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Review

Electronic communication in heterobinuclear organometallic complexes through unsaturated hydrocarbon bridges

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Contents

Abstract

Much of the interest about the construction of model compounds suitable for investigating the phenomena associated with the interaction of two or more metal centers, the so-called cooperative effect, has been concentrated on homobimetallic complexes and less attention has been paid to the class of heterobimetallic derivatives. This review will feature experimental detection and the effects of the electronic communication in heterobinuclear organometallic complexes through unsaturated hydrocarbon bridges. The described systems are classified according to the nature of the bridging ligand, in three main groups: (i) carbon σ-bonded molecular wires; (ii) fulvalene and fulvalene-like bridges; (iii) fused delocalized polycyclic bridges. In this contribution, we discuss the flexibility of heterobimetallic complexes, and more in general of asymmetric bimetallic species, in terms of tailoring the cooperative effects, i.e. of controlling and tuning the reactivity of one metal center by acting on the adjacent one. Satisfactory quantitative estimate of the degree of metal to metal communication through the bridging ligand is obtained in illustrative examples combining efficient electrochemical and spectroscopic techniques with consolidated theories. A review with almost 350 references.

Keywords: Heterobimetallic complexes; Electron transfer; Molecular wires; Mixed-valence chemistry; Cooperative effects

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Abbreviations: Bpy, bipyridine; CHT, 1,3,5-cycloheptatriene; COD, 1,5-cyclooctadiene; COT, 1,3,5,7-cyclooctatetraene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; CV, cyclic voltammetry; DMAD, dimethylacetylenedicarboxylate; dppe, 1,2-bis-(diphenylphosphino)ethane; dppf, 1,1′-bis-(diphenylphosphino)ferrocene; dppm, bis(diphenylphosphino)methane; EHMO, extended Huckel molecular orbitals; ET, electron transfer; Fv, fulvalene; Ic, indacene; Ind, indenyl anion; Ind*, heptamethylindenyl anion; IR/NIR, infrared/near-infrared; IVCT, inter valence charge transfer; MP, methylpropiolate; NBD, norbornadiene; NLO, non-linear optics; TMEDA, *N*,*N*,*N*,*N*-tetramethylethylenediamine; Tp′, hydridotris(3,5-dimethylpyrazolyl)borate

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1. Introduction

1.1. General overview

The presence of two metal centers within the same molecule profoundly affects both the physical properties and the reactivity of the molecule [1–5]. It results either in a significant modification of the individual properties or in the development of novel characteristics which do not occur in monometallic compounds. In particular, the physical properties of one of the two metals (luminescence, fluorescence, non-linear optical (NLO) activity, redox properties, etc.) can vary substantially [6–9]. Moreover, in polymetallic complexes, in which it is possible to analyze the effects of chemical, electrochemical, or photochemical modifications of one metallic center on the properties of the other, the reciprocal interaction between the active centers often brings surprising results. Amongst the phenomena which have been increasingly studied, there are the chemical and electrochemical transport of electrons and energy in certain classes of compounds. These are often closely correlated with natural biosynthesis phenomena and the development of unique chemical and physical characteristics which allow for the production of novel products, new and more efficient catalytic systems, and modern materials devised for electronics (“molecular devices”) [5,10–14]. Many of the techniques employed to study the different phenomena associated with the communication between the metal centers are applied to mixed-valence (MV) species. Among the physical properties which afford information on these properties, two of these, the $\Delta E_{1/2}$ values relative to the redox potential of the two metal centers, and the optical intervalence transfer (IT) band in the near-infrared (NIR) [5,15] are widely used to classify the extent of interaction between the metals. Other specific techniques are suitable to study the electronic (ESR spectroscopy) and nuclear interaction (^{57}Fe-Mössbauer spectroscopy) between metal centers, whilst NMR spectroscopy and X-ray crystallography give useful structural information in solution and solid state.

The great interest for transition metal complexes arises not only from the aforementioned particularities but also from the wide range of arrangements which can be created due to the huge flexibility of the organometallic structures. Besides the availability of a large number of transition metals, it is often sufficient through simple reactions to vary either the nature of the auxiliary ligands bound to the metals or the oxidation state of the metals themselves in order to induce peculiar chemical and physical properties in the system.

1.2. Scopes and limitations

In this review we will focus on heterobinuclear organometallic complexes containing unsaturated hydrocarbon bridges, in particular on those systems in which the extent of electronic communication and consequently the physical and/or chemical characteristics of one metal are modified by the presence of a different metal.

Since the synthesis of the Creutz–Taube [16,17] mixed valence ions, continuing investigations in a series of di-ruthenium complexes on the way in which two or more metals linked by a bridging ligand interact have been directed in the building up of bimetallic complexes [18–20]. However, in the present review complexes where the two active sites are connected by nitrogen containing bidentate ligands or other complexes in which the metals are connected through sulfur or other heteroatoms will not be considered, since they have been exhaustively described in several reviews [21–23].

Considerable attention has been paid during the last two decades to studying those complexes in which two equivalent metals are bonded through a hydrocarbon bridge, i.e. homobimetallic complexes, and most of the information on the phenomena of electronic communication comes from investigation on this class of compounds. These results have been also extensively reviewed [24–27]. They will be taken into consideration in the course of this report whenever the homobimetallic complexes represent a reference model for analogous heterobimetallic compounds. With regard to the last systems, although considerable efforts have been and are currently devoted to the development of synthetic methods in order to provide new heterobinuclear transition metal complexes, less data, describing how the physical and chemical properties of one metal are modified by the presence of a different one in the same molecule, are at present available. A recent review by Wheatley and Kalck [28] deals with the structure and reactivity of early-late heterobimetallic complexes.

Moreover, in this review, we will not discuss the class of organometallic polymers in which homo- and heterobimetallic subunits are present. For an overview of some of these systems, we recommend the review by Manners and coworkers [29].

This last limitation leads to the classification of the complexes considered here in essentially three classes, on the basis of the hydrocarbon bridging ligand nature:

(i) unsaturated carbon chains with odd or even numbers of C-atoms with σ-bonded metals at the *termini* (*molecular wires*);
(ii) metal π-coordinated aromatic rings linked directly (such as fulvalene) or separated by a hydrocarbon chain;
(iii) metal π-coordinated bi- and tri-cyclic fused systems (*fused aromatic bridges*).

The heterobimetallic complexes are intrinsically *asymmetric* systems and since the *asymmetry* plays a significant role in the electronic communication we will also mention the few examples of homobimetallic complexes in which asymmetry is due to the presence of substituents in the bridge, the nature of the ancillary ligands, and the coordination mode.

The phenomena associated with the electronic communication between the metal centers can emerge in the fundamental state of the molecules manifesting enhanced or unique reactivity in stoichiometric and catalytic reactions. Besides bimetallic complexes are often precursors of mixed valence species generated by chemical or electrochemical activation, whose redox, optical and magnetic properties depend on the extent of the electronic interaction between the metals.

A rationale for this experimental evidence arises mainly from the classical Marcus–Hush theory and its subsequent derivations.

1.3. Theoretical aspects

In bimetallic complexes cooperative effects and the possibility of tuning the properties of one metal center M_1 by acting on the oxidation state of the second coordinated metal M_2 depend on the strength of the electronic interaction between the two metals, which is modulated by the ability of the conjugated bridging ligand to mediate the transfer of one electron through itself [30].

According to the classification proposed by Robin and Day [31], the strength of electronic interaction between the oxidized and reduced sites ranges from essentially zero (Class I) to moderate (Class II), to very strong electronic coupling (Class III). Apart the Coulombic repulsion, in general the experimentally detected separation between the redox potentials of M_1 and M_2 is ascribed to the electronic communication [15]. In the intermediate potential domain the complex exists in a mixed-valence state and can undergo optically induced electron transfer. In homobimetallic systems, which contain two equivalent redox centers ($M_1 = M_2$), the ΔE separation between the two reversible (in the chemical and electrochemical sense) redox events is indicative of an interaction between the two sites. ΔE values close to zero are characteristic of non-interacting metal sites, i.e. of Class I complexes. Small ΔE separations correspond to a weak interaction between the metals and to a smaller K for the equilibrium of Scheme 1; the valences are described by a mixed-valence state involving trapped-valence systems (Class II).

Finally, larger ΔE values correspond to a stabilization of the mixed-valence complexes involving the totally delocalized Class III systems, and to a very large comproportionation constant K for the equilibrium of Scheme 2.

According to Mountford and coworkers [32], in the case of heterobimetallic complexes ($M_1 \neq M_2$), the ΔE which is indicative of the metal–metal interactions is no longer that between the two subsequent reversible redox waves, but it is the difference between the redox potential of the reversible second wave and the redox potential of the reversible wave of the corresponding monometallic species, except eventually the substituent effect due to the presence of the other metal.

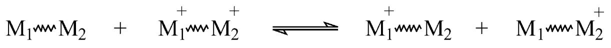
Recently, Geiger and coworkers [33] have introduced a "charge distribution parameter" $\Delta\rho$ which allows to use IR spectral shifts to calculate the actual ground–state charge distributions between two IR-active centers (typically carbonyl groups) in mixed valence systems:

$$\Delta\rho = \frac{\Delta\nu_{\mathrm{ox}} + \Delta\nu_{\mathrm{red}}}{2[\nu'(\mathrm{ox}) - \nu'(\mathrm{red})]} \tag{1}$$

where $\Delta\nu_{\mathrm{ox}} = \nu'(\mathrm{ox}) - \nu'_{\mathrm{meas}}(\mathrm{ox})$, $\Delta\nu_{\mathrm{red}} = \nu'_{\mathrm{meas}}(\mathrm{red}) - \nu'(\mathrm{red})$, and $\nu'(\mathrm{ox})$ and $\nu'(\mathrm{red})$ are the frequencies of the fully oxidized and reduced redox centers, respectively. $\Delta\rho$ as well as ΔE increases with the increasing strength of metal–metal interaction. In particular in a series of homobimetallic complexes of Cr and Mn [34], a very good linear correlation was found and a value of $\Delta\rho = 0.50$ indicated that equal charge resides on the two metal centers.

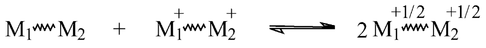
Intramolecular metal-to-metal communication can be theoretically investigated using the electron transfer (ET) theory introduced by Marcus [35–38]. In this section, we summarize its main concepts since it is central to an appreciation of the topic of electronic communications in the discussed compounds. The model system for a binuclear complex is sketched in Fig. 1. The two metals represent the *donor* and the *acceptor*, i.e. the two sites between which ET occurs, and they are connected by the spacer (or bridging ligand); the molecule is surrounded by a solvation sphere whose equilibrium polarization is in general different before and after ET.

Marcus' intuition was that the fluctuations in the various nuclear coordinates, such as in the orientation of the individual solvent molecules and in any other coordinate whose most probable distribution for the products differ from that of the reactants, i.e. vibrational coordinates, can lead the system to a transition state where electron transfer is energy neutral and occurs rapidly ("in the dark") [38]. In this case, both Franck–Condon and energy conservation principles are satisfied. The potential energy surfaces of the initial state (reactant plus solvent) and of the final state (product plus solvent) are functions of N relevant coordinates. Neglecting electronic coupling, they intersect on a $(N-1)$ dimensional surface which constitutes the transition state of the reaction [38]. The electronic coupling causes a splitting of the two surfaces in the vicinity of their intersection: a



$$\mathrm{M_1{\sim}M_2} + \mathrm{\overset{+}{M}_1{\sim}\overset{+}{M}_2} \rightleftharpoons \mathrm{\overset{+}{M}_1{\sim}M_2} + \mathrm{M_1{\sim}\overset{+}{M}_2}$$

Scheme 1.



$$\mathrm{M_1{\sim}M_2} + \mathrm{\overset{+}{M}_1{\sim}\overset{+}{M}_2} \rightleftharpoons 2\,\mathrm{\overset{+1/2}{M}_1{\sim}\overset{+1/2}{M}_2}$$

Scheme 2.

Fig. 1. Schematic representation of a binuclear metal complex.

lower and an upper surface are generated. ET is a frequent event on the lower surface (adiabatic conditions). When the coupling is very weak (non-adiabatic conditions), ET becomes a relatively rare event and the probability of successful electron jump is small and can be calculated using quantum-mechanical approach [39–43].

Marcus introduced rigorously a global reaction coordinate q in this many dimensional (N) coordinate space of the reacting system. The potential energies in the many dimensional coordinate space are functions of both the vibrational coordinates and of the hundreds of relevant solvent coordinates. In the limit of linear response approximation, in which any hypothetical change in charge of the reactant produces a proportional change in the dielectric polarization of the solvent, the free energies of the reagent and of the product are simple quadratic functions of the global reaction coordinate. Such an approach permits a depiction of the reaction in terms of the well-known parabolic free energy plots [44]. It is worth to remind that in Marcus theory the curve of the reactant and of the product is assumed to be the same and its validity is restricted to weakly coupled systems.

The expression of the kinetic constant for a generic ET process is taken from transition state theory:

$$k_{\mathrm{ET}} = \kappa_{\mathrm{el}}\nu_{\mathrm{n}} \exp\left[-\frac{(\lambda + \Delta G^{\circ})^2}{4\lambda k_{\mathrm{B}}T}\right] \tag{2}$$

where κ_{el} is the transmission coefficient, ν_{n} is the frequency of passage (nuclear motion) through the transition state, k_{B} is the Boltzmann constant and T is the temperature. In addition, these important quantities must be explicitly defined: (i) the reorganization energy λ, defined as the change in Gibbs energy if the reactant state remained unchanged at the equilibrium configuration but ET occurs and (ii) ΔG°, the difference in Gibbs energy between the equilibrium configuration of the product and reactant states. These important relations for $\Delta G^{\#}$, the Gibbs activation energy for forward ET, come out from purely geometrical considerations: (i) $\Delta G^{\#} = \lambda/4$, in reactions of zero ΔG°; (ii) $\Delta G^{\#} = (\lambda + \Delta G^{\circ})^2/4\lambda$ in all cases when $\Delta G^{\circ} \neq 0$. For moderately exergonic reactions $\Delta G^{\#}$ will decrease and k_{ET} will consequently increase, as ΔG° becomes more negative. When $-\Delta G^{\circ} = \lambda$, $\Delta G^{\#} = 0$ and k_{ET} reaches its maximum value of $\kappa_{\mathrm{el}}\nu_{\mathrm{n}}$. As ΔG° becomes even more negative, $\Delta G^{\#}$ will increase again and thus k_{ET} will surprisingly decrease as the reaction becomes highly exergonic in what is called the Marcus *inverted region*.

Hush applied the Marcus conceptual framework to the problem of intervalence transitions [45–47]. The energy surface for thermal ET is obtained from a two-state classical model in which the electronic interaction between diabatic surfaces, those who would be occupied for a Class I compound, is the off-diagonal matrix element H in a 2 × 2 secular determinant. The solution gives the adiabatic energy surfaces:

$$E_{\pm} = 0.5\{(H_0 + H_1) \pm [(H_0 - H_1)^2 + 4H^2]^{1/2}\} \tag{3}$$

Eq. (3) is used to calculate the solid curves represented in Fig. 2 from the dashed diabatic states, both for a symmetric (Fig. 2a–c) and an asymmetric system (Fig. 2b–d).

Symmetric Class II compounds have their diabatic minima at the same energy, i.e. at 0 and 1 in a suitably scaled coordinate system, and a vertical separation equal to Marcus's reorganization energy λ (see Fig. 2a). The electronic mixing H causes the ground state adiabatic surface to be a double minimum well with a maximum at an energy value of $\lambda/4 - H$. When H is large enough to observe it this model predicts there will be an intervalence charge transfer (IT) band with an optical transition energy at the band maximum, $\tilde{\nu}_{\max} = \lambda$. The quantity $\tilde{\nu}_{\max}$ is also called E_{op} and is invariant with H for Class II compounds [48].

The positions of the two minima approach each other towards 0.5 as H increases. The thermal ET barrier is given by

$$\Delta G^{\#} = \left(\frac{\lambda}{4} - H\right) + \frac{H^2}{\lambda} \tag{4}$$

and disappears at $H = \lambda/2$, when the compound becomes a Class III delocalized system for this and higher values of H.

In the case of strong coupled Class III systems, for which it is no longer appropriate to use the perturbation theory, the magnitude of H has become so great that $E_{\mathrm{th}} = 0$. The odd electron is now delocalized between metal centers and $E_{\mathrm{op}} = 2H$ (see Fig. 2c).

Class II and Class III behavior for an asymmetric system is represented in Fig. 2b and d.

For Class II systems, Hush derived the following relationships of intervalence band properties.

Symmetric systems:

$$E_{\mathrm{op}} = 4E_{\mathrm{th}}, \qquad \Delta\tilde{\nu}_{1/2}\,(\mathrm{cm}^{-1}) = (2310\tilde{\nu}_{\max})^{1/2} \tag{5}$$

Asymmetric systems:

$$E_{\mathrm{op}} = \lambda + E_0, \qquad \Delta\tilde{\nu}_{1/2}\,(\mathrm{cm}^{-1}) = [2310(\tilde{\nu}_{\max} - E_0)]^{1/2} \tag{6}$$

The band width of a Gaussian shaped IT band, symmetrical about $\tilde{\nu}_{\max}$, is given in the high temperature limit by the more generic expression [49]:

$$\Delta\tilde{\nu}_{1/2} = (16RT\ln 2\tilde{\nu}_{\max})^{1/2} \tag{7}$$

At room temperature this formula reduces to Eq. (5).

Many Class II intervalence compounds with transition metal centers lie near the borderline II/III and therefore have exceptionally fast thermal ET. A definition of these complexes can be given introducing a mixing coefficient α, approximated as $H/\tilde{\nu}_{\max}$. This approximation becomes increasingly poor as the borderline is approached. A criterion to distinguish between Class II and Class III compounds can be either the adiabatic minima separation or the disappearance of $\Delta G^{\#}$. We assume that the latter is the best definition of Class II/Class III borderline [48].

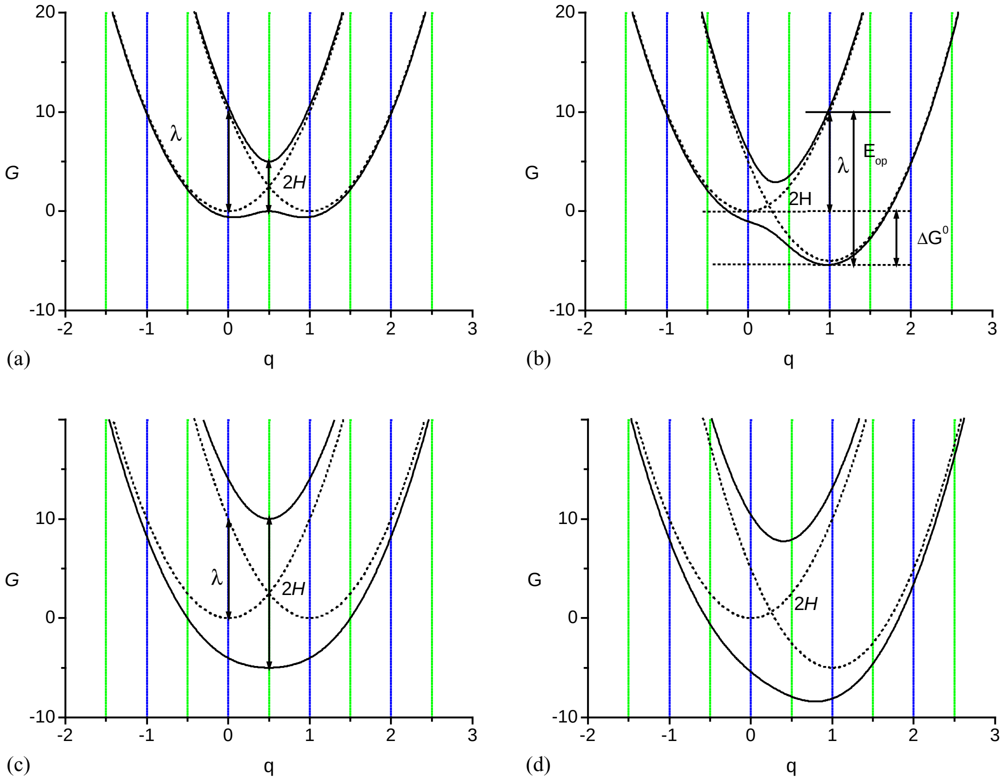


Fig. 2. Energy plots of Hush two state model: (a and b) Class II intervalence compound drawn for $H = \lambda/4$; (c and d) Class III intervalence compound drawn for $H = 3\lambda/4$. Parabolic diabatic energy surfaces are shown as dotted lines; the adiabatic surfaces calculated using Eq. (3) are shown as solid lines. Both the isoergonic (a and c), $\Delta G^\circ = 0$, and the exergonic cases (b and d), $-\Delta G^\circ = 5$, are shown.

A recent review on these Class II/Class III complexes, focussing on the transition from localized to delocalized systems in MV chemistry, is that by Meyer and coworkers [50].

The Hush model is the preferred method of analysis of mixed valence complexes because of its readily understandable derivation, its overlap with Marcus theory and the facility of its application. However it is applicable only to weakly coupled Class II complexes. Two fundamental reviews rich in examples about the application of Hush theory to MV complexes of transition metal centers are those by Creutz [1] and by Crutchley [3] on binuclear ruthenium species.

Other theoretical approaches were developed which have validity for all classes of MV complexes. For example Piepho, Krauz and Schatz have developed a vibronic coupling model (PKS model) that is applicable to both Class II and Class III mixed-valence complexes [51,52]. Ondrechen developed a realistic three-site model for delocalized Class III bridged mixed valence complexes [53].

Creutz et al. revisited the Hush model and demonstrated that it can be used to calculate also metal–ligand coupling elements for any donor–acceptor system, provided overlap may be neglected and the charge transfer transition dipole moment lies along the donor–acceptor bonding axis [54]. An example of application of both Hush and Creutz–Newton–Sutin models to binuclear mixed valence ruthenium complexes, exhibiting from valence trapped to nearly delocalized behavior can be found in the work of Evans et al. [55].

The rapidly evolving advances in theoretical, experimental and computational techniques allowed enormous recent progress in quantitative understanding of ET processes at the molecular level. The availability of ab initio and of the promising density functional theory (DFT) methods is of great value for a chemically accurate description of both ground and excited state systems [56], including those of our interest. From recent examples of application of these methods [33,57,58] it is clear that computational results might provide in the near future better rationalization of intramolecular ET in mixed valence complexes.

2. Carbon σ-bonded molecular wires

One of the most fascinating classes of bimetallic complexes spanned by an organic spacer is represented by those rod-like molecules where two metal centers are σ-bonded to an unsaturated hydrocarbon chain, the so called carbon σ-bonded molecular wires. Their one-dimensional and semi-rigid structures facilitate the tuning of the electronic communication between the two redox active termini and makes them intriguing materials for their potential applications as molecular devices, switches and current rectifiers [5,13].

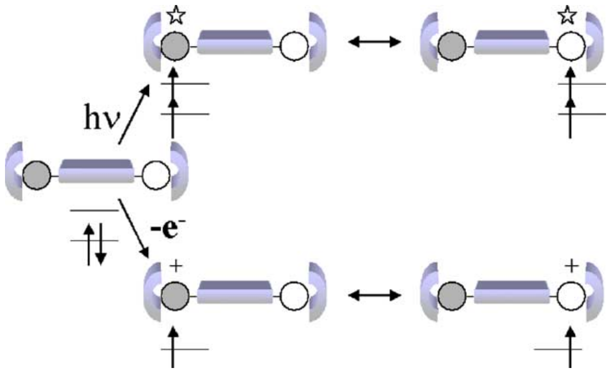


Fig. 3. Molecular wires: photonic and electrochemical activation.

