkynyls reported by Nast and Urban in 1957, *in situ* generated nitrosamine being the chemical oxidant, and potassium amide the base in that particular case [132]. Related coupling reactions have been reported since [133,173,175,320].

Complex **27** was isolated as a thermally stable but air sensitive, brown complex. The bis-vinylidene salt **24** does not constitute an interesting wire model for the study



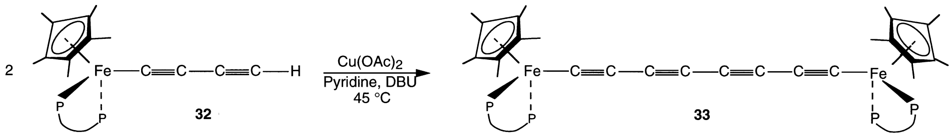
Scheme 12.

of electronic delocalization. No other stable oxidation state of this compound could be found in the usual redox range [204].

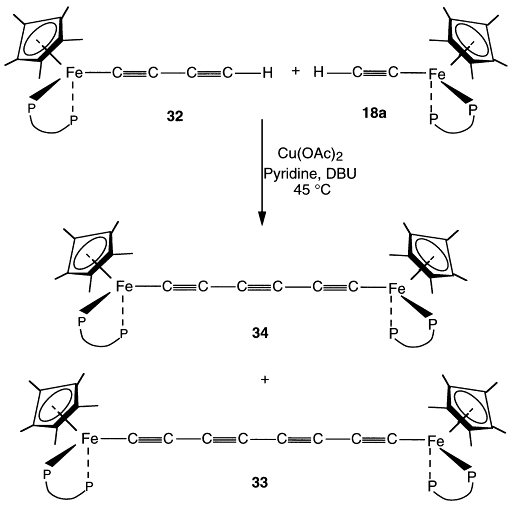
A similar approach based on coupling was used to access compounds containing longer bridges or with different substitution at both ends, from the mono-metallic butadiynyl synthon (dppe)Cp*Fe–C≡C–C≡C–H (**32**). Such a compound did not undergo a similar oxidatively induced coupling as its C_2 analogue did (**18a**); however, homocoupling promoted by copper allowed quantitative access to the C_8-bridged dinuclear complex **33** with fair yields (see Scheme 13) [143]. With two different organoiron alkynyl starting synthons, this coupling gives a statistical mixture from which the C_6-bridged complex **34** could be characterized as the main product (see Scheme 14) [204]. Such synthetic approaches, based on the Eglinton coupling, have already been used by other researchers [62,100, 134,138,160,136].

Finally, access to non-symmetrically substituted complexes **37** and **38** could be achieved with good yields, using the alkynyl-activation reaction on carbonyl-iron butadiynyl complexes **35** and **36** (see Scheme 15) [144]. In these molecules, an electron-rich center (dppe)Cp*Fe is connected to an electron-poor center, giving a model of a “polarized wire”.

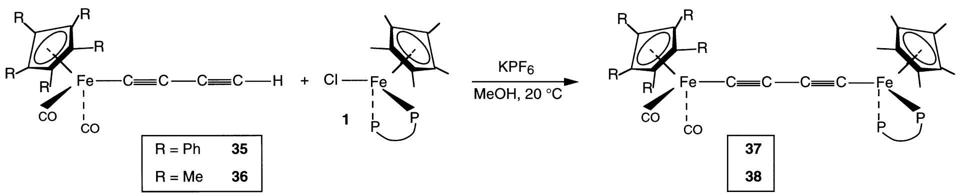
In conclusion, monometallic alkynyl or butadiynyl complexes such as **18a** or **32**, **35** and **36** constitute convenient building blocks for elaboration of more sophisticated compounds with polyynyl-type bridges. This is further evidenced by our recent success in implementing the Sonogashira catalytic coupling reaction with haloaromatics using such building blocks (see Scheme 16) [321].



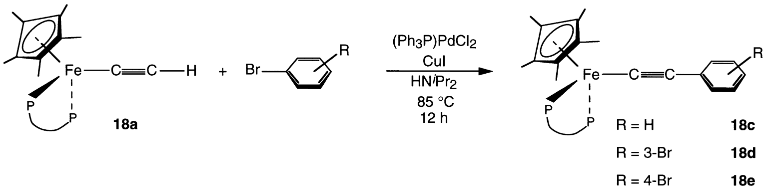
Scheme 13.



Scheme 14.



Scheme 15.

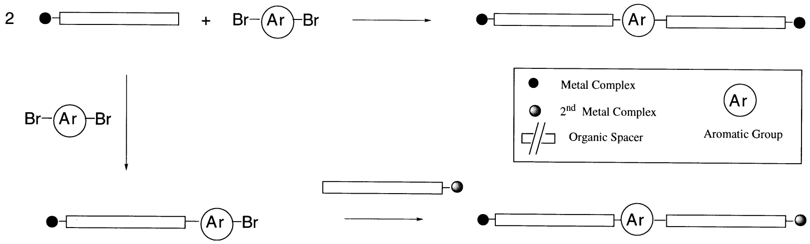


Scheme 16.

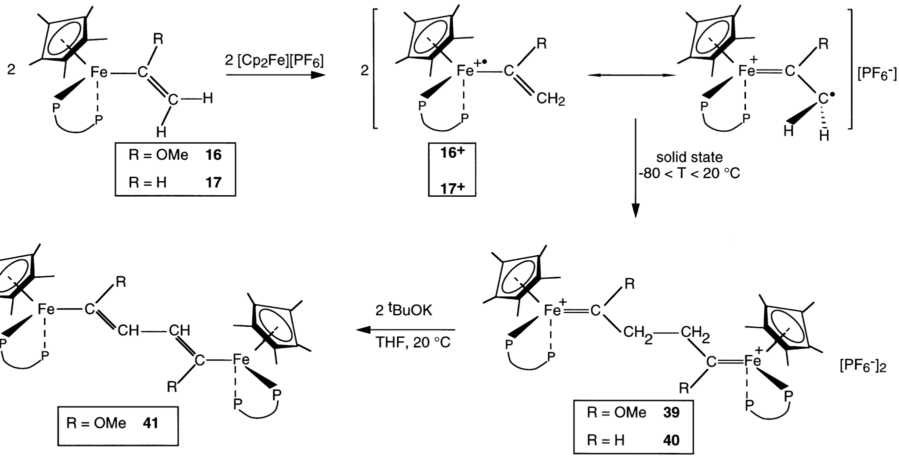
This reaction should allow us to access a broad range of phenylene-containing bridged organoirons containing the (dppe)Cp*Fe unit, starting from polyhalogenated haloaromatics (i.e. *S2*-bis reaction type; see Scheme 17).

4.1.2. Polyenyl-based complexes

As an alternative to pure polyyne-based C_x bridges, we have also tried to develop a route to analogous compounds with polyene-based linkers. Access to the butadienediyl was realized using an oxidative-coupling reaction (see Scheme 18). Here again the propensity of the corresponding iron(III)–methoxyvinyl cation toward



Scheme 17.

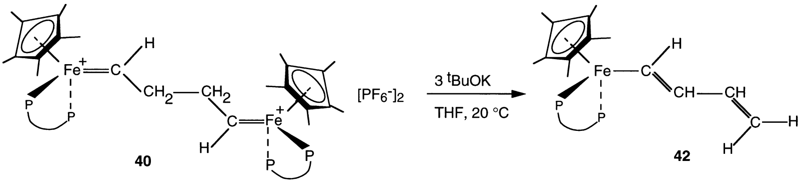


Scheme 18.

dimerization at low temperature was used efficiently to form the corresponding bis-carbenes **39** and **40**. Compound **39** was subsequently deprotonated to give the expected dinuclear compound **41** [293].

Such reactions could also be achieved with iron vinylidenes containing a carbonyl ligand and lead to mixtures of diastereoisomeric complexes. This was the first example of such a reaction induced by chemical oxidation [322]. Related examples of metal-promoted oxidative coupling leading to similar molecules can, however, be found [173,269]. Recently, we were able to find an easy synthetic access to the corresponding butadienyl complex **42**, using a selective mono-demetallation from bridged bis-carbene precursor **40** (see Scheme 19) [308]. Since preliminary experiments indicate that such a complex presents a similar redox behavior to **17**, we will attempt to develop thereby an access to bridged di-iron octatetraenilidenediyl complexes.

In summary, we could isolate in fair yields by use of diverse synthetic approaches a broad range of neutral polynuclear architectures featuring two or three (dppe)Cp*Fe units ligated through a central unsaturated organic core, differing in structure. In the case of a ligand-mediated electronic interaction between these units,



Scheme 19.

the stepwise oxidation of each metal center should occur and lead to the formation of the corresponding oxidized states possessing unpaired electrons. Investigation of the electron transfer in those oxidized forms, and particularly in the MV states, will be representative of the potential for each family of compounds to constitute molecular wires or other nanoscopic devices, depending on the structure of the organic bridge.

4.2. Synthesis and study of electronic interaction in the MV state

4.2.1. CV of the complexes

In all these compounds, the (dppe)Cp*Fe units were easily oxidized and presented the lowest oxidation potentials ever reported for neutral molecular wires redox termini. Apart for **28**, ΔE^0 was always above 200 mV in our polynuclear organoiron complexes. Since no neat structural change takes places, through-bridge interaction can be considered as being a determining factor of the magnitude of K_c. Except **37** and **38**, all compounds exhibited a reversible redox behavior at usual scan rates ($0.1\ \mathrm{V\,s^{-1}}$), giving two well-separated 1-e$^-$ processes. Representative values of the redox potentials for our compounds are given in Tables 12 and 13. The CV reversibility of the first oxidation wave and the strong corresponding comproportionation

Table 12
Redox potentials[a] and comproportionation constants for the dinuclear compounds

Compound	E_1^0 [ΔE] (V)	E_2^0 [ΔE] (V)	ΔE (V)	K_c	Refs.
27[b]	−0.63 [0.06]	0.08 [0.06]	0.70	1.6×10^{12}	[162]
34	−0.42 [0.06]	0.11 [0.06]	0.53	1.0×10^{9}	[204]
33	−0.19 [0.06]	0.24 [0.06]	0.43	2.0×10^{7}	[143]
37	−0.28 [0.06]	0.93 [0.07]	1.21	/	[144]
38	−0.36 [0.07]	0.74 [0.07]	1.10	/	[144]
28	−0.28 [0.05]	−0.19 [0.05]	0.09	3.3×10^{1}	[302]
29	−0.27 [0.07]	−0.01 [0.07]	0.26	2.6×10^{4}	[257]
30	−0.22 [0.09]	−0.10 [0.08]	0.13	1.3×10^{2}	[241]
41	−1.04 [0.08]	−0.61 [0.07]	0.43	2.2×10^{7}	[179]

[a] Conditions: CH_2Cl_2, [^{n}Bu$_4$N][PF$_6$], 0.1 M, 20 °C relative to SCE calibrated with ferrocene at 0.460 V, Pt electrode, sweep rate $0.100\ \mathrm{V\,s^{-1}}$.

[b] A third redox wave was also observed at 0.97 V for this compound.

Table 13
Redox potentials[a] in V vs SCE and K_c for the trinuclear compound **31** [265]

E^0_{1-3}	ΔE (ΔEp)	K_c
0.00 (0.06)	/	/
−0.12 (0.07)	0.130	1.3×10^2
−0.25 (0.07)	0.130	1.0×10^2

[a] Conditions: CH_2Cl_2, [$^nBu_4N$][PF_6], 0.1 M, 20 °C relative to SCE calibrated with ferrocene at 0.460 V, Pt electrode, sweep rate 0.100 V s^{-1}.

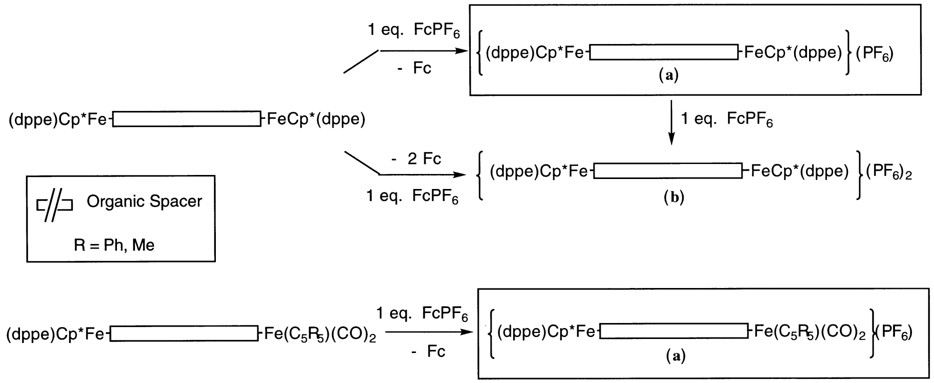
constants (see Table 12) indicated that our MV complexes might be isolable after chemical oxidation.

4.2.2. Isolation and characterization of the oxidized states

Isolation of the mono- (MV) and di-oxidized compounds was usually possible after chemical oxidation using 1 or 2 equiv. of ferricenium hexafluorophosphate. For **37**$^+$ and **38**$^+$, only the MV complex could be isolated (see Scheme 20). All displayed a CV spectrum similar to the one obtained from their neutral parents. The mono- and di-oxidized complexes were generally thermally stable strongly colored compounds, and in some cases were even air stable.

