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Use of the Electron-Reservoir [Fe^{I}Cp(arene)] Sandwiches as Efficient and Selective Electrocatalysts: Syntheses of Homo- and Heterodinuclear Zwitterionic Transition-Metal Fulvalene Complexes

David S. Brown,[†] Marie-Hélène Delville,[‡] K. Peter C. Vollhardt,[†] and
Didier Astruc*[,‡]

Department of Chemistry, University of California, and Chemical Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, and Laboratoire de Chimie Organique et Organométallique, URA CNRS No. 35, Université Bordeaux I, 351, Cours de la Libération, 33405 Talence Cédex, France

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The electron-reservoir complexes [Fe^{I}Cp(C$_6$H$_6$)], [Fe^{I}Cp(C$_6$Me$_6$)], and [Fe^{I}Cp*(C$_6$Me$_6$)] (Cp $= \eta^5$-C$_5$H$_5$; Cp* $= \eta^5$-C$_5$Me$_5$) have been used as initiators in THF for the electron-transfer-chain-catalyzed (electrocatalyzed) synthesis of the homobimetallic zwitterions $[(CO)_3M^-FvM^+(CO)_2(PR_3)_2]$ (M = Mo, W; Fv $= \mu_2$-η^{10}-fulvalene; R = Me, OMe) from [M$_2$Fv(CO)$_6$] and PR$_3$ and of the heterobimetallic zwitterions $[(CO)_3M^1FvM^2(CO)(PR_3)_2]$ (M^1 = Mo, W; M^2 = Fe, Ru) from $[M^1M^2Fv(CO)_5]$ and PR$_3$. Cyclic voltammetry (CV) experiments (DMF, 0.1 M *n*-Bu$_4$NBF$_4$, Pt, 0.400 V s^{-1}) show that the CV's of the homobimetallic starting materials are unchanged in the presence of PR$_3$ (R = Me, OMe) whereas those of the heterobimetallic complexes in the presence of PMe$_3$ show only the CV's of the zwitterions. This indicates that the electrocatalytic process of the homobimetallic complexes is slow on the electrochemical time scale whereas that of the heterobimetallic complexes with PMe$_3$ is fast on the same time scale. This dichotomy is taken into account in terms of the very low concentration of the primary radical anion responsible for the reactivity with PR$_3$ in the case of the homodinuclear systems due to an intrinsically high disproportionation constant (K_{disp}); with heterodinuclear complexes, the dissymmetry is responsible for a relatively good thermodynamic stability and, thus, a higher concentration of the primary radical anion $[(CO)_3M^{1\,-}FvM^2(CO)_2^{\bullet}]$, which reacts with PR$_3$. The effect of the PMe$_3$ concentration is also important, consistent with second-order kinetics. Subsequently, the K_{disp} values are qualitatively found in the following order, which is opposite to that of the electrocatalytic reactivity: RuRu (unreactive) $\gg$ WW $>$ MoMo $>$ 1 $>$ RuMo, RuW $>$ FeW. In THF, initiation with [Fe^{I}Cp(C$_6$Me$_6$)] of the reaction of $[(CO)_3\overline{WFvR}u(CO_2)]$ with PR$_3$ yields the monophosphine zwitterionic adduct $[(CO)_3W^-FvRu^+(CO)_2(PMe_3)]$, whose formation is partially driven by its insolubility. On the other hand, with [FeCp*(C$_6$Me$_6$)] as the initiator, the bis(phosphine) zwitterion $[(CO)_3W^-FvRu^+(CO)(PMe_3)_2]$ is formed as a result of the stronger driving force in the initiation electron-transfer step. The synergistic roles of the insolubility of the monophosphine intermediate and of the driving force provided by the electron-reservoir initiator are confirmed for electrocatalytic experiments in solvents of high dielectric constants (synthesis in MeCN or electrochemistry in DMF) in which the monophosphine zwitterion is neither formed nor detected. In conclusion, initiation of electrocatalytic reactions by the electron-reservoir [Fe^{I}Cp(arene)] complexes is very useful (cobaltocene is inefficient in many cases), highly efficient (no side reactions), and highly selective (as a function of the number of Me groups on the ligands providing a wide range of redox potentials).

Introduction

Since the seminal work by Mueller-Westerhoff and Cowan on biferrocenylene,[1] electron-transfer reactions in bimetallic fulvalene complexes have attracted a great deal of attention.[2] In the 1970s, the studies concentrated on the homonuclear bimetallic bifulvalene[5−8] and

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[†] University of California and Lawrence Berkeley Laboratory. Telefax: (510) 643-5208. E-mail: vollhardt@cchem.berkeley.edu.

[‡] Université Bordeaux I. Telefax: Int. code + (56) 84 66 46. E-mail: astruc@cribx1.u-bordeaux.fr.