Alkyl spacers are far less suited for intramolecular electronic communication than alkene, polyene, alkyne or polyyne units, which constitute interesting carriers for long-range ET. Polyalkynyl bridges are strongly favored for their relative rigidity which allows a stricter control of the molecular geometry.

Synthetic problems precluded a rapid development of organometallic molecular wires and the bridge maximal length of molecules able to transfer electrons from one end to the other is much smaller than the lengths of their purely organic homologues [59,60]. ET can be activated electrochemically or by photo-induction, as it is sketched in Fig. 3. Moreover, very few of the molecular wire compounds that have been prepared have been experimentally tested and evaluated for their electron conduction capability. Electron conduction capacity is difficult to prove. It can be observed [13] directly by measuring the bulk conductivity of the material or by looking at the electronic interaction between the two metals using electrochemistry (CV, cyclic voltammetry), or, when odd-electron states are stable, NIR spectroscopy. In presence of photo-switchable redox groups (photonic molecular wires) ET can be studied by time-resolved UV-Vis spectrometry and fluorimetry. Finally, since heterobinuclear molecular wires are polarized molecules, some qualitative information on electronic delocalization within the wire comes from measuring NLO properties.[1] In principle, electron conduction capacity can be obtained by directly measuring the conductivity of the single molecule, an innovative investigation that has been seldom performed experimentally on real molecules. This method requires molecules that are well defined in size and shape and with a sufficient length (at least 10 nm), to satisfy the technological problem of properly interfacing the molecule ends with macroscopic conductors.

Among the studies on bimetallic molecular wires which have been carried out essentially in the last 20 years, those regarding synthetic aspects represent the great majority, while those focusing on the electronic communication aspects are far less numerous, in particular for those complexes characterized by an asymmetry of the two metal centers. Purely synthetic studies have been reviewed by Lapinte and will not be repeated here [13]. On the other hand, specific complete studies on electronic communication have been conducted mainly on homobimetallic species and they will be here mentioned for a comparison with the results obtained in structurally related heterobimetallic complexes.

Adopting the designation by Paul and Lapinte [13] we can classify the molecular wires with a σ-bonded carbon bridge according to the structure of the organic spacer: all-carbon sp bridge, carbon based sp^2 bridge or other carbon based sp/sp^2 bridge.

2.1. All-carbon sp bridged molecular wires

Among polyalkynyl bridged binuclear complexes one can distinguish between compounds with an even number of carbon atoms and those with an odd number of carbon atoms. The HC_nH series is known only for even n and this is due to the different nature of the ground states for compounds with an even and an odd number of carbon atoms; a stable closed shell singlet in the former case and an unstable open shell triplet in the latter case [65].

Bridged binuclear compounds with a C_n bridge[2] are by far more common than C_{n+1} bridged ones, especially derivatives of butadiene [66]. Depending on the d electronic configuration of the metals, the C_4 chain displays either a polyynic (reduced) form or a cumulenic (oxidized) structure. The communication between the two metals can be expressed by three valence structures related to the C_n chains which are formally related by two-electron oxidations (see Scheme 3).

It has been calculated both at semi-empirical and DFT level of theory that the geometrical structure is essentially determined by the nodal pattern of the highest molecular orbitals of d_π–p_π character of the bridge. With good approximation the valence formulations can be forecasted on the basis of the d^n configurations of the endgroups: d^5-polyynic structure I, d^6-cumulenic structure II and d^7-polyynic structure III. A detailed theoretical description can be found in [13].

Very few compounds have been synthesized with an odd number of carbons in the bridge with a length greater than one and only non-symmetrical examples are known, i.e. heterobimetallic complexes or homobimetallic species with different ancillary ligands. This is due mainly to synthetic difficulties, the chain assembling being much easier by coupling of C≡C building blocks which lead only to even number bridges. For those odd-carbon complexes two dif-

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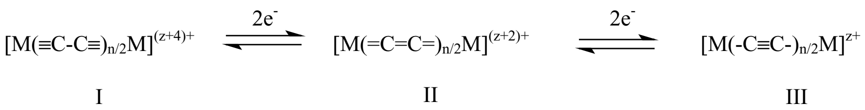
[1] Although non-linear optics (NLO) studies are very interesting and provide insight into the intramolecular electronic communication, we do not discuss this phenomenon in detail in this review. An extensive treatment of organometallic dipoles with NLO properties can be found in specific literature [61–64].

[2] Here and in the following, n denotes an even number.



$$[M(\equiv C\text{-}C\equiv)_{n/2}M]^{(z+4)+} \underset{}{\overset{2e^-}{\rightleftharpoons}} [M(=C=C=)_{n/2}M]^{(z+2)+} \underset{}{\overset{2e^-}{\rightleftharpoons}} [M(\text{-}C\equiv C\text{-})_{n/2}M]^{z+}$$

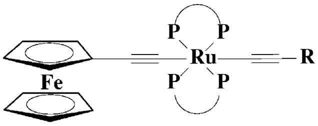
I II III

Scheme 3.

ferent valence structures are possible: a cumulenic structure M=C=(C=C)$_n$ = M′ and polyynyl/carbyne structure M–(C≡C)$_n$–C≡M′ with a metal–carbon single bond on one end and a metal–carbon triple bond on the other [67].

In this section, we present an overview of the major studies on all-carbon sp bridged molecular wires following a chronological and structural order.

In the 1980s, several workers described σ–σ-ethynide-bridged complexes of transition metals, like gold(I) [68,69], palladium(II), platinum(II) [70], rhenium(I) [71] and tungsten [72]. For example, the molecular and electronic structure of $(OC)_5ReC\equiv CRe(CO)_5$ was studied [71] to investigate the interactions occurring between the two rhenium atoms and the bridging acetylide ligand. Complexes with C_2 ligands bonded to two metals are quite rare, but they represent the shortest example of sp wires [73–76]. A series of novel heterobimetallic bis(acetylide) ferrocene complexes featuring a bis[1,2-bis(diphenylphosphino)-methane]Ru center and seven various aromatic acetylene ligands have been more recently synthesized and characterized (**1**) [77].[3]



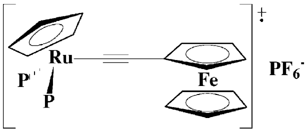
1

R = Ph, 4-Ph-C_6H_4, 4-Me-C_6H_4, 4-$NO_2C_6H_4$, 3-Me,4-NO_2-C_6H_3, 2-NO_2-C_6H_4, ferrocenyl

The electrochemical behavior of these systems is greatly affected by the degree of metal–metal interaction. The electronic spectra contain an inter-valence charge transfer (IVCT) band in the NIR region, indicating that the mixed valence species belong to Robin and Day Class II.

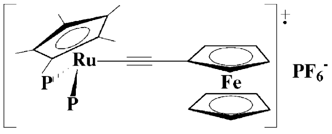
Other ferrocenylacetylide ruthenium complexes (**2** and **3**) were studied by Sato et al. [78]. CV data suggest a large electronic delocalization between the Fe atom and the Ru(II) atom in the corresponding one-electron oxidized species. A detailed study based on X-ray diffraction, NIR and Mössbauer spectroscopy, allowed to assign the radical cation of **2** to Class II.

Recently, Sato et al. [79] studied the oxidatively induced reductive elimination in *cis*-aryl platinum(II) complexes (Scheme 4), a rare example in which a chemical reaction is initiated by the metal–metal interaction. This reaction is induced by the oxidation of the ferrocenyl moiety and is promoted by electron donating substituents on the aryl ligand. The ferrocenyl part is first oxidized giving a radical cation; then an electron transfer occurs from the Pt part through the C≡C bond and the electron density on platinum decreases, accelerating the reductive elimination.



2

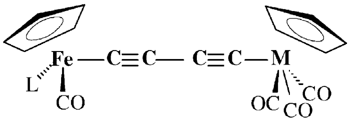
P = PPh_3
P_2 = dppf



3

P = PPh_3

Increasing the length of the C_x spacer we find examples of C_3 and C_4 bridged complexes. The first example of heterobimetallic complexes containing the C_4 ligand was presented by Wong et al. in 1990 [80]. The employed metals were Fe, Mo and W; the ancillary ligands of these half-sandwich complexes were Cp (Cp: cyclopentadienyl), CO and PPh_3 (**4**). However, information on the electronic interaction between the metals was obtained only for the analogous homobimetallic Fe compound, studying the effect on IR (infrared) spectra of the substitution of one CO by PPh_3. A significant variation of ν_{CO} of the CO on the second iron fragment was observed, suggesting that the butadiynediyl ligand is effective in conveying electronic information between the two metal centers in the same molecule.



4

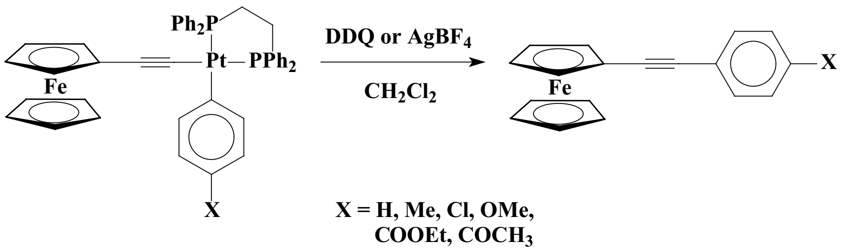
M = Mo, W, Fe; L = CO, PPh_3

Much of the pioneering work of synthesis and characterization of polyynyl molecular wires is due to Gladysz and coworkers. In 1993, they described a mixed valence complex of formula Cp*Re(NO)(PPh_3)(C≡C–C≡C)(Ph_3P)(ON)ReCp* in which both metals are stereocenters [81,82]. The radical cation was isolated, and IR and ESR measurements established that the odd electron is fully delocalized between the two rhenium atoms.

Almost contemporarily, Lapinte reported a study on the achiral radical cation of the related C_4 species Cp*Fe(dppe)(C≡C–C≡C)(dppe)FeCp* and provided further evidence for the ready accessibility to multiple redox states in μ-butadiynediyl compounds [83]. A delocalized

---

[3] In this and few other complexes, the hydrocarbon bridge is σ-bonded to one metal, but is in general linked to a Cp moiety on the opposite side, as in fulvalene-like bridged complexes. We will describe these ‘hybrid’ examples, that cannot be classified according to the proposed scheme, in this section.



Scheme 4.

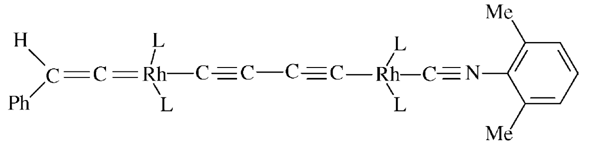
ground state was assigned also on the basis of IR and Mössbauer data.

The work on the ReC$_4$Re assembly was later completed [84]. Three *consanguineous* (species derived from a common ancestor and differing only in electron count) complexes were isolated. ReC$_4$Re and $^+$ReC$_4$Re$^+$ were crystallographically characterized. ESR spectra of the radical cation indicate spin delocalization over the two rheniums; IR spectra give only one ν_{NO} band, positioned between those of the neutral and of the dicationic complexes. Important evidence for electronic communication came from NIR spectra of the radical cation: by its analysis an assignment to Class III was established by the authors. This investigation on the family of compounds characterized by an acetylenic wire capped at each end by a redox active rhenium fragment was further elaborated until the longest molecule to date containing a C$_{20}$ bridge between two metal atoms was reported [85–87].

Another example of C$_4$ bridged rhenium(I) wires was given by Yam et al. [88], who initiated a program to investigate the possibility of incorporating rhenium(I) diimine luminophores into the bis-acetylide backbone. They presented the synthesis, photophysics and electrochemistry of $Re(^tBu_2bpy)(CO)_3(C{\equiv}C{-}C{\equiv}C)Re(^tBu_2bpy)(CO)_3$. To date the authors have not examined the electronic communication between the two metal nuclei, but rather the electrochemical and spectroscopic studies have been mainly centered on the bridging ligand properties, and on the MLCT $d\pi(Re) \rightarrow \pi^*(^tBu_2bpy)$ (bpy: bipyridine) transitions in the bimetallic and in the monometallic acetylide Re(I) complex.

Heterobinuclear buta-1,3-diynyl compounds of formula $Cp(CO)_3W(C{\equiv}C{-}C{\equiv}C)M(CO)_xCp$, where M can be W, Mo or Fe, were synthesized by Bruce et al. [89], but no specific studies on electronic communication were carried out. More recently the same authors have given new contributions to the oxidation chemistry of metal bonded C$_4$ chains, with a spectroelectrochemical and computational study on the complex $\{Cp(PPh_3)(PR_3)Ru\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ (R = Ph, Me, Cp) which can be obtained in an unprecedented series of five oxidation states [90]. On the basis of experimental data the mixed valence radical cations are assigned to Class III with the unpaired electron delocalized over the Ru–C$_4$–Ru six-atom fragment (estimated *H* values are about 0.7 eV). Theoretical calculations, carried out on the model complexes $[\{Cp(PH_3)_2Ru\}_2(\mu\text{-}C_4)]^{n+}$ ($n = 0$–4), indicate that the oxidation affects both the metal centers and the carbon atoms of the C$_4$ bridge, since the process corresponds to the removal of electrons housed in MOs delocalized over all atoms of the Ru–C$_4$–Ru chain. An interesting investigation on these model complexes with different ancillary ligands was carried out. Bruce et al. [91] have described also the synthesis, structures and spectroelectrochemistry of $\{Cp^*(PP)Ru\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ (PP = dppm, dppe) (Cp*: pentamethylcyclopentadienyl; dppe: 1,2-bis-(diphenylphosphino)ethane; dppm: bis(diphenylphosphino)methane) and of the corresponding mono and dications. A Class III description seems appropriate also for these mixed valence di-ruthenium molecular wires.

Asymmetric di-iron complexes of formula $(\eta^5\text{-}C_5R_5)(dppe)Fe{-}C_4{-}Fe(CO)_2Cp^*$ (R = CH$_3$, phenyl) were synthesized and characterized by Lapinte and coworkers [92,93], who included a comparison with the corresponding mononuclear species. In the bimetallic complexes the IR frequencies of the carbonyl groups indicate the existence of electronic communication between the metal centers through the C$_4$ spacer. The ^{57}Fe-Mössbauer spectrum established that the electron density on the two iron atoms is quite different. In fact, the spectrum of the pentamethylcyclopentadienyl species displays two well separated doublets, both with almost the same quadrupolar splitting. The isomeric shifts of the two doublets are quite different ($\delta = 0.257/0.192$ and $0.029/-0.033\,mm\,s^{-1}$ at 80/293 K, respectively) and this is in agreement with a strong polarization of the homobinuclear compound. The isomeric shifts at δ 0.257 and 0.029 are assigned to the iron centers of Cp*Fe(dppe) and Cp*Fe(CO)$_2$ building blocks on the basis of the isomeric shifts of the analogous monometallic species; the isomeric shift of the binuclear complex is temperature dependent and the separation between the two doublets is almost constant. Cyclic voltammograms give further support to strong metal-to-metal interaction. ESR, Mössbauer spectroscopy and Hush analysis of the IT band observed in the NIR region were carried out to study the radical cation species, which was assigned to Class II. Lapinte highlighted the efficiency of the C$_4$ backbone, which provides rigidity to the molecular structure. Thanks to a large degree of covalency of the metal–carbon bonds, which favors mixing of the orbitals of the carbon linkage with those of the transition metals, the C$_4$ bridge induces possible new properties that the mononuclear components do not possess. Then, such molecules can be considered interesting models of polarized molecular wires.



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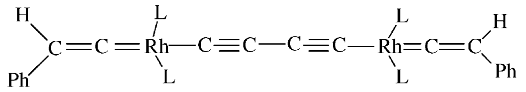
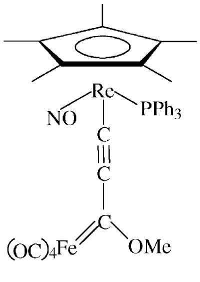


6

Symmetrical and unsymmetrical Rh(I) complexes containing a C_4 bridge were reported by Werner and coworkers [94,95]. The effect of a different coordination sphere at the metal centers on both sites of the C_4 chain was investigated by absorption spectroscopy. For example, the comparison of the two complexes **5** and **6** gives a hint as to the strength of the mutual electronic interaction between the metal centers through the C_4 chain. The red shift of the absorption maxima (439 and 638 nm) of **5** compared to the corresponding maxima of **6** (429 and 621 nm) is due to the better donor ability of the isocyanide compared with the vinylidene ligand, indicating that there is a push-pull interaction between the $Rh(CNR)L_2$ and the Rh(=C=CHPh) units. Werner et al. [96] isolated also two binuclear iridium(III) compounds with a C_4 bridge.

In 1993, Gladysz presented a study on a C_3 chain spanning two different transition metals, rhenium and manganese [97]. From speculations on the cationic carbyne species by UV-Vis spectroscopy, charge transfer from rhenium to the adjacent metal center was evidenced. These studies on electronic communication in wirelike cumulenic odd number (three and five) carbon bridged bimetallic complexes of Re, Fe, W and Mn were continued [98,99]. The investigated molecular structures are **7**, **8**, and **9**.



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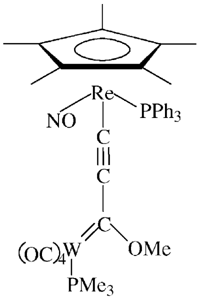

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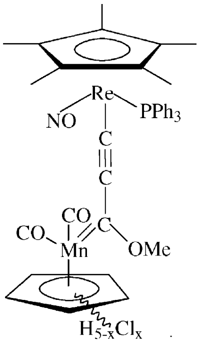
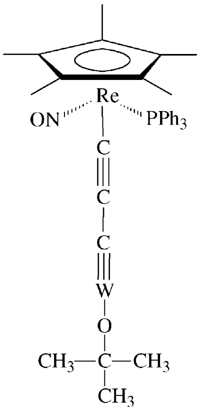


9 (x=0,1,5)

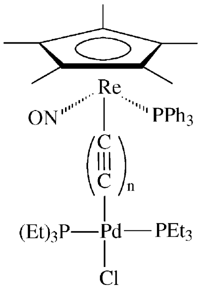
By reaction with excess BF_3 gas, complexes **7** and **9** give the corresponding cationic carbyne complexes, while the methoxy group is removed. It is interesting to notice in the IR spectra of the oxidized fully chlorinated **9** that a cumulenic resonance form with the charge localized on rhenium dominates over the polyynic one and the shifting of maxima to longer wavelengths in UV-Vis spectra, as the number of cyclopentadienyl chlorine increases, suggests an appreciable rhenium-to-manganese charge transfer character (see Fig. 4).

On the contrary, in the three-carbon chain complex **10**, no special metal–metal interaction has been detected by NMR and IR, and crystallographic data establish dominant the polyynic form [100].

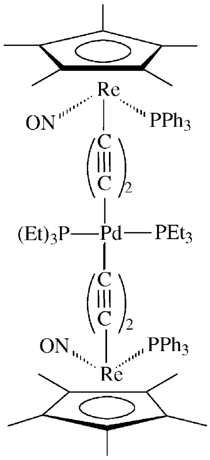


10

Hetero- bi- and tri-metallic half-sandwich carbon complexes, where the spacer is formed by one or two alkyne units, the metals Re, Rh and Pd and the ancillary ligands CO, PPh_3 and PEt_3, were also synthesized and studied by Gladysz and coworkers [101]. They are **11** and **12**.



11 (n=1,2)



12

The oxidation of complex **11** ($n = 1$) generates a radical cation that could be rhenium centered, palladium centered or delocalized: this represents the first radical cation derived from an heterobimetallic complex. By CV of complex **11**, the localized nature of the radical cation was evidenced, since rhenium is much more readily oxidized than palladium (see Fig. 5 and Table 1). Comparing oxidation in complexes **11** with $n = 1$ and 2, it was clear

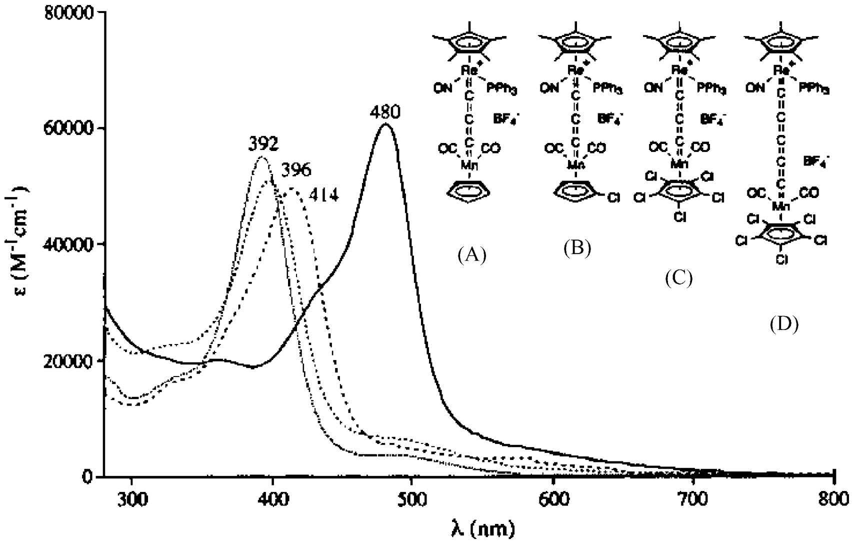


Fig. 4. Representative UV-Vis spectra of C_3 and C_5 complexes (CH_2Cl_2, ambient temperature). Reproduced with permission from [99]. Copyright by the American Chemical Society.

Table 1
Cyclic voltammetry data

Compound	$E_{\mathrm{p,a}}$ (V)	$E_{\mathrm{p,c}}$ (V)	E° (V)	ΔE (mV)	$E'_{\mathrm{p,a}}$ (V)
[Re*]CH_3	0.32	0.25	0.29	70	
[Re*]C≡CCH_3	0.40				
[Re*]C≡CC≡CCH_3	0.52				
[Re*]C≡C[Pd]Cl	0.12	0.05	0.08	70	1.25
[Re*]C≡CC≡C[Pd]Cl (**11**, $n = 1$)	0.35	0.28	0.32	70	1.29
[Re*]C≡CC≡C[Pd]C≡C C≡C[Re*] (**12**)	0.36	0.28	0.32	80	1.29
[Re*]C≡CC≡C[Re*]	0.15	0.06	0.11	90	0.68
PhC≡C[Pd]C≡CPh	1.48				

Re* = Cp*(NO)PPh_3Re and Pd* = Pd(PEt_3). Reproduced with permission from [101]. Copyright by the American Chemical Society.

that the process becomes thermodynamically less favorable as the sp carbon segments are lengthened. Moreover, on the basis of the E° values of [Re*]C≡C–C≡C[Re*] and [Re*]C≡C–C≡C[Pd]Cl (0.11 and 0.32 V, respectively), it is to note that the substitution of a [Re*] with a [Pd]Cl group hampers the electron delocalization between the metal termini through the C_4 bridge. In our opinion this effect can be ascribed to the molecular asymmetry due to the different electronic nature of [Pd]Cl in regard to [Re*] group which increases the barrier for the electron transfer and consequently inhibits the interaction between adjacent metals. A comparison might be performed also with the trimetallic species **12** in which the presence of palladium presumably inhibits the electron delocalization between the two rhenium atoms whilst in the homobimetallic [Re*]$(C{\equiv}C)_4$[Re*] a metal–metal electronic interaction is encountered [87].