4.2.3. Study of the different redox states

For all these dinuclear compounds, as for their mononuclear counterparts, characteristic low spin metal-centered single radicals were obtained after oxidation. The MV state of the complexes exhibit three typical ESR-tensors in dichloromethane–dichloroethane glasses at 77 K (see Tables 14 and 15). An ESR investigation of some of the fully oxidized complexes indicated the existence of a ferromagnetic interaction between the unpaired spins through the bridge, in the di- and tri-metallic *meta*-substituted phenylethynyl complexes **30**$^{++}$ and **31**$^{+++}$. Hyperfine coupling between phosphorus and unpaired electrons was seldom observed.



Scheme 20.

Table 14
ESR parameters for selected MV compounds (77 K)[a]

Compound	$\Delta m_s = \pm 1$			Refs.
	g_1	g_2	g_3	
37$^+$	1.987	2.051	2.347	[144]
38$^+$	2.008	2.089	2.139	[144]
29$^+$	2.031	2.043	2.199	[257]
30$^+$	1.975	2.033	2.464	[246]
31$^{+\ b}$	1.982	2.034	2.450	[246]
31$^{2+\ c}$	1.978	2.030	2.409	[246]
41$^+$	g = 2.025[d]			[179]

[a] In $CH_2Cl_2/ClCH_2CH_2Cl$ (1:1) glass.
[b] Coupling: $a_3 = 12$ G.
[c] Coupling: $a_3 = 15$ G; for $\Delta m_s = \pm 2$, $g = 4.637$.
[d] Isotropic signal observed in solution at 258 K.

Table 15
ESR parameters for selected bis/tris-Fe^{III} compounds (77 K)[a]

Compound	$\Delta m_s = \pm 1$			$\Delta m_s = \pm 2$	$\Delta m_s = \pm 3$	Refs.
	g_1	g_2	g_3	g	g	
27^{++}	ESR silent compound					[162]
37^{++}	Unstable					[144]
38^{++}	Unstable					[144]
29^{++}	1.967	2.036	2.114	/	/	[257]
30^{++}	1.934	2.097	2.281	4.540	/	[246]
31^{+++}	1.981	2.130	2.601	4.461	7.973	[246]

[a] In $CH_2Cl_2/ClCH_2CH_2Cl$ (1:1) glass.

The use of Mössbauer spectroscopy for the study of the mono-oxidized relative to the neutral and di-oxidized complexes was also particularly interesting, since it allowed the precise knowledge of the different oxidation states for iron centers detected in the MV complex (see Table 16). Thus an estimate of the rate of the electron exchange relative to the acquisition time of this technique can be obtained. Measurements being effected on solid samples, this technique alone cannot be diagnostic of localized valence [310], since solid state effects have been shown to induce a localization of the valence in some cases. Thus, other spectroscopic techniques such as IR also proved to be a useful complement, especially regarding evaluation of the electron transfer rate.

Magnetism studies performed either in solution by NMR [323] or with solid samples (squid) on the oxidized states confirmed the occurrence of an antiferromagnetic interaction between the unpaired electrons on remote centers in fully oxidized butadiynediyl (**27**$^{++}$) and the *para*-phenylethynyl (**29**$^{++}$) complexes, whereas similar investigations conducted on the di- and trimetallic *meta*-substituted ones (**30**$^{++}$ and

Table 16
Mössbauer parameters for selected MV compounds (80 K)[a]

Compound	ΔE_Q *vs* Fe (mm s^{-1})	δ *vs* Fe (mm s^{-1})	%	Refs.
27$^+$	1.320	0.210	100	[162,302]
33$^+$	1.910	0.240	21	[309]
	1.450	0.210	58	
	1.090	0.190	21	
37$^+$	1.922	−0.048	50	[144]
	0.865	0.160	50	
38$^+$	1.990	−0.028	50	[144]
	0.922	0.206	50	
29$^+$	1.96	0.250	14	[257]
	1.110	0.200	72	
	0.710	0.250	14	
30$^+$	2.000	0.249	50	[246]
	0.854	0.254	50	
31$^+$	1.992	0.254	65	[246]
	0.680	0.375	8	
	0.948	0.239	27	
31^{++}	1.714	0.190	22	[246]
	0.492	0.437	6	
	0.862	0.248	72	
41$^+$	2.010	0.270	100	[179]

[a] Measurement effected in dichloromethane at 25 °C.

31^{+++}) were much more in favor of a ferromagnetic interaction. In the MV compounds **27**$^+$, **29**$^+$ and **30**$^+$ the presence of a single unpaired electron was confirmed each time [162,246,257].

Finally, whenever possible, the electronic coupling parameter V_{ab} was calculated or bracketed using the characteristics of the ICT band (see Section 2.1.2). For such an experimental evaluation, one has to be able to observe clearly the ICT band(s), which can be masked by other electronic transitions [48]. Fortunately, regarding our MV compounds, one isolated ICT band was observed each time in the NIR range. In one case (**38**), however, V_{ab} was obtained with a rather large experimental uncertainty due to the weakness of this absorption. Another difficulty arises when the MV complex is on the borderline between class-II and class-III, no appropriate formula allowing computation of V_{ab} being available. Differences between the experimental bandwidth and the theoretical one expected from Eq. (2b) provide additional evidence for such cases, a much narrower bandwidth, in general, being typical of class-III compounds and limiting cases.[19] In those cases, the V_{ab} value was calculated using both formulas (Eqs. (2a) and (3)) and its real value can be considered to lie between those extremes. Typical parameters of the ICT bands and corresponding V_{ab} values are given in Table 17 for all our MV compounds.

Often for strongly coupled complexes, V_{ab} values follow the same trend as K_c

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[19] Some class-II exceptions are known, however; see for instance Ref. [324] and references cited therein.

values (Tables 12 and 13); however, especially for class-II MV complexes, V_{ab} is a much more accurate measure of electron delocalization [52]. Thus, as a representative parameter for electronic interaction, V_{ab} was preferred to K_c in the following discussions, the latter also often being sensitive to other factors, as stated earlier (see Section 2.1.2) [49,51,62].

4.3. Discussion of the results

We will now analyze more closely the experimental data given for our molecular wires models and discuss it in the light of other results published in the literature.

4.3.1. Symmetric polyyne-diyl-based wires [143,162]

The CV study of the symmetrical series of polyyne-based molecular wires (dppe)Cp*Fe(C≡C)$_n$FeCp*(dppe) ($n=2$: **27**; 3: **34**; 4: **33**) indicated the presence of a strong potential separation between the reversible redox waves ΔE^0 that decreased upon lengthening of the wire. Large comproportionation constants could be inferred for the corresponding MV complexes (Table 12). This was suggestive of good electronic communication through the polyynic spacers for all the wires and only a slight weakening was observed with increasing distance.

Whereas the C_6 (**34**) compound was characterized in mixture with the C_8 (**33**), both the C_4 (**27**) and the C_8 (**33**) compounds were studied as pure samples and their MV and dioxidized states were isolated. These salts were more strongly colored than the neutral compounds and proved to be thermally and air stable. The dioxidized compounds possessed two unpaired electrons on each iron(II) center, antiferromagnetically coupled through the bridge, as indicated by magnetism, and Mössbauer and ESR spectroscopies.

In solution, for the MV states the unpaired electron is delocalized all-over the molecule at the time scale of UV and IR spectroscopy. For complex **33**$^+$, in the solid at low temperature, Mössbauer spectroscopy indicated that localization of valence occurred. An averaged signal corresponding to the delocalized valence compound with two other signals in a 1:1 ratio, corresponding to the localized Fe^{II}–Fe^{III} valence compound, were observed. The ratio between the signals changed with temperature and the proportion of delocalized valence relative to localized valence increased when the sample was brought back to room temperature. Solid-state effects could be responsible for this behavior, but no crystals of **33**$^+$ could be grown in order to check this hypothesis. In solution, all compounds behaved as typical class-III complexes. Accordingly, the ICT transition in the NIR spectral region proved to be solvent independent in each case and theoretical bandwidth calculations using the Hush model did not fit the experimental data. Additional evidence for large electronic delocalization comes from the solid state crystallographic structure of the MV C_4 complex **27**$^+$ which is centrosymmetric (see Fig. 8). The slight disymmety observed in the ICT band shape of **27**$^+$ is suggestive of the occurrence of two overlapping transitions, as observed with other class-III complexes [62]. We considered it, however, as a single band in the calculations, since $\nu_{1/2}$ does not intervene in the calculations of V_{ab} for class-III complexes. The coupling constants V_{ab} were estimated to be 0.47 eV and 0.32 eV for the C_4 (**27**$^+$) and C_8 (**33**$^+$) wires respectively.

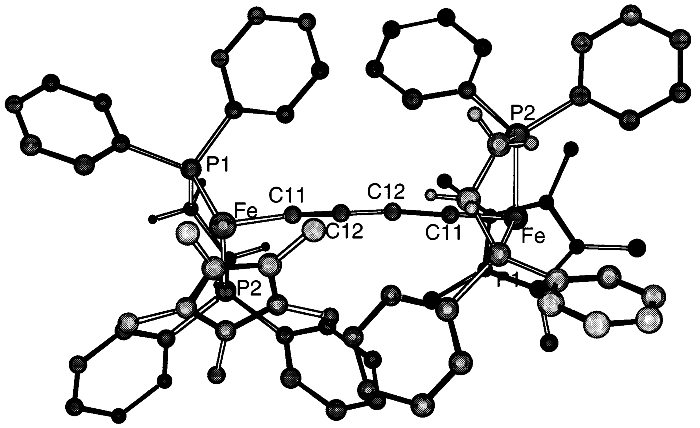

Fig. 8. Crystal structure of **27**$^{+}$. Selected bond distances (Å) and angles (deg):; Fe–P1, 2.238(2); Fe–P2, 2.206(2); Fe–C11, 1.830(8); Fe–$Cp^{*}_{(\mathrm{Centroid})}$, 1.766; Fe–$Fe_{(\mathrm{Intra})}$, 7.43; C11–C12, 1.236(9); C12–C12, 1.36(1); P1–Fe–P2, 84.65(8); P2–Fe–C11, 84.4(2); P1–Fe–C11, 93.4(2); Fe–C11–C12, 167.0(6); C11–C12–C12, 177(1).

The V_{ab} values for the C_4 and C_8 compounds **27**$^{+}$ and **33**$^{+}$ are close to theoretical values obtained by Sponsler for quite similar di-iron bis-carbonyl compounds, considering the fact that the diphosphine ligands should decrease the coupling parameter relative to carbonyl ligands [164]. Such high values are quite remarkable, especially in the case of the C_8 bridge, where the distance spans more than 12 Å (**33**). These compounds, therefore, constitute a promising class for the elaboration of molecular wires. This statement is in accordance with the results published by Gladysz and coworkers for very similar bis-rhenium complexes. Despite a decreased K_c (1.1×10^{9} *vs* 1.6×10^{12} respectively), they also report a class-III behavior for a butadiynediyl complex with V_{ab} values of 0.70 eV and 0.62 eV due to the observation of distinct ICT bands [62]. Increasing the length of the chain in the rhenium series produces a decrease of the potential separation between the two oxidation processes, which suggests a decrease of electronic communication between the metal centers, i.e. the rhenium termini behave increasingly as independent centers and the comproportionation constant of the corresponding MV decreases also [134]. Moreover, a loss of the reversibility is found for bridge lengths containing more than six carbon atoms, indicating that, above this chain-length, the MV complex is no longer sufficiently stable to be isolated (see Fig. 9). The decrease of K_c upon lengthening of the chain was predictable. The curve obtained when ΔE^{0} is plotted against the number of carbon atoms in the chains allows extrapolation of the maximum length of the all-carbon bridge where an observable potential separation will be observed, i.e. where the metal–metal interaction is sufficiently strong to stabilize the MV. This is of great concern for the elaboration of molecular wires or other nanoscopic devices. From semi-empirical calculations it seems that rhenium behaves differently from iron upon oxidation [62]. A cumulenic form is favored upon oxidation in rhenium(II/III) dimers, whereas the polyyne-like structure is maintained for

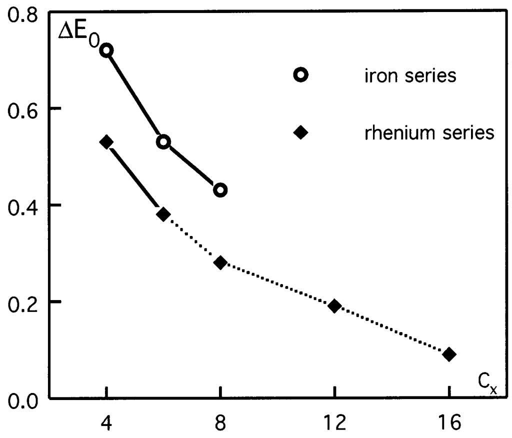

Fig. 9. Comparative evolution of the oxidation potential difference ΔE^0 upon chain increase in the di-iron (○) and di-rhenium series (◆). The dashed line indicate irreversible redox events in CV.

iron(II/III) homologues. This seems in agreement with the increased electronic delocalization observed for the butadiyne-diyl MV complexes in the rhenium series.