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bimetallocene[9−11] complexes. More recently, attention has focused on homobimetallic monofulvalene complexes with carbonyl and phosphine ligands.[12−15] On the other hand, biferrocenes,[16,17] diiron fulvalene bis(arene),[18] and dinuclear bis(fulvalene)[19] complexes have still been the subject of recent studies due to the great potential for multiple electron transfers and mixed valences of these delocalized systems. Bimetallic fulvalene complexes now constitute a broad class of organometallic chemistry owing to synthetic routes using biferrocenes,[15] redox chemistry,[20−23] or the fulvalene dianion.[24−30]

In this context, our goal was initially to study intramolecular electron transfer between two metals linked by a delocalized bridging fulvalene ligand.[14,15] We then turned to applications of selective electron-transfer reactions involving redox recognition in heterodinuclear fulvalene complexes and their synthetic consequences.[31] A targeted application was the synthesis of zwitterionic fulvalene complexes using electron-transfer chain catalysis. Indeed, zwitterions are of interest in the context of nonlinear optics.[33−36] The thermal route from bimetallic (fulvalene) carbonyl complexes to zwitterions is not straightforward, since prolonged reaction times are required and sometimes lead to the loss of one metal (see the recent extensive full paper by Tilset[30]). Electron-transfer-chain catalysis[37−43] is a very efficient way to perform inorganic and organometallic reactions such as ligand exchange,[38−43] isomerization, chelation, decomplexation, insertion, and oxidative addition.[44] Few reactions involve an overall redox change. Tyler has disclosed photochemically initiated disproportionations of metal carbonyl dimers in the presence of phosphines that were shown to proceed according to the electron-transfer-chain mechanism; “19-electron” species were involved in the propagation chain.[45−50]

The delocalized bimetallic fulvalene framework provides an electron sink for the extra electron required in reductively induced electrocatalytic reactions. In former papers, we have detailed the electrochemistry and stoichiometric electron-transfer chemistry of heterodi-

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Scheme 1

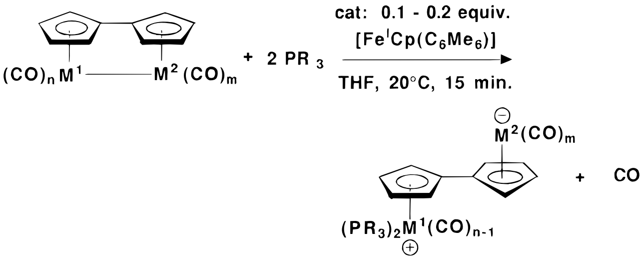

Table 1. Summary of the Starting Materials and Products for the Reaction in Scheme 1

starting material	product	M^1	M^2	*n*	*m*	R
1	**2**	Mo	Mo	3	3	Me
3	**4**	W	W	3	3	Me
5	**6**	Fe	W	2	3	OMe
5	**8**	Fe	W	2	3	Me
9	**10**	Ru	Mo	2	3	Me
11	**13**	Ru	W	2	3	Me

nuclear fulvalene complexes [WMFv(CO)$_5$] (Fv = fulvalene; M = Fe, Ru). Along this line, we now report electrocatalytic reactions of these complexes as well as those of the homodimers [M$_2$Fv(CO)$_6$] (M = Mo, W) with PMe$_3$ and P(OMe)$_3$, including the synthetic and analytical aspects.[54] In synthetic-scale reactions, we use three electron-reservoir [Fe^{I}Cp(arene)] complexes as electrocatalysts and will show their selectivity depending on their redox potential values.

Results

Electrocatalytic Syntheses of the Zwitterions Using Electron-Reservoir Fe^I Complexes as Initiators. The homobimetallic dimolybdenum (**1**), ditungsten (**2**), and diruthenium (**14**) complexes were tested in the electrocatalytic syntheses of zwitterions in the presence of trimethylphosphine or trimethyl phosphite and of the initiator in THF at 20 °C. The standard initiator was the electron-reservoir complex [Fe^{I}Cp(C$_6$Me$_6$)], whose redox potential (Fe$^{I/II}$: −1.55 V vs SCE in DMF) is more negative than the reduction potentials of the MoMo and WW complexes (−0.860 and −0.940 V vs SCE, respectively).[55] Indeed, both **1** and **2** gave good yields of the zwitterions **2** and **4** (60% and 70%, respectively, after a few minutes at 20 °C), in which one carbonyl ligand in the starting material has been replaced by two trimethylphosphine ligands (Scheme 1, Tables 1 and 2). Both compounds were readily identified by comparison of their spectral data with those previously reported.[28,30] Complex **2** did require a large excess of PMe$_3$ (20 equiv) to give efficient conversion, as the use of lower PMe$_3$ concentrations resulted in the need for larger amounts of reducing agent, which in turn resulted in the formation of the dianion. Only disubstituted products were obtained. In order to compare the efficiency of the electrocatalytic process and of the uncatalyzed reactions performed by Tilset,[30] we have gathered the yields and conditions of both methods in Table 2. It is noteworthy that, for **1** and **2**, no electrocatalytic process is observed on the electrochemical time scale, even upon continuous cyclic voltammetry scanning.

Table 2. Comparison of Catalyzed and Uncatalyzed Syntheses of Homobimetallic Zwitterions[a]

compd	product	catalyst	temp	time	yield
1 (Mo−Mo)	**2**	no	ambient	12 h	51%
1 (Mo−Mo)	**2**	[Fe^{I}Cp(C$_6$Me$_6$)]	ambient	20 min	70%
3 (W−W)	**4**	no	0 °C	3 days	63%
3 (W−W)	**4**	[Fe^{I}Cp(C$_6$Me$_6$)]	ambient	15 min	56%

[a] Reaction times have not been optimized. The electrocatalytic processes were shown to be slower than the electrochemical time scale (scan rate 0.4 V s^{-1}; see text). Modest yields (after chromatography) in the catalytic experiments are due to the small scale (see Experimental Section), but no side products were observed.