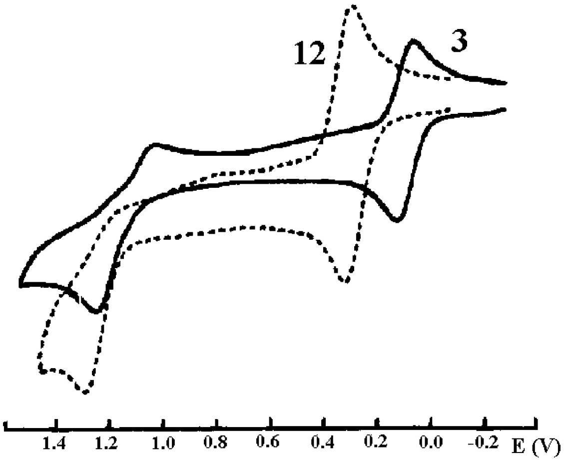
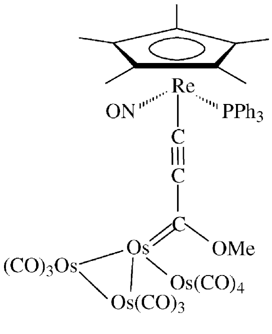


Fig. 5. Cyclic voltammograms of complexes **11** ($n = 1$) and **12** recorded in CH_2Cl_2 at 100 mV s^{-1} ($E^{\circ\prime}$(ferrocene) = 0.56 V). Reproduced with permission from [101]. Copyright by the American Chemical Society.

The authors draw the same conclusions analyzing ESR spectra, which show that the odd electron is localized on one rhenium.

Another class of heteropolymetallic complexes studied by Gladysz is characterized by a new form of coordinated carbon in which a three carbon atom chain links two metals which are bonded to a third metal in a cluster fashion [102]. An example of rhenium/osmium complex of this type is **13**. The terminal trimetallic cluster is a versatile architecture which allows many modes of chain attachment: other examples of asymmetric tetrametallic complexes can be found in [103,104] (**14**).



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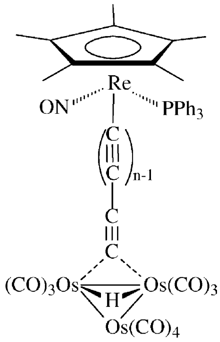
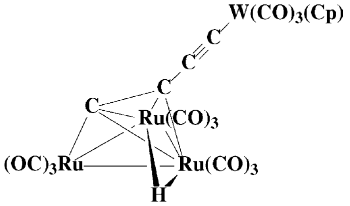


14

The oxidation of these complexes have no counterparts in $[Os_3(CO)_{10}(L)_2]$ compounds and the potentials are much less favorable thermodynamically than those of other analogous rhenium derivatives. The less facile oxidation versus other rhenium complexes or the more facile oxidation versus other tri-osmium complexes can be explained in terms of a great contribution by zwitterionic resonance forms $^{+}Re{=}(C{=}C)_n{=}(Os)_3{}^{-}$. In contrast to symmetrical rhenium complexes the longer chain adducts are more easily oxidized. This can be rationalized by a slight decrease in zwitterionic character with chain length, rendering the rhenium more electron rich, which is consistent with IR data.

An unusual heterobinuclear complex formed by tungsten connected to a tri-ruthenium cluster by a diynyl bridge was described by Bruce et al. [105]. The X-ray structure of the complex **15** suggests that there is a tungsten–carbene interaction with Ru(3), but no further studies on electronic communication were presented.



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A *conjugal* (featuring two unlike metal fragments) family of butadiynediyl bridged complexes of Re/Fe has been described by Gladysz and Lapinte [106] (**16**). In their paper data are carefully compared to those of the analogous consanguineous di-iron and di-rhenium complexes. Both the iron and the rhenium endgroups prove particularly effective in ET capabilities. The complex was structurally characterized by X-ray analysis and the corresponding mono and dication were characterized in detail by CV, IR, NMR, NIR, ESR and ^{57}Fe Mössbauer spectroscopies: this paper represents the first complete systematic study of hetero-substituted polyynediyl complexes.

Table 2
Electrochemical data

Compound	ΔE_p (V)	$E°$ (V)	i_c/i_a	$\Delta E°$ (V)
16	0.07	−0.50	1	0.73
$ReCp^*(NO)(PPh_3)C_4SiMe_3$	0.25	0.35	3	
$FeCp^*(NO)(PPh_3)C_4SiMe_3$	0.09	0.00	1	

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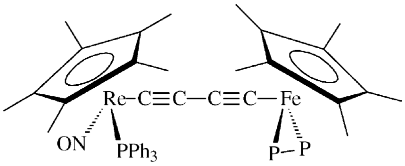

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Comparing the CV data (see Fig. 6 and Table 2) with those of the related monometallic species the radical cation has dominant iron character; the first oxidation occurs at the iron center, the second oxidation occurs at rhenium. These conclusions are further supported by the comparison of the CV curves with those of the structurally related homobimetallic complexes: the replacement of one of the iron endgroup with a rhenium endgroup decreases the electron density at iron, making its oxidation more difficult. Interesting information comes from the NIR spectrum of the radical cation: an IVCT band is observed, and on the basis of the Hush model the complex is assigned to Class II.

As previously mentioned great contributions to the research on electronic communication in binuclear molecular wires have come also from Lapinte. He presented a complete paper on synthesis and characterization of the diiron half-sandwich complex of formula Cp*Fe(dppe)(C≡C–C≡C)(dppe)FeCp* and its consanguineous derivatives [107]. The radical cation is a stable centrosymmetric mixed valence cation: a NIR intense band allowed its assignment to Class III. From the NIR data the coupling element *H* was calculated to be 0.47 eV. It is interesting to compare this value

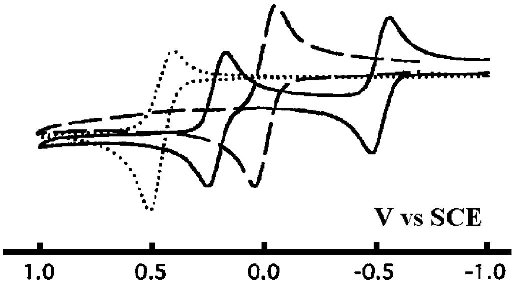


Fig. 6. Cyclic voltammograms of complex **16** (solid line) and related monometallic complexes (Fe, dashed line, and Re, dotted line) in 0.1 M n-$Bu_4N\ PF_6/CH_2Cl_2$ (Pt electrode; V versus SCE; scan rate 0.100 V s^{-1}; 20 °C). Reproduced with permission from [106]. Copyright by the American Chemical Society.

to that reported in [92] for the asymmetric mixed valence complex with the same backbone FeC_4Fe (0.021 eV), which is discussed above. While the symmetric complex is assigned to Class III, the asymmetric species is undoubtedly a valence trapped Class II species, showing that the overlap between the electronic wavefunctions of the donor and acceptor groups decreases abruptly with the energy difference between the donor and acceptor centers.

The dication was characterized by CV, IR, ESR, NMR, Mössbauer and electronic spectroscopy and no evidence of cumulenic structure was encountered. It was also attempted to extend the C_n bridge to longer and linear carbon chains, in order to investigate the effects of distance on the electronic communication. $[\{FeCp^*(dppe)\}_2(\mu{-}C_8)]$ was synthesized and characterized [108]. From CV measurements on the neutral complex, a greater coupling is observed than in di-rhenium analogous compounds by Gladysz. The mixed valence radical cation was characterized by CV, IR, UV-Vis, NIR and on the basis of Hush model it was assigned to Class III, evidencing a noticeable electronic communication between the metal termini. Recently Lapinte synthesized also a new mixed valence complex of formula $[Cp^*(dppe)Fe{-}C{\equiv}C{-}X{-}C{\equiv}C{-}Fe(dppe)Cp^*][PF_6]$ ($X = 2,5\text{-}C_4H_2S$) [109]. This work is particularly interesting since the properties of the species are compared to those of the related all carbon bridged complex ($X = {-}C_4{-}$) by characterization through cyclic voltammetry, IR and NIR, ^{57}Fe-Mössbauer, UV-Vis and ESR spectroscopies. The introduction of thiophene into the C_4 chain constitutes an attractive mean to expand the size and to increase the rigidity of molecular wires. In fact, the Class III electronic communication at the molecular level is apparently not affected by inclusion of the thiophene unit with the advantage that the synthesis is greatly facilitated with respect to the C_8 analogous species [108].

A recent study on homobimetallic complexes of tungsten and chromium with conjugated C_4, C_6, C_{10} and C_{14} bridges was carried out by Fischer and coworkers [110]. From a comparison of the IR and NMR spectra of the C_6, C_{10} and C_{14} bridged symmetric species with the C_2 one, only weak π-interactions between the metal fragments through the bridge could be identified.

2.2. Carbon based sp^2 bridged molecular wires

Among sp^2 bridges we can distinguish polyalkenes, polyphenylenes and mixed alkene/phenylene spacers.

The *para*-substituted polyphenylene units are conjugated linkers of fixed geometry composed of sp^2 carbon atoms, but they show some disadvantages with respect to polyalkynyl and polyalkenyl bridges. These include higher activation barriers for intramolecular ET with increasing length owing to the loss of aromaticity, and a decrease of π-orbital overlap in successive para substituted units owing to rotation of the units in the bridge, implying a reduced electronic interaction [13]. Despite these disadvantages the 1,4-phenylene unit is attractive regarding its stability and synthetic potential. It can be incorporated in bridges composed of several different spacers, providing more stability, rigidity of the wire core and allowing geometric modifications and multi-branching to be achieved.

Polyethylene bridged complexes are another investigated class of hydrocarbon bridged complexes, but most of them contain identical metals bonded to the $-(CH)_n-$bridge [111–114].

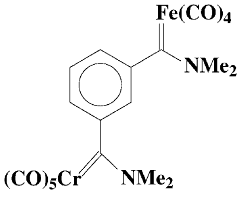
A particularly interesting set of studies by Sponsler and coworkers [115] was carried out on the di-iron complexes, Cp(CO)LFe(CH=CHCH=CH)Fe(CO)LCp (L= CO, PMe_3, PPh_3). These authors synthesized butadienediyl-bridged di-iron complexes and oxidized them to their radical cation and dication species. X-ray crystal structures of the dication, cyclic voltammetry and electronic absorption spectroscopy provided evidence for a strong coupling between the metal nuclei through the C_4 bridge. Other interesting works by Sponsler deal with Cp(dppm) Fe(CH=CHCH=CH)Fe(dppm)Cp [116,117] and on the bisalkylidene di-ruthenium complex $[(Cy_3P)_2Cl_2Ru]_2$ (μ-CHCH=CHCH) [118].

Methylene bridged complexes in which the $-CH_2-$ bridge links two metals of disparate electronic properties are relatively rare; examples of their reactions and structural features can be found in [119–122].

Some polyalkenyl bridges are connected to cyclopentadienyl moieties in sandwich or half-sandwich complexes; thus they will be described in the Section 3 dedicated to fulvalenes.

A mixed chromium-iron μ-bis(aminocarbene) complex (**17**) was synthesized and characterized by X-ray diffraction by Dvorak and coworkers [123]. No examination of the electronic communication between the metal termini was reported.

Another example of a novel heterobinuclear complex (**18**) was presented by Fischer et al. [124].



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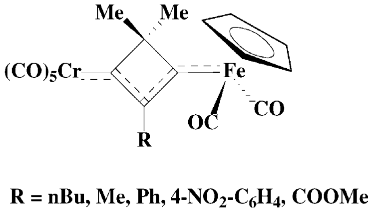


18

The spectroscopic data as well as the X-ray structural analysis of complex **18** indicate strong electronic communication between the metal centers in this cyclobutenylidene heterobinuclear complex.

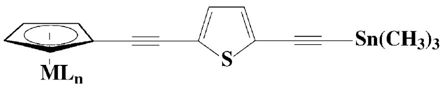
Homo-bi- and poly-nuclear platinum complexes with a biphenyl bridge were designed and synthesized in the attempt to obtain nanoscale organoplatinum macrocycles with unique mechanical, chemical and optical properties [125]. The characterization was performed by IR, NMR and mass spectroscopy, but no specific investigation on electronic communication was carried out.

2.3. Other carbon based sp/sp^2 bridged molecular wires

Mixed sp/sp^2 unsaturated bridges are mainly those where a polyynic chain is interrupted by a ethylenic sequence or by an aromatic ring which increases the system rigidity.

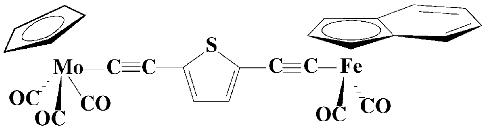
Ruthenium and ferrocenyl homobimetallic, RuPdRu and FePdFe heterotrimetallic complexes connected by unsaturated carbon-rich $–C{\equiv}CC_6H_4C{\equiv}C–$ bridges have been synthesized by Dixneuf and coworkers [126]. Electrochemistry studies have shown that the electrochemical behavior of bimetallic complexes is strongly dependent on the nature of the connection between the two terminal organometallic fragments and the 1,4-diethynylbenzene bridge. In fact ruthenium is σ-bonded to the spacer, but the ferrocenyl group is connected in fulvalenyl fashion. Moreover, the presence of the palladium moiety in trimetallic species seems to inhibit communication between the two terminal inorganic groups, a phenomenon already observed in $L_nRe–C{\equiv}C–Pd–(PBu_3)_2–C{\equiv}C–ReL_n$ [101] and discussed in Section 2.1.

Lo Sterzo and coworkers studied palladium-catalyzed carbon–carbon and metal–carbon coupling and prepared a molybdenum–iron heterobimetallic bis(acetylide) derivative of 2,5-diethynylthiophene and poly(metallacetylide) tethers [127,128] (**19** and **20**).



$ML_n = W(CO)_3CH_3, Re(CO)_3$

19



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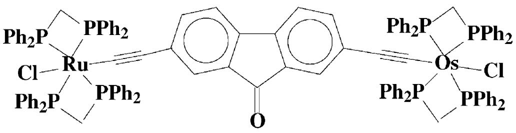
Raithby's group synthesized a binuclear ruthenium/osmium complex with a fluorenyl derivative in the bridging ligand (**21**). The homo di-ruthenium and di-osmium and the heterobimetallic species were characterized by IR and electronic absorption spectroscopy [129].



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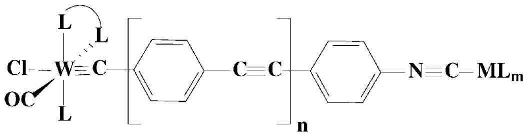
Electronic communication between metal centers across the ligands 4-isocyanobenzylidyne (**22**, $n = 0$) and 4-(4-isocyanoethynylbenzene)benzylidyne (**22**, $n = 1$) was investigated by Wing-Wah Yam [130]. From IR measurements it is evident that the palladium and platinum metal complex fragments are stronger electron acceptors than the rhenium moiety. In fact, palladium and platinum derivatives exhibit higher IR stretching frequencies for the isocyanide groups than the rhenium complexes. Electronic absorption spectroscopy proves that the employed ligands are appropriate for photoinduced electron transfer from the metal alkylidyne fragment to the isocyanide-coordinated metal. Another example of trimetallic species is the Pt(II) complex **23** [131]. It was synthesized and characterized (X-ray structure, optical, electrochemical and thermal properties) by Raithby and coworkers in an attempt to explore new classes of spacer units in novel organometallic polyyne systems. The presence of a pendant ferrocenyl donor unit in the side appears to be efficient in reducing the energy difference of HOMO–LUMO separation.



L_2 = TMEDA, n = 0, ML_m = *fac*-ReCl(CO)$_3$, *cis*-PdCl$_2$, *trans*-PtI$_2$
L_2 = dppe, n = 1, ML_m = *fac*-ReCl(CO)$_3$, *cis*-PdI$_2$, *trans*-PtI$_2$

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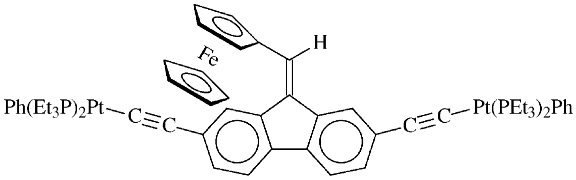

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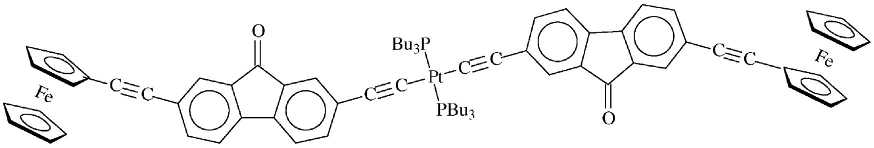
The presence of studies on electronic communication in heterobinuclear molecular wires in the very recent literature is proof of the growing interest in the field. In this regard recent work by Choi and coworkers [132] on new ferrocenyl heterometallic complexes of 2,7-diethynylfluoren9-one should be noted. The bridge in this case is analogous to that of complex **21**, but the metals employed are iron/platinum ($FeCp_2$, $Pt(PEt_3)Ph$), iron/mercury ($FeCp_2$, HgMe), iron/gold ($FeCp_2$, $Au(PPh_3)$). The oxidation of the ferrocenyl moiety is facilitated by the presence of the heavy metal center and by the conjugation in the chain through the ethynyl and fluorenone linkage units. In a trimetallic species formed by two ferrocenyl end groups and a platinum central unit (**24**), the communication through the fluorenyl system is interrupted.

These complexes were fully characterized by spectroscopic, electrochemical and structural methods and the authors drew the conclusion that delocalization of π electrons continues through the metal center to different extent and the conjugation is greater for the Pt(II) complexes than the Au(I) and Hg(II) species.



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Finally, there are some studies on mixed sp/sp^3 chains, in which the lack of conjugation in principle switches off the electronic communication. For example, the heterobinuclear complex of formula Tp′(CO)$_2$Mo≡C–CH$_2$–C≡M(CO)$_2$Tp′ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate), where M indicates molybdenum or tungsten, was synthesized by Templeton [133,134], who employed it as a 'generator' of derivative binuclear chemistry but unfortunately no systematic studies on the electronic communication were attempted.

3. Fulvalene and fulvalene-like bridges

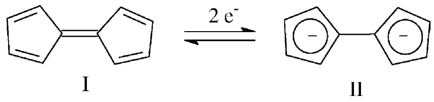
In this section, we will illustrate a wide class of heterobimetallic complexes spanned by bridging ligands containing two identical or different aromatic rings, in particular Cp, phenyl and tropylium linked directly, i.e. fulvalene like ligands, or by a hydrocarbon chain. The most common sub classes for heterobimetallic systems may be differentiated by the ring types present in the bridging ligand, such as: (i) fulvalene, (ii) phenyl-cyclopentadienyl, and (iii) other fulvalenyl-like bridges.

As for the previous classes examined in this review, we will focus on those studies including a description of the physical properties which evidence the electronic interaction between the metal centers in the ground state and in the mixed valence state.

3.1. Fulvalene complexes

3.1.1. The concept of fulvalene

Among the bridging ligands considered in this subsection, fulvalene (Fv) I and its reduced form fulvalene dianion (bicyclopentadienyl) II have attracted the most attention in the chemistry of bimetallic complexes and are still a subject of continuing investigations.

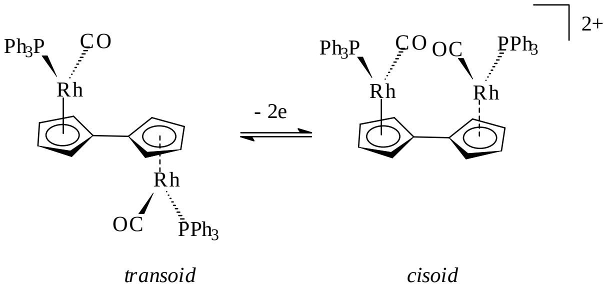


The fulvalene bridge, in fact, is notably efficient in transmitting the electronic effects between two redox centers. In particular, bi-sandwich fulvalene complexes have been thoroughly investigated as a model for the electronic communication between the metal centers when at least one undergoes reversible reduction or oxidation and the system may behave as a molecular switch or wire [135]. Exhaustive reviews on this class of binuclear organometallic complexes have appeared in the 1990s [136,137]. In the last year, a selective update of Vollhardt group's studies was published and we refer to it for a deep insight on the topic [138].

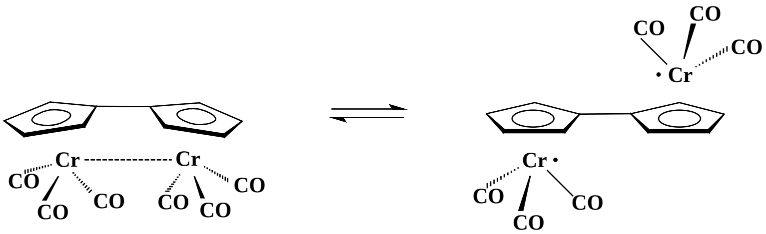
In the present work, we will cite some significant examples of asymmetric (homo- and especially heterobimetallic) organometallic complexes of this ligand. Nevertheless, some selected examples of symmetric homobimetallic complexes will be illustrated for a description of the main fulvalene peculiarities.

Bimetallic fulvalene complexes exhibit unique properties with respect to those of the corresponding monometallic analogues. The main reason is that the conjugated π system of the fulvalene system allows an efficient through-ligand intramolecular electron transfer between the metal centers regardless of whether or not there is a metal–metal bond, and whether the metal atoms are in *cisoid* or *transoid* geometry with respect to the bridging ligand [136–141]. A simple EHMO diagram of fulvalene [142] shows that two low level orbitals in the π system provide significant bonding interaction between the two Cp rings. Further support for the existence of electronic communication through the fulvalene ligand was given by the physico-chemical properties of bimetallic complexes obtained with different techniques. In fact, the cyclic voltammetry of Fv[Rh(CO)PPh$_3$]$_2$ showed a reversible two-electron oxidation at a potential about 400 mV less positive than the monometallic CpRh(CO)(PPh$_3$) analog indicating a strong stabilization of the radical cation in the homobimetallic system [143]. In order to explain this finding the authors proposed the presence of a structural rearrangement suggested by the X-ray structures showing a *transoid* conformation for the neutral complex and a *cisoid* one for the dication (Scheme 5).

In addition, the ^{57}Fe-Mössbauer spectra of the radical cations [FvFe$_2$(C$_6$R$_6$)$_2$]$^+$ (R = H, Me) at 4.2 K showed that the electron change between the iron centers is faster than 10^9 s^{-1} indicating that they belong to the Class III of the mixed valence complexes [144]. Finally, it was found that the radical cation [FvMn$_2$(CO)$_4$(μ-Ph$_2$CH$_2$PPh$_2$)]$^+$ shares the



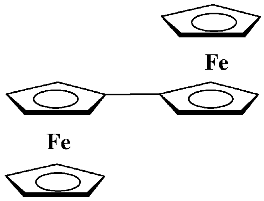
Scheme 5.



Scheme 6.

characteristics of both trapped valence (Class II) and fully delocalized systems (Class III). In fact, this radical cation has a delocalized electron on the near-IR (10^{-13} s^{-1}) and ESR time scale (10^{-8} s), along its electrochemical behavior (detrapped valence, Class III). On the other hand on the IR time scale (10^{-12} s) the radical cation was classified as a valence trapped species (Class II) [33,34,145]. This apparent incongruity was overcome by designing the system as having borderline Class II–Class III behavior [34,48,146] and a correlation of ΔE with IR spectral properties was found.

The fulvalene is a flexible bridge and in the metal–metal bonded derivatives the ligand is often bent away from the planarity. As a consequence, whereas the Cp centroid distance in the complexes bi-ferrocenyl (**25**) [147] and Fv_2Fe_2 (**26**) [148] with planar fulvalene is 4 Å, in the $FvM_2(CO)_6$ (M = Cr, Mo, W) (**27**) is less than 3.5 Å [149–151]. Such a bending causes a strain in the molecule which induces a lengthening of the M–M bond and consequently may translate into unique physical and chemical properties [152,153]. Nevertheless, it was found that in the case of $FvCr_2(CO)_6$, the fulvalene ligand stabilizes the Cr–Cr bond with respect to both enthalpy and entropy. In fact, despite the Cr–Cr bond elongation in the solid phase, the enthalpy of dissociation of the complex of type **27** (Scheme 6) is equal to or slightly higher than that of its cyclopentadienyl analog **28**. This finding is attributed to the special electronic characteristics of the fulvalene ligand. A less favorable entropy also disfavors the bond rupture with respect to **28**, since the resulting radicals are not free to dissociate and only rotational freedom is gained [153].