In our mind, the difference in electronic density distribution between the metal centers and the all-carbon bridge in both families of MV compounds explains their different respective stabilities (see Fig. 9). Whereas for similar bridge lengths the stability of the di-iron compounds is slightly greater, the magnitude of the metal–metal interaction is slightly decreased. These data suggest that a chain length above C_8 may still allow a strong electronic interaction to take place and could exhibit sufficient stability for isolation in the di-iron series. This is of course very interesting, and we are currently trying to synthesize higher homologues in order to verify this belief. Along the same lines, we are also studying analogues presenting a more electron-releasing diphosphine [318]. This constitutes another way to impart stability to the oxidized states and to influence the magnitude of the coupling parameter V_{ab} [62,146]. Finally, in order to better understand the specific role exerted by each metal on the butadiynediyl spacer, in collaboration with Gladysz's group, we are currently studying non-symmetric Fe–Re homologues [172].

4.3.2. Non-symmetric polyyne-diyl-based wires [144]

Considering now the disymmetrically functionalized butadiyne-diyl wires **37** and **38**, the electronic interaction between the metal centers was evidenced by a strong difference in the measured oxidation potentials of these compounds relative to the corresponding mononuclear butadiynyl complexes **35** and **36** (see Table 12). As mentioned previously, the reversibility of the first oxidation waves made the MV state a viable synthetic target for each complex. The redox wave corresponding to the dioxidized form was accessible as well, but not reversible. Confirmation of a strong polarization of the butadiynyl bridge was visible from polynuclear NMR data on the neutral compounds. The crystal structure of the neutral compound **38** indicated a strong steric shielding of the (dppe)Cp*Fe side of the molecule, compared with the other (see Fig. 10).

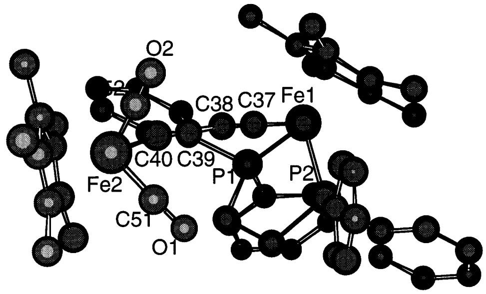

Fig. 10. Crystal structure of **38**. Selected bond distances (Å) and angles (deg): Fe1–P1, 2.190(3); Fe1–P2, 2.172(3); Fe1–C37, 1.886(9); Fe2–C51, 1.76(1); Fe2–C52, 1.73(1); Fe2–C40, 1.90(1); Fe1–$Cp^*_{(Centroid1)}$, 1.740(3); Fe2–$Cp^*_{(Centroid2)}$, 1.706(3); Fe1–$Fe2_{(Intra)}$, 7.57; C37–C38, 1.21(1); C38–C39, 1.36(1); C39–C40, 1.24(1); C51–O1, 1.13(1); C52–O2, 1.15(2); P1–Fe1–P2, 85.7(1); P2–Fe1–C37, 83.4(3); P1–Fe1–C37, 83.8(3); Fe1–C37–C38, 177.8(8); C51–Fe2–C52, 95.3(5); C52–Fe2–C40, 90.4(5); C51–Fe2–C40, 87.3(5); Fe2–C40–C39, 172.0(1); Fe2–C51–O1, 176(1); Fe2–C52–O2, 178.0(1); C37–C38–C39, 175(1); C40–C39–C38, 178.4(9).

Both MV compounds were isolated and studied. ESR and Mössbauer spectrometries were, each time, indicative of the localization of the unpaired electron on the electron-rich metal end, whereas IR data were suggestive of reversal of the polarity of the all-carbon bridge upon oxidation. These results were characteristic of class-II MV complexes. Spectrometric investigation of the intervalence transition was effected with complex $\mathbf{38}^+$ and indicated no clear solvatochromism. We had here a typical example of a limiting case between class-II and class-III for an MV complex and, accordingly, the electronic coupling parameter was bracketed using Eqs. (2a), (2b), (2c) and (3). Values comparable with those for other class-II/class-III complex ($\mathbf{29}^+$) were obtained (see Section 4.3.4). Regardless of the equations used, the values were each time smaller than those for the symmetric butadiyne-diyl complex $\mathbf{27}^+$, indicating that disruption of the symmetry results in decreased electronic communication, possibly because of the poorer energetic match between the MOs of the (dppe)Cp*Fe, $(CO)_2(C_5R_5)Fe$ (R = Me, Ph) and the butadiyne-diyl bridge.

Thus, disruption of the symmetry produced a polarized molecular wire. The decrease in the conduction is possibly due to localization of the valence resulting from the inequivalence of the two end-groups. Preliminary results with homologues possessing different metals, such as (dppe)Cp*Fe and $(NO)(PPh_3)Cp^*Re$, indicate that this behavior seems to be general, regardless of the nature of the metal involved [172]. An interesting feature in these compounds is the fact that oxidation results in an opposite polarization of the bridge. Such behavior could be interesting for elaboration of more sophisticated molecular devices, such as redox-switchable molecular rectifiers.[20]

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[20] Comparable or lower electronic coupling parameters were reported by Sato *et al.* for a family of non-symmetric dinuclear C_2-bridged class-II/III MV complexes containing the (dppe)Cp*Fe moiety linked to a ferrocene group ($V_{ab} = 2.3 \times 10^{-2}$–$0.9 \times 10^{-2}$ eV), even with a shorter (C_2) spacer [91]. This brings additional support to the idea that direct 6-linkage of the bridge to the metal has a dramatic influence on the electron delocalization properties.

4.3.3. *Alkyl-bis-ethynyl-based wires [302]*

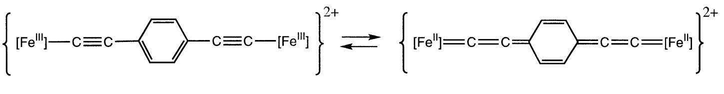
CV of compound **28** indicated that only a very weak electronic interaction was observable between the metal centers, since the two single-electron reversible redox waves were barely resolved (Table 12). Thus the comproportionation constant for the MV state was quite small (*ca* 35) and only the di-oxidized form may have been isolable with sufficient purity. As usually stated, introduction of a saturated spacer in the bridge results in strongly decreased electronic communication [76], and such a unit can be envisioned as being a typical insulator.

4.3.4. *Phenyl-bis-ethynyl-based wires [241,246,257]*

A strong reduction of solubility of neutral compounds was found for these complexes. This effect has been detrimental for most spectrometric analyses of the *para* complex **29** in solution. For the bis-ethynyl compounds **29** and **30**, CV revealed the occurrence of two separated reversible redox waves; however, ΔE^0 was smaller for the *meta*-substituted complex than for the para-substituted one. The comproportionation constants are much smaller than the previous ones found for pure polyynediyl bridges (see Table 12).

The MV and the doubly oxidized salts $\mathbf{29}^{++}$ and $\mathbf{30}^{++}$ were isolated and studied. As usual, both compounds were thermally and air-stable. From Evans measurements, and ESR and Mössbauer spectroscopies, the dioxidized complexes appeared to be bis-$\mathrm{Fe^{III}}$ compounds. Complex $\mathbf{29}^{++}$ showed an antiferromagnetic coupling, whereas $\mathbf{30}^{++}$ exhibited a ferromagnetic coupling. Unfortunately, the hyperfine coupling between iron and phosphorus could not be observed by ESR. Thus, although improbable from Mössbauer data, the participation of a cumulenic and diamagnetic $\mathrm{Fe^{II}/Fe^{II}}$ form to the description of the structure (see Scheme 21) still remains an open question for $\mathbf{29}^{++}$ [257].

For the MV complex $\mathbf{29}^{+}$ a trapped and a delocalized valence state were observed simultaneously in the solid state using Mössbauer spectrometry, as was observed for the octatetrayne-diyl complex $\mathbf{33}^{+}$. On an IR basis, however, the unpaired electron appeared to be delocalized in solution. Thus, localization of the charge was proposed to occur only in the solid state and the $\mathbf{29}^{+}$ MV compound was classified as a frontier class-II/class-III complex [257]. Unfortunately, no crystal structure could be obtained for the MV state of compound **29** and the cause of valence localization could not be ascertained. Here, apart from crystal polymorphism, the simultaneous presence of two bridge orientational conformers with respectively localized and delocalized electrons can be tentatively proposed as an alternative explanation [117]. The switching capability of the *para*-phenylene unit upon rotation has been mentioned previously (see Section 2.2.2). On the other hand, the MV complex $\mathbf{30}^{+}$ presented a clearly localized charge in solution at the Mössbauer time



Scheme 21.

scale (10^{-8} s). The crystal structure of this compound could be solved and revealed that this feature was still valid in the solid form, where localization of the hexafluorophosphate counter ion was clearly visible [246].

For **29**$^+$, from the intervalence band, electronic coupling parameters (V_{ab}) of 6.4×10^{-2} eV or 0.31 eV could be calculated depending on the formulas used (Eqs. (2a) and (3) respectively), whereas a V_{ab} value of 1.4×10^{-2} eV was obtained for **30**$^+$ (see Table 15). For **29**$^+$ and **30**$^+$ the ICT band displayed no marked solvatochromism, indicating that the outer-sphere contribution for the reorganization energy was possibly not determining in the electron transfer process. Although good for **29**$^+$, the match between experimental and theoretical data using the Hush formula (Eq. (2b)) was not satisfactory for **30**$^+$. In this case, this could be related to the large experimental error made in the determination of the bandwidth by deconvolution. In conclusion, introduction of a *para*- or *meta*-disubstituted phenylene unit in the wire caused a diminution in the electronic coupling parameter relative to the plain C_8 (**33**$^+$) bridge. This result was not completely unexpected, since the 1,4-phenylene unit was known to be less prone to delocalization than pure polyyne bridges (see Section 2.2.2). More interestingly, it appears that changes in the branching position produce changes in the electronic interaction, *para*-substitution giving the better results, in accordance with electrochemical data. Nevertheless, electronic communication is not interrupted in any case and both compounds can still be visualized as molecular wires incorporating a molecular resist, where the electron exchanges over a distance estimated to be 11.89 Å for **29**$^+$ and 10.25 Å for **30**$^+$ [246].

Electrochemical data reported for related *para*-phenylene diethynyl complexes indicates that the electronic interaction between metal centers is stronger in **29** with the (dppe)Cp*Fe^{II} end-group than with the Cl(depe)$_2$Fe^{II} end-group (ΔE = 0.2 V, $K_c = 2.4 \times 10^3$), where a high spin class-II mixed valence complex with axial symmetry was inferred [256]. It is, however, less important than when Cl(depe)$_2$Ru^{II} (ΔE = 0.36 V, $K_c = 1.3 \times 10^6$) are used as capping groups [98]. Unfortunately, no V_{ab} values have been reported for the MV state of these compounds. Those would constitute a much more accurate parameter for discussing electron delocalization. Nevertheless, this further illustrates that electronic interaction in such complexes is not solely related to the nature of the organic bridge, but that the terminal capping groups have a determining influence on it as well.

Better coupling in *para* than in *meta* positions is in accordance with results obtained by Richardson and Taube on related type *III-1* complexes (see Fig. 2). Indeed, such a pronounced diminution of the V_{ab} parameter for meta-branching *vs* *para*-branching had already been observed, concomitantly with a decrease in intensity ϵ for the ICT band in type *III-1* (see Fig. 2) MV compounds [53]. The occurrence of electronic communication "through" the ligand for meta-branching can seem somewhat surprising from very simple electronic considerations usually invoked for electron delocalization through a phenyl spacer (see Fig. 4). However, one has to realize that such "bonding isomers" which present in fact a re-hybridization of mainly ligand-located MOs with metal termini in the same oxidation state are very pictorial since, in the Lewis formulation, they are based on localized double bonds in an uncharged phenyl ring. Moreover experimental values of v_{ab} are obtained from a charged odd-electron containing species. A density functional calculation (DFC) analysis of these compounds revealed that the electronic structures of neutral **29** and **30** complexes were quite comparable regardless of the substitution pattern, especially concerning the HOMOs of the complexes where oxidation took place. A large energy gap separates the occupied and unoccupied orbitals in both complexes, the gap being slightly smaller for the *para*-substituted compound.(1.45 *vs* 1.66 eV). The respective energy ordering of the HOMOs correlates well with the experimental oxidation potentials found for these complexes. In accordance with related theoretical studies [163,165,166,258], the HOMO results mainly from a destabilizing 4-e^- two-orbitals interaction between the d_z electrons of the metal and out-of-plane π-electrons of the phenylethynyl spacer. Thus, the HOMO contains several nodes strongly localized on the iron centers and rather poorly located on the spacer, but actually spans over the whole molecule [241]. Taken together with our experimental results, these data indicate that the phenylethynyl spacer constitutes a suitable connector for electron conveyers in *ortho, meta* or *para* positions. Conceptually, a phenyl unit can be seen as an adjustable molecular resist[21], the value of which will depend on the branching positions.

Another interesting issue was to study the poly-branched trimetallic complex **31** realized from the same building blocks. The identity of the neutral complex was confirmed by X-ray crystallography (see Fig. 11) [241], and CV was indicative of an electrostatic interaction between the three metal centers of the same amplitude as that the reported for the previous compound **30** (see Table 13). Consequently, the two MV and the tris-oxidized states were isolated and studied.

The tris-oxidized complex featured three low spin Fe^{III} units as usual. Much more interesting with this latter complex, however, was the occurrence of a strong ferromagnetic coupling between the three low spin paramagnetic iron centers at such an intramolecular distance, as indicated by ESR data and solid state magnetic studies [325]. Such unusual behavior is currently being studied in our group.