With the diruthenium complex, which displayed an extremely negative reduction potential (−2.0 V vs SCE),[58] neither [Fe^{I}Cp(C$_6$Me$_6$)] nor [Fe^{I}Cp*(C$_6$Me$_6$)] ($E°$ = −1.85 V vs SCE in DMF) afforded a reaction. The use of stronger reducing agents such as Na/K alloy failed to give any substitution product. The desired bimetallic zwitterion was not observed either during the uncatalyzed substitution reaction, which, upon extended heating, led to the loss of one ruthenium moiety.[30] On the other hand, the heterobimetallic FeW (**5**), RuMo (**9**), and RuW (**11**) complexes offered excellent possibilities for the desired reactivity since their reduction potentials were less negative than that of [Fe^{I}Cp(C$_6$Me$_6$)]. For **5**, the two one-electron-reduction waves are separated,[31,32] whereas they are not for **9** and **11**.[55] Thus, the regioselectivity problem was especially challenging for these last two complexes. Compound **9** displayed electrocatalytic substitution to give the zwitterion **10** (60% yield), which was readily identified by comparison of the spectral data with those known.[26] The fact that substitution had occurred exclusively at the ruthenium center was easily confirmed as well by this comparison. Thus, the easy and fast electrocatalytic pathway offered a viable alternative to the previous synthesis of **10**. The behavior of complex **5** proved to be similar, giving the new zwitterions **6** and **8** upon reactions with P(OMe)$_3$ and PMe$_3$, respectively. Since the zwitterion **6** was the first one obtained in the series, suitable crystals were grown by slow cooling of a saturated acetonitrile solution and the X-ray diffraction study was carried out by Boese. The results were reported in a preliminary communication,[54] and the ORTEP drawing is shown in Figure 1. The X-ray structure confirmed the proposed formulation of the product and showed a trans orientation of the metal centers with respect to the fulvalene

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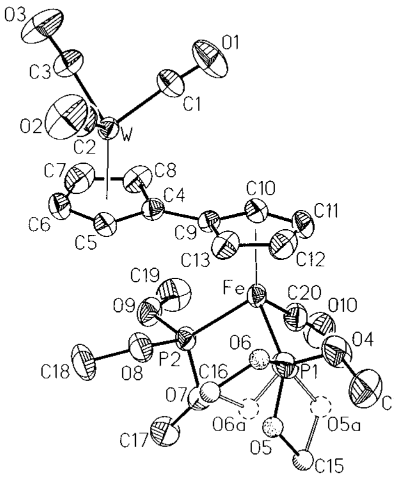
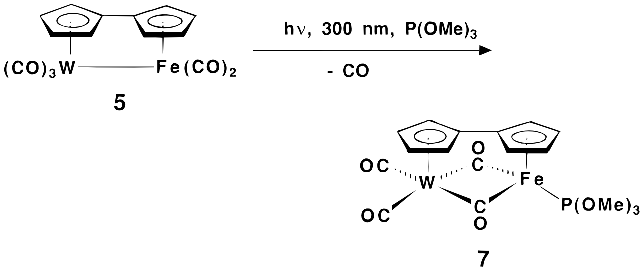


Figure 1. Crystal structure of **6**. Reproduced from ref 54.

Scheme 2



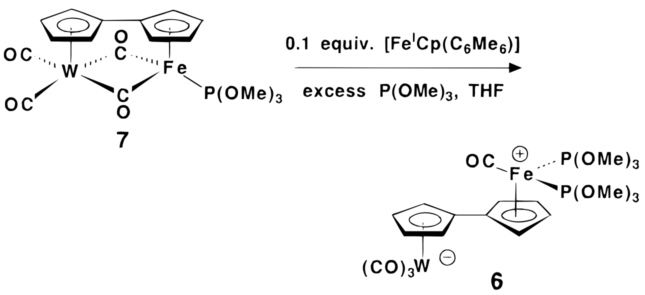
ligand, an arrangement which is always observed in bimetallic complexes lacking a metal−metal bond.

The electrocatalytic reaction of **5** to form a zwitterion could be initiated not only by [Fe^{I}Cp(C_6Me_6)] but also by [Fe^{I}Cp(C_6H_6)]. The redox potential of the latter is $E° = -1.30$ V vs SCE in DMF, just between the two reduction peaks of **5**, $E_{p1} = -1.05$ V and $E_{p2} = -1.60$ V vs SCE. The use of [Fe^{I}Cp(C_6Me_6)] as the initiator is justified by an excellent thermal stability and ease of handling. On the other hand, the electrosynthesis could not be initiated by cobaltocene, as expected by the insufficiently negative $E°$ value of the cobaltocene/cobaltocenium redox couple ($E° = -0.9$ V vs SCE).[61]

The mono(phosphine)-substituted compound **7** was desired in order to check whether it was an intermediate in the electrocatalyzed formation of the zwitterion **6** from **5**. Photolysis of **5** seemed to be an independent and thus attractive route to **7**. Indeed, photolysis of complex **5** at 300 nm in the presence of P(OMe)$_3$ gives a single carbonyl substitution by a phosphite to produce **7**. The product was easily purified by chromatography followed by recrystallization. The ^{31}P NMR spectrum confirmed that the phosphite ligand was on the iron center, as no coupling to the ^{183}W nucleus was observed. The ^{1}H NMR spectrum showed a doublet at δ 3.61 ppm that was integrated to nine hydrogens for the P(OMe)$_3$ ligand and a symmetrical fulvalene signal of four peaks consistent with the proposed structure **7**. The absorptions at 1880 and 1866 cm^{-1} in the IR spectrum confirmed that bridging carbonyl groups were present (Scheme 2).