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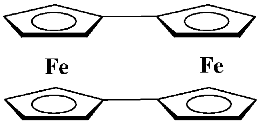

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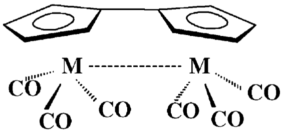

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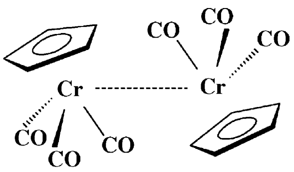

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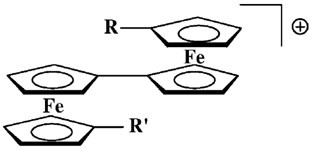
3.1.2. Homobimetallic asymmetric fulvalene complexes

In general, there are three main factors which control the rate of the electron transfer in mixed valence bimetallocenyl cations: (i) the electronic coupling between the two metal centers and their vibronic coupling which is a measure of the bond length in the metallocenyl moieties in the two different oxidation states, (ii) the zero-point energy difference between the two states, and (iii) the intermolecular cation-cation and cation–anion interactions.

The electronic interaction between the two iron centers in a series of symmetric and asymmetric mixed-valence biferrocenium cations were widely investigated by mean of their structural, electrochemical, and spectroscopic characteristics [154–163]. In particular, the main strategies were to use mixed-valence biferrocenium cations (**29**) with short [164–167] and long alkyl [168,169], and aryl [170–172] substituents at the Cp rings.



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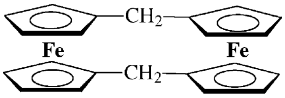
In a recent paper [173], Dong et al. compared the effect of the asymmetry in solution and solid state and demonstrated that minor perturbations caused by the alkyl substituents with terminal bromide have significant effect on the rate of the electron transfer. The magnitudes of the peak-to-peak separation ($\Delta E_{1/2}$) obtained by electrochemical measurements and the Fe–Fe distances by X-ray structure determinations indicate that the electronic and vibronic coupling between the two Fe sites are similar in solution and the zero-point energy difference between the vibronic states is small in the examined cations. On the other hand, the ^{57}Fe-Mössbauer spectra established significant differences of the intramolecular electron transfer rate and the authors suggested that the most important factor is the symmetry of the cation and the zero-point energy difference owing to intermolecular interactions which induce asymmetry between the two ferrocenyl moieties. The effect of the asymmetric substitution in mixed valence biferrocenyl cations has been probed by Cowan and coworkers [174] by single substitution either at the fulvalene ligand or at one Cp. For an asymmetric biferrocenyl cation, the two metals are not equivalent and one vibronic state is more stable than the other one and the electron transfer will result in the formation of an energetically unfavorable valence isomer. In agreement with the Hush theory, the displacement to higher energy of IT electronic absorption and a decrease of its intensity for the monosubstitued biferrocenyl cation relative to the IT band of the unsubstituted case suggested that "asymmetry reduces the rate of the electron transfer". However, in almost all biferrocenyl complexes reported, the symmetrical derivative and the corresponding asymmetrically substituted one belong to the same Class II of localized mixed valence complexes. The only example of totally delocalized (Class III) unsubstituted biferrocenyl cation is $\mathbf{26}^{+}$ which was characterized by using Mössbauer and EPR techniques [175]. Surprisingly, the 3-acetyl substitued cation [176] still appeared to be a Class III delocalized mixed valence complex, contrary to the expectation based on its asymmetry and the zero-point energy difference introduced by an electron-withdrawing group. A direct Fe–Fe interaction was found in the parent cation and it is apparently maintained in the substituted cation. This interaction decreases when the Fe–Fe distance is increased as in the cation of the [1,1]ferrocenophane (**30**) [175] system in which the ferrocene moieties are spanned by two CH_2 bridges. In fact, ^{57}Fe-Mössbauer spectroscopy (time scale of 10^{-7} s) showed that the I^{3-} salt of the cation of **30** gives a spectrum that can be interpreted as a superposition of both Class II and Class III mixed valence species. Interestingly, lowering the temperature led to an increase of the Class III species. The authors interpreted this behavior with a phase transition wherein the Fe–Fe distance is changed permitting greater exchange interaction.



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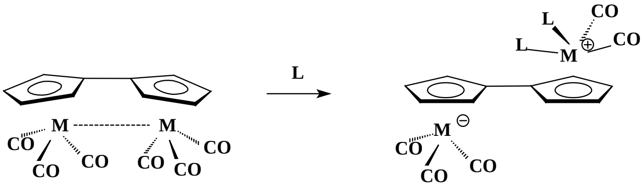
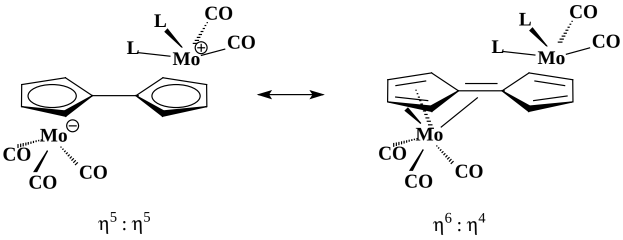
Specific factors such as lattice dynamics [177–179], structural micromodifications [180], as well as the tilt of Cp rings [181,182] have been considered for the analysis of metal–metal interaction in several biferrocenyl complexes.

The addition under thermal or photochemical conditions of basic phosphines (PMe_3, $Me_2PCH_2PMe_2$) to complexes of type **27** (M = Mo, W) generates the corresponding asymmetric zwitterions [183–186] (Scheme 7).

The Mo zwitterion was structurally characterized and presents the two metals bonded to the fulvalene in *trans* orientation with η^5:η^5 hapticity rather than η^6:η^4 (Scheme 8). Both η^6 and η^4 hapticities were found in the monometallic complexes η^6-$M(CO)_3$(fulvene) [187] and η^4-$M(CO)_2L_2$(diene) (M = Cr, Mo, W; L = PR_3) [188–190].



Scheme 7.



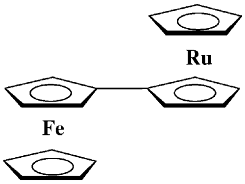
Scheme 8.

The zwitterionic nature and the contribution of the fulvalene-diene form are consistent with the reactivity of these species. In fact, the Mo and W complexes add electrophiles at the anionic group and the nucleophiles at cationic one. Conversely, the decomplexation of the Mo zwitterion when treated with an excess of PMe_3 is unexpected, as the anionic site should be unreactive for electronic reasons and the cationic site should be protected by steric hindrance. The proposed mechanism [183], illustrated in Scheme 9, involves hapticity changes which allow for the addition of the phosphine to anionic site.

3.1.3. Heterobimetallic fulvalene complexes

The main reason for the great interest raised by heterobimetallic complexes is that the presence of two different metals induces a polarization of the molecule and can create a polar M–M bond when the inorganic groups are in close proximity. Consequently, unique reactivity and physical properties may be produced by synergistic interactions between the metals.

The first example of heterobimetallic fulvalene complex, the ferrocenylruthenocene $FvFeRu(Cp)_2$ (**31**) was reported by Neuse and Loonat in 1981 [191].



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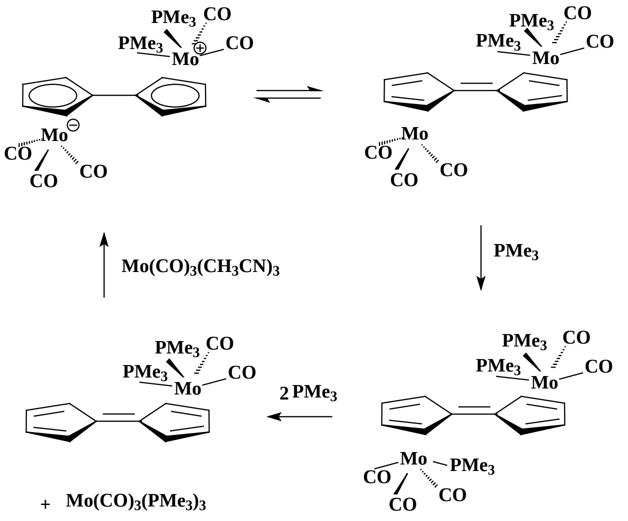
Afterwards, Sano and coworkers [192,193] studied the redox, spectroscopic, and magnetic properties of the neutral compound and its cationic derivatives. The oxidation of **31** with different reagents gives a mono-oxidized $\mathbf{31}^{+}(BF_4^{-})$ salt with sulfuric acid–NH_4BF_4, and a trioxidized $\mathbf{31}^{3+}(BF_4^{-})_3$ with *p*-benzoquinone–$BF_3(Et_2O)$.

The absence of peaks in the ^{1}H and ^{13}C NMR spectra in acetonitrile of the monocation indicates that it is paramagnetic but sharp signals were observed in ^{13}C-CP-MAS NMR spectra in the solid state. The magnetic susceptibility study showed that the BF_4^{-} salt is diamag-

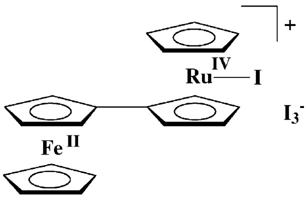


Scheme 9.

netic from 78 to 300 K. In the ^{57}Fe-Mössbauer spectra only one kind of iron was observed and the parameters correspond to those of the neutral complex itself indicating that **31** is not oxidized to its ferrocenium salt in the solid state. On the basis of these results the authors suggested the existence in the solid state of a dimeric structure $[CpFe(II)FvRu(III)CpRu(III)CpFvFe(II)Cp]^{+3}(BF_4^-)_2$ with an antiferromagnetic Ru(III)–Ru(III) chemical bond which is unstable in solution and dissociates giving a monomeric paramagnetic cation $[CpFe(III)FvRu(II)Cp]^+$. This conclusion was confirmed by the ^{57}Fe-Mössbauer spectra of the **31**$^+$ cation dissolved in acetonitrile and then dispersed in a poly(methylmetacrylate) matrix in which two kinds of iron atoms were observed, one in Fe(II) state and the other in Fe(III) state. It can be concluded that in solution the dissociation of the dimeric BF_4^- salt gives the monomeric **31**$^+$ cation. In contrast to the diamagnetic BF_4^- salt, in the solid state the PF_6^- salt is paramagnetic and on the basis of Mössbauer and magnetic properties it can be mainly described as $[CpFe(III)FvRu(II)Cp]^+PF_6^-$. Cyclic voltammetry showed that the ferrocenyl moiety is oxidized at almost the same potential of ferrocene (0.45 V versus Ag/AgCl) whilst the ruthenocene moiety in two one-electron steps at 0.85 and 0.92 V, associated with the Ru(III)–Ru(III) antiferromagnetic bond formation.

The trication **31**$^{3+}$ is a paramagnetic species as shown by its magnetic susceptibility (2.1 B.M.) which was found to be somewhat smaller than that of the ferrocenium (BF_4^-) salt (2.5 B.M.). The Mössbauer spectrum from 4.2 to 300 K gave a well resolved quadrupolar splitting with the doublets ascribed to a low spin Fe(III), although most of ferrocenium salts show a broad singlet line because of the fast relaxation related to a negligible energy difference between the two Kramer doublets. These results suggest that the trication is represented by the structure $[CpFe(III)FvRu(IV)Cp]^{3+}$ in which some kind of electronic interaction of the ruthenocenium moiety on the ferrocenium is present.

Complex **31** also reacts with I_2 giving the diamagnetic iodoferrocenylruthenocenyl (I_3^-) salt (**32**) [194] whose structure in solid state and at a low temperature in solution (183 K) was assigned on the basis of ^{1}H, ^{13}C, ^{13}C-CP-MAS NMR and ^{57}Fe-Mössbauer data. A weak interaction between the metal groups was suggested [195].



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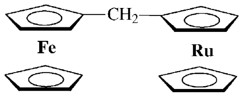
Interestingly, at higher temperatures this species became paramagnetic and an intramolecular electron transfer between Fe(II) and Ru(IV) occurred accompanied by exchange of the iodide atom between the metals. Similar behavior was found for the homobimetallic ruthenium analog [196,197].

Information about the chemical state of iron atoms in a series of heterobimetallic bimetallocene cations (**33**–**35**), in which the two metallocene moieties are connected by different linkers, were provided by means of the same physico-chemical measurements [193,194].



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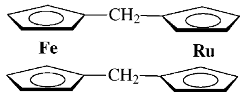

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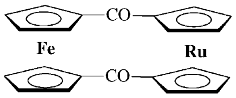

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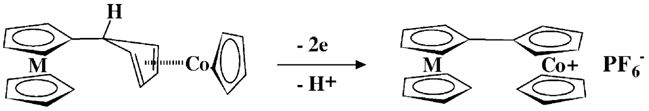
Similarly to **31**, the BF_4^- cations of [1]ferroceno[1] ruthenocenophane (**34**) is expressed by a dimeric structure with an antiferromagnetic Ru(III)–Ru(III) bond with a small amount of monomeric cation, while the ratio of the two species is reversed in the case of carbonyl linked [1]ferroceno[1]ruthenocenophane-1,13-dione (**35**) probably because of the effect of the electron attractive carbonyl groups. Also for complex **35** the nature of the counteranion has an important role. In fact, for the PF_6^- salts of **35**, as in the case of the directly linked bimetallocene, the amount of monomeric structure increases indicating that the Ru(III)–Ru(III) bond in the dimeric structure is less stable. Finally, the ferrocene moiety in the cation ferrocenylruthenocenemethane (**33**) is so separated from the ruthenocene that iron and ruthenium cannot directly interact with each other.

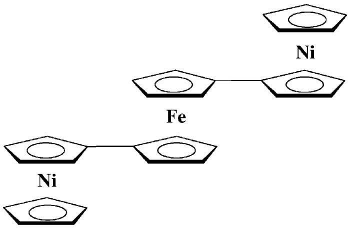
It was found [198], on the basis of the molecular structure and ^{13}C-CP-MAS NMR, that the oxidation of **34** with one equivalent of iodoruthenocenium$^+BF_4^-$ produces not a monocationic ferrocenium but the cationic salt [Fe(II)($C_5H_4CH_2C_5H_4$)$_2$Ru(IV)I]$^+$ owing to the stabilization energy of the Ru(IV)–I bond, with some interaction between the two metals. Besides, the oxidation with 1.5 eq. or with a large excess of iodine gave the monocation [Fe(III)($C_5H_4CH_2C_5H_4$)$_2$Ru(II)]$^+$$I_3^-$ and the dication [Fe(III)($C_5H_4CH_2C_5H_4$)$_2$Ru(IV)I]$^{2+}$$I_3^-$·0.5($I_3^-$)$_2$·0.5($I_2$), respectively, which were structurally characterized [199]. Selective oxidation of iron site can occur only with iodine as oxidant.

A series of heterobimetallic bimetallocene complexes with different metal couples, [$C_{20}H_{18}$CoFe]$^+$ (**36**) [200,201], [$C_{20}H_{18}$CoOs]$^+$ (**37**) [202], [$C_{20}H_{18}$CoRu]$^+$ (**38**) [202], [$C_{20}H_{18}$FeRh]$^+$ (**39**) [203], $C_{20}H_{18}$FeNi (**40**) [204], [$C_{20}H_{18}$CoNi]$^+$ (**41**) [201,205], and of heteronuclear bisfulvalene [$C_{20}H_{16}$CoFe]$^+$ (**42**) [206–208], $C_{20}H_{16}$FeNi (**43**) [204], [$C_{20}H_{16}$CoRu]$^+$ (**44**) [207,208] were synthesized and characterized by Schwarzhans, Schottenberger and coworkers. In particular, information on the electronic communication between the metals were provided for some of them. The electrochemically generation of the bimetallocene cations **36** and **41** by oxidative deprotonation in dichloromethane of $C_{20}H_{19}$CoFe and $C_{20}H_{19}$Co–Ni, respectively, was proposed by the authors [201].



M = Fe (**36**)
Ni (**41**)

The formation of the cation **36** was suggested by the appearance of a new reversible wave in the cathodic scan after oxidation of the starting compound followed by proton abstraction, and by the positive shift of the redox potential of the ferrocenyl moiety. Such a shift is generally observed in case of electronic interaction between the metal centers of binuclear metallocene complexes. The assignment was confirmed by the comparison with the redox behavior of an authentic sample of the cationic species. Though in the case of **41** no comparable electrochemical data exist [205], its redox generation in dichlorometane occurs most likely by proton abstraction after oxidation of the corresponding hydride [NiCoH]. Also in this case, the positive shift of the redox potential of Ni^{2+}/Ni^{3+} oxidation of the nickelocene moiety in **41** yielding the corresponding dication can be explained by the existence of electronic interaction between the two metal centers, though, surprisingly, similar effect was not observed for other nickelocene-containing bi- and termetallocenes such as binickelocene [205], ferrocenylnickelocene [204] and 1,1′-dinickelocenyl-ferrocene [209] (**45**).



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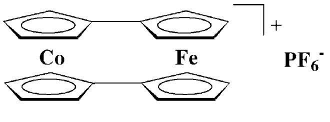
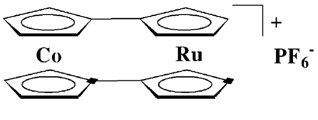
In order to study the range of valence states accessible in heterobimetallic complexes and the extent of delocalization of the valence electrons, Schottenberger and coworkers [207] investigated the redox behavior of the bisfulvalene [$C_{20}H_{16}$CoFe]$^+$ (**42**) and [$C_{20}H_{16}$CoRu]$^+$ (**44**) cations in comparison with the analogous homobimetallic [$C_{20}H_{16}Fe_2$]$^+$ (**26**), [$C_{20}H_{16}Co_2$]$^+$ (**46**) and [$C_{20}H_{16}Co_2$]$^{2+}$ (**47**), and the monometallic metallocenes.





42 **44**

The cyclic voltammogram in acetonitrile of the homonuclear cation **46** (or dication **47)** shows three one-electron electrochemically reversible waves, at −0.06, −0.81, and −1.77 V versus Ag/AgCl (Scheme 10).

The cyclic voltammogram in acetonitrile of **42** exhibits three one-electron electrochemically reversible waves, at 0.83, −0.81, and −1.77 V versus Ag/AgCl (Scheme 11).

In contrast, in the cyclic voltammogram of **44** one irreversible at 1.45 and two reversible waves at −0.77 and −1.75 V were observed (Scheme 12).

The oxidation wave is most likely a one-electron process and it was attributed to the ruthenium moiety despite the oxidation of the mononuclear ruthenocene at 1.04 V be a two-electrons process in the same experimental conditions. The authors suggested that the charge effect arising from the proximity of Co(III) center as well as the electron delocalization between the metals in the mixed valence dication renders the abstraction of a second electron a high energy process.

Concerning the subsequent reduction waves, a comparison among **42**, **44** and **46** indicates delocalization of the valence electrons and interaction between the metals on the basis of the comparably large Δ*E*° values between succes-

$$[\mathrm{Co^{III}Co^{III}}]^{2+} \underset{-0.06}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{III}Co^{II}}]^{+} \underset{-0.99}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{II}Co^{II}}] \underset{-1.83}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{I}Co^{II}}]^{-}$$

Scheme 10.

$$[\mathrm{Co^{III}Fe^{III}}]^{2+} \underset{0.83}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{III}Fe^{II}}]^{+} \underset{-0.81}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{II}Fe^{II}}] \underset{-1.77}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{I}Fe^{II}}]^{-}$$

Scheme 11.

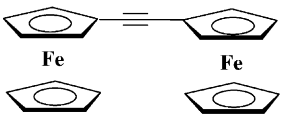
$$[\mathrm{Co^{III}Ru^{III}}]^{2+} \underset{1.45}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{III}Ru^{II}}]^{+} \underset{-0.77}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{II}Ru^{II}}] \underset{-1.75}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Co^{I}Ru^{II}}]^{-}$$

Scheme 12.

sive electron transfers. We further note that the ΔE° differences between the $E^{+/0}$ and $E^{0/-}$ potentials, −0.96, −0.98 and −0.84 for the cations **42**, **44** and **46**, respectively, corresponding to two subsequent monoelectronic reductions of the cobalt moiety, are similar and hence the asymmetry in the heterobimetallic complexes does not seem to decrease as expected the extent of the electronic interaction between the metals. Nevertheless, the substituent effect raising from the different nature of the adjacent metals should be taken into account and the results reconsidered in detail. On the contrary, the positive shift of the oxidation potential of the iron, ruthenium and cobalt moiety with respect to the corresponding mononuclear metallocenes, increases for the three cationic complexes in the order **44** $\approx$ **42** (0.42) $<$ **46** (0.83). In our opinion and according with several authors [173,174,210], this effect can be ascribed to the metal asymmetry in the sense that the different electronic nature of Ru and Fe in regard to Co increases the barrier for the electron transfer and consequently decreases the interaction between adjacent metals. As a consequence, the oxidation of the heterobimetallic compounds is more favorable than that of the homobimetallic one. We assume that the electrostatic contribution [211] due to presence of the positive charge in the bimetallic cations is roughly the same and small with respect to the electronic contribution due to the charge delocalization, especially in the case of large electronic interactions [5].

Schwarzhans and coworkers [212] compared the crystallographic structures of homo- and heterobimetallic bisfulvalene **26** and **42** PF_6^- salts, establishing that the two compounds reveal very similar lattices and nearly uniform charge distribution over both metallocene units. This provided evidence for a valence averaged delocalization for both molecules. Nevertheless, the heterobimetallic cations are not randomly oriented in the counter-ion environment and the lattice layers are slightly displaced rendering the crystal packing deformed in contrast to the homobimetallic complex. Very probably an asymmetric charge distribution is present on the different metals.

In view of the remarkable valence averaging behavior of some ethyne-linked biferrocenes [213–215] such as **48** and **49**, they extended the study of the intervalence transfer phenomena to related systems **50** [201] and **51** [216].



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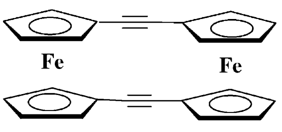

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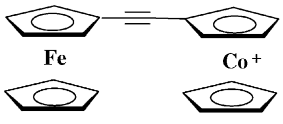

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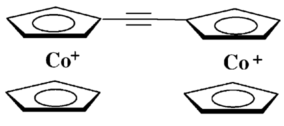
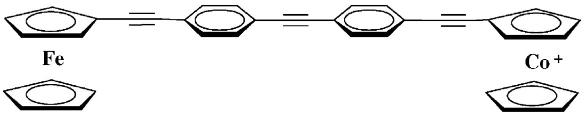


51

The diamagnetism found by ^{1}H NMR for **50** indicates that the positive charge is localized at the cobaltocene part. The voltammetric behavior of the PF_6^- salt of **50** is represented by two reversible redox waves at 0.64 and −0.78 V versus Ag/AgCl, corresponding to the oxidation of the ferrocene and to the reduction of the cobaltocene moieties, respectively. We can compare the voltammetric results with those of the directly linked bimetallocene **42** and observe that the oxidation potential of ferrocene is at a slightly more positive potential (30 mV), whereas the reduction potential occurs definitely at less negative potential (210 mV) suggesting that in the ethyne-linked complex **50** the positive charge may be more localized at the cobaltocene part. The larger distance between the metals and the minor efficiency of the ethyne with respect to the direct linkage of the Cp rings disfavor the electronic communication between the metal groups. The efficiency of ethyne linkage can be evaluated in the corresponding homobimetallic complex of iron (**48**) and cobalt (**51**). Cyclic voltammetry of **48** gave two reversible oxidation waves at 0.63 and 0.76 V versus SCE; **51** showed two reversible reduction waves at −0.66 and −0.84 V versus Ag/AgCl. The ΔE° values (130 and 180 mV) are typical of Class II mixed valence systems. Nevertheless, a second ethyne linkage can enforce the metal–metal interaction [214,215]. In fact, it has been shown that the cation of [2,2]ferrocenophane-1,13-diyne (**49**) has properties which are quite different from the Class II cation **48**$^+$, and it is a fully delocalized class III mixed valence compound on the basis of the electrochemistry, EPR, electronic absorption and ^{57}Fe-Mössbauer spectroscopy. In view of these properties, the development of an efficient synthesis of heterobimetallic complexes of analogous structure of complex **49** is desirable.