The MV states behaved as class-II in the classification of Robin and Day complexes. As with $\mathbf{30}^+$, their NIR ICT absorption displayed no marked solvatochromism. Their electronic coupling parameters were determined using an approach already used by Launay and coworkers [326,327] for purely organic tri-centered mixed valence compounds and were quite similar to the previous ones (see Table 17). Here again the match between experiment and theory (see Eq. (2b)) was poor [246].

A DFC performed on the neutral form led to very similar conclusions as with dinuclear complexes: localization of the electron density is quite similar and the HOMO–LUMO gap is comparable (1.74 eV) [241]. Thus, as surmised with our compounds, the phenyl unit can be used as well as a multiple-connector allowing the linking of several molecular wires together, and permitting transmission of information through its core. Again, its high internal “resistance” relative to the

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[21] As pointed out by one referee, the term “resist” usually refers to an ohmic situation, which is obviously not the case at the molecular (quantified) level with these compounds. Although not very appropriate in a pure sense, we have chosen to maintain this appellation which makes sense in the present context.

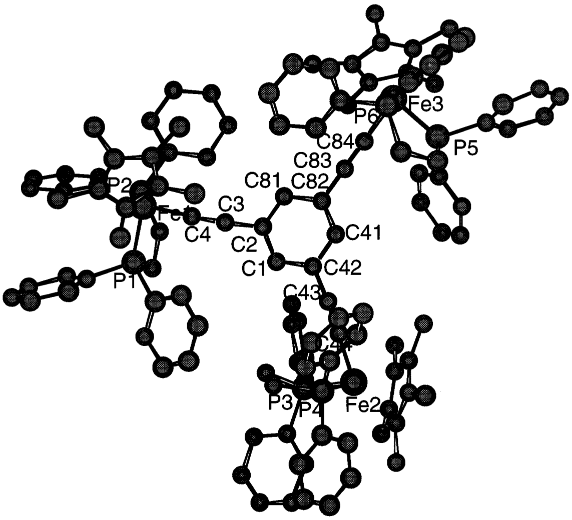

Fig. 11. Crystal structure of **31**. Selected bond distances (Å) and angles (deg); Fe1–P1, 2.178(3); Fe1–P2, 2.166(3); Fe2–P3, 2.161(3); Fe3–P4, 2.168(3); Fe3–P5, 2.181(4); Fe3–P6, 2.170(3); Fe1–$Cp^*_{(Centroid1)}$, 1.750; Fe2–$Cp^*_{(Centroid2)}$, 1.742; Fe3–$Cp^*_{(Centroid3)}$, 1.738; Fe1–C4, 1.90(1); Fe2–C44, 1.89(1); Fe3–C84, 1.92(1); Fe1–$Fe2_{(Intra)}$, 10.05; Fe1–$Fe3_{(Intra)}$, 10.48; Fe2–$Fe3_{(Intra)}$, 10.32; C3–C4, 1.24(2); C43–C44, 1.23(2); C83–C84, 1.21(1); C1–C2, 1.38; C2–C81, 1.39(1); C81–C82,1.41(1); C41–C82, 1.38(2); C41–C42, 1.39(1); C1–C2, 1.41(1); P1–Fe1–P2, 84.7(1); P3–Fe2–P4, 85.7(1); P5–Fe3–P6, 85.9(1); P1–Fe1–C4, 84.8(3); P2–Fe1–C4, 84.8(3); P3–Fe2–C44, 83.7(2); P4–Fe2–C44, 83.5(3); P5–Fe3–C84, 84.1(4); P6–Fe3–C84, 83.7(4); Fe1–C4–C3, 178(1); Fe2–C44–C43, 177.4(9); Fe3–C84–C83, 178.4(8); C4–C3–C2, 173(1); C4–C43–C42, 177.0(1); C84–C83–C22, 175.5(9).

alkyne units of the bridge results in diminished electronic conduction. Comparison of our results with another 1,3,5-phenyl-tris-ethynyl trimetallic complex recently reported and bearing three ferrocenyl units is interesting [328]. No apparent interaction between the iron centers was visible from the CV spectrum of that complex. This can be attributed to the absence of a direct σ-bond between the bridge core and the metals.

4.3.5. Butadiene-diyl-based wires [179]

Complex **41** exhibited two reversible well-separated 1-e^- waves in CV indicative of a strong electronic interaction of the metal sites through the bridge (Table 14). These values are comparable with the values reported by Sponsler and coworkers for quite similar di-iron compounds [63]. The di-oxidized and mono-oxidized compounds could be isolated and were studied as usual. As expected, ΔE is much larger than values reported for type *III-1* (Fig. 2) dipyridylbutadiene-bridged complexes [48,71].

The dioxidized air-stable compound $\mathbf{41}^{++}$ possessed two low spin Fe^{III} centers, and an analogue with the (CO)(PMe_3)Cp*Fe capping groups in place of (dppe)Cp*Fe could even be characterized by X-ray diffraction [179,329].

The MV complex $\mathbf{41}^{+}$ belonged to the class-III of Robin and Day. Its ESR solution spectrum presented the typical features of a delocalized radical coupled to four equivalent phosphorus atoms, whereas its Mössbauer spectrum was also typical of a delocalized electron, since only an average signal corresponding to iron centers in a 2.5 oxidation state could be observed. From the ICT band located in the NIR range, the calculated coupling parameter amounted to 0.54 eV for this compound (see Table 17) [179]. Although the comproportionation constant K_c was lower than for the corresponding MV complex with a butadiynyl bridge (**27**$^+$), the V_{ab} value was higher than for **27**$^+$. This further illustrates the inadequacy of the sole redox $K_c/\Delta E^0$ parameters for discussing electron delocalization in these compounds (see Section 2.1.2).

The V_{ab} value obtained for **41**$^+$ is quite close to the experimental and theoretical values reported by Sponsler for the related class-III [(dppm)CpFe(CH)$_4$ FeCp(dppm)]$^+$ MV complex (0.48 eV). Thus, the change in ancillary ligands on the metal centers (Cp* *vs* Cp and dppm *vs* dppe) as well as the presence of methoxy groups on the bridge seem only to have a minor influence upon electron delocalization in butadienediyl complexes [164].[22] Moreover, it seems that electron delocaliza-

Table 17
ICT parameters for the MV compounds[a]

Compound	Class[b]	λ_{max} (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	E_{op} (cm^{-1})	$R^c_{MM'}$ (Å)	$\nu_{1/2\ exp}$ [ν_{theo}] (cm^{-1})	V_{ab} (eV)	Refs.
27$^+$	III	1326	11700	7541	7.4	3250[d] [4173]	0.47 (1.9×10^{-1})[e]	[162]
33$^+$	III	1958	31000	5107	12.6	1300 [3434]	0.32 (1.0×10^{-1})[e]	[143,309]
38$^+$	II–III	1600	360	6250	7.6	1762 [3799]	0.38 (2.1×10^{-2})[e]	[144]
29$^+$	II–III	2016	5940	4960	11.9	3017 [3385]	0.31 (6.4×10^{-2})[e]	[257,302]
30$^+$	II	1833	320	5455	10.3	1670 [3550]	1.4×10^{-2} [e]	[246]
31$^+$	II	1830	583	5464	10.3	2130 [3553]	1.5×10^{-2} [f]	[246]
31^{++}	II	1836	407	6446	10.3	1733 [3547]	1.1×10^{-2} [f]	[246]
41$^+$	III	1150	3350	8696	7.6[g]	3996 [4482]	0.54 (1.1×10^{-1})[e]	[179]

[a] Measurement effected in dichloromethane at 25 °C.

[b] Following Robin and Day classification [46].

[c] Through-space M–M value obtained from RX structures or molecular modeling.

[d] Overestimated experimental value due to assymmetry in the band (possibly due to two overlapping ICT bands.

[e] Value calculated using Hush formula (Eq. (2a)).

[f] Preliminary values calculated using modified Hush formulas for trimetallic compound (see text).

[g] Through-bond distance calculated from RX data.

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[22] As mentioned, the presence of the two methoxy groups on the butadiendiyl spacer does not apparently affect drastically the conductivity of the bridge. However, this functional group has an influence in the localization of the HOMO of the complex, as indicated by a Hückel molecular diagram [179]. Indeed, the methoxy bridge induces a more extensive mixing of the ligand-based orbitals in the HOMO, and, depending on the nature of the iron complex chosen as a capping group, oxidation can also take place on the organic bridge. For instance, results from our group using the (CO)(PMe$_3$)Cp*Fe^{II} end-group indicate that the MV complex has its odd electron mainly located on the bridge, whereas the dioxidized form appears to be a bis-iron(II) carbene complex. Thus, with such a bridge, the localization of the electron density in the complex may change importantly, depending on the ligands surrounding the metals [179,329].

tion may be higher for complexes incorporating this type of bridge than for butadiynediyl spacers. This idea finds additional support in many independent studies performed on different type *III-1* (see Fig. 2) organometallic MV compounds [41]. Consequently, such compounds may also constitute interesting molecules for the development of efficient molecular wires. Investigations with longer homologues are now desirable, since Sponsler's study indicates that octatetraenylidene bridges should also present high V_{ab} coupling constants (with approximately 10% decrease) [164]. Non-symmetrical substitution is another point of interest to investigate in order to determine the effect of bridge polarization on these molecules. Regarding these questions, complex **42** constitutes a particularly interesting starting compound for access to such molecules. This task may, however, be more difficult than with rigid bridges owing to the possible interference of conformers or isomers of these compounds. Thus, very selective homocoupling reactions will have to be devised in the first place.

5. Conclusions and perspectives

At this point, we hope to have convinced the reader that type *III-3* organometallic dinuclear molecules possessing electroactive end-groups constitute very interesting models for the elaboration and study of effective molecular wires. These organometallics possess promising potential for the development of new nanoscopic devices in molecular electronics. Linking directly the spacer to the metal by a σ metal-carbon bond seems to promote electronic coupling in comparison with more conventional dative coordination at least with iron. Curiously, apart from ferrocene, organoiron building blocks have only been seldom used for the elaboration of electronic devices and especially for molecular wire construction. However, iron in itself is attractive for the study of such molecules since it constitutes a convenient Mössbauer probe and useful information on the electronic environment of the metal center is thereby available. Additionally, it is also a cheap starting material which can make quite strong metal–carbon bonds compared with other transition metals. In that respect, the (dppe)Cp*Fe fragment represents a particularly interesting capping group. Its interest rests mainly in its redox properties, since such a unit presents the lowest oxidation potentials for molecular wire termini reported to date.

Our studies with organometallic type *III-3* molecular wire models incorporating this unit prove to be complementary with studies effected by other groups, with other metals on similar organic bridges. They indicate that polyynyl bridges may give rise to very interesting molecular wires using such an organoiron end-group. For now, we could realize symmetric wires where electron delocalization occurs through the bridge over a distance of approximately 15 Å, but longer wires should constitute viable synthetic targets as well. Such a belief rests on the statement that the electronic density after oxidation is still located mainly on the metal center, which is efficiently protected by the bulk of the ligands in (dppe)Cp*Fe. This may be the clue for achieving the realization of stable wires upon lengthening of the all-carbon chain and current work in our laboratory is actually underway to probe this hypothesis.

Evidence for the strong influence of the nature of the metallic capping sites on the properties of the bridge also comes from other compounds studied in our group. Thus, upon differentiation of both iron ends by using different ligand environments, polarized wires where the odd electron is located mainly on the electron-rich site of the molecule were isolated. Such compounds constitute exciting models of electronic rectifiers, and work is still in progress to understand the effect of the nature of the metal on the properties of such polyyne-diyl bridges.

The influence of the nature of the organic bridge was also tested. Incorporation of various units in the core of a symmetric polyyne bridge was achieved and the new di-iron complexes were studied. In accord with data gathered from other organic or organometallic architectures, a linear alkyl fragment inhibits quite completely the electronic interaction and thereby can be seen as an insulating device, whereas a phenylene group can be seen as a resistor since the new wire proves to have diminished electronic delocalization in its MV state. We could also establish that the "resistive value" of such a unit will be dependent on the way branching is effected, para-substitution leading to the lowest resistive value. Finally and more interestingly, a model of a polybranched wire could be realized, always by use of a phenyl group. This illustrates the potential of the phenyl unit to be used as a connecting device. In particular, this property may be useful for establishing derivative circuits on a main molecular wire in more sophisticated molecular devices. Moreover, this unit has proven to be suited for transmission of antiferro- and ferromagnetic coupling between remote (dppe)Cp*Fe^{III} moieties, uncovering here another fascinating interest for use of such building blocks in molecular electronics. Thus, we were able to isolate the first trinuclear organometallic compound where intramolecular ferromagnetic coupling was evidenced.

Finally, we studied some models containing butadienediyl bridges. In line with what is often observed for purely organic bridges, the polyene spacer appears to be more "conducting" than the polyyne bridge in similar model compounds. However, we would like to recall that in order to design efficient molecular wires, conductivity alone cannot be the only factor to take into consideration for a given linker. Its relative rigidity, insuring a constant geometry of the molecular architecture, might also be an important issue. In this respect, polyynyl bridges are still important models for future elaboration of molecular devices despite apparent decreased conduction properties.