In the presence of PMe$_3$ and [Fe^{I}Cp(C_6Me_6)] as the catalyst, complex **7** undergoes electrocatalytic synthesis

Scheme 3



of the same zwitterion (**8**) as that obtained starting from **5**, which means that P(OMe)$_3$ was selectively exchanged in **7** rather than CO (Scheme 3). For complex **7**, [Fe^{I}Cp(C_6H_6)] is not a strong enough reducing agent to catalyze the reaction.

We now turn to the electrocatalytic reaction of complex **11**, which is peculiar. Treatment of a THF solution of **11** with a catalytic amount of [Fe^{I}Cp(C_6Me_6)] in the presence of PMe$_3$ resulted in the rapid formation of a precipitate which was isolated and purified in the usual way. Although this complex was expected to be the known zwitterion **13**, the spectral data revealed that it was a new complex. The ^{1}H NMR spectrum showed a doublet at 1.68 ppm which was integrated to nine hydrogens, indicating that only one PMe$_3$ ligand was present. The absence of coupling to the ^{183}W nucleus in the ^{31}P NMR spectrum confirmed that the phosphine was bonded to ruthenium. This complex is insoluble in THF but soluble in acetonitrile. It was characterized by ^{1}H, ^{13}C, and ^{31}P NMR and FAB mass spectroscopy, which gave the molecular peak. All of these data support the formulation of the complex as a zwitterion with two CO and one PMe$_3$ ligand on the ruthenium center. This compound, **12**, then, represented the only case in which monosubstitution was achieved by electrocatalysis.

The formation of the monosubstituted zwitterion **12** was unexpected, and it was postulated that this product reflected a dependence of the reaction on the potential of the reducing agent. In order to test this hypothesis, the reaction was carried out in THF using [Fe^{I}Cp*(C_6Me_6)] as the reductant, and in this case, the known zwitterion **13** was obtained. Furthermore, it was possible to convert **12** into **13** by treating **12** in acetonitrile with a catalytic amount of either [Fe^{I}Cp(C_6Me_6)] or [Fe^{I}Cp*(C_6Me_6)]. Thus, the nature of the solvent also plays an important role in the reaction. It was determined that **12** does not react with PMe$_3$ in the absence of an initiator (as for all the electrocatalytic reactions in this paper) (Scheme 4).

Electrochemical Characterization of the Electrocatalytic Reactions. Whereas the cyclic voltammograms of the homodinuclear MoMo and WW complexes did not change upon addition of PMe$_3$ even upon continuous scanning, dramatic changes were observed when such experiments were carried out with all the heterodinuclear complexes. Indeed, with **5**, **7**, **9**, and **11** the cathodic reduction wave of the starting material was rapidly replaced by a new cathodic wave.

For the MoRu complex **9**, the two-electron wave of the starting complex is observed at $E_p = -1.415$ V vs SCE at a scan rate of $v = 400$ mV s^{-1}, and the reoxidation is observed in a two-electron anodic wave at +0.035 V. The

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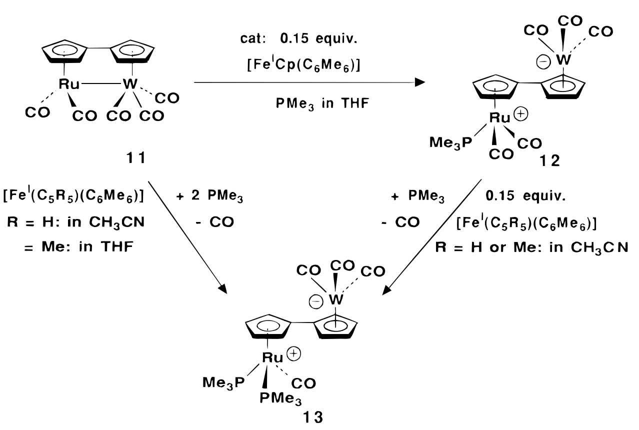
[61] (a) Vlček, A. A. *Collect. Czech. Chem. Commun.* **1965**, *30*, 952. (b) Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632. (c) Gubin, S. P.; Smirnova, S. A.; Denisovitch, L. I. *J. Organomet. Chem.* **1971**, *30*, 257.

Scheme 4. ETC Reactions Starting with 11



addition of 20 equiv of PMe_3 leads to a new cathodic wave at -1.930 V vs SCE (cathodic shift: 0.515 V), whereas the cathodic wave of **9** completely disappears. No change is observed on the oxidation side, as no new wave appears upon continuous scanning.

For **5**, the addition of excess PMe_3 to the cell provokes the disappearance of the two cathodic waves at $E_p = -1.155$ and -1.665 V vs SCE and of the reoxidation wave at $+0.065$ V ($v = 400$ mV s^{-1}). Instead, new waves appear on the cathodic side at $E_p = -1.710$ V (cathodic shift: 0.555 V) and anodic side at $E_p = +0.090$ V vs SCE. The transformation is so fast that it is impossible to observe the waves of both compounds at the same time. In the case of the addition of $P(OMe)_3$, both waves can be observed. In DMF, the CV of the WRu complex **11** shows a two-electron cathodic wave at $E_p = -1.565$ V vs SCE and an oxidation wave at $E_p = 0.0$ V vs SCE (the CV depends very much on the solvent[31,58]). Upon addition of excess PMe_3 in the cell and scanning, these waves disappear and a new cathodic wave appears at $E_p = -1.970$ V (cathodic shift: 0.405 V vs SCE; Figure 2).