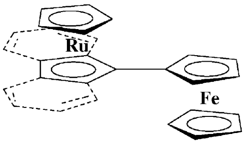
It is well known that the chain length and increased planarity of the conjugated π-system play an important role on electronic and NLO properties. A straightforward synthetic concept was found by Schottenberger and coworkers [217] for the modular construction of stable polyaromatics with designed extent of conjugation, generating a series of homo and heterobimetallic complexes. The paraphenyleneacetylene-linked Co–Fe complex (**52**) is a typical donor–acceptor system which satisfies the prerequisites for compounds with nonlinear optical properties:



52

Substituted cyclopentadienes may be prepared by reaction of a lithium or magnesium organyl with cyclopentenones [218,219]. Plenio [220] adopted this strategy to reactions of ferrocenyl lithium and opened up the possibility of synthesizing heterobimetallic bimetallocene and bifulvalene complexes with functionalized cyclopentadienes. The preparation and characterization by IR and NMR spectroscopy of (η^5-9-ferrocenylfluorenyl)

(η^5-pentamethylcyclopentadienyl)ruthenium(II) (**53**) [221] and the molecular structure of [ferrocenyl(η^5-C_5Me_4)]$_2$$ZrCl_2$ (**54**) and (η^5-9-ferrocenylindenyl)$_2$(η^5- C_5Me_5)$_2$$ZrCl_2$ (**55**) [222] were reported.



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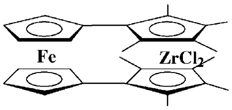

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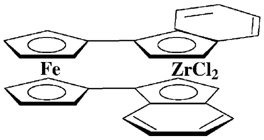

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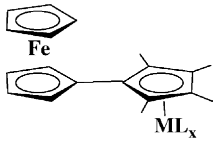
Moreover, the suitable route by Plenio [220] and also Scott et al. [222] for the synthesis of some ferrocenyl–cyclopentadiene and ferrocenyl–indene complexes allowed the preparation of fulvalene-bridged heterobimetallic complexes of the type ferrocenyl–(C_nR_m)ML_x, where –(C_nR_m)ML_x is not a metallocenyl-like moiety (**56**).



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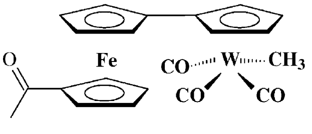
These complexes are attractive targets since the ferrocenyl has well defined redox properties and is chemically robust in both Fe(II) and Fe(III) oxidation states, and the electronic and redox properties of the second metal centers ML_x can be modulated by varying the metal or the ancillary ligands.

Until the early 1990s, the unique example of such heterobimetallic complexes, 1′-acetylferrocenyl–(C_5H_4)W(CO)$_3$ CH_3 (**57**), was prepared in 1988 by Moulton and Bard [223] via electrochemical reduction of diacetylbiferrocene (**58**), followed by addition of W(CO)$_3$(PrCN)$_3$ and then CH_3I.



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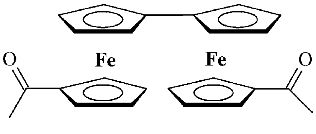

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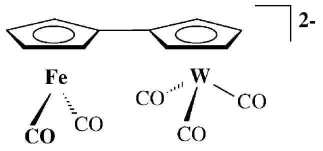
The reduction of complex **57** by cyclic voltammetry showed two waves, the first irreversible followed by the cleavage of the W–CH_3 bond generating the anion 1′-acetylferrocenyl–(C_5H_4)W(CO)$_3^-$, the second reversible corresponding to the reduction of the anion produced at the level of the first wave. The peak splitting for the second reduction ($\Delta E_p = 65\,mV$) suggests faster heterogeneous kinetics than in the reduction of diacetylbiferrocene. The electrolysis of the anion 1′-acetylferrocenyl–(C_5H_4)W(CO)$_3^-$ under CO gave the percarbonylated heterobimetallic dianion (**59**):



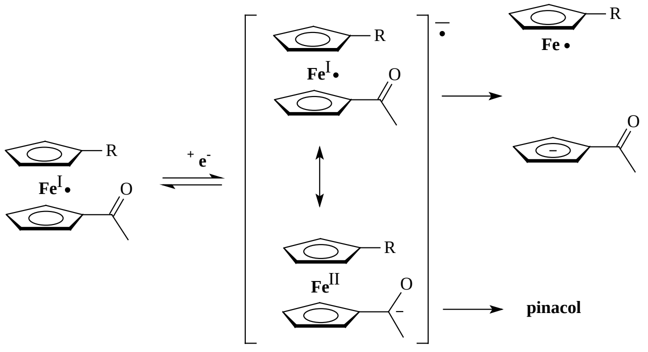
59

The work-up of the solution with excess of I_2 gave fulvaleneFeW(CO)$_5$$I_2$ **(60)** but also 1′-acetylferrocenyl–(C_5H_4) W(CO)$_3$I which may be formed by oxidation (or autoxidation) of the pinacol dimer [223].

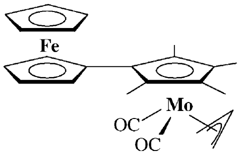
The authors explained the electrochemical behavior and the reactivity of acylated ferrocene anion in terms of the canonical structures of the radical anion (Scheme 13).

To the extent the unpaired electron is localized on the antibonding Fe-ring LUMO orbital, decomplexation may occur. On the other hand, electron density on the carbonyl group increases the probability of the pinacolization, limiting the synthesis of fulvalene complexes from acetylferrocene. By analogy with Plenio's synthesis, Mountford and coworkers [224,225] reported the convenient synthesis of a series of heterobimetallic complexes of the type ferrocenyl–(C_nR_m)ML_x (**61–63**):

The authors discussed in detail the ν_{CO} stretching and the electrochemical data for the oxidation of the Fe–Mo complexes compared with those of the monometallic [Mo(CO)$_2$(η-C_3H_5)(ring)] (ring $= C_5Me_5$, C_5H_5, C_9H_7) and ferrocene. The average ν_{CO} for the heterobimetallic complexes decreases in the order **63** > **62** > **61** (M = Mo) indicating that it is possible to 'tune' the electron density at the molybdenum center. The ν_{CO} values of the indenyl and C_5Me_4 derivatives are so close to those of the monometallic compound that the authors concluded that there is negligible 'leakage' of electron density between the iron and the molybdenum centers in the heterobimetallic complexes. In the case of $C_5H_2Me_2$– **62** and C_9H_6-containing **63** binuclear complexes, they assigned the first oxidation to the Fe and the second to the Mo on the basis of the $E_{1/2}$ values of the monometallic complexes (320 and 170 mV, respectively), which are essentially the same of those found for the cor-



Scheme 13.



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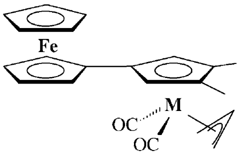

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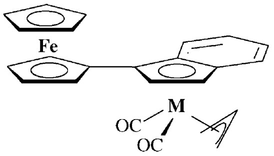
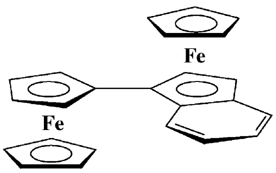


M = Mo, W

63

responding bimetallic complexes. On the other hand, in the case of the C_5Me_4 derivative (**61**), the difference in $E_{1/2}$ for the two subsequent oxidation processes (160 mV) is twice as larger as that anticipated from the $E_{1/2}$ values for the model complexes (80 mV), indicating a strong interaction between the two metal centers. For **62** and **63**, the authors suggested that there is no significant interaction between the Mo and the Fe and that their cations are described as Class I in the Robin and Day classification. For **61**, the results were reminiscent of a Class II mixed valence system. In fact, it is possible that the first oxidation does occur at Fe giving a Fe^{III}Mo^{II} species but that a significant equilibrium concentration of the corresponding Fe^{II}Mo^{III} valence isomer exists, as expected from the Nernst equation. On the basis of respective model complexes, there is a larger difference between the oxidation potentials of ‘isolated’ metal centers in the first two complexes than in the latter. This corresponds to a greater ΔG° in the Marcus–Hush theory. In conclusion, as the degree of interaction between the metal centers decreases with increased asymmetry, the different electrochemical behavior of **61** can be attributable to a smaller degree of asymmetry than found in the other two complexes, so that decreasing the difference in redox potential between the two different metal centers can lead to a greater interaction between them in the monocation.

Chung and coworkers [226] examined the electrochemical properties of the asymmetric (ferrocenyl-indenyl)cyclopentadienyliron compounds (**64** and **65**) in order to evaluate the influence of the indenyl on the oxidation potential of ferrocene.



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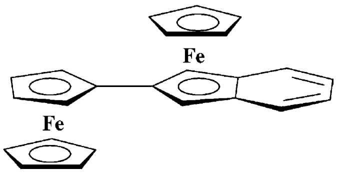


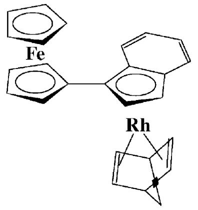
65

In comparison to the biferrocenyl **25**, the introduction of an indenyl group increases the difference in $E_{1/2}$ for the two subsequent oxidation processes because the indenyl is more electron-donating than the cyclopentadienyl. The indenyl-cyclopentadienyliron moiety oxidizes at less positive potential than ferrocene (−0.14 V), hence this must be taken into account when comparing the electrochemical data of **64** and **65** compounds with those of **25**. The $\Delta E_{1/2}$ values of the two indenyl derivatives are almost identical (0.46 and 0.44 V) indicating that the position of the ferrocenyl group has little influence.

The same authors developed the synthesis of some fulvalene bridged heterobimetallic complexes of type ferrocenyl–(C_nR_m)ML_x ((C_nR_m)ML_x = (C_5H_4)Mn(CO)$_3$, (C_5H_4)Cr(CO)$_2$NO, (2-MeC$_5$H$_3$)Mn(CO)$_3$, 1,3-Me$_2$C$_5$H$_2$)Mn(CO)$_3$) [227,228] but no electrochemical data were reported.

In this context and as a part of our continuing program to expand the chemistry of heterobimetallic indenyl complexes we were involved in the synthesis of a series of ferrocenyl containing heterobimetallic complexes [η^5-(1-ferrocenyl)-indenyl]-ML$_2$ (M = Rh, Ir; L$_2$ = COD, NBD, L = CO, COE) in anticipation that the close proximity of an iron (and of its oxidized species) to a rhodium or iridium centers associated with the coordinative flexibility of the indenyl ligand will result in unusual structural and chemical properties [229,230].

The crystal structure determined for RhNBD (**66**), Rh(CO)$_2$ (**67**) and Ir(CO)$_2$ (**68**) derivatives established that the metals are in a *transoid* configuration in the NBD complex probably to avoid steric repulsion, and in a *cisoid* configuration in the carbonylated complexes due to the presence of stabilizing π-hydrogen bonds between the M(CO)$_2$ group and the hydrogens of the unsubstituted Cp ring.



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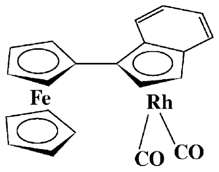

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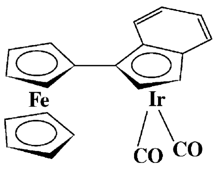
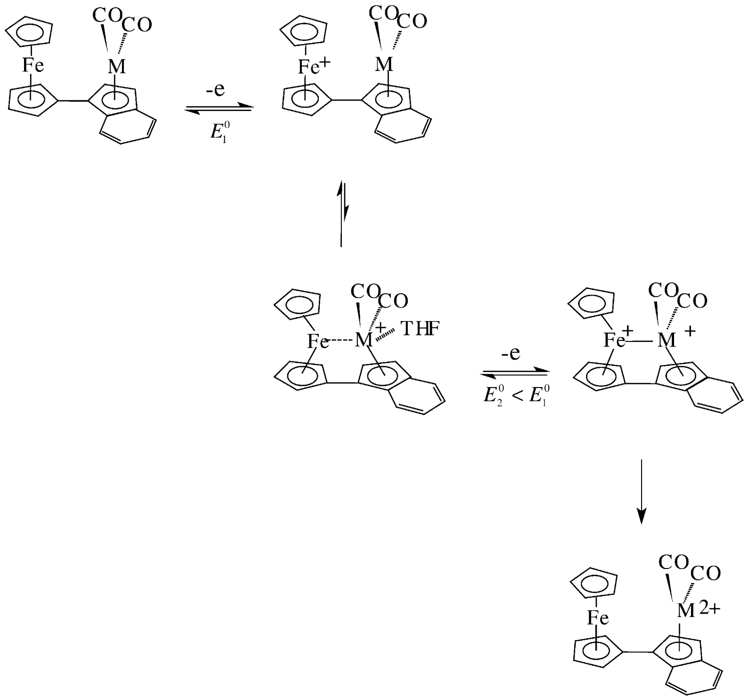


68

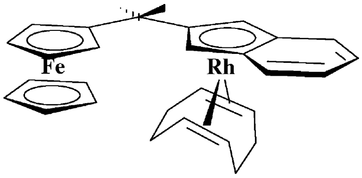
The electrochemical studies on the carbonylated **67** and **68** compounds revealed a strong metal–metal interaction favored by the relative proximity of the metal groups in the ground state configuration. Oxidation proceeds through an EC$_{rev}$E route (Scheme 14) in which the iron works as a sink of electrons supplied by rhodium (or iridium) with the consequence that the oxidative activation of rhodium and iridium mediated by the ferrocenyl group is possible at a potential far shorter than that required for direct oxidation



Scheme 14.

of the metal. We suggested that the driving force is the internal electron transfer from rhodium (or iridium) to iron concomitant with the rearrangement of the bridging ligand from a planar to a bent fulvalene frame and formation of a metal–metal dative bond.

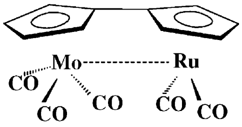
The methylene-linked Fe–Rh analog (**69**) was synthesized by Gaede [231]. A comparative electrochemical study would be interesting to evaluate the possibility of the through-space electron transfer when the through-ligand mechanism is disfavored by lack of conjugation.



69

The successful synthesis of homobimetallic fulvalene complexes $(C_{10}H_8M_2CO_4)$ (M = Co, Ru) and $(C_{10}H_8M_2CO_6)$ (M = Cr, Mo, W) developed by Vollhardt and Weidman [232] in 1984, opened the possibility of preparing heterobimetallic fulvalene complexes of type $(C_{10}H_8)ML_nM'L_m$, in which both the metal moieties are of the *half-sandwich* type. In the same paper the authors reported the synthesis of the complex $(C_{10}H_8)Mo(CO)_3Ru(CO)_2$ (**70**) in a slightly better than statistical yield.

Afterwards, electrochemical studies [233] showed that in oxidation these complexes behave similarly giving a two-electron irreversible wave, whereas in reduction they are reduced in a two-electron process to form a dianion which upon oxidation produces the starting substance. An ECE type mechanism was proposed and shown in Scheme 15.

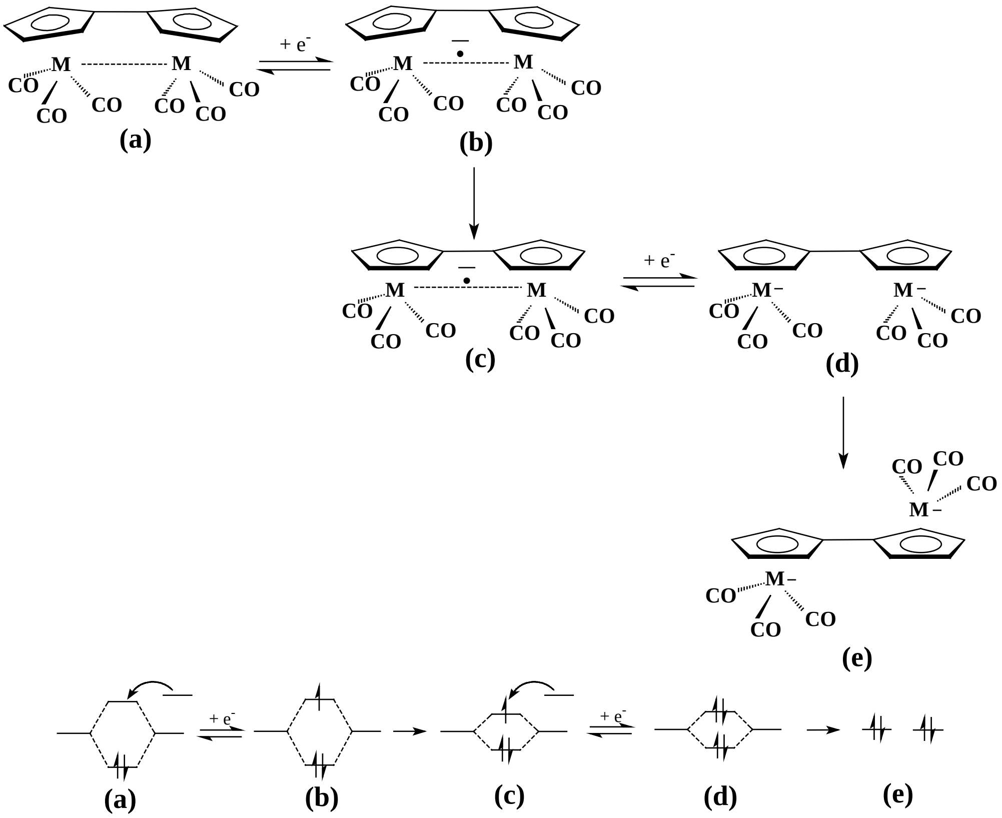


70

The first electron is introduced into the metal–metal antibonding LUMO orbital, reducing the bond order and yielding an anion radical (b) in an unfavorable geometry in which the metal–metal distance is too short so that the molecule relaxes in a less strained geometry increasing the metal–metal distance in (c). As a consequence, the second electron transfer occurs at less negative potential than the starting complex (a) since the SOMO of the radical anion results stabilized by the chemical rearrangement. Thus, an overall two-electron wave is observed. After the second electron transfer (d) the dianion may rearrange probably to a *trans* configuration (e).

The heterobimetallic **70** is similarly reduced in a single two-electron wave at a potential (−1.25 V versus NHE) which is intermediate of those of Mo–Mo (−0.77 V) and Ru–Ru (−1.65 V) homobimetallic homologues. On the anodic scan a main oxidation wave was observed at roughly the same potential of the Ru–Ru dianion (−0.5 V), suggesting that it corresponds to the two-electron oxidation of a Ru-centered dianion affording the original metal–metal bonded material.

Few years later, Vollhardt and coworkers [234] developed the first controlled approach to heterobinuclear

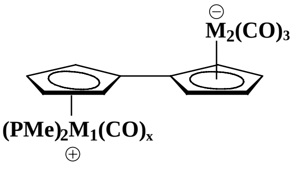


Scheme 15.

derivatives based on the remetallation of the previously described (Scheme 9) monometallic ring slippage product of $FvRu_2(CO)_4$ and $FvMo_2(CO)_6$. A series of zwitterionic binuclear complexes were obtained (Scheme 16).

A second, more efficient synthetic strategy utilized a cyclopentadienyl–cyclopentenone as a precursor to fulvalene, allowing a selective step-wise preparation of several heterobimetallic complexes with different transition metals (Scheme 17) [234,235].

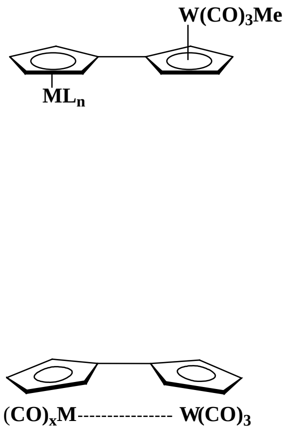
The efficient preparation of heterobimetallic complexes allowed the investigation of their chemistry and some examples were recently reviewed [138]. Here, we cite one significant example. In the presence of alkynes the homobimetallic $FvRu_2(CO)_4$ [236] and $FvMo_2(CO)_4$ [150] undergo upon irradiation to metal–metal and fulvalene C–C bond homolysis followed by formation of bridging alkyne complexes for the former, and symmetrical addition of alkynes to the metal–metal bond for the latter. In contrast, the heterobimetallic **70** in the presence of alkynes undergoes selective photo substitution at the Mo center only (Scheme 18) [237].



$M_1 = M_2 = Mo$, $x = 2$
$M_1 = Mo$, $M_2 = Cr$, $x = 2$
$M_1 = Ru$, $M_2 = Cr$, $x = 1$
$M_1 = Ru$, $M_2 = Mo$, $x = 1$
$M_1 = Ru$, $M_2 = W$, $x = 1$

Scheme 16.

The role of the ruthenium changes from that of a spectator to that of an active participant when using terminal alkynes providing the first heterobinuclear side-on bridging four-electron donating alkyne–alkenylidene **71** as an isomer mixture owing to vinylidene rotation. A non bridging intermediate was proposed by the authors on the basis of the X-ray analysis of complex (**72**) obtained by carbonylation of complex (**71**) (Scheme 19).



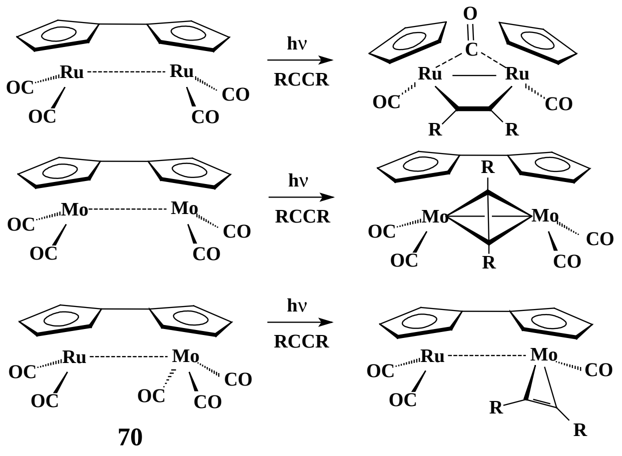
ML_n

Cp^*ZrCl_2
$V(CO)_4$
$Mo(CO)_3Me$
$Mn(CO)_3$
$Re(CO)_3$
$Co(CO)_2$
$Rh(CO)_2$
$Rh(C_2H_4)$
$Ir(CO)_2$

$M(CO)_x$

$Cr(CO)_3$
$Mo(CO)_3$
$Fe(CO)_2$
$Ru(CO)_2$

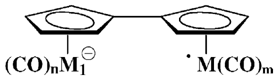
Scheme 17.