Clearly, incorporation of the (dppe)Cp*Fe or, more generally, (P_2)Cp*Fe moieties in various unsaturated organic architectures will lead to the realization of a wealth of interesting molecules for molecular electronics. Further development of the synthetic chemistry allowing selective and easy introduction of these organoiron units in various organic environments is a main subject of concern in our group. Currently, we continue to implement the available set of reactions allowing access to new exciting molecules bearing these synthons. Obvious future synthetic targets for us are analogous molecules to those already made, but possessing an organic spacer of increased size. This is in order to study the evolution of their electronic properties and stability, but also to make available molecules best suited for macroscopic interfacing.

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Appendix 1: Relevant publications published during the reviewing process

In this section are included some recent references related to the topics discussed in this review that appeared in the literature during the reviewing process. Those references have not been discussed in the text, but their connection to this work is briefly outlined in the following. Whenever possible, these data have been integrated in the tables.

Synthesis and characterization of type *III-3* additional dinuclear complexes:

- **A1** Fe complexes [141];
- **A1** Ir complexes [151];
- **C2** complexes; convenient synthetic bridge precursors [331];
- **C3** Pd and Pt complexes and corresponding II/IV MV states [232];
- **D4**/**Ar4** Pt complexes [265].

General data about bridge conductivity and electron transfer are as follows.

- Discussion of the validity of the "$E_{op}/2 = V_{ab}$" formula for MV class-III complexes. Comparison of attenuation factors between organic and metal-containing MV depending on the bridge structure [77].
- Discussion of the topological effects on the ICT transition intensity through differently substituted *meta*-phenyl linkers [332].
- Attenuation factor for electron transfer through "$-[C{\equiv}C(C_6H_4)]_n-$" bridges [70].
- Attempt to investigate the conductivity of a single one-dimensional rigid molecule [333].
- Synthesis and study of organic wire models; thienylenevinylene oligomers [334].
- DFC on the metal–alkyne bond for selected transition metal complexes [335].

Appendix 2:

Tables 18 and 19 contain selected data for C_2 complexes.

Table 18
Selected examples of ethyne-diyl complexes (structural type **A1**, $x=1$)

Entry	$[M_1]$	$[M_2]$	RX: global charge of the complex	Obs./isol. redox. st.[a]	Synthesis type	Refs.
A1	$(CO)_3CpW^{II}$	$(CO)_3CpW^{II}$	yes: 0	1/1	*S4*	[126]
A2	$(CO)_5Mn^{I}$	$(CO)_5Mn^{I}$	yes: 0	1/1	*S0*	[336]
A3	$(CO)_5Re^{I}$	$(CO)_5Re^{I}$	yes: 0	1/1	*S1*	[337]
A4	$(CO)_2Cp^*Fe^{II}$	$(CO)_2Cp^*Fe^{II}$	yes: 0	1/1	*S1*	[128,141,338]
A5	$(CO)_2CpRu^{II}$	$(CO)_2CpRu^{II}$	yes: 0	1/1	*S2*	[339]
A6	$Cl(PMe_3)_2Pd^{II}$	$Cl(PMe_3)_2Pd^{II}$	no	1/1	*S0*	[340]
A7	$Cl(PMe_3)_2Pt^{II}$	$Cl(PMe_3)_2Pt^{II}$	yes: 0	1/1	*S0*	[340]
A8	$Cl(PPh_3)_2Pt^{II}$	$Cl(PPh_3)_2Pt^{II}$	yes: 0	1/1	*S1*	[341]
A9	$Cl(PBu_3)_2Pt^{II}$	$Cl(PBu_3)_2Pt^{II}$	no	1/1	*S3*	[341]
A10	$Cl(PBu_3)_2Pt^{II}$	$[(PBu_3)_3Pt^{II}]^+$	no	1/1	*S3*	[341]
A11	$(NO)(PPh_3)Cp^*Re^{II}$	$Cl(PPh_3)_2Pd^{II}$	yes: 0	1/1	*S1′*	[135]
A12	$(PhCCPh)(CO)CpW^{II}$	$(PMe_3)_2CpRu^{II}$	yes: 0	1/1	*S2*	[342]
A13	$(PhCCPh)(CO)CpW^{II}$	$[P(OMe)_3]_2CpRu^{II}$	no	1/1	*S2*	[342]
A14	$(PhCCPh)(CO)CpW^{II}$	$(PMe_3)_2CpFe^{II}$	no	1/1	*S2*	[342]
A15	$(PhCCPh)(CO)CpW^{II}$	$[P(OMe)_3]_2CpFe^{II}$	no	1/1	*S2*	[342]
A16	$(PhCCPh)(CO)CpW^{II}$	$(dppp)CpFe^{II}$	no	1/1	*S2*	[342]
A17	$(dppe)Cp^*Fe^{II}$	$ClCp_2Zr^{II}$	yes: 0	1/1	*S1′*	[343]
A18	$(CO)_2CpRu^{II}$	$ClCp_2Zr^{II}$	yes: 0	1/1	*S1′*	[203]

[a] Observed and isolated redox states of the compound (without skeletal changes).

Table 19
Selected examples of ethene-diyl or biscarbene complexes (structural type **B1**, $x=1$ or **D5**, $x=y=0$)

Entry	Structural type	$[M_1]$	$[M_2]$	/R/R′ or G (R = R′ most often)	RX: global charge of the complex	Obs./Isol Redox. St.[a]	Synthesis type	Refs.
A1	**B1**	$Cl(C_5H_4Me)_2Zr^{II}$	$Cl(C_5H_4Me)_2Zr^{II}$	H/Me	yes: 0	1/1	*S1′*	[344]
A2	**B1**	$(PMe_3)_2CpRu^{II}$	$(CO)_2CpRu^{II}$	Me	yes: 0	1/1	*S1′*	[202]
A3	**B1**	$K_3[(CN)_5Co^{III}]$	$K_3[(CN)_5Co^{III}]$	C(O)OMe	no	1/1	*S0*	[345–347]
A4	**B1**	$(PPN)_3[(CN)_5Co^{III}]$	$(PPN)_3[(CN)_5Co^{III}]$	C(O)OMe	yes: 6	1/1	*S3*	[347]
A5	**B1**	$(OEP)Rh^{II}$ [b]	$(OEP)Rh^{II}$ [b]	H, Ph	no	1/1	*S0*	[348]
A6	**B1**	$(PMe_3)Au^{I}$	$(PMe_3)Au^{I}$	CF_3	yes: 0	1/1	*S0*	[349]
A7	**B1**	$(PPh_3)Au^{I}$	$(PPh_3)Au^{I}$	CF_3, Me	no	1/1	*S0*	[200,201,350]
A8	**B1**	$(PMe_3)Au^{I}$	$(PMe_3)(Me)_2Au^{III}$	CF_3	no	1/1	*S0*	[351]
A9	**B1**	$(PMe_2Ph)Au^{I}$	$(PMe_2Ph)(Me)_2Au^{III}$	CF_3	no	1/1	*S0*	[351]
A10	**B1**	$(PMePh_2)Au^{I}$	$(PMePh_2)(Me)_2Au^{III}$	CF_3	no	1/1	*S0*	[351]
A11	**B1**	$(PMePh_2)Au^{I}$	$(PMePh_2)(Et)_2Au^{III}$	CF_3	no	1/1	*S0*	[351]
A12	**B1**	$(PMe_2Ph)Au^{I}$	$(PMe_2Ph)Au^{I}$	CF_3	no	1/1	*S0*	[349]
A13	**B1**	$(PPh_3)(CO)CpFe^{II}$	$(CO)_5Re^{I}$	Me	no	1/1	*S1′*	[202]
A14	**B1**	$[P(OPh)_3](CO)CpFe^{II}$	$(CO)_5Re^{I}$	Me, Ph	no	1/1	*S1′*	[202]
A15	**B1**	$(PPh_3)(CO)CpFe^{II}$	$(CO)_2CpRu^{II}$	Me	no	1/1	*S1′*	[202]
A16	**B1**	$(CO)_2CpRu^{II}$	$ClCp_2Zr^{II}$	H	yes: 0	1/1	*S3*	[203]
A17	**B1**	$(PMe_3)_2CpRu^{II}$	$(CO)_5Mn^{I}$	CO_2Me	no	1/1	*S1′*	[202]
A18	**B1**	$(PMe_3)_2CpRu^{II}$	$(CO)_5Re^{I}$	CO_2Me	no	1/1	*S1′*	[202]
A19	**D5**	$(TMP)Ru^{II}$ [c]	$(TMP)Ru^{II}$ [c]	H	no	1/1	*S0*	[285]
A20	**D5**	$(CO)_5Cr^{0}$	$(CO)_5Cr^{0}$	NEt_2	yes: 0	1/1	*S2*	[284]

[a] Observed and isolated redox states of the compound (without skeletal changes).

[b] OEP = octaethylporphyrin.

[c] TMP = tetramesitylporphyrin.

References

[1] R.M. Baum, C&EN, July 30, 1997, p. 39.
[2] R. Dagani, C&EN, January 22, 1996, p. 22.
[3] J.-P. Launay, L'Actualité Chimique, July-August, 1994 p. 37.
[4] J.-P. Launay, C. Joachim, A. Gourdon, J. Bonvoisin, C. Coudret, Sci. Chim. Lett. Dep. Sci. C.N.R.S. 54 (1995) 1.
[5] D. Astruc, in: Electron Transfer and Radical Processes in Transition-Metal Chemistry, VCH, 1995, p. 283.
[6] J.M. Lehn, in: Supramolecular Chemistry—Concepts and Perspectives, VCH, 1995, pp. 106, 111, 195.
[7] V. Mujica, M. Kemp, M.A. Ratner, J. Chem. Phys. 101 (1994) 6856.
[8] M.D. Ward, Chem. Ind. 15 (1996) 568.
[9] C. Joachim, New. J. Chem. 15 (1991) 223.
[10] A. Aviram, M.A. Ratner, Chem. Phys. lett. 29 (1974) 277.
[11] J.K. Young, J.C. Nelson, J.S. Moore, J. Am. Chem. Soc. 116 (1994) 10841.
[12] J.S. Schumm, D.L. Pearson, J.M. Tour, Angew. Chem. Int. Ed. Engl. 33 (1994) 1360.
[13] J.M. Tour, Chem. Rev. 96 (1996) 527.
[14] A. Fehn, O. Briel, W. Beck, Chem. Ber. Rcl. 130 (1997) 1467.
[15] A. Hradsky, B. Bildstein, N. Schuler, H. Schottenberger, P. Jaitner, K.-H. Ongania, K. Wurst, J.-P. Launay, Organometallics 16 (1997) 392.
[16] R.P. Hsung, C.E.D. Chidsey, L.R. Sita, Organometallics 14 (1995) 4808.
[17] I. Manners, Angew. Chem. Int. Ed. Engl. 35 (1996) 1603.
[18] A. Bolognesi, M. Catellani, S. Destri, in: Sir G. Allen, J.C. Bevington (Eds.), Comprehensive Polymer Science, vol. 4, Pergamon Press, Oxford, 1989, p. 143.
[19] M. Soga, T. Nakagawa, K. Ogawa, Jpn. J. Appl. Phys. Part 1: 35 (1996) 1908.
[20] D. Bloor, in: Sir G. Allen, J.C. Bevington (Eds.), Comprehensive Polymer Science, vol. 2, Pergamon Press, Oxford, 1989, p. 687.
[21] M.P. Samanta, W. Tian, S. Data, Phys. Rev. B 53 (1996) R7626.
[22] R.J. Crutchley, Adv. Inorg. Chem. 41 (1994) 273.
[23] A. Harriman, R. Ziessel, Chem. Commun. (1996) 1707.
[24] J.-P. Sauvage, J.-P. Colin, J.-C. Chambron, S. Guillerez, C. Coudret, Chem. Rev. 94 (1994) 993.
[25] R.W. Wagner, J.S. Lindsey, J. Am. Chem. Soc. 116 (1994) 9759.
[26] A.C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn, B. Marczincke, J. Phys. Chem. 98 (1994) 7798.
[27] N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.
[28] V. Mujica, M. Kemp, M.A. Ratner, J. Chem. Phys. 101 (1994) 6849.
[29] V. Mujica, M. Kemp, M.A. Ratner, J. Chem. Phys. 101 (1994) 5172.
[30] C. Joachim, J.F. Vinuesa, Europhys. Lett. 33 (1996) 635.
[31] M. Kemp, A. Roitberg, V. Mujica, T. Wanta, M.A. Ratner, J. Phys. Chem. 100 (1995) 8349.
[32] C. Joachim, J.-P. Launay, S. Woitellier, Chem. Phys. 147 (1990) 131.
[33] C. Joachim, J.K. Gimzewski, Europhys. Lett. 30 (1995) 409.
[34] C. Joachim, J.K. Gimzewski, R.R. Schlitter, C. Chavy, Phys. Rev. Lett. 74 (1995) 2102.
[35] F.-R.F. Fan, J. Kwak, A.J. Bard, J. Am. Chem. Soc. 118 (1996) 9669.
[36] F.-R. Fan, A.J. Bard, Science 277 (1997) 1791.
[37] L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones, II, D.L. Allara, J.M. Tour, P.S. Weiss, Science 271 (1996) 1705.
[38] J. Liu, H. Dai, J.H. Hafner, D.T. Colbert, R.E. Smalley, S.J. Tans, C. Deekker, Nature 385 (1997) 780.
[39] P.G. Collins, A. Zettl, H. Bando, A. Thess, R.E. Smalley, Science 278 (1997) 100.
[40] S.-I. Kugimiya, T. Lazrak, M. Blanchard-Desce, J.M. Lehn, J. Chem. Soc. Chem. Commun. (1991) 1179.
[41] M.D. Ward, Chem. Soc. Rev. 24 (1995) 121.
[42] J.-P. Launay, C. Joachim, J. Phys. Chem. 85 (1988) 1135.