In all cases, the CV's of the zwitterions were recorded independently, and it was found that the new waves appearing after addition of excess PMe_3 or $P(OMe)_3$ to the cell containing the starting materials were always exclusively those belonging to the zwitterions (Table 3).

In particular, in the case of **11**, for which the electrocatalytic synthesis in THF using [Fe^{I}Cp(C_6Me_6)] as catalyst led to the simple phosphine addition product **12**, the CV of **12** was recorded, but its waves were never found in the CV of **11** + PMe_3 (Figure 2). It can be concluded that, under the electrochemical conditions, the electrocatalytic process always directly leads to the bis-PMe_3 or bis-$P(OMe)_3$ zwitterions when a group VI metal (Fe or Ru) is involved. The CV of **12** in the presence of PMe_3 also shows the electrocatalytic formation of **13** on the electrochemical time scale, as monitored by the appearance of the wave of **13** after one cycle.

Discussion

Use of Fe^I Electron-Reservoir Complexes as Electrocatalysts. Electron-reservoir complexes (such as [Fe^{I}Cp(arene)] complexes) have been defined as having at least two stable oxidation states.[4,41,51,75,76] The reduced form must be sufficiently electron-rich to be able to reduce a wide range of substrates. Indeed, [Fe^{I}Cp(arene)] electron-reservoir complexes are the most electron-rich neutral molecules known, on the basis of their ionization potentials measured by He(I) photoelectron spectroscopy.[51b] They can effect: (i) stoichiometric reductions (e.g. C_{60},[52a] O_2,[52b] etc.[4,41]); (ii) redox catalysis (for instance, NO_3^- and NO_2^- reduction);[4] (iii) initiation of electron-transfer chain reactions (electrocatalysis). Previous examples of this latter class are found in the initiation of the electrocatalytic decomplexation of the [Fe^{II}Cp(arene)]$^+$ salts[53a] and of the electrocatalytic ligand exchange of the arene ligand in these salts by a set of three two-electron neutral ligands such as phosphines.[53b] However, the present study is the first one for which the Fe^I electron-reservoir complexes serve for the electrocatalytic reaction of another system.

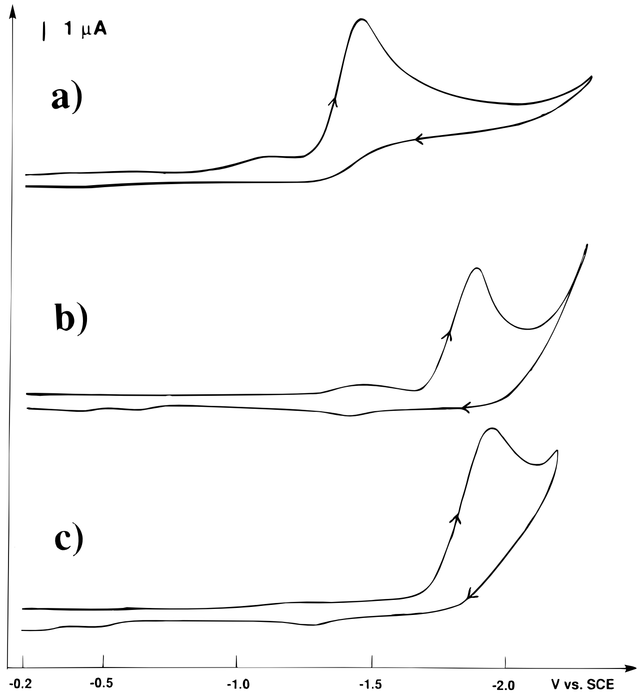


Figure 2. Cyclic voltammograms (CV) of **11** showing the electrocatalytic process on the CV time scale (Pt electrode, DMF, scan rate 0.4 V s^{-1}; room temperature; n-Bu_4NBF_4): (a) starting material **11**; (b) starting material **11** + PMe_3, showing the formation of the zwitterion **13** on the electrochemical time scale; (c) isolated zwitterion **13** (compare with b). The anodic wave of **11** at 0.0 V in DMF was not scanned for clarity (see Table 3 for the anodic wave of the zwitterion).

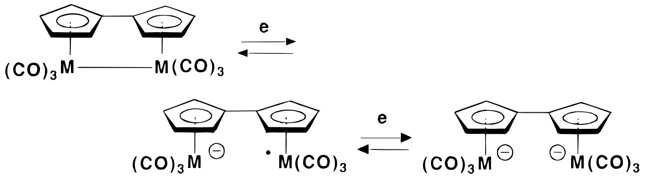
Concerning the synthesis of the bimetallic fulvalene zwitterions, the fact that the uncatalyzed reaction involved extended reaction periods in every case and eventually led to the loss of one metal contributed to the appeal of an alternative route to the same compounds. Furthermore, the electrochemistry of the starting materials was already known.[52,53,55] The stoichiometric electron-transfer chemistry of the FeW and RuW compounds was also known to lead to the tetranuclear complexes, indicating that dimerization was the exclusive radical-type reaction of the radical anions of the starting materials. Thus, the choice of the initiator in the wide range of potentials provided by the Cp and arene substituents of the [Fe^{I}Cp(arene)] series was dictated by the cathodic reduction potential of the starting materials. Since the organometallic species involved are fairly large and the charges involved in the redox changes very low, we concluded that the electrostatic factor intervening in the ergonicity of the electron