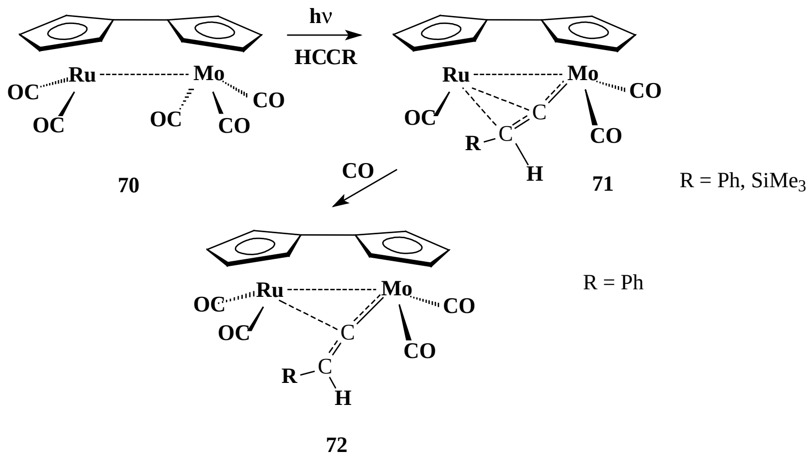
Scheme 18.

This reactivity represents a remarkable demonstration of heterobinuclear diversity from the corresponding homobimetallic analogues [138]. Further evidence of the peculiar behavior of heterobimetallic complexes was found by Astruc and coworkers [238] studying the electrocatalytic synthesis of zwitterionic complexes starting from homo- and heterobimetallic Mo–Mo, W–W, Fe–W, Ru–Mo and Ru–W carbonyl fulvalenes in the presence of PMe$_3$ and [Fe^I(C$_5$R$_5$)(C$_6$R$_6$)] (R = H, Me) as electrocatalyst (Scheme 20).

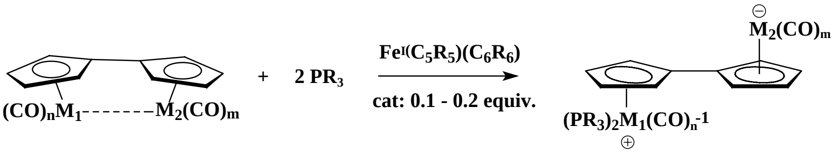
Zwitterions are of interest in the context of NLO [239]. The thermal synthesis of fulvalene zwitterions from bimetallic carbonyl complexes is not straightforward, since prolonged reaction times are required leading sometimes to loss of one metal [183]. Electron-transfer-chain catalysis [240] is a very efficient way to perform inorganic and organometallic reactions such as ligand exchange [241–247], isomerization, chelation, decomplexation, insertion, and oxidative addition [248]. Previous electrochemical studies [233,249,250] of the starting complexes indicated that the reduction process occurs, as figured out in Scheme 15, in a two separated one-electron waves for Fe–W complex, or in a two-electron wave for the other compounds. The initiation step of the electrocatalytic reaction is the formation of the radical anion followed by the propagation step which consists in the addition of the phosphine to the radical anion. The rate and efficiency of the overall catalytic process depends on the reactivity and stability of the radical anion which can be represented by a limit structure in which the negative charge is centered on one metal and the odd electron on the other one.



A fast second-order addition of the phosphine to the 17-electron metal center occurs generating a 19-electron moi-

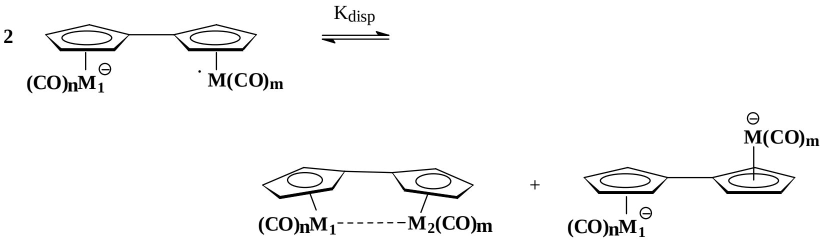


Scheme 19.



$M_1 = M_2 =$ Mo, $n = m = 3$
$M_1 = M_2 =$ W $n = m = 3$
$M_1 =$ Fe, $M_2 =$ W, $n = 2$, $m = 3$
$M_1 =$ Ru, $M_2 =$ Mo $n = 2$, $m = 3$
$M_1 =$ Ru, $M_2 =$ W $n = 2$, $m = 3$

Scheme 20.



Scheme 21.

ety, since the energy levels of 17- and 19-electron states are very close [241,251]. Delocalization of the negative charge and of the spin density may occur over the molecule, drastically slowing down the reactivity of the radical frame. However, this delocalization prevents side radical reactions and the selectivity and efficiency of the electrocatalytic process increase.

The behavior of homobimetallic fulvalene complexes compared with those of heterobimetallic ones indicated that the electrocatalytic process is faster for the heterobinuclear systems, since the process could be observed in the time scale of CV only in the case of the latter complexes, although the electrocatalytic reactions are over in few minutes. This evidence was explained on the basis of the reduction mechanism of the starting complexes. In fact, in the reduction of homobimetallic fulvalenes, since the two electrons are transferred at the same potential, the radical anion disproportionates to the neutral and dianionic species (Scheme 21) with $K_{\mathrm{disp}} \gg 1$ and consequently its concentration is very low.

Very low concentration accounts for the low reaction rate of homobimetallic complexes. On the other hand, in heterobimetallic Fe–W complex the two reduction steps occur at different potentials. Instead, Ru–Mo and Ru–W derivatives, still exhibit a two-reduction wave but this does not exclude that two one-electron reductions could proceed at very close potentials which would appear in the same wave envelope. Anyway, the asymmetry due to the presence of different metals renders the situation more favorable than in homobimetallic complexes. In conclusion, the electrocatalytic reactivity was found in the order Fe–W > Ru–Mo, Ru–W > Mo–Mo > W–W ≫ Ru–Ru which is opposite to that of the K_{disp} values.

Notable synthetic efforts have been dedicated to the preparation and characterization of heterobimetallic *ansa*-metallocene, in which two cyclopentadienyl rings are linked by organic groups such as CR_2, CROH and CO. Some example are reported hereafter.

Heterobimetallic derivatives of bis(cyclopentadienyl)methane have been reported by Härter and Werner and their coworkers. Härter et al. [252], adapting a reaction reported by Mueller-Westerhoff and coworkers [253], obtained a series of $Mn(CO)_3$-based derivatives by metallation of 6-[$CpMn(CO)_3$]fulvenyl (Scheme 22).

Werner [254] prepared similar complexes ($M' = Co(CO)_2$, $Rh(CO)_2$, $CpTiCl_2$) by deprotonation of the pendant cyclopentadiene ring followed by metallation of the monometallic $M(CO)_2C_5H_4CH_2C_5H_5$ (M = Rh, Ir).

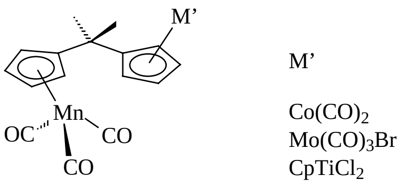
Heck and Körnich [255–257] have prepared several heterobimetallic compounds having the cyclopentadienyl and tetramethylcyclopentadienyl rings coupled by a ketone carbonyl (Scheme 23). Depending on the reaction conditions and on the nature of the metal groups it is possible to obtain the complexes in the *transoid* and/or metal–metal bonded *cisoid* configuration.

Bitterwolf et al. [258,259] found a convergent synthetic strategy for the preparation of a series of heterobimetallic compounds in which two half-sandwich moieties are linked by CROH, CO and CR_2 groups (Scheme 24).

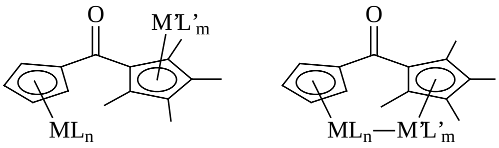
The crystal structure of Cr–Mn alcohol ($R = CH_3$) revealed that the two metal moieties assume a configuration between *syn* and *anti* orientation. It would be interesting to investigate the electrochemical and optical properties due to eventually electronic communication modulated by different linkages which connect different metal moiety.

In their research for new Ziegler–Natta and Fischer–Tropsch catalysts, Green and coworkers [260–262], have prepared a series of homo and heterobimetallic *ansa*-metallocene complexes of (2,2-dicyclopentadienyl)- and (2,2-cyclopentadienyl)(indenyl)-propane involving both early and late transition metals. Some examples obtained by reaction of $ClMn(CO)_5$ and $[ClRh(CO)_2]_2$ with $ZrCl(\eta^5\text{-}C_5H_5)[\eta^5,\eta^2\text{-}C_5H_4C(CH_3)_2C_9H_6]$ are shown in Scheme 25.

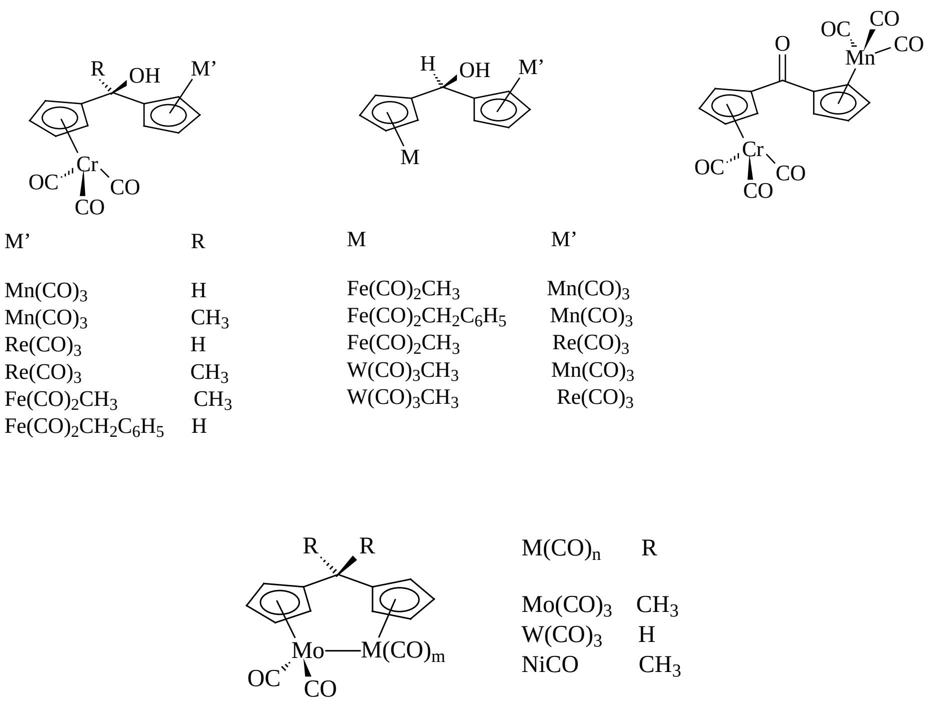
The alkylation reaction of the dichlorozirconocene part with $AlMe_3$, which plays an important role in the initiation step of polymerization catalysis, has been recently



Scheme 22.



Scheme 23.

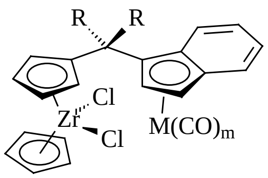


M'	R
$Mn(CO)_3$	H
$Mn(CO)_3$	CH_3
$Re(CO)_3$	H
$Re(CO)_3$	CH_3
$Fe(CO)_2CH_3$	CH_3
$Fe(CO)_2CH_2C_6H_5$	H

M	M'
$Fe(CO)_2CH_3$	$Mn(CO)_3$
$Fe(CO)_2CH_2C_6H_5$	$Mn(CO)_3$
$Fe(CO)_2CH_3$	$Re(CO)_3$
$W(CO)_3CH_3$	$Mn(CO)_3$
$W(CO)_3CH_3$	$Re(CO)_3$

$M(CO)_n$	R
$Mo(CO)_3$	CH_3
$W(CO)_3$	H
NiCO	CH_3

Scheme 24.



$M(CO)_m$
$Rh(CO)_2$
$Mn(CO)_3$
$CpZrCl_2$

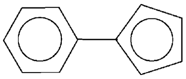
Scheme 25.

investigated in this type of heterobimetallic complexes [263].

3.2. Fulvalene-like bridges

3.2.1. The phenyl-cyclopentadienyl ligand

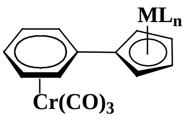
Phenyl-cyclopentadienyl is a bifunctional ligand containing two aromatic rings of different nature, a negative charged cyclopentadienyl and a neutral arene, connected by a σ bond.



Considering the different reactivity and wide applications of arene and cyclopentadienyl transition metal complexes, it is easily understandable that heterobimetallic complexes containing both types of these systems held in close proximity by a C–C bond are of particular interest. Much effort was devoted towards the synthesis of several heterobimetallic complexes of this bridging ligand [264–270], but unfortunately few studies on the electronic communication between the two metal centers were reported.

Chung and coworkers [265], Qian et al. [267] and also Ceccon and coworkers [270] were involved in the synthesis of heterobimetallic phenyl-cyclopentadienyl complexes containing the $Cr(CO)_3$ group coordinated to the arene ring. They found that (η^6-phenyl-cyclopentadiene)$Cr(CO)_3$, which can be prepared in excellent yield as reported by Ceccon et al. [271], is a good starting material for the preparation of several $Cr(CO)_3$-containing complexes (Scheme 26).

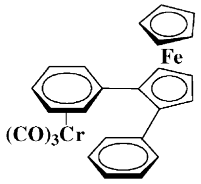
Chung and coworkers [268] also developed a convenient method for the synthesis of mixed ferrocenes, which are starting materials for the preparation of bi- (**73**) and trimetallic (**74**) compounds, using [(fluorenyl)FeCp]PF_6 as an effi-



ML_n = FeCp
$Fe(CO)_3^+$
$Cr(CO)_3^-$
$Mo(CO)_3^-$
$W(CO)_3^-$
$Cr(CO)_2NO$
$Mo(CO)_2NO$
$W(CO)_2NO$
$Mn(CO)_3$
$Co(C_4Ph)_4$
$RuCl(PPh_3)_2$
$TiCl_2Cp$
$ZrCl_2Cp$
$MoCH_3(CO)_3$
$WCH_3(CO)_3$
$Co(CO)_2$
$Rh(Et)_2$
$Rh(CO)_2$
$Rh(PPh_3)_2$

Scheme 26.

cient CpFe transfer reagent to other Cp′.



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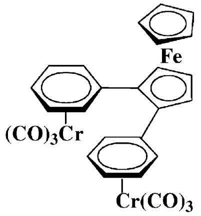

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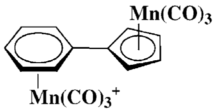
Moreover, together with Sweigart and Pike, they found a general synthetic route for the transfer of the $Mn(CO)_3{}^+$ group from (η^6-polyarene)$Mn(CO)_3$ complexes to an arene ring [272]. When applied to phenyl-cyclopentadienyl derivatives, this method gave a series of bi- (**75**) and trimetallic (**76**,**77**) complexes [268].



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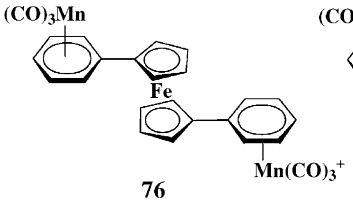

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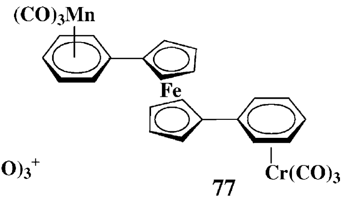

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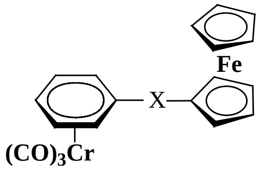
A detailed electrochemical study of the complex $Cr(CO)_3$(phenyl-cyclopentadienyl)CpFe [264] and correlated derivatives in which the aromatic rings are spanned by different organic groups (Scheme 27) was reported by Degrand and coworkers [273,274], and Sweigart and Chung [275] in different solvents.

In DMF and CH_3CN, Degrand observed that the arene $Cr(CO)_3$ moiety of those complexes in which the electronic delocalization between the two metal groups exists, undergoes assisted electrooxidation induced by the ferrocenyl moiety which is first oxidized at the electrode. One or two oxidation waves were observed depending on the efficiency of the assisted oxidation of chromium site. When the metal groups are adjacent or conjugated as in complex **78a** and **78c**, the assisted oxidation is total and only one wave with number of electrons much more than 1 is observed. On the other hand, when the assisted oxidation is partial (**78b** and **78d**) or absent (**78e**), a second wave at more positive potential appears, corresponding to the direct oxidation of the chromium moiety. The conjugation of the two metal groups through the bridging ligand as well as via space allows intramolecular electronic exchange from chromium to iron. The efficiency of assisted oxidation is related to the generated intermediate Cr(I) species and to the distance between the metal sites. This efficiency increases when the metal–metal distance decreases and the nucleophilicity of the solvent increases (DMF > CH_3CN). A CO substitution in the $Cr(CO)_3$ group of the radical cation intermediate by a molecule of solvent was suggested to occur, accounting for the lower efficiency in CH_3CN. Sweigart and Chung [275] demonstrated that, in a less nucleophilic solvent such as CH_2Cl_2, the ferrocenyl group attached to the benzene ring of complex **78a** functions as a reversible redox switch for the ligand substitution and addition reactions at the chromium center (Scheme 28).



	X
78a	-
78b	CH=CH
78c	CO
78d	CH2
78e	CH2CH(OH)

Scheme 27.

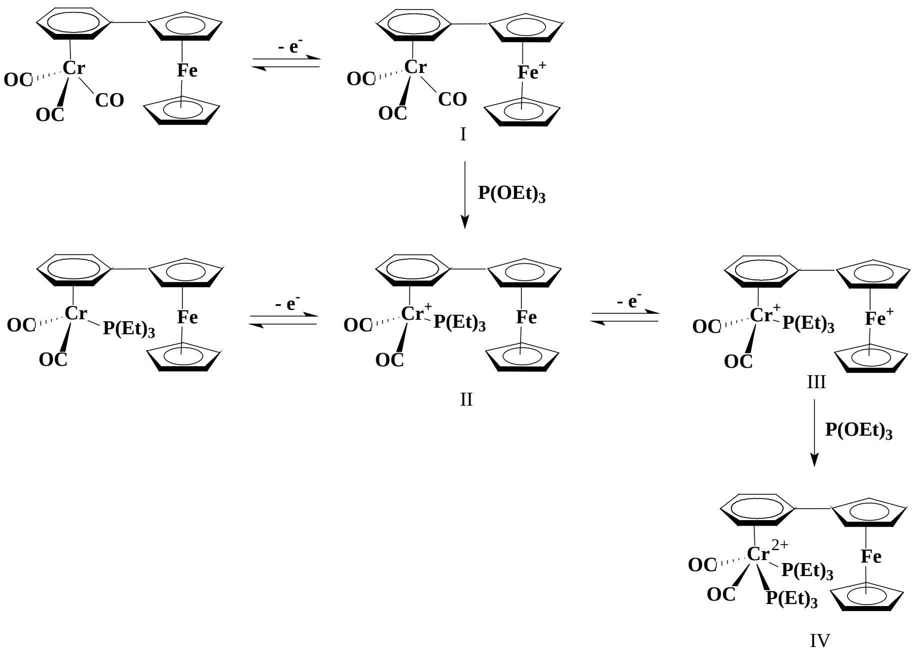
It was reported that organometallic complexes undergoing chemically reversible oxidation or reduction may behave as effective redox switches which can be turned on and off by electron transfer [233,234,276–283]. In this work, the authors showed that the ferrocenyl moiety functions as a self-closing redox switch which facilitates the substitution of a CO by a $P(OEt)_3$. "Turning on" the ferrocenyl switch by oxidation allows rapid substitution since a very rapid equilibrium between the valence isomers of the primary radical cation is active, even if it lies far to the right (Scheme 29) ($K_{eq} = 2.4 \times 10^3$, $k_{-1} = 1.5 \times 10^7$, $k_1 = 6 \times 10^3\ s^{-1}$).

The chromium-centered radical cation is the active species which undergoes facile substitution reaction. The conclusion is that internal electron transfer from chromium to iron accompanies this CO substitution, with the result that the ferrocenium reverts to ferrocenyl closing the redox switch. The oxidative activation at the chromium occurs at potentials far shorter than that for its direct oxidation. Moreover, the oxidation of II (Scheme 28) reopens the switch activating the chromium towards the addition of a second $P(OEt)_3$ which is accompanied by further internal electron transfer from chromium to iron. The automatic switch closing generates a product with 18-electron centers (IV). Since the efficiency of the activation is related to the difference of the chromium and iron oxidation potentials, the authors suggested that the attachment of a remote redox switch may be a useful general methodology for the quantitative control of the reactivity at a metal center.

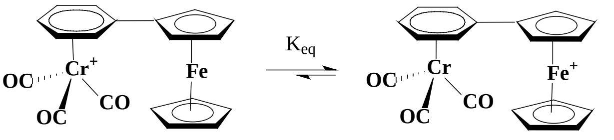
Alkenyl- and alkynyl-linked ferrocenyl and arene-$Cr(CO)_3$ (Scheme 30) have been synthesized by Peris and coworkers [284], and also Müller and coworker [285,286], and their optical and NLO properties were reported in the context of designing systems with fine-tuning electronic properties upon connecting electron donor and electron acceptor metallorganic groups.

3.2.2. *Other fulvalene-like bridges*

A few heterobimetallic complexes of different bridging ligands containing two aromatic or olefinic rings linked directly, such as biphenyl (**79**) [287] and phenyl-



Scheme 28.

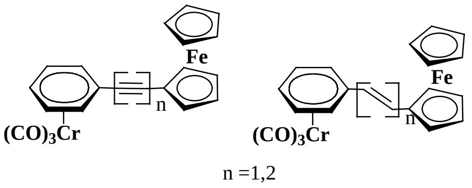


Scheme 29.

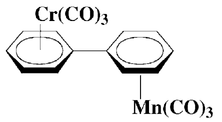
cycloheptatriene (**80**) [288,289], or through alkenyl chains (**81**) and (**82**) [287] were synthesized and some examples are hereafter reported but no systematic studies on their electronic communication were conducted.

In particular, Cooper and coworkers [289] established for the first time that benzene and tropylium can be selectively cross coupled in complexes **83** and **84**. The sequence involving reductive activation of complex **83** and subsequent annulation of benzene (Scheme 31) could have potential application in transition metal-mediated organic synthesis.

The electronic communication in heterobimetallic complexes of the 3-(**85**) and 4-(**86**) cyclopentadienyl-pyridine which are bridging ligands structurally similar to the above described phenyl-cyclopentadienyl, were recently investigated [290,291] by mean of cyclic voltammetry, and UV-Vis and near-IR spectroscopy.



Scheme 30.