[43] S.F. Nelsen, R.F. Ismagilov, D.R. Powell, J. Am. Chem. Soc. 119 (1997) 10213.
[44] C. Creutz, H. Taube, J. Am. Chem. Soc. 91 (1969) 3988.
[45] N.S. Hush, Prog. Inorg. Chem. 8 (1967) 391.
[46] M.B. Robin, P. Day, Adv. Inorg. Chem. Radiochem. (1967) 247.
[47] N.S. Hush, Coord. Chem. Rev. 64 (1985) 135.
[48] A.-C. Ribou, J.-P. Launay, K. Takahashi, T. Nihara, S. Tarutani, C.W. Spangler, Inorg. Chem. 33 (1994) 1325.
[49] J.E. Sutton, P.M. Sutton, H. Taube, Inorg. Chem. 18 (1979) 1017.
[50] Y. Hoshino, T. Suzuki, H. Umeda, Inorg. Chim. Acta 245 (1996) 87.
[51] J.E. Sutton, H. Taube, Inorg. Chem. 20 (1981) 3125.
[52] K.A. Goldsby, T.J. Meyer, Inorg. Chem. 23 (1984) 3002.
[53] D.E. Richardson, H. Taube, J. Am. Chem. Soc. 105 (1983) 40.
[54] D. Osella, L. Milone, C. Nervi, M. Ravera, J. Organomet. Chem. 488 (1995) 1.
[55] K.Y. Wong, P.N. Schatz, Prog. Inorg. Chem. 28 (1981) 369.
[56] S.B. Piepho, E.R. Krausz, P.N. Schatz, J. Am. Chem. Soc. 100 (1978) 2996.
[57] J.R. Reimers, N.S. Hush, Inorg. Chem. 29 (1990) 3686.
[58] B. Mayoh, P. Day, J. Am. Chem. Soc. 94 (1972) 2885.
[59] C. Creutz, Prog. Inorg. Chem. 30 (1983) 1.
[60] R. de la Rosa, P.J. Chang, F. Salaymeh, J.C. Curtis, Inorg. Chem. 24 (1985) 4229.
[61] Y. Dong, J.T. Hupp, Inorg. Chem. 31 (1992) 3170.
[62] M. Brady, W. Weng, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Böhme, J.A. Gladysz, J. Am. Chem. Soc. 119 (1997) 775.
[63] B.A. Etzenhouser, Q. Chen, M.B. Sponsler, Organometallics 13 (1994) 4176.
[64] L.O. Spreer, A. Li, D.B. Mac Queen, C.B. Allan, J.W. Otvos, M. Calvin, R.B. Frankel, G.C. Papaefthymiou, Inorg. Chem. 33 (1994) 1753.
[65] L.O. Spreer, C.B. Allan, J. Am. Chem. Soc. 116 (1994) 2187.
[66] J.M. Manriquez, M.D. Ward, W.M. Reiff, J.C. Calabrese, N.L. Jones, P.J. Caroll, E.E. Bunel, J.S. Miller, J. Am. Chem. Soc. 117 (1995) 6182.
[67] M. Beley, S. Chodorowski-Kimmes, J.-P. Colin, P. Lainé, J.-P. Launay, J.-P. Sauvage, Angew. Chem. Int. Ed. Engl. 33 (1994) 1775.
[68] T.J. Meyer, Acc. Chem. Res. 11 (1978) 94.
[69] G.L. Closs, J.R. Miller, Science 240 (1988) 440.
[70] S.B. Sachs, S.P. Dudek, R.P. Hsung, L.R. Sita, J.F. Smalley, M.D. Newton, S.W. Feldberg, C.E.D. Chidsey, J. Am. Chem. Soc. 119 (1997) 10563.
[71] A.C. Ribou, J.P. Launay, M.L. Sachtleben, H. Li, C.W. Spangler, Inorg. Chem. 35 (1996) 3735.
[72] F. Barigelletti, L. Flamigni, J.-P. Collin, J.-P. Sauvage, Chem. Commun. (1997) 333.
[73] V. Grosshenny, A. Harriman, R. Ziessel, Angew. Chem. Int. Ed. Engl. 34 (1995) 1100.
[74] R. Ziessel, A. Harriman, Sci. Chim. Lett. Dep. Sci. C.N.R.S. 55 (1996) 11.
[75] V. Grosshenny, A. Harriman, M. Hissler, R. Ziessel, Platinum Met. Rev. 40 (1996) 26.
[76] A.C. Benniston, A. Harriman, V. Grosshenny, R. Ziessel, New J. Chem. 21 (1997) 405.
[77] S.F. Nelsen, H.Q. Tran, M.A. Nagy, J. Am. Chem. Soc. 120 (1998) 298.
[78] W.M. Laidlaw, R.G. Denning, J. Chem. Soc. Dalton Trans. (1994) 1987.
[79] L. Karki, J.T. Hupp, J. Am. Chem. Soc. 119 (1997) 4070.
[80] E.M. Kober, K.A. Goldsby, D.N.S. Narayana, T.J. Meyer, J. Am. Chem. Soc. 105 (1983) 4303.
[81] V. Marvaud, J.-P. Launay, C. Joachim, Chem. Phys. 177 (1993) 23.
[82] P.A. Lay, R.H. Magnuson, H. Taube, Inorg. Chem. 27 (1988) 2364.
[83] C.G. Atwood, W.E. Geiger, J. Am. Chem. Soc. 116 (1994) 10849.
[84] J.M. Williams, Inorg. Synth. 21 (1989) 141.
[85] J.S. Miller, in: Extended Linear Chain Compounds, vol. 1, Plenum Press, 1981.
[86] J.M. Williams, Inorg. Synth. 20 (1980) 1.
[87] J.M. Williams, Inorg. Synth. 19 (1979) 1.
[88] M. Sato, H. Shintate, Y. Kawata, M. Sekino, M. Katada, S. Kawata, Organometallics 13 (1994) 1956.
[89] M. Sato, E. Mogi, Organometallics 14 (1995) 3157.

[90] M. Sato, E. Mogi, M. Katada, Organometallics 14 (1995) 4837.

[91] M. Sato, Y. Hayashi, S. Kumakura, N. Shimizu, M. Katada, S. Kawata, Organometallics 15 (1996) 721.

[92] C.F. van Nostrum, R.J.M. Nolte, Chem. Commun. (1996) 2395.

[93] M.J. Irwin, G. Jia, N.C. Payne, R.J. Puddephatt, Organometallics 15 (1996) 57.

[94] M.S. Khan, S.J. Davies, A.K. Kakkar, D.J. Schwartz, B. Lin, F.G. Johnson, J. Lewis, J. Organomet. Chem. 424 (1992) 87.

[95] M.H. Chisholm, Angew. Chem. Int. Ed. Engl. 30 (1991) 673.

[96] N. Hagihara, K. Sonogashira, S. Takahashi, Adv. Polym. Sci. 41 (1981) 149.

[97] C. Hartbaum, H. Fischer, Chem. Ber. Rcl. 130 (1997) 1163.

[98] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184.

[99] N.D. Jones, M.O. Wolf, Organometallics 16 (1997) 1352.

[100] M.I. Bruce, M. Ke, P.J. Low, J. Chem. Soc. Chem. Commun (1996) 2405.

[101] K. Wärnmark, J.A. Thomas, O. Heyke, J.-M. Lehn, Chem. Commun. (1996) 701.

[102] N.C. Brown, G.B. Carpenter, N.G. Connelly, J.C. Crossley, A. Martin, A.G. Orpen, A.L. Rieger, P.H. Rieger, G.H. Worth, J. Chem. Soc. Dalton Trans. (1996) 3977.

[103] J. Hock, A.M.W.C. Thompson, J.A. Mac Cleverty, M.D. Ward, J. Chem. Soc. Dalton Trans. (1996) 4257.

[104] V.A. Ung, D.A. Bardwell, J.C. Jeffery, J.P. Maher, J.A. Mac Cleverty, M.D. Ward, A. Williamson, Inorg. Chem. 35 (1996) 5290.

[105] A.R. Rezvani, C.E.B. Evans, R.J. Crutchley, Inorg. Chem. 34 (1995) 4600.

[106] W. Beck, B. Niemer, M. Wieser, Angew. Chem. Int. Ed. Engl. 32 (1993) 923.

[107] J.N. Onuchic, D.N. Beratan, J. Am. Chem. Soc. 109 (1987) 6711.

[108] K. Otha, G.L. Kloss, K. Morokuma, N.J. Green, J. Am. Chem. Soc. 108 (1986) 1319.

[109] S. Larsson, J. Am. Chem. Soc. 103 (1981) 4034.

[110] J.A. Thomas, C.J. Jones, T.A. Hamor, J.A. Mac Cleverty, F. Mabbs, D. Collison, C. Harding, Mol. Cryst. Liq. Cryst. 234 (1993) 103.

[111] J. Roncali, Chem. Rev. 97 (1997) 173.

[112] T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, Macromolecules 25 (1992) 1214.

[113] L.M. Tolbert, X. Zhao, Y. Ding, L.A. Bottomley, J. Am. Chem. Soc. 117 (1995) 12891.

[114] T. Yamamoto, T. Maruyama, Z. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, K. Kubota, J. Am. Chem. Soc. 116 (1994) 4832.

[115] F. Barigelletti, L. Flamingni, V. Balzani, J.-P. Colin, J.-P. Sauvage, A. Sour, E.C. Constable, A.M.W.C. Thompson, J. Am. Chem. Soc. 116 (1994) 7692.

[116] P. Sautet, C. Joachim, Chem. Phys. Lett. 153 (1988) 511.

[117] S. Woitellier, J.-P. Launay, C. Joachim, Chem. Phys. 131 (1989) 481.

[118] R.D. Markwell, I.S. Butler, A.K. Kakkar, M.S. Khan, Z.H. Al-Zahkawani, J. Lewis, Organometallics 15 (1996) 2331.

[119] Q. Zhou, P.J. Caroll, T.M. Swagger, J. Org. Chem. 59 (1994) 1294.

[120] U.H.F. Bunz, Angew. Chem. Int. Ed. Engl. 35 (1996) 969.

[121] H. Lang, Angew. Chem. Int. Ed. Engl. 33 (1994) 547.

[122] R. Eastmond, T.R. Johnson, D.R.M. Walton, Tetrahedron 28 (1972) 4601.

[123] R. Eastmond, D.R.M. Walton, Tetrahedron 28 (1972) 4591.

[124] T.R. Johnson, D.R.M. Walton, Tetrahedron 28 (1972) 5221.

[125] R.J. Lagow, J.J. Kampa, H.-C. Wei, S.L. Battle, J.W. Genge, D.A. Laude, C.J. Harper, R. Bau, R.C. Stevens, J.F. Haw, E. Munson, Science 267 (1995) 362.

[126] Y.-L. Yang, L.J.-J. Wang, Y.-C. Lin, S.-L. Huang, M.-C. Chen, G.-H. Lee, Y. Wang, Organometallics 16 (1997) 1573.

[127] P. Belanzoni, N. Re, M. Rosi, A. Sgamellotti, C. Floriani, Organometallics 15 (1996) 4264.

[128] M. Akita, Y. Moro-Oka, Bull. Chem. Soc. Jpn. 68 (1995) 420.

[129] S. Takahashi, E. Murata, S. Sonogashira, N. Hagihara, J. Polym. Sci. Polym. Chem. Ed. 18 (1980) 661.

[130] K. Sonogashira, S. Kataoka, S. Takahashi, N. Hagihara, J. Organomet. Chem. 160 (1978) 319.

[131] J. Kim, H. Masai, K. Sonogashira, N. Hagihara, Inorg. Nucl. Chem. Lett. 6 (1970) 181.

[132] R. Nast, F. Urban, Z. Anorg. Allg. Chem. 289 (1957) 244.

[133] B.E. Woodworth, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 119 (1997) 828.

[134] T. Bartik, B. Bartik, M. Brady, R. Dembinski, J.A. Gladysz, Angew. Chem. Int. Ed. Engl. 35 (1996) 414.

[135] W.Q. Weng, T. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 117 (1995) 11922.

[136] J.W. Seyler, W. Weng, Y. Zhou, J.A. Gladysz, Organometallics 12 (1993) 3802.

[137] Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 115 (1993) 8509.

[138] V.W.-W. Yam, V.C.-Y. Lau, K.-K. Cheung, Organometallics 15 (1996) 1740.

[139] R. Crescenzi, C. Lo Sterzo, Organometallics 11 (1992) 4301.

[140] A. Wong, P.C.W. Kang, C.D. Tagge, D.R. Leon, Organometallics 9 (1990) 1992.

[141] M. Akita, C.-M.Chung, A. Sakurai, S. Sugimoto, M. Terada, M. Tanaka, Y. Moro-Oka, Organometallics 16 (1997) 4882.

[142] N. Le Narvor, C. Lapinte, J. Chem. Soc. Chem. Commun. (1993) 357.