Table 3. Electrocatalytic Reactions: Cyclic Voltammetry Data of the Substrate and Products[a]

substrate	E_{pc} (V)	product	E_{pc} (V)	$\Delta E_{pc}/\Delta \log v$ (mV)	E_{pa} (V)	$\Delta E_{pa}/\Delta \log v$ (mV)
MoMo, **1**	−0.860	Mo$^+$Mo$^-$, **2**	−1.990	13.7	−0.080	20.0
WW, **3**	−0.940	W$^+$W$^-$, **4**	−1.920	45.6	+0.055	
FeW, **5**	−1.155 (1st wave)	Fe$^+$W$^-$, **8**	−1.750	18.3	+0.075	49.2
RuMo, **9**	−1.415	Ru$^+$Mo$^-$, **10**	−1.960	22.6	+0.160	13.7
RuW, **11**	−1.565	PRu$^+$W$^-$, **12**	−1.540	35.7	+0.098	14.4
RuW, **11**	−1.565	P$_2$Ru$^+$W$^-$, **13**	−1.970		+0.080	

[a] The data for the heterodinuclear zwitterionic products were the same for isolated products and those formed on the electrochemical time scale from the starting material + PMe$_3$. The peak potentials were measured at a scan rate $v = 0.4$ V s^{-1} (Pt electrode, DMF, E_p vs SCE). The cathodic and anodic CV waves of the zwitterions are irreversible and independent of each other. For a monoelectronic reduction or oxidation process, $\Delta E_p/\Delta \log v = 60$ mV indicates a $\vec{E}_{irrev}$ mechanism, 30 mV indicates a $\vec{E}_{rev}C_{irrev}$ mechanism, and 0 indicates a $\vec{E}_{rev}C_{rev}$ mechanism. Intermediate values indicate intermediate mechanisms (for instance, see ref 4, Chapter 2).

Scheme 5



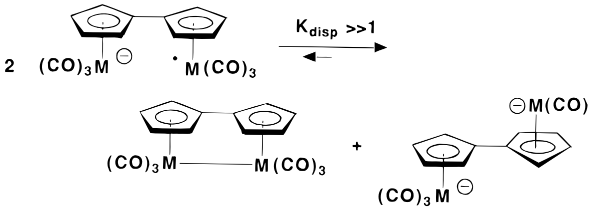
transfer of the initiation step was negligible in THF, which has the dielectric constant $\epsilon = 7.6$.[56] Under these conditions, the ergonicity is approximated by the simplified Weller equation: $\Delta G°$ (kcal mol^{-1}) $\simeq 23.06(E_D - E_A)$. In other words, the redox potential of the initiator must be more negative than the reduction potential of the starting material, so that the initiation step be exergonic. The cathodic reduction of the latter is always irreversible, but since the odd electron of the radical formed is largely delocalized over the bimetallic fulvalene frame, it is expected that the dimerization of the radical is not dramatically fast. Thus, the thermodynamic redox potentials of $[M^1M^2FvL_n]^{0/-}$ must be very close to the reduction potential (especially at low scan rate), and the comparison between $E°$ of the initiator and E_p of the starting material still holds.

Primary Radical Anion Involved in the Reaction with the Phosphine: Electronic Structure and Concentration. The previous electrochemical studies of the homo- and heterobimetallic fulvalene complexes[52,53,55] indicate that the two-electron-reduction process, whether it occurs at the same potential or not, can be depicted in Scheme 5.

If the two electrons are transferred at the same potential, the concentration of the intermediate radical anion is low (*vide infra*). Since both the neutral starting material and the dianion are 18-electron complexes which are inert toward phosphine and phosphite under ambient conditions on the electrochemical time scale, the only reactive species is the radical anion. The first step (initiation) of the electrocatalytic process is indeed the generation of this radical anion, and we anticipated (*vide infra*) that the second step, propagation, involves the simple addition of the phosphine to this radical anion (Scheme 6).

Subsequent to the monoelectronic reduction by the Fe^I electron-reservoir initiator, an ion pair is formed in which the radical anion is relatively stabilized by the large organoiron counterion.[59,60] Before we discuss the mechanism further, let us make another remark concerning these radical anions. It is understandable that a fast addition of phosphine to the 17-electron metal center occurs, since 17- and 19-electron states have very close energy levels and the 17-electron radical does not suffer from sterically demanding constraints. In fact, it is probable that delocalization of the negative charge as well as of the spin density occurs over the bimetallic fulvalene framework. This delocalization drastically slows down the reactivity of the "radical" metal center.[60b,62] However, we already know that it also prevents side radical reactions which are found, for instance, in homoleptic metal carbonyl radical anions.[59,63] Overall, this delocalization is thus very favorable for the efficiency and selectivity of the electrocatalytic process despite the kinetic restriction indicated above.[64]