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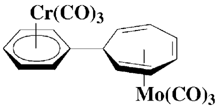

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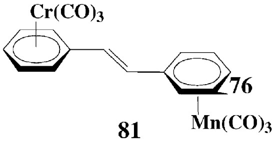

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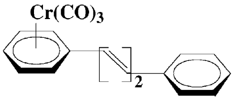

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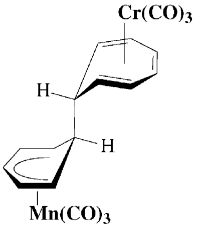

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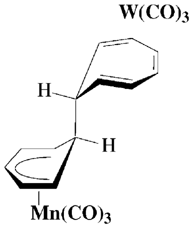

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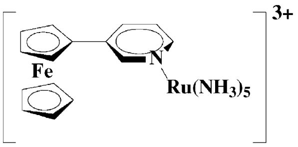

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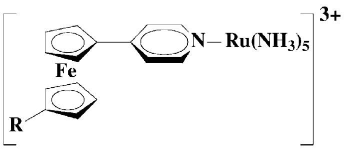

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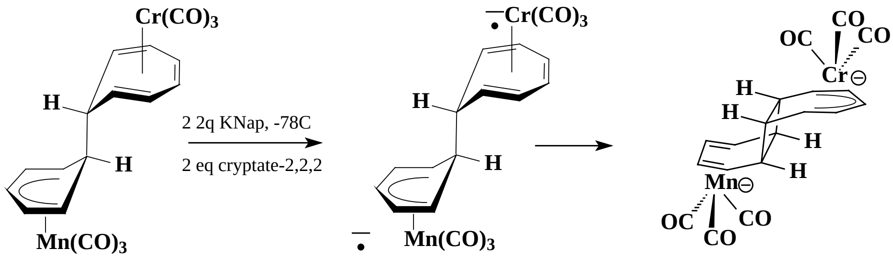
In particular, the mixed valence species generated by chemical oxidation with ferrocenium hexafluorophosphate show Class II behavior and the oxidized metal site is ruthenium. The $\Delta E^{\circ}_{1/2}$, that is the potential difference between

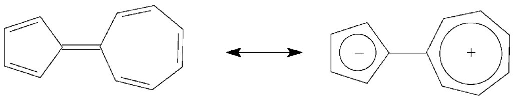


83

Scheme 31.

the reversible oxidation of the acceptor site (pyridine-$Ru(NH_3)_5$) and the reduction of donor site (ferrocene), and the IT bands in the near-IR are solvent dependent. Good linear relationship between $\Delta E^{\circ}_{1/2}$ and the Gutmann solvent donicity (DA), and between the energy of the IT bands and $\Delta E^{\circ}_{1/2}$ exists and allowed the evaluation of the solvent reorganization energy $(l)_s$ and the total vibronic energy (l) values, the latter being in agreement with those calculated from the Hush equation.

Particular attention was devoted by Heck and coworkers to the sesquifulvalene ligand, whose mono- [292] and heterobimetallic [293–296] complexes are of interest in the context of NLO. Very often the charge transfer states, which are very important for high hyperpolarization properties, can be represented by a polar resonance structure and this also holds for sesquifulvalene.

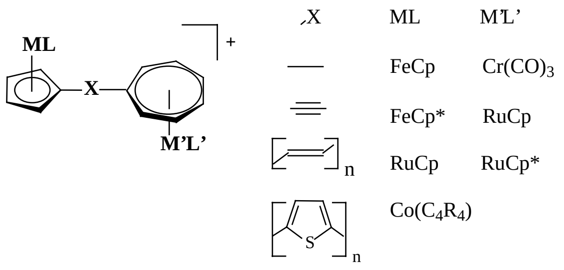


A number of heterobimetallic sandwich and half-sandwich type complexes of sesquifulvalene were synthesized by the Hamburg group and their electrochemical, optical and NLO properties were reported and already reviewed by the same authors [296]. We refer the readers to the review for a deeper insight in this topic and here we will show a general overview of this class of complexes. Their general structure, in which the two rings are connected directly or by an unsaturated chain, is shown in Scheme 32.

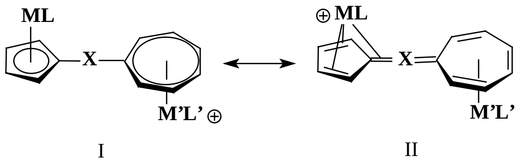
The bonding situation of binuclear complexes which demonstrate weak or strong NLO effects is described by two different mesomeric forms. The ground state is mainly represented by the polar bis(aromatic) form I as demonstrated by several structural determinations, whereas the excited state CT state should have more contribution from the cross-conjugated form II (Scheme 33) [292,293].

The dipole change $\Delta\mu$ between the ground and excited states by varying the polarity of the solvent is relevant for the first hyperpolarizability β [297–299].

In recent work, Heck and coworkers [295] investigated the donor–acceptor interaction in mono and binuclear sesquifulvalene complexes with X = –, ML = FeCp and $M'L'$ = $Cr(CO)_3$, RuCp* and RuCp. The NMR data indicate an increased positive charge delocalization from M' to M (=FeCp) in the order $M'L'$ = $Cr(CO)_3$ < RuCp* < RuCp < none, clearly elucidating a strong donor (ferrocene)–acceptor (tropylium moiety) interaction in the ground state and an increased contribution of the mesomeric form II to the electronic ground state. The UV-Vis spectra exhibit two intense CT bands in the visible and near-UV regions with negative solvatochromism (blue-shift on increasing the solvent polarity) which implies a greater polarity for the ground state than for excited state, or an inversion of the polarity upon excitation from I to II. The lower energy absorption was attributed to the donor–acceptor charge-transfer transition donor–acceptor CT and it decreases in energy in the order $M'L'$ = $Cr(CO)_3$ > RuCp* > RuCp > none. Moreover, on the basis of the redox properties of the complexes measured by cyclic voltammetry, assuming that the oxidation potentials correlate roughly with the energy of the HOMO and the reduction potentials with that of the LUMO, the authors concluded that the HOMO–LUMO gap qualitatively decreases in the order $M'L'$ = $Cr(CO)_3$ > RuCp* > RuCp > none, as well as the energy of the donor–acceptor CT band. Finally, NLO properties were determined by measuring the first hyperpolarizability β and calculating the static hyperpolarizability β_0. β was obtained and β_0 calculated only for the ruthenium derivatives. The



Scheme 32.



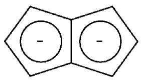
Scheme 33.

larger values were found for the RuCp derivative which was shown to be the stronger electron-accepting moiety by NMR and cyclic voltammetry studies. Concerning the π-linker X between the donating and acceptor groups, despite the relatively short dipole lengths strong NLO effects can be obtained which are very promising with respect to longer π-linkers. In conclusion, the variation of the electronic properties of the donors and acceptors as well as of the π-linkers opens the possibility of a fine tuning of the NLO properties.

4. Fused delocalized polycyclic bridges

Condensed polycyclic arenes represent excellent bridges in donor–acceptor systems since they form a rigid molecular backbone suitable for a strict control of ET path distances and they exhibit electronic delocalization. Their potentially wide application in the construction of heterobinuclear complexes is inhibited mainly by synthetic difficulties. Besides low yields there is the necessity of discovering stereospecific routes to prepare pure isomers. In fact, two isomers can be obtained with a cisoid or transoid disposition of the metal groups, i.e. they can be grafted on the same or on the opposite face of the plane of the bridging ligand, respectively. Factors that can favor a specific configuration are steric hindrance and the mechanism of the metallation which is still a vexing problem and has not been completely investigated yet. A non-stereospecific synthetic approach would require the final separation of the mixture, but this is most of the times inefficient due to the low stability of the complexes and the high similarity of the isomer properties. During the synthetic or purification procedure there is also the possibility of an isomerization process which converts the kinetic isomer into the thermodynamically more stable isomer as it has been shown during the synthesis of $Cr(CO)_3IndRhNBD$ complex (NBD: norbornadiene) [300].

A classification of fused aromatic ring-bridged heterobimetallic complexes can be made according to the type and number of condensed rings and the charge of the spacer. In the following sections heterobimetallic complexes of the spacers pentalene-diide **(87)**, indenyl anion **(88)**, as-indacene-diide **(89)** and s-indacene-diide **(90)** will be presented, highlighting their reactivity, catalytic, and intramolecular communication properties.



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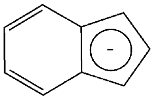

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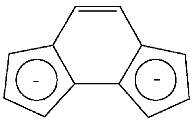

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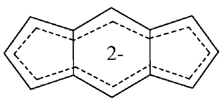

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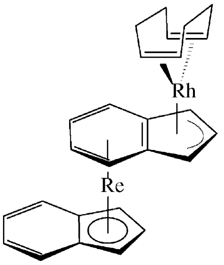
4.1. Indenyl, indacene and pentalene derivatives

The indenyl anion (Ind) is an aromatic 10-π electron system. Two quite recent reviews on the state of the art of the chemistry of indenyl metal complexes are those by Gimeno and coworkers [301] and by Stradiotto and McGlinchey [302].

The first example of a heterobinuclear rhenium/rhodium complex containing the indenyl bridge was prepared by Green et al. [303,304] (**91**), who predicted a transoid configuration of the metal groups on the basis of steric reasons.

In 1989, Ceccon et al. [305] published the synthesis and the structural characterization of η^6-$Cr(CO)_3$-Ind-η^3-Rh-η^4-C_8H_{14} (**92**). The results of X-ray diffraction confirmed that the metal units are situated *anti* with respect to the indenyl ligand. While the pattern of the chromium-arene distances is very similar to that observed for other neutral bicyclic η^6-$Cr(CO)_3$ benzenoid complexes, and the $Cr(CO)_3$ adopts an *exo* conformation, the position of rhodium with respect to the cyclopentadienyl moiety is slightly distorted towards allylic hapticity, forced by the strong coordination ability of the tricarbonyl chromium unit *versus* π-electron sextets.



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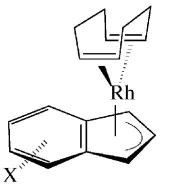

X = -, p-NO_2, $Cr(CO)_3$

92

Departure of the ML_2 unit from η^5 hapticity in indenyl complexes is very important because it represents a way of favoring coordinative unsaturation that can be responsible for the enhanced reactivity of the substrates with respect to cyclopentadienyl analogues [306]. In the elegant study of Basolo on the associative substitution reactions of Cp- and Ind-$M(CO)_n$ complexes [307,308] the high rate enhancement displayed by the indenyl derivatives ($\approx 10^8$ times, the so-called 'indenyl effect') was attributed to a stabilization of the transition state structure owing to the greater coordinative flexibility of the indenyl ligand as compared to that of the cyclopentadienyl ligand. In fact in the cyclopentadienyl species, the slippage of the metal from η^5 to η^3 coordination would produce a disruption of the aromaticity of the five-membered ring to form an allyl-ene electronic structure of higher energy; on the contrary, it induces an increase of the aromatic character of the benzene ring in the indenyl complexes causing stabilization of the η^3 intermediate. For a d^8-ML_2 fragment, slippage from η^5 to η^3 coordination renders the resulting 16-electron species more susceptible to nucleophilic attack from an external σ-donor. The Ind-ML_2 monometallic adducts already exhibit incipient slippage in

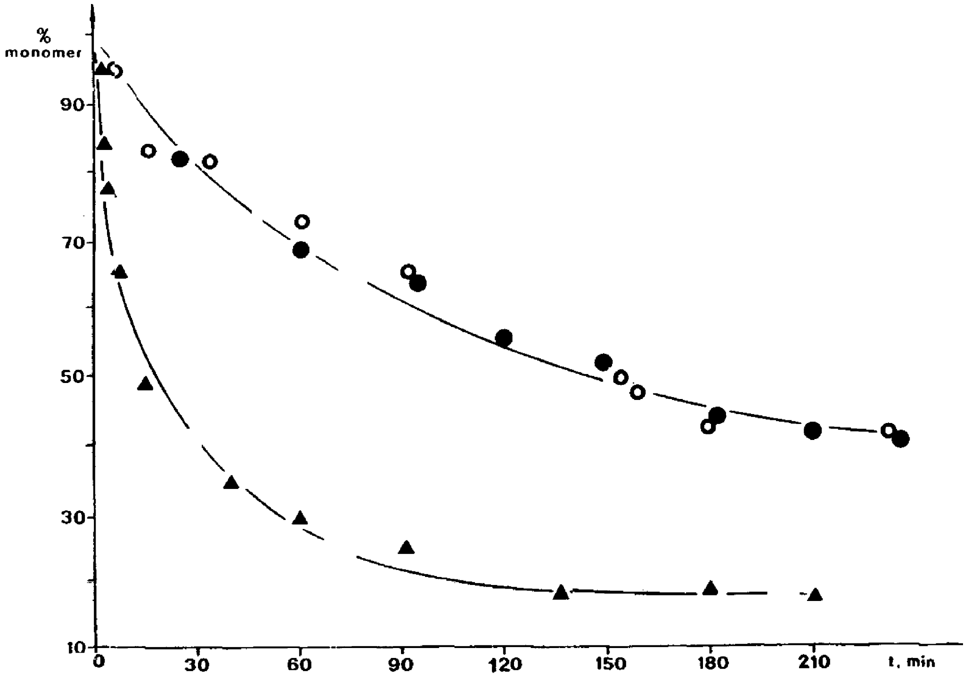

Fig. 7. Monomer disappearance in the MP trimerization reaction catalyzed by *anti*-Cr(CO)$_3$-Ind-Rh(COD) (filled triangle), Ind-Rh(COD) (filled circle), *p*-NO$_2$-Ind-Rh(COD) (empty circle). [Monomer] = 0.5 mol dm^{-3} in cyclohexane; [monomer]/[catalyst] = 1000, $T = 50\,^{\circ}$C. Reproduced with permission from [310]. Copyright by Elsevier Sequoia.

the ground state: the shift of the projection of the metal from the center of the pentagon is at least 0.15 Å in the direction opposite to the C–C junction with the hexagon.

The reactivity of heterobinuclear indenyl derivatives (**92**) was investigated and compared with that of mononuclear indenyl complexes. It was known [309] that the monometallic Ind-Rh(COD) (COD: 1,5-cyclooctadiene) is an efficient catalyst for the trimerization reaction of alkynes to benzenes. Ceccon et al. [310] studied the trimerization of methylpropriolate (MP) and dimethyl-acetylenecarboxylate (DMAD) promoted by three catalysts: *anti*-Cr(CO)$_3$-Ind-Rh(COD), Ind-Rh(COD), *p*-NO$_2$-Ind-Rh(COD).[4] The two monometallic species display almost the same catalytic activity; on the other hand, coordination with Cr(CO)$_3$ in *anti* disposition causes a dramatic increase of the efficiency of the catalyst (see Fig. 7).

The permethylation of the indenyl frame influences both the stability and the reactivity of the bimetallic indenyl complexes [313]. It is well recognized that η^5-pentamethylcyclopentadienyl ligand is a valid alternative to cyclopentadienyl ligand in $C_5R_5ML_n$ ($R = H, CH_3$) complexes, due to the exceptional blend of stability and reactivity induced by the permethylation [314]. Some permethylated monometallic indenyl complexes were synthesized by Basolo and coworkers, who tested in particular the reactivity of Ind*-M(CO)$_n$ complexes (Ind* = heptamethylindenyl) [314,315].

Therefore the studies on catalytic activity were focused also on the two bimetallic complexes *anti*-[Cr(CO)$_3$Ind*]Rh (CO)$_2$ and *anti*-[Cr(CO)$_3$Ind*]Rh(COD), while no catalytic activity was encountered in the *syn* isomers. For the monometallic derivatives, the trimerization reaction stops after ≈20 and 40% conversion with Ind*Rh(COD) and Ind*Rh(CO)$_2$, respectively probably because of poisoning of the catalyst (Fig. 8). The catalytic efficiency of the bimetallic substrates is much higher. The use of Cr(CO)$_3$Ind*Rh(COD) leads to quantitative conversion of MP to trimers and the reaction follows a pseudo-first order kinetic law ($v = k_{\text{obs}}[\text{monomer}]$, where $k_{\text{obs}} = k_2[\text{catalyst}]$). Under the same conditions by using Cr(CO)$_3$Ind*Rh(CO)$_2$ as catalyst, the same kinetic law is obeyed up to 70% reaction. The monomer conversion is anyway completed after a longer time.

The results lead to the conclusion that the permethylation of the indenyl frame further increases the stability of the catalyst with a moderate reduction of the reaction rate with respect to the *anti*-(Cr,Rh) indenyl species.

A detailed mechanism of the trimerization of DMAD catalyzed by *anti*-[Cr(CO)$_3$Ind*]Rh(CO)$_2$ is presented in [316].

A huge increase of the reaction rate (≈10^3) caused by the *anti* coordination with Cr(CO)$_3$ in indenyl rhodium complexes was also observed in the substitution reaction of CO with COD at the rhodium center, an effect dubbed '*extra* indenyl effect'.

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[4] It is known that the electron withdrawing effect of the nitro-group is comparable to that of Cr(CO)$_3$; their Hammet σ value is almost the same [311,312].

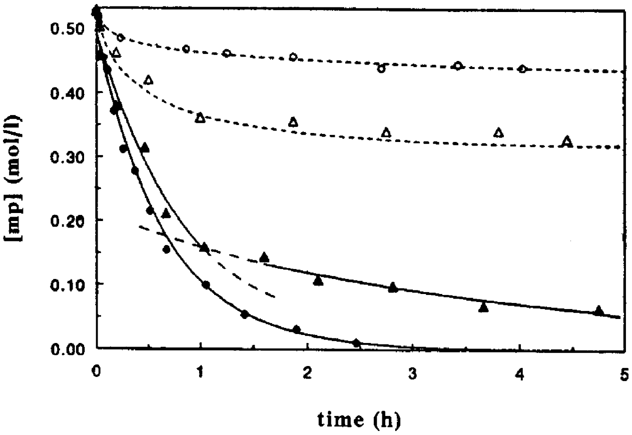


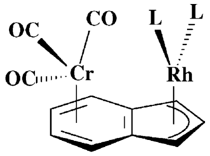
Fig. 8. Monomer disappearance in the methyl propiolate cyclotrimerization reaction catalyzed by Ind*-Rh(COD) (empty circles), Ind*-Rh(CO)$_2$ (empty triangles), Cr(CO)$_3$-Ind*-Rh(COD) (filled circles), and Cr(CO)$_3$-Ind*-Rh(CO)$_2$ (filled triangles). [Monomer]$_0$ = 0.526 mol dm^{-3} in cyclohexane; [monomer]/[catalyst] = 1000; $T = 50.0 \pm 0.1\,^{\circ}$C. Reproduced with permission from [313]. Copyright by Elsevier Science.

The results obtained from catalytic and ligand exchange experiments show that the accelerating effect of Cr(CO)$_3$ can be attributed only in part to its electron-withdrawing power. In fact, most of the effect is due to an enhanced coordinative unsaturation at rhodium which arises from the simultaneous *anti* coordination of the two metal units to the same 10-π-electron indenyl ligand.

An anomalous reactivity was observed also at the chromium center in the exchange reaction of the Cr(CO)$_3$ group with 1,3,5-cycloheptatriene (CHT). The exchange process is quantitative for naphthalene–Cr(CO)$_3$; instead it takes place to the extent of 55% in Cr(CO)$_3$IndRh(COD), and it is not observed at all in case of η^6-indene-Cr(CO)$_3$. The reactivity is correlated to the slippage of chromium from an unreactive η^6-bonding mode towards an η^4 one.

Actually, the geometrical parameters of rhodium-Cp moiety in the bimetallic species are not too different from those found for the monometallic one [317]. The structural characteristics however, obtained by X-ray measurements, refer to the solid state and do not reflect the dynamic processes which might occur in solution. Thus, the attempt was made to explain this extra-indenyl effect and the strong catalytic activity on the basis of spectral parameters, i.e. NMR $\delta(^1\text{H})$, $\delta(^{13}\text{C})$ and $\delta(^{103}\text{Rh})$ [318]. In fact, the ligand hapticity and the electron density at the metal greatly affects the ^{103}Rh chemical shift values. For example, in monometallic Rh(COD) derivatives with cyclopentadienyl (quasi perfect η^5 hapticity) the ^{103}Rh resonance is 768 ppm upfield with respect to the cyclooctenyl analogue (η^3 hapticity). In the η-Ind-Rh(COD) complex ^{103}Rh resonates at an intermediate value, suggesting that the situation is well described by a $\eta^3 + \eta^2$ coordination. In this case, the organic fragment is no longer a fully delocalized carbocycle and this reduces the ΔE between the HOMO and LUMO molecular orbitals for this type of compound compared to the corresponding η^5-Cp–Rh complexes. The electron withdrawing substituents like nitro-group shift the resonance downfield, but it is to note that the coordination of the benzene ring with Cr(CO)$_3$ in *anti* disposition shifts the ^{103}Rh resonance to higher values and consequently the effect of Cr(CO)$_3$ cannot be justified by its electron withdrawing properties alone. This leads to the conclusion that the rhodium–indenyl bonding mode is different in the mono- and bis- complexed species and this fact can be represented by an increased importance of an η^3 hapticity in the bimetallic complexes.

When the bridging ligand is a rigid arene structure, in contrast with highly flexible spacers like 1,3,5,7-cyclooctatetraene (COT) which can coordinate two *synfacial* metals adopting different conformations [319–322], more severe molecular constraints are required to allow the formation of a *syn* complex, including the bending of the arene frame. During the preparation of *anti*-[Cr(CO)$_3$(Ind)]Rh(COD) the presence of a *syn* isomer was not observed among the reaction products; on the other hand, the *syn* isomer was the only thermodynamically stable product if NBD instead of COD was used as an ancillary ligand [300]. *Syn*-[Cr(CO)$_3$(Ind)]RhL$_2$ (L$_2$ = NBD or L = CO) (**93**) are the first examples of *syn* heterobimetallic complexes of the indenyl ligand, the only related species being the homobimetallic complex *syn*-di-indenyl–di-vanadium [323].



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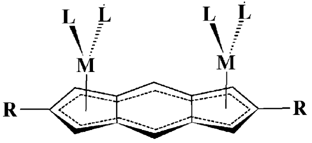
It is interesting to note that the bridge planarity is lost in the *syn* isomer: the doubly bent geometry of the indenyl ligand promotes an incipient coordinative unsaturation of both the metal units and favors the onset of a direct rhodium–chromium interaction.

A theoretical attempt to explain the indenyl and the extra-indenyl effect on the basis of extended Huckel molecular orbitals (EHMO) calculations is described in [324]. In the series CpRh(CO)$_2$, IndRh(CO)$_2$ and *anti*-[Cr(CO)$_3$Ind]Rh(CO)$_2$ the progressively reduced donor capabilities of the cyclic polyene towards the Rh(CO)$_2$ fragment induce a larger electrophilicity at the rhodium center, justifying the reactivity scale. Instead in the cofacial heterobimetallic species a direct heterodox Cr–Rh interaction has been detected, which is presumably responsible for the inhibition of reactivity. A summary on the results obtained for heterobimetallic Cr(CO)$_3$IndRhL$_2$ complexes can be found in [325].

The indacenyl dianion (Ic) in the isomeric forms *as*-(**89**) and *s*-(**90**) is a 14-π electron aromatic species. Investigations on the class of homobimetallic complexes with this bridging ligand have been carried out by different research groups. Thus, the coordination with FeCp of the two terminal cyclopentadienyls of the as-indacene was described in the 1970s [326]. Homobinuclear metallocene derivatives (M = Fe, Co, Ni) of this ligand were prepared and studied by Manriquez et al. [327]. Half-sandwich homobinuclear complexes of manganese and molybdenum of *s*- and as-indacene-diide have been synthesized and described in [328,329]. O'Hare and coworkers [330] characterized and studied some di-iron(CO)$_3$ and di-cobalt(CO)$_2$ complexes of the symmetric indacene-diide bridge. Ceccon and coworkers deeply studied mono- and bimetallic derivatives of rhodium and iridium of *s*- and *as*-indacene in a series of papers since 2000, with the main purpose of observing cooperative effects.

The synthesis of RhL$_2$ and IrL$_2$ (L = CO; L$_2$ = COD, NBD) homobimetallic complexes of *s*-indacene-diide, 2,6-dimethyl-*s*-indacene-diide, *as*-indacene-diide and 2,7-dimethyl-*as*-indacene-diide (**94**–**97**) is described in [331]. Whatever the cause for the different isomer ratio, a topic extensively treated in the paper, it has been ascertained that by changing the nature of the ancillary ligands one can obtain mixtures with a large preference for the *syn* with L$_2$ = COD or NBD (**94**, **96**) or for the *anti* with L = CO (**95**, **97**).