[143] F. Coat, C. Lapinte, Organometallics 15 (1996) 476.

[144] F. Coat, M.-A. Guillevic, L. Toupet, F. Paul, C. Lapinte, Organometallics 16 (1997) 5988.

[145] M.I. Bruce, P. Hinterding, E.R.T. Tiekink, B.A. Skelton, A.H. White, J. Organomet. Chem. 450 (1993) 209.

[146] M.I. Bruce, L.I. Denisovich, P.J. Low, S.M. Peregudova, N.A. Ustynyuk, J. Chem. Soc. Mendeleev Commun. (1996) 200.

[147] H.B. Fyfe, M. Mlekuz, D. Zargarian, N.J. Taylor, T.B. Marder, J. Chem. Soc. Chem. Commun. (1991) 188.

[148] T. Rappert, O. Nürnberg, H. Werner, Organometallics 12 (1993) 1359.

[149] O. Gevert, J. Wolf, H. Werner, Organometallics 15 (1996) 2806.

[150] P.J. Stang, R. Tykwinski, J. Am. Chem. Soc. 114 (1992) 4411.

[151] H. Werner, R.W. Lass, O. Gevert, J. Wolf, Organometallics 16 (1997) 4077.

[152] S. Takahashi, Y. Ohyama, E. Murata, S. Sonogashira, N. Hagihara, J. Polym. Sci. Polym. Chem. Ed. 18 (1980) 349.

[153] B.E. Woodworth, J.L. Templeton, J. Am. Chem. Soc. 118 (1996) 7418.

[154] W. Weng, J.A. Ramsden, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 115 (1993) 3824.

[155] W. Weng, T. Bartik, J.A. Gladysz, Angew. Chem. Int. Ed. Engl. 33 (1994) 2199.

[156] S.F. Falloon, W. Weng, A.M. Arif, J.A. Gladysz, Organometallics 16 (1997) 2008.

[157] M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Chem. Soc. Dalton Trans. (1996) 3151.

[158] S.F. Falloon, A.M. Arif, J.A. Gladysz, Chem. Commun. (1997) 629.

[159] H. Hagihara, K. Sonogashira, S. Takahashi, Adv. Polym. Sci. 41 (1981) 149.

[160] M. Brady, W. Weng, J.A. Gladysz, J. Chem. Soc. Chem. Commun. (1994) 2655.

[161] T. Bartik, R. Dembinski, B. Bartik, A.M. Arif, J.A. Gladysz, New J. Chem. 21 (1997) 739.

[162] N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129.

[163] M. Springborg, R.C. Albers, Phys. Rev. Condens. Matter B: 53 (1996) 10626.

[164] M.B. Sponsler, Organometallics 14 (1995) 1920.

[165] G. Frapper, M. Kertesz, Inorg. Chem. 32 (1993) 732.

[166] O. Lhost, J.M. Toussain, J.L. Bredas, H.F. Wittmann, K. Fuhrmann, R.H. Friend, M.S. Khan, J. Lewis, Synth. Met. 5557 (1993) 4525.

[167] U.H. Bunz, Chem. Unserer Zeit 29 (1995) 96.

[168] A.M. Sladkov, in: M. E. Vol'pin (Ed.), Chemistry Reviews, Soviet Scientific Reviews/sect.B, vol. 3, Harwood, Moscow, 1981, p. 75.

[169] G.H. Worth, B.H. Robinson, J. Simpson, Organometallics 11 (1992) 501.

[170] G.H. Worth, B.H. Robinson, J. Simpson, J. Organomet. Chem. 387 (1990) 337.

[171] P. Blenkiron, G.D. Enright, N.J. Taylor, A.J. Carty, Organometallics 15 (1996) 2855.

[172] F. Paul, W. Meyer, J.A. Gladysz, C. Lapinte, in preparation.

[173] A. Geisbauer, S. Mihan, W. Beck, J. Organomet. Chem. 501 (1995) 61.

[174] H.H. Fox, J.-K. Lee, L.Y. Park, R.R. Schrock, Organometallics 12 (1993) 759.

[175] A. Rabier, N. Lugan, R. Mathieu, G.L. Geoffroy, Organometallics 13 (1994) 4676.
[176] M.R. Churchill, J. Wormald, Inorg. Chem. 8 (1969) 1936.
[177] R.E. Davies, J. Chem. Soc. Chem. Commun. (1968) 1218.
[178] B.A. Etzenhouser, M.D. Cavanaugh, H.N. Spurgeon, M.B. Sponsler, J. Am. Chem. Soc. 116 (1994) 2221.
[179] V. Morvan-Mahias, Thesis, University of Rennes I, 1997.
[180] C.J. Lawrie, K.P. Gable, B.K. Carpenter, Organometallics 8 (1989) 2274.
[181] F. Maassarani, M. Pfeffer, G. Le Borgne, E. Wehman, G. van Koten, J. Am. Chem. Soc. 106 (1984) 8002.
[182] H.P. Xia, R.C.Y. Yeung, G. Jia, Organometallics 16 (1997) 3557.
[183] V. Guerchais, personal communication.
[184] S. Kotani, K. Shiina, K. Sonogashira, J. Organomet. Chem. 429 (1992) 403.
[185] D.G. Sekutowski, G.D. Stucky, J. Am. Chem. Soc. 98 (1976) 1376.
[186] J.H. Teuben, H.J. de Liefde Meijer, J. Organomet. Chem. 17 (1969) 87.
[187] T. Cuenca, R. Gomez, P. Gomez-Sal, G.M. Rodriguez, P. Rogo, Organometallics 11 (1992) 1229.
[188] U. Rosenthal, A. Ohff, A. Tillack, W. Baumann, H. Görls, J. Organomet. Chem. 468 (1994) C4.
[189] W. Weng, T. Bartik, M.T. Johnson, A.M. Arif, J.A. Gladysz, Organometallics 14 (1995) 889.
[190] G.G. Aleksandrov, V.V. Skripkin, N.Y. Kolobova, Y.T. Struchkov, Koord. Khim. 5 (1979) 453 (English translation)
[191] N.Y. Kolobova, V.V. Skripkin, G.G. Alexandrov, Y.T. Struchkov, J. Organomet. Chem. 169 (1979) 293.
[192] A. Davison, J.P. Solar, J. Organomet. Chem. 155 (1978) C8.
[193] B.E. Boland-Lussier, R.P. Hugues, Organometallics 1 (1982) 635.
[194] R.M. Bullock, J. Am. Chem. Soc. 109 (1987) 8087.
[195] H. Fischer, F. Leroux, G. Roth, R. Stumpf, Organometallics 15 (1996) 3723.
[196] H. Fischer, F. Leroux, R. Stumpf, G. Roth, Chem. Ber. 129 (1996) 1475.
[197] M.I. Bruce, G.A. Koutsantonis, M.J. Liddell, E.R.T. Tiekink, J. Organomet. Chem. 420 (1991) 253.
[198] M.R. Churchill, J. Wormald, W.P. Giering, G. Emerson, J. Chem. Soc. Chem. Commun. (1968) 1217.
[199] A. Sanders, W.P. Giering, J. Organomet. Chem. 104 (1976) 67.
[200] C.J. Gilmore, P. Woodward, J. Chem. Soc. Chem. Commun. (1971) 1233.
[201] C.M. Mitchell, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1972) 102.
[202] J. Bremair, M. Steigmann, B. Wagner, W. Beck, Chem. Ber. 123 (1989) 7.
[203] R.M. Bullock, F.R. Lemke, D.J. Szalda, J. Am. Chem. Soc. 113 (1991) 8466.
[204] V. Guillaume, V. Morvan-Mahias, C. Lapinte, unpublished results.
[205] R. Aumann, B. Jasper, R. Fröhlich, S. Kotila, J. Organomet. Chem. 502 (1995) 137.
[206] R. Neidlein, S. Gürtler, C. Krieger, Helv. Chim. Acta 77 (1994) 2303.
[207] N.P. Robinson, L. Main, B.K. Nicholson, J. Organomet. Chem. 430 (1992) 79.
[208] S.L. Buchwald, E.L. Lucas, J.C. Derwan, J. Am. Chem. Soc. 109 (1987) 4396.
[209] F.H. Köhler, W. Prössdorf, U. Schubert, Inorg. Chem. 20 (1981) 4096.
[210] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolbova, A.A. Ioganson, Dolk. Akad. Nauk SSSR 175 (1966) 358 (English translation)
[211] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolbova, Izv. Akad. Nauk SSSR Ser. Khim. (1963) 1348 (English translation).
[212] R. Chukwu, A.D. Hunter, B.D. Santasiero, S.G. Bott, J.L. Atwood, J. Chassaignac, Organometallics 11 (1992) 589.
[213] A.D. Hunter, A.B. Szigety, Organometallics 8 (1989) 2671.
[214] J. Blackmore, M.I. Bruce, P.J. Davidson, M.Z. Iqubal, F.G.A. Stone, J. Chem. Soc. A: (1970) 3153.
[215] M.I. Bruce, J. Organomet. Chem. 21 (1970) 415.
[216] S.C. Cohen, J. Chem. Soc. Dalton Trans. (1973) 553.
[217] O. Bekarö̈glu, Chim. Acta Turc. (1974) 131.
[218] B. Hipler, E. Uhlig, J.I. Vogel, J. Organomet. Chem. 218 (1981) C1.
[219] R. MacDonald, K.C. Sturge, A.D. Hunter, L. Shilliday, Organometallics 11 (1992) 893.
[220] R. MacDonald, K.C. Sturge, A.D. Hunter, B.D. Santarsiero, Organometallics 11 (1992) 3056.

[221] W.D. Müller, H.A. Brune, J. Organomet. Chem. 119 (1986) 759.
[222] J. Manna, C.J. Kuehl, J.A. Whiteford, P.J. Stang, Organometallics 16 (1997) 1897.
[223] J. Manna, J.A. Whiteford, P.J. Stang, J. Am. Chem. Soc. 118 (1996) 8731.
[224] S. Trofimenko, J. Am. Chem. Soc. 93 (1971) 1808.
[225] S.J. Loeb, G.K.H. Shimizu, J. Chem. Soc. Chem. Commun. (1993) 1395.
[226] P. Steenwinkel, S.L. James, D.M. Groove, H. Kooijman, A.L. Spek, G. van Koten, Organometallics 16 (1997) 513.
[227] J.-P. Sutter, D.M. Grove, M. Beley, J.-P. Collin, N. Veldman, A.L. Spek, J.-P. Sauvage, G. van Koten, Angew. Chem. Int. Ed. Engl. 33 (1994) 1282.
[228] M. Beley, J.-P. Colin, R. Louis, B. Metz, J.-P. Sauvage, J. Am. Chem. Soc. 113 (1991) 8521.
[229] M. Beley, J.-P. Colin, J.-P. Sauvage, Inorg. Chem. 32 (1993) 4539.
[230] M. Beley, S. Chodorowski-Kimmes, J.-P. Colin, J.-P. Sauvage, F. Flamigni, F. Barigeletti, Inorg. Chem. 33 (1994) 2543.
[231] F. Barigeletti, F. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowski-Kimmes, J.-P. Colin, J.-P. Sauvage, Inorg. Chem. 35 (1996) 136.
[232] M.-C. Lagunas, R.A. Gossage, A.L. Spek, G. van Koten, Organometallics 17 (1998) 731.
[233] S.L. Buchwald, E.L. Lucas, W.D. Davis, J. Am. Chem. Soc. 111 (1989) 397.
[234] J.D. Scott, R.J. Puddephatt, Organometallics 5 (1986) 1538.
[235] N.A.A. Al-Jabar, A.G. Massey, J. Organomet. Chem. 275 (1984) 9.
[236] J.E. Dobson, J.P. Wiggen, R.G. Miller, J. Am. Chem. Soc. 93 (1971) 554.
[237] M. Beley, S. Chodorowski, J.-P. Colin, J.-P. Sauvage, Tetrahedron Lett. 34 (1993) 2933.
[238] N.A. Richardson, M.B. Hall, Organometallics 12 (1993) 1338.
[239] A.D. Hunter, Organometallics 8 (1989) 1118.
[240] A.D. Hunter, J.L. Mac Lernon, Organometallics 8 (1989) 2679.
[241] T. Weyland, C. Lapinte, G. Frapper, M.J. Calhorda, J.-F. Halet, L. Toupet, Organometallics 16 (1997) 2024.
[242] R. Tykwinski, P.J. Stang, Organometallics 13 (1992) 3203.
[243] M.S. Khan, D.J. Schwartz, N.A. Pasha, A.K. Kakkar, B. Lin, P.R. Raithby, J. Lewis, Z. Anorg. Allg. Chem. 616 (1992) 121.
[244] N. Ohshiro, F. Takei, K. Onitsuka, S. Takahashi, Chem. Lett. (1996) 871.
[245] I.R. Whittall, M.G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid, D.C.R. Hockless, J. Organomet. Chem. 544 (1997) 277.
[246] T. Weyland, Thesis, University of Rennes I, 1997.
[247] H.P. Xia, W.F. Wu, W.S. Ng, I.D. Williams, G. Jia, Organometallics 16 (1997) 2940.
[248] C. Hartbaum, G. Roth, H. Fischer, Chem. Ber. Rcl. 130 (1997) 479.
[249] N.A. Ustynyuk, V.N. Vinogradova, V.G. Adrianov, Y.T. Struchov, J. Organomet. Chem. 268 (1984) 73.
[250] K.-Y. Shih, R.R. Schrock, R. Kempe, J. Am. Chem. Soc. 116 (1994) 8804.
[251] S.A. Krouse, R.R. Schrock, J. Organomet. Chem. 355 (1988) 257.
[252] E.O. Fischer, W. Röll, N.H. Tran Huy, K. Ackermann, Chem. Ber. 115 (1982) 2951.
[253] N.Q. Dao, H. Fevrier, M. Jouan, E.O. Fischer, W. Röll, J. Organomet. Chem. 275 (1984) 191.
[254] E. Viola, C. Lo Sterzo, R. Crescenzi, G. Frachey, J. Organomet. Chem. 493 (1995) C9.
[255] S.J. Davies, B.F.G. Johnson, J. Lewis, M.S. Khan, J. Organomet. Chem. 401 (1991) C43.
[256] L.D. Field, A.V. George, F. Laschi, E.Y. Malouf, P. Zanello, J. Organomet. Chem. 435 (1992) 347.
[257] N. Le Narvor, C. Lapinte, Organometallics 14 (1995) 634.
[258] M.S. Khan, A.K. Kakkar, S.L. Ingham, P.R. Raithby, J. Lewis, B. Spencer, F. Wittmann, R.H. Friend, J. Organomet. Chem. 472 (1994) 247.
[259] A. Santos, J. Lopez, J. Montoya, P. Noheda, A. Romero, A.M. Echavarren, Organometallics 13 (1994) 3605.
[260] H. Werner, T. Rappert, J. Wolf, Israel J. Chem. 30 (1990) 377.
[261] R. Nast, A. Beyer, J. Organomet. Chem. 194 (1980) 125.
[262] S. Takahashi, H. Morimoto, E. Murata, S. Kataoka, S. Sonogashira, N. Hagihara, J. Polym. Sci. 20 (1982) 565.
[263] U. Behrens, K. Hoffmann, J. Kopf, J. Moritz, J. Organomet. Chem. 117 (1976) 91.