It is now striking to compare the behavior of the homodinuclear MoMo and WW fulvalene complexes with that of the heterodinuclear ones. For neither of the homodinuclear complexes could be observe the electrocatalytic process by CV, although the electrocatalytic reactions are over in a few minutes. In contrast, the changes are instantaneous in the CV of all the heterodinuclear complexes in the presence of excess of the same phosphine, PMe$_3$, and it is not even possible to observe both the starting material and the zwitterionic product at the same time. It is also not possible to observe any intermediate such as **12**, which results from the simple addition of PMe$_3$ before the substitution of CO by the second PMe$_3$. There is previous evidence that rapid substitution by phosphine occurs at the 17-electron molybdenum center in [MoCp(CO)$_3$]$^•$.[45] In the homobimetallic fulvalene complexes, however, the simultaneous two-electron reduction has been shown.[55] Thus, it is clear that the concentration of the reactive intermediate radical anion in eq 1 is very low, since this species disproportionates to the neutral species and the dianion with a disproportionation constant $K_{disp} \gg 1$.[65]



(1)

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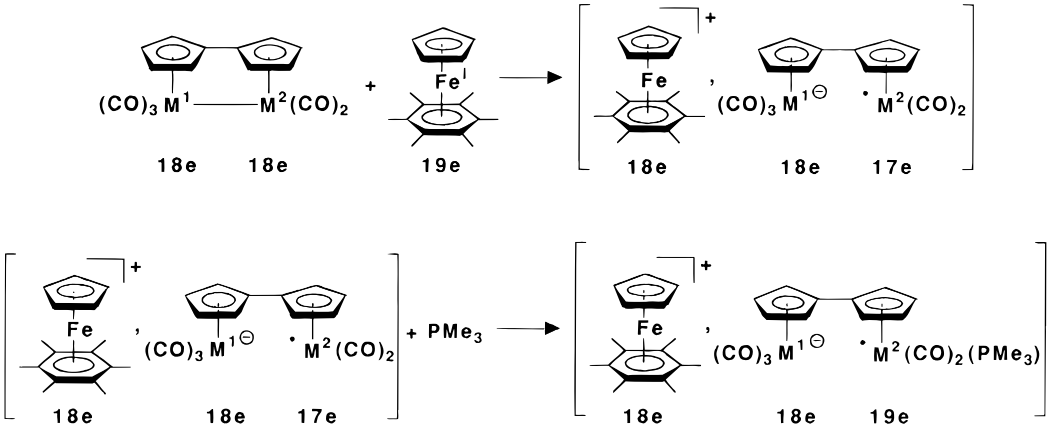
[62] For previous examples of cathodically induced substitution of CO by more electron-releasing ligands in mononuclear complexes bearing an electron-sink ligand, see: (a) Lahuerta, P.; Latorre, J.; Sanan, M.; Kisch, H. *J. Organomet. Chem.* **1985**, *286*, C27. (b) Olbrich-Deussner, B.; Gross, R.; Kaim, W. *J. Organomet. Chem.* **1989**, *366*, 155.

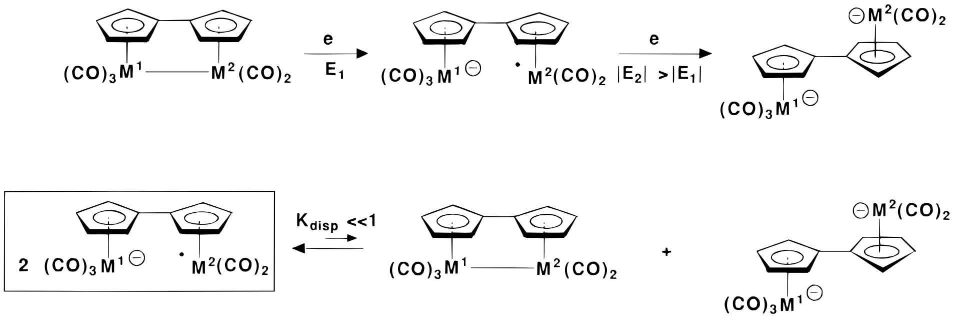
[63] Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265.

[64] A similar delocalization is encountered in cathodically induced substitution of CO by phosphorus donors in transition-metal clusters; see refs 40, 41, and 61 (pp 434−443). For examples, see: Bruce, M. I. *Coord. Chem. Rev.* **1987**, *76*, 1.

Scheme 6



Scheme 7



The classical trend in the substitution of CO by another ligand in 17-electron radicals is that the reaction is second order,[66] $k = [\text{17e radical}][\text{ligand}]$, and it is likely that the PMe_3 addition reaction follows the same rate law here. Thus, we believe that the very low radical anion concentration accounts for the low reaction rate for homobimetallic complexes. On the other hand, the situation is different in heterodinuclear complexes. The two reduction steps should, in principle, occur at different potentials since the two metal carbonyl moieties are different (Scheme 7). This is true for **5**.[52,53] In the case of **9** and **11**, Bard has reported a two-electron reduction,[55] but this does not exclude the possibility that two one-electron reductions proceed at close potentials which would appear in the same wave envelope.[67] In the most unfavorable case, where a structural reorganization would bring the second potential at less negative value,[68] the situation would still be much more favorable, due to the dissymmetry, than in the homobimetallic complexes above.

It may also be noted that, in the case of the WW complex **2**, an even larger excess of PMe_3 was required in order to obtain a good yield, which means that the very low concentration of radical anion, due to the presumably very large K_{disp} value, had to be compensated by a very high PMe_3 concentration in order to ensure an acceptable rate. This trend confirms the favorable influence of the PMe_3 concentration on the rate and gives even more credit to the validity of the hypothesis of the second-order rate constant. The fact that, at insufficiently high PMe_3 concentrations, the dianion $[W_2Fv(CO)_6]^{2-}$ was found in addition to the starting material **2** is another argument in favor of the high K_{disp} value.

Let us now consider the lack of success of the electrocatalytic reaction of the RuRu complex **14** in the presence of PMe_3 and of Na/K alloy. In light of the above reasoning, we can now explain this failure in terms of an insignificant radical anion concentration due to a too large K_{disp} value. Indeed, we know that, in two-electron *versus* two one-electron reduction processes, two-electron reduction processes are usually favored for late second-row metals as compared to the late first-row metals of the same group. This is true, for example, for $[M(C_6Me_6)_2]^+$ (Ru[69] versus Fe) and for $[MCp^*(C_6Me_6)]^{2+}$ (Rh[70,71] versus Co). The reason for this is that the metal orbitals have higher energy levels for second-row than for first-row metals, and consequently, the HOMO's have essentially ligand character in the second-row late-transition-metal complexes. Ligand rearrangement occurs upon the second electron transfer, which decreases the second reduction potential to the level of the first one. Thus, the RuRu complex **14** is reduced in a two-electron wave, with a second reduction potential

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(65) (a) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1985**, *60*, 107. (b) *Inorg. Chem.* **1981**, *20*, 1278. (c) *J. Am. Chem. Soc.* **1983**, *105*, 40.

(66) See ref. 4, Chapter 5 (pp 333−337), and for example: (a) Shi, Q. Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71; **1982**, *104*, 4032. (b) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; J. Organomet. Chem. Libr. 22; Elsevier: New York, 1990; Vol. 22, p 67.

(67) For the EE and ECE mechanisms see, for instance, ref 4, Chapter 2 (pp 123−128), and: Heinze, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831.

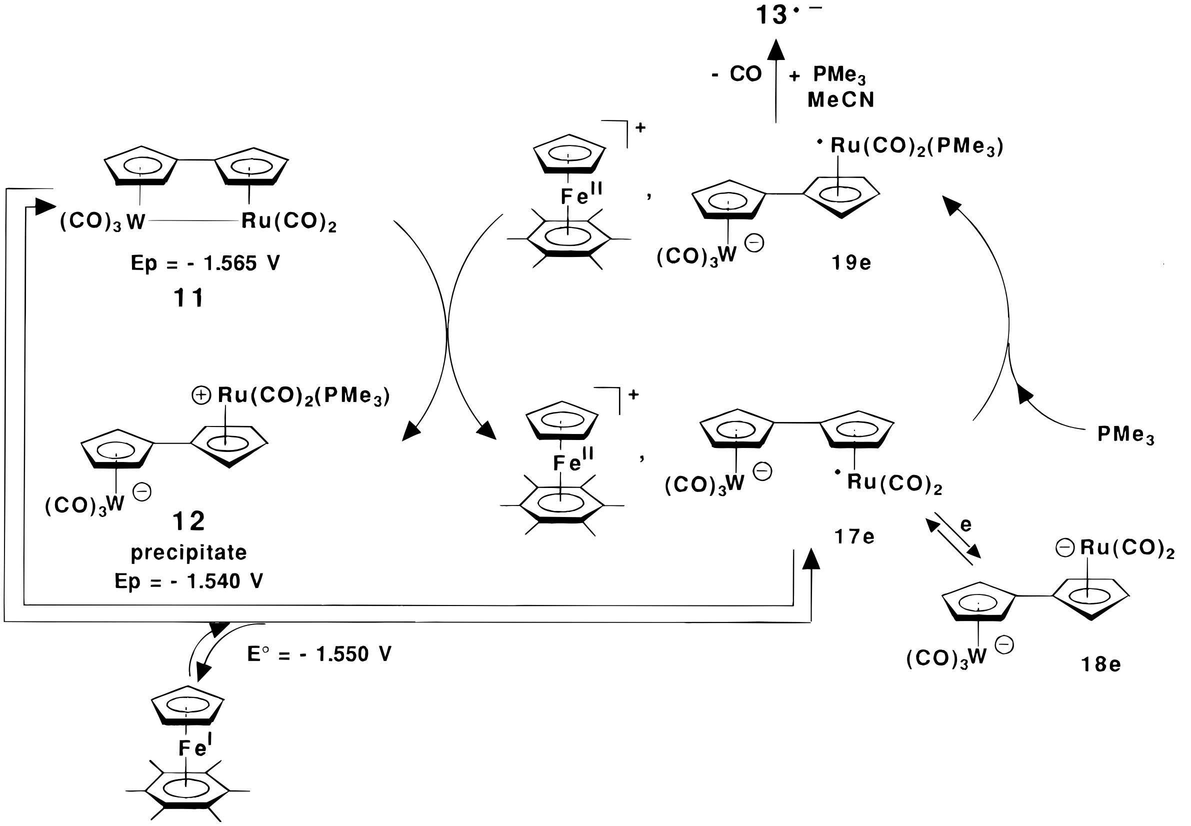
(68) For a thoroughly characterized example, see: (a) Astruc, D.; Lacoste, M.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1990**, 558. (b) Lacoste, M.; Rabaâ, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548.

(69) (a) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347. (b) Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* **1984**, *3*, 1079.

(70) (a) Bower, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191. (b) Merkert, J.; Nielson, R. M.; Waever, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084.

(71) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275.

Scheme 8. Mechanism of the Selective Electrocatalytic Syntheses of the Zwitterion 12 Initiated by the Electron-Reservoir Complex [$Fe^ICp(C_6Me_6)$] in THF