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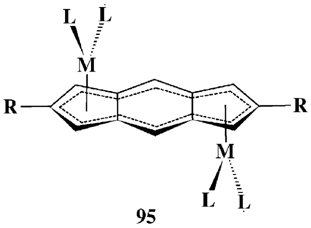

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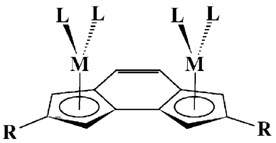

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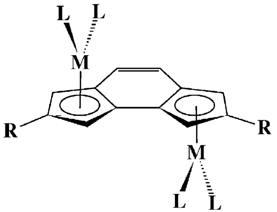

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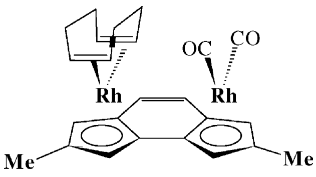
(M=Rh, Ir; R=H, CH$_3$, L$_2$=COD, NBD, L=CO, Ethylene)

An interesting aspect of the reactivity of the homobimetallic *as*-indacene-diide-[M(COD)]$_2$ species connected with cooperative effects is represented by its carbonylation. In the case of rhodium complexes the *syn* isomer reacts at a low temperature to produce the asymmetric substituted intermediate *syn*-(COD)Rh-2,7-dimethyl-*as*-Ic-Rh(CO)$_2$ (**98**), the concentration of which reaches a maximum in a very short time; afterwards it decreases slowly to give the final symmetric *syn*-tetracarbonylated product. The *anti* isomer behaves similarly but the exchange rate is a little slower. Notably, it was shown that, in both the isomers, the substitution of the first COD is much faster than that of the second one. It follows that the substitution of COD with two COs at one Rh center greatly influences the rate of substitution of the second COD unit. This result is clear evidence of the importance of a cooperative effect on reactivity, i.e. of electronic communication between the two metal centers mediated by the π-electron cloud of the bridging ligand. Finally, the factors responsible for the different reactivity exhibited by the two isomers in the first carbonylation step, can be probably referred mainly to their different ground state energies.

Carbonylation of the *syn* and *anti* isomers of iridium complexes, investigated under similar conditions, revealed that the mechanism of carbonylation in this case is quite different [331]. Evidence of cooperative effects in these isomers of iridium are lacking.



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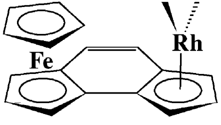
Manriquez and coworkers carried out EHMO calculations to shed some light on the electronic structure of the *s*- and as- indacene dianions and to understand their structural and physical properties [332]. They found a noticeable difference in the HOMO–LUMO gap, on the basis of which the asymmetric species is stabilized with respect to the symmetric one. Once complexed with two Cp*M (M = Fe, Co, Ni) units, assuming a singlet state, the *s*-indacene diide ligand has seven π-type electron pairs, of which six are of appropriate symmetry to interact in a bonding way, for example, with the six accepting frontier orbitals of the [Cp*Fe · · · FeCp*]$^{2+}$ fragment. In this case the calculated HOMO–LUMO gap is 1.3 eV. Instead in the case of *as*-indacene diide bridged diiron complex this energy difference is 2.7 eV. These results predict correctly and explain the different stability of both the dianions and their homobinuclear complexes.

The first example of heterobimetallic derivatives of *as*-indacene-diide was recently presented in [333]. The authors synthesized the *syn* and *anti* isomers CpFe-as-indacene-diide-RhL$_2$ (L$_2$ = COD, NBD; L = ethylene) (**99** and **100**) and investigated their chemical and electrochemical oxidation.



(L$_2$=COD, NBD; L=ethylene)

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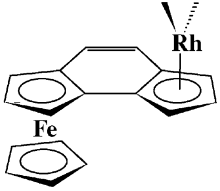

(L$_2$=COD, NBD; L=ethylene)

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A comparison of the reactivity of homo- and heterobimetallic indacene-diide complexes was carried out by testing the reaction of substitution of the ancillary ligands NBD

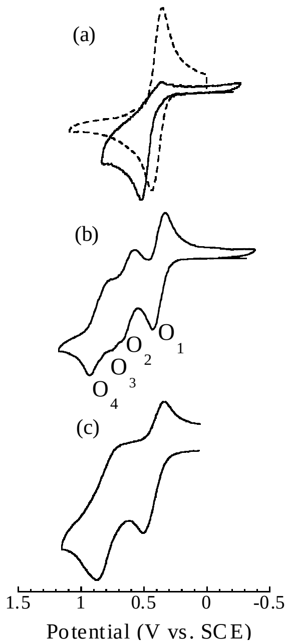


Fig. 9. Cyclic voltammetry scan at 0.5 mm diameter gold-disk electrode ($T = 20\,^{\circ}C$, solvent THF/0.2 M n-Bu_4NBF_4, scan rate $\nu = 0.5\,V\,s^{-1}$): (a, dashed line) 3 mM CpFe(η^5-hydro-as-indacenide) (as-**1**); (a, solid line) 3 mM (η^5-hydro-as-indacenide)RhCOD (as-**5**); (b) 3 mM mixture (1/1.5) of *syn*-CpFe(as-indacene-diide)Rh(COD) (*syn*-**2**) and *anti*-CpFe(as-indacene-diide)Rh(COD) (*anti*-as-**2**); (c) 1 mM *anti*-CpFe(as-indacene-diide)Rh(NBD) (*anti*-as-**3**). Reproduced with permission from [333]. Copyright by American Chemical Society.

or COD with CO. While the reactivity of the homobinuclear rhodium derivatives is similar to that of IndRh(COD) and contrasts with the inertness of the CpRh(olefin)$_2$ [270], surprisingly, no substitution product was obtained when CO was bubbled in solutions of complexes **99** and **100**. Only under forced conditions the carbonylated complex was obtained (50 °C, 10 atm) [334]. This lack of reactivity in the heterobimetallic complexes is probably due to the very strong η^5 coordination of iron to the Cp ring of the bridging ligand, which causes a quenching of the π-electron delocalization so that RhL$_2$ is forced to coordinate in a strict η^5 fashion as well. Hence its inertness is similar to that of CpRh(olefin)$_2$ and the complex assumes a fulvalene-like structure with an ethylene bridge. This reduced aromatic character of the six-membered ring is confirmed also by NMR spectroscopy. A CV study was carried out on the couple of isomers (see Fig. 9 and Table 3). From the peak separation *anti*-[CpFe as-indacene-diide]RhCOD was identified as a borderline Class II/Class III mixed valence system. Instead, *syn*-[CpFe as-indacene-diide]RhCOD can be interpreted as almost the sum of two isolated metal systems (Class I). This is likely due to the folding of the indacenyl skeleton induced by steric requirements determining a minor delocalization of the π-electron system of the indacene-diide ligand.

In the NIR time scale ($\approx 10^{-13}$ s), the results indicate that the radical cation of the *anti* complexes are valence detrapped (Class III) and the characteristic Gaussian-shaped band was recorded (see Fig. 10 and Table 4).

Table 3
Cyclic voltammetric data

Compound	E^1_p (V)	ΔE^1_p (V)	E^2_p (V)	ΔE^2_p (V)
Cp_2Fe	0.65	0.085		
As-**1**	0.44	0.085		
As-**5**	0.57[a]	0.07[a]		
Syn-**2**	0.66	0.100	0.75	[b]
Anti-as-**2**	0.42	0.100	0.92	0.15
Anti-as-**3**	0.50	0.150	0.87	0.20

Conditions: solvent THF/0.2 M n-Bu_4BF_4; potential vs. SCE at a 0.5 mm diameter gold disk electrode; $T = 20\,^{\circ}C$; potential scan rate $0.5\,V\,s^{-1}$.

[a] Estimated at high scan rate.

[b] Not measured due to the overlapping of the cathodic waves. Reproduced with permission from [333]. Copyright by American Chemical Society.

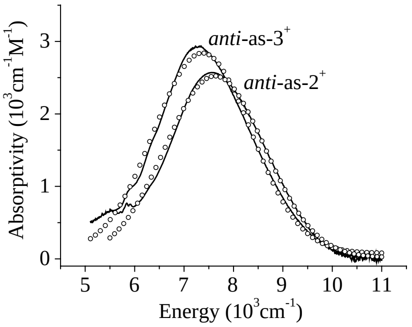
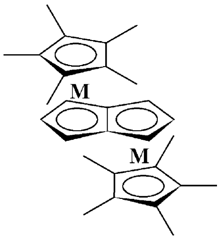


Fig. 10. Near IR spectra of 1 mM *anti*-**2** and *anti*-**3** (solid line, experimental curves; open circles, Gaussian fitting) in THF ($T = -78\,^{\circ}C$). Reproduced with permission from [333]. Copyright by American Chemical Society.

The 10-π electron pentalene dianion is an aromatic species formed by two condensed cyclopentadienyl rings. Studies on homo- and hetero-bimetallic derivatives of this bridging ligand were carried out mainly by Manriquez and coworkers [335,336]. They established a convenient synthetic procedure to prepare bridged metallocenes of formula *anti*-(Cp*M)$_2$(pentalene) (M = Ru, Fe, Co, Ni) (**101**). The first studies on the electronic communication were based on ^{57}Fe-Mössbauer spectroscopy (time scale ≈100 ns).



(M = Ru, Fe, Co, Ni)

101

Both the homobinuclear MV Fe(II)/Fe(III) pentalene-diide complexes and the analogous s- and as-indacene-diide derivatives were investigated in order to examine delocalized systems with larger metal–metal distances. While the

Table 4
Near IR data

Compound	$\nu_{\max}$ (cm^{-1})	ε ($cm^{-1} M^{-1}$)	$\Delta\nu_{1/2}$ (cm^{-1})	
			Found	Theory[a]
Anti-as-**2**$^+$	7580	2570	2020	3800
Anti-as-**3**$^+$	7310	2760	1980	3900

Conditions: solvent THF; $T = -78\,°C$.

[a] From Hush equation. Reproduced with permission from [333]. Copyright by American Chemical Society.

MV di-iron pentalene-diide complex is a fully averaged species, both the MV homobinuclear indacene-diide derivatives exhibit a Mössbauer signal typical of trapped Fe(II) and Fe(III) valences at low temperature [335].

The heterobinuclear case is particularly unusual illustrating the high degree of metal–metal interaction in pentalene-diide complexes. In fact the heterobimetallic (Cp*Fe-pentalene-RuCp*)$^{0,+1}$ shows a unique iron environment for the monocationic system over the entire range of temperature 1.5–300 K [327,335,336] (see Fig. 11), while a similar system, the dimethylene-bridged [1.1] ferrocenylruthenocenophane^{+1}, in which the two metals are coupled *via* CH_2 groups, exhibits a transition from trapped Fe(II)/Ru(III) to Fe(III)/Ru(II) as the temperature is increased [337]. A possible reason for the different behaviors of these (Fe/Ru)$^+$ complexes might be the fused nature of the pentalene-diide bridge, which allows a better electronic communication. Moreover, it should be noticed that, in contrast to fulvalene systems, the electronic communication appears unaffected by the heterobimetallic asymmetry.

The heterobimetallic consanguineous (Cp*Fe-pentalene-CoCp*)$^{0,+1}$ [338] give a ferrocene like Mössbauer spectrum. In the neutral complex, the electron spin resides on the low-spin Co(II); in the monocation the ferrocene-like behavior attests to the great stability of the diamagnetic low spin d^6 configuration of Co(III). In fact, the oxidation of the neutral hetero-complex to the monocation corresponds to loss of an electron from the spin doublet Co(II) center and little if any perturbation of the iron centers. The formation of the dication involves loss of an electron by Fe(II) to give Fe(III) and also this is consistent with the observed Mössbauer spectrum, which is similar to that of ferrioceinium.

^{57}Fe-Mössbauer studies were extended and completed with CV, NIR and ESR measurements in [327] where Manriquez and coworkers reported the structural characterization and the physical properties of $[Cp^*M(Pentalene)M'Cp^*]^{n+}$ (M, M′ = Fe, Fe; Co, Co; Ni, Ni; Ru, Ru; Fe, Ru; Fe, Co; $n = 0, 1, 2$) and the analogous homobimetallic derivatives of *s*- and *as*-indacene. In all cases Cp*M moieties are disposed in *anti* configuration, reflecting the dominance of steric effects. These complexes generally exhibit behavior consistent with significant electronic interactions between metal centers, including large electrochemical potential separations between successive one-electron redox events, and for the MV complexes IVCT absorption bands. In particular, CV curves with large ΔE separations of the heterobimetallic pentalene-diide complexes of Fe/Co and Fe/Ru exhibit two redox waves, assignable on the basis of the known electrochemical behavior of the iron and cobalt/ruthenium metallocenes. The MV heterobimetallic complexes present IVCT bands in the NIR region, which are not observed for the neutral and dicationic species, and the analysis based on Hush theory allows their assignment to Class III. The ESR spectrum of the neutral Fe/Co complex is that expected for spin doublet ground state Co(II), while that of the monocation is silent, as expected for low spin Fe(II) and Co(III). The dication spectrum exhibits large anisotropy as expected for the ferrocenium Fe(III). These results are in agreement with the Mössbauer data above discussed. In contrast the ESR spectrum of (Cp*Fe-pentalene-RuCp*)$^+$ $[BF_4]^-$ (see Fig. 12) reflects a significant reduced g-factor anisotropy, which indicates the approach to an averaged state, again corresponding to valence detrapping as suggested by its Mössbauer spectra.

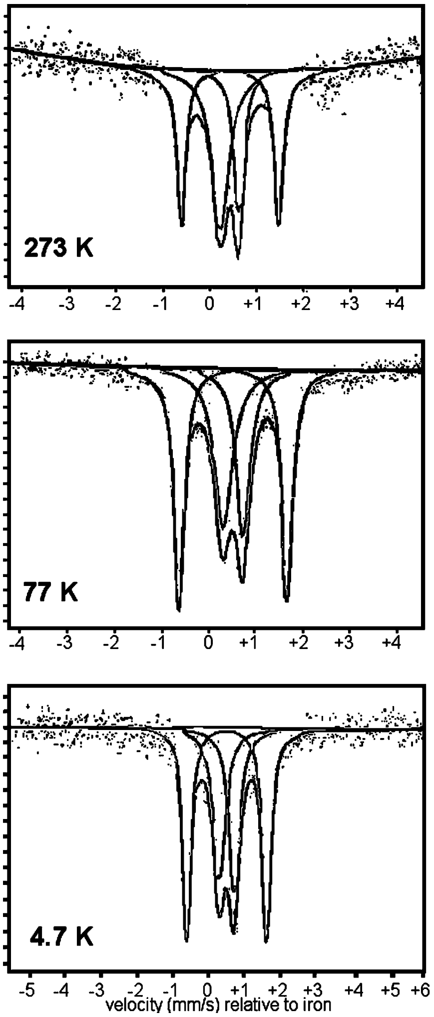


Fig. 11. Mössbauer spectra of $[Cp^*Fe(Pentalene)RuCp^*]^+$ as a function of temperature. Reproduced with permission from [327]. Copyright by American Chemical Society.

A search in the chemical literature before 2001 reveals no binuclear pentalene-diide compounds containing rhodium as

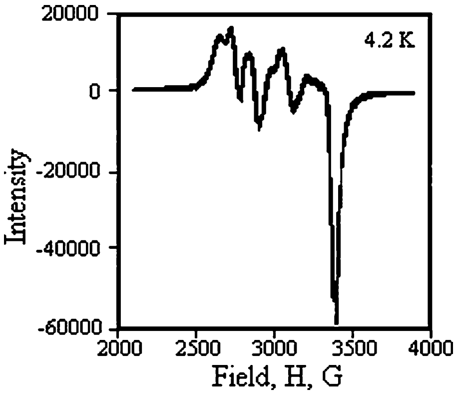
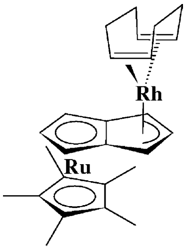


Fig. 12. EPR spectra of [Cp*Fe(Pentalene)RuCp*]$^+$[BF$_4$]$^-$ at 5 K. Reproduced with permission from [327]. Copyright by American Chemical Society.

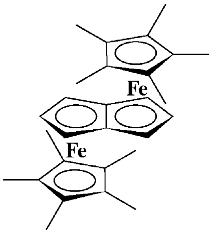
metal center. Recently, Manriquez and coworkers presented a new heterobimetallic Ru/Rh complex with dianionic pentalene as bridging ligand (**102**) [339]. X-ray characterization indicates that the ruthenium atom is symmetrically coordinated to one of the fused cyclopentadienyl rings and the rhodium atom coordinates to the other ring, in *anti* conformation, in a η^3-allyl mode.



102

The IR and NMR characterizations of the product of carbonilation of **102** indicated the displacement of the COD ligand to afford the binuclear complex [Cp*Ru(μ-C$_8$H$_6$)Rh(CO)$_2$]. Catalytic studies were also started on dehydrogenative silylation reaction of styrene and the activity and selectivity of [Cp*Ru(μ-η^5,η^3-C$_8$H$_6$)Rh(η^4-COD)] were found to be similar to that of one of the most active rhodium catalysts reported for dehydrogenative silylation, [Rh(COD)$_2$]BF$_4$/PPH$_3$.

It is noteworthy to compare the high reactivity of this pentalene-diide complex with the non-reactivity of both the isomers CpFe(indacene-diide)RhCOD towards carbonylation (see above discussion). Studies on the catalytic activity of related binuclear pentalene-diide complexes are currently underway. The strong electron conveying capability of pentalene dianion is confirmed by another recent study by Manriquez and coworkers [210]. He has investigated the effect of asymmetry in binuclear pentalene-diide bridged complexes which can be due to i) adjacent different metals or ii) different ancillary ligands in four complexes of formula Cp*Fe C$_8$H$_6$ MCp* and (C$_8$H$_7$)Fe C$_8$H$_6$ MCp* (M = Fe, Co) (**99–102**). The asymmetry in general introduces a barrier and, as a consequence, the electronic communication decreases. This reduction is strong when comparing a homobinuclear complex with its analogous heterobimetallic complex and can cause a change from delocalized to localized behavior. On the other hand the barrier introduced by an asymmetry in the terminal ligand must be low. A comparative analysis of the results on the four complexes **103–106** demonstrates that the different nature of Co in regard to Fe produces a dramatic change in the barrier for electron transfer, reflected in a change of behavior from delocalized to localized. The effect of changing a terminal ligand on the barrier is different from delocalized compounds than for localized ones; specifically in this last case it induces a complete loss of electronic communication.



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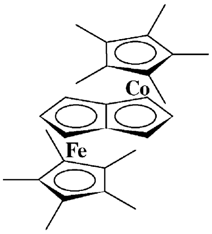

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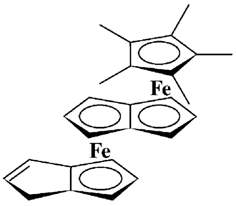

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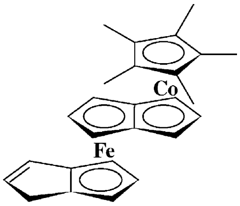


106

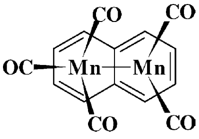
It should be mentioned that recently Barlow and O'Hare [340] have reported the synthesis of homobinuclear Mn and Re carbonyl derivatives of pentalene, their redox chemistry and they describe a strong interaction between the two metals via the π bridging ligand. In particular they investigated the electronic communication in the dimanganese complex, whose mono-reduction product can be classified as Class III on the basis of NIR data.

4.2. Polycyclic derivatives

The most common neutral spacer employed in the synthesis of bimetallic complexes is naphthalene. The paucity of examples of homo- and hetero-binuclear complexes is due mainly to synthetic difficulties.

Homo-bimetallic complexes of naphthalene were prepared and in all but very few cases an *anti* disposition of the two metal groups has been assigned by X-ray structures or by analogy with similar complexes. The *anti*-naphthalene-(FeCp)$_2$ [341], (Cr-arene)$_2$ [342] and (RuCOD)$_2$ [343] complexes can be classified as 'slipped triple decker' complexes where coordination of both metals to the two six-membered rings is characterized by the shift of the metals towards the peripheral carbons of the ligand naphthalene (distorted η^6 hapticity). Jonas and coworkers prepared also heterobimetallic naphthalene sandwich and half-sandwich derivatives containing Fe/Co, Cr/Co and Cr/V [341]. They observed that the planarity of the bridging naphthalene is generally modified depending on the nature of the bonded metal groups and found that the magnitude of the fold angle vary from 14° for the bis-(FeCp) complex to 30–40° for an heterobimetallic Cr–Co complex.

Sweigart and coworkers set up a general route to homo and heterobinuclear *syn* and *anti* complexes with naphthalene-type ligands [344,345]. By controlled reduction (1 eq. of cobaltocene) of naphthalene-Mn(CO)$_3{}^+$ they obtained syn-facial asymmetric bimetallic η^4:η^6 naphthalene complexes (**107**), one manganese bearing three carbonyl ligands and the second bearing only two.



107

The *syn* arrangement facilitates metal to metal communication, which was confirmed by ESR experiments [345]. Similarly, i.e. by controlled reduction of a mixture of Napth-Mn(CO)$_3{}^+$ with appropriate metal complexes that have a free arene ring available, they prepared the analogous *syn* Mn/Fe derivative and the antifacial complexes [(C$_6$Me)$_6$Ru-Napth-Mn(CO)$_3$]$^+$ and [(CpFe-Napth-Mn(CO)$_3$]. Even if these works on arenemanganese carbonyl chemistry are mainly synthetic, they have a great importance, due to the scarce examples of naphthalene-bridged bimetallic complexes.

5. Conclusions and perspectives

In this review we have focused the attention on the electronic communication in metal–metal carbon bridged heterobimetallic and asymmetric homobimetallic complexes. The bridging ligands considered are sp and sp^2 hydrocarbon chains, fulvalene, fulvalene-like and fused aromatic spacers. The effects on the electronic communication have been mainly evaluated on the basis of the reactivity studies and of the results of ^{57}Fe-Mössbauer, ESR, optical and electrochemical measurements of the mixed valence species, which give information on the rate of the intramolecular electron transfer or on electron delocalization. The numerous examples reported have been classified according to the structural features of the bridging ligand. In fact, as well as in homobimetallic symmetric complexes, the efficiency of the intramolecular electronic communication depends on the strength of the coupling between the termini, the nature of the metals, their oxidation state, and the structure of the bridging ligand playing a fundamental role. Rigid and semi-rigid unsaturated spacers proved to be efficient in conveying electrons, since they provide highly conjugated pathways. However, the electronic communication falls down with increasing the distance between the termini and in the molecular wires this limits the length of the carbon chain. Fulvalene and fused aromatic spacers are also suitable linkers to promote electronic communication, unless steric requirements break their planarity inducing loss of aromaticity. Typically, this is encountered in *cisoid* fused complexes when the hindrance of the ancillary ligands imposes a bended shape to the whole molecular structure. These considerations are general and subsist both for a homobimetallic M-*spacer*-M and an analogous heterobimetallic M-*spacer*-M′ complex. The peculiarity of the latter is connected to its strong asymmetry which governs the extent of the electronic interaction between the metal centers. In fact by replacing one end-capping metal group in a homobimetallic complex by a different one it is possible in principle to achieve a fine tuning of the communication in order to control the metal-to-metal electron transfer. The reported examples show that asymmetry reduces the electronic communication and the presence of a different metal group can even interrupt the intramolecular ET. This can be rationalized in the framework of electron transfer theory, since asymmetry raises the thermal barrier. In case of weak coupling asymmetry can inhibit the electronic communication but in strongly adiabatic conditions Class III behavior is often found. Thus, it seems that the extent of the electronic coupling might be tuned by accurately designing the complexes and to this purpose most of the heterobinuclear species discussed in this review are ideal candidates for catalysts and devices in which the activity of one metal center can be finely controlled at molecular level acting on the adjacent one. Systematic studies on reactivity and catalytic activity are required at both theoretical and experimental level.

In spite of the quite large number of heterobimetallic complexes reported, much less are those for which the reactivity and the physico-chemical properties have been investigated. There is a “gold mine” of material waiting to be re-examined.

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