[264] R. Nast, J. Moritz, J. Organomet. Chem. 117 (1976) 81.
[265] J. Lewis, N.J. Long, P.R. Raithby, G.P. Shields, W.-Y. Wong, M. Younus, J. Chem. Soc. Dalton Trans. (1997) 4283.
[266] G. Jia, R.J. Puddephatt, J.D. Scott, J.J. Vittal, Organometallics 12 (1993) 3565.
[267] E. Viola, C. Lo Sterzo, F. Trezzi, Organometallics 15 (1996) 4352.
[268] R.L. Beddoes, C. Bitcon, A. Ricalton, M.W. Whiteley, J. Organomet. Chem. 367 (1989) C21.
[269] R.S. Iyer, J.P. Selegue, J. Am. Chem. Soc. 109 (1987) 910.
[270] C. Löwe, H.-U. Hund, H. Berke, J. Organomet. Chem. 1989 (1989) 295.
[271] N.H. Tran Huy, P. Lefloch, J. Organomet. Chem. 327 (1987) 211.
[272] T. Albrecht, J. Sauer, Tetrahedron Lett. 35 (1994) 561.
[273] W.A. Herrmann, J. Plank, G.W. Kriechbaum, M.L. Ziegler, H. Pfisterer, J.A. Atwood, R.D. Rogers, J. Organomet. Chem. 264 (1984) 327.
[274] N.E. Kolobova, O.S. Zhvanko, L.L. Ivanov, A.S. Batsanov, Y.T. Struchkov, J. Organomet. Chem. 302 (1986) 235.
[275] N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, Izv. Akad. Nauk SSSR Ser. Khim. (1984) 1667 (English translation).
[276] S. Guesmi, D. Touchard, P.H. Dixneuf, Chem. Commun. (1996) 2773.
[277] M. Havraneck, M. Husak, D. Dvorak, Organometallics 14 (1995) 5024.
[278] L.K. Myers, D.M. Ho, M.E. Thompson, C. Langhoff, Polyhedron 14 (1995) 57.
[279] G. Jia, W.F. Wu, R.C.Y. Yeung, H.P. Xia, J. Organomet. Chem. 539 (1997) 53.
[280] R. Aumann, H. Heinen, Chem. Ber. 120 (1987) 537.
[281] V. Peron, E. Porhiel, V. Ferrand, H. Le Bozec, J. Organomet. Chem. 539 (1997) 201.
[282] R.P. Hsung, J.R. Babock, C.E.D. Chidsey, L.R. Sita, Tetrahedron Lett. 36 (1995) 4525.
[283] O. Lavastre, L. Ollivier, P.H. Dixneuf, S. Sinbandhit, Tetrahedron 52 (1995) 5495.
[284] E.O. Fischer, D. Wittmann, D. Himmelreich, D. Neugebauer, Angew. Chem. Int. Ed. Engl. 21 (1982) 444.
[285] N. Rajapakse, B.R. James, D. Dolphin, Can. J. Chem. 68 (1990) 2274.
[286] R. Faust, F. Diederich, V. Gramlich, P. Seiler, Chem. Eur. J. 1 (1995) 111.
[287] F. Diederich, R. Faust, V. Gramlich, P. Seiler, J. Chem. Soc. Chem. Commun. (1994) 2045.
[288] C. Roger, P. Marseille, C. Salus, J.-R. Hamon, C. Lapinte, J. Organomet. Chem. 336 (1987) C13.
[289] C. Roger, P. Hamon, L. Toupet, H. Rabaë, J.-Y. Saillard, J.-R. Hamon, C. Lapinte, Organometallics 10 (1991) 1045.
[290] P. Hamon, L. Toupet, J.-R. Hamon, C. Lapinte, Organometallics 15 (1996) 10.
[291] J.-R. Hamon, D. Astruc, P. Michaud, J. Am. Chem. Soc. 103 (1981) 758.
[292] N. Nlate, C. Lapinte, V. Guerchais, Organometallics 12 (1993) 4657.
[293] V. Mahias, S. Cron, L. Toupet, C. Lapinte, Organometallics 15 (1996) 5399.
[294] S. Nlate, Thesis, University of Rennes I, 1993.
[295] S. Cron, Thesis, University of Rennes I, 1993.
[296] C. Roger, C. Lapinte, J. Chem. Soc. Chem. Commun. (1989) 1598.
[297] M. Brookhart, W.B. Studabaker, Chem. Rev. 87 (1987) 411.
[298] R.R. Schrock, J. Am. Chem. Soc. 97 (1975) 6577.
[299] W. Tam, G.-Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong, J.A. Gladysz, J. Am. Chem. Soc. 104 (1982) 141.
[300] M.I. Bruce, Chem. Rev. 91 (1991) 197.
[301] N.G. Connelly, M.P. Gamasa, J. Gimeno, C. Lapinte, E. Lastra, J.P. Maher, N. Le Narvor, A.L. Rieger, P.H. Rieger, J. Chem. Soc. Dalton Trans. (1993) 2775.
[302] N. Le Narvor, Thesis, Universty of Rennes 1, 1993.
[303] M.D. Johnson, in: G. Wilkinson, F.G.A. Stone, E. Abel (eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon, Oxford, 1982, Chapter 31.2., p 331.
[304] P. Hamon, L. Toupet, J.-R. Hamon, C. Lapinte, Organometallics 11 (1992) 1429.
[305] K.-T. Smith, C. Romming, M. Tilset, J. Am. Chem. Soc. 115 (1993) 8681.
[306] D. Astruc, Chem. Rev. 88 (1988) 1189.
[307] M.C. Baird, Chem. Rev. 88 (1988) 1217.
[308] V. Guillaume, V. Morvan-Mahias, C. Lapinte, J. Organomet. Chem. (in press).

[309] F. Coat, Thesis, University of Rennes I, 1996.
[310] N.N. Greenwood, in: Mössbauer Spectroscopy, Chapman and Hall, 1971.
[311] W.H. Morrison, D.N. Hendrickson, J. Chem. Phys. 59 (1973) 380.
[312] C. Le Vanda, K. Bechgaard, D.O. Cowan, J. Org. Chem 41 (1976) 2700.
[313] C. Le Vanda, D.O. Cowan, C. Leitch, K. Bechgaard, J. Am. Chem. Soc. 96 (1974) 6788.
[314] P. Hamon, J.-R. Hamon, C. Lapinte, J. Chem. Soc. Chem. Commun. (1992) 1602.
[315] P.H. Rieger, Coord. Chem. Rev. 135–136 (1994) 203.
[316] I. Bertini, C. Luchinat, in: A.B.P. Lever, H.B. Gray (Eds.), NMR of Paramagnetic Molecules in Biological Systems, Physical Bioinorganic Chemistry Series, Benjamin/Cummings, 1986, p. 319.
[317] V. Guillaume, P. Thominot, F. Coat, A. Mari, C. Lapinte, J. Organomet. Chem. 565 (1998) 75.
[318] M. Guillemot, L. Toupet, C. Lapinte, Organometallics 17 (1998) 1928.
[319] A.W. Kaplan, R.G. Bergman, Organometallics 16 (1997) 1106.
[320] R.G. Beevor, M.F. Freeman, M. Green, C.E. Morton, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1985) 68.
[321] R. Denis, T. Weyland, F. Paul, C. Lapinte, J. Organomet. Chem. 545–546 (1997) 615.
[322] S. Cron, V. Morvan, C. Lapinte, J. Chem. Soc. Chem. Commun. (1993) 1611.
[323] D.F. Evans, J. Chem. Soc. (1959) 2003.
[324] C.G. Atwood, W.E. Geiger, J. Am. Chem. Soc. 115 (1993) 5310.
[325] T. Weyland, K. Costuas, A. Mari, J.-F. Halet, C. Lapinte, Organometallics 17 (1998), in press.
[326] J. Bonvoisin, J.-P. Launay, W. Verbouwe, M. Van der Auweraer, F.K. De Schryver, J. Phys. Chem. 100 (1996) 17079.
[327] J. Bonvoisin, J.-P. Launay, M. Van der Auweraer, F.K. De Schryver, J. Phys. Chem. 98 (1994) 5052.
[328] H. Fink, N.J. Long, A.J. Martin, G. Opromolla, A.J.P. White, D.J. Williams, P. Zanello, Organometallics 16 (1997) 2646.
[329] V. Morvan-Mahias, V. Guillaume, C. Lapinte, in preparation.
[330] C.J. Lawrie, A.E. Dankosh, B.K. Carpenter, J. Organomet. Chem. 411 (1991) C7.
[331] P. Steenwinkel, J.T.B.H. Jatrzebski, B.-J. Deelman, D.M. Groove, H. Kooijman, N. Veldman, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 16 (1997) 5486.
[332] C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, Inorg. Chem. 36 (1997) 5037.
[333] M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, Science 278 (1997) 252.
[334] E.H. Elandaloussi, P. Frère, P. Richomme, J. Orduna, J. Garin, J. Roncali, J. Am. Chem. Soc. 119 (1997) 10774.
[335] F. de Angelis, N. Re, M. Rosi, A. Sgamellotti, C. Floriani, J. Chem. Soc. Dalton Trans. (1997) 3841.
[336] J.A. Davies, M. El-Ghanam, A.A. Pinkerton, D.A. Smith, J. Organomet. Chem. 409 (1991) 367.
[337] J. Heidrich, M. Steigmann, M. Appel, W. Beck, J.R. Phillips, W.C. Trogler, Organometallics 9 (1990) 1296.
[338] M. Akita, M. Terada, S. Oyama, Y. Moro-Oka, Organometallics 9 (1990) 816.
[339] G.A. Koutsantonis, J.P. Selegue, J. Am. Chem. Soc. 113 (1991) 2316.
[340] H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, Y. Yamaloto, H. Yamazaki, Organometallics 7 (1988) 2257.
[341] K. Sünkel, U. Birk, C. Robl, Organometallics 13 (1994) 1679.
[342] K.G. Frank, J.P. Selegue, J. Am. Chem. Soc. 112 (1990) 6414.
[343] M.B. Sponsler, personal communication.
[344] G. Erker, W. Frömberg, K. Angermund, R. Schlund, C. Krüger, J. Chem. Soc. Chem. Commun. (1986) 372.
[345] M.E. Kimball, J.P. Martella, W.C. Kaska, Inorg. Chem. 6 (1967) 414.
[346] P.S. Santos, K. Kawai, O. Sala, Inorg. Chim. Acta (1977) 155.
[347] K.D. Grande, A.J. Kunin, L.S. Sthul, B.M. Foxman, Inorg. Chem. 22 (1983) 1791.
[348] J.I. Setsune, Z.-I. Yoshida, H. Ogoshi, J. Chem. Soc. Perkin Trans. I: (1982) 983.
[349] J.A.J. Jarvis, J. Chem. Soc. Chem. Commun. (1973) 373.
[350] C.M. Mitchell, F.G.A. Stone, J. Chem. Soc. Chem. Commun. (1970) 1263.
[351] A. Johnson, R.J. Puddephatt, J. Chem. Soc. Dalton Trans. (1978) 980.
[352] A. Antoniolo, A. Otero, M. Fajardo, C. Garcia-Yebra, R. Gil-Sanz, C. Lopez-Mardomingo, A. Martin, P. Gomez-Sal, Organometallics 13 (1998) 4679.
[353] L. Toupet, unpublished results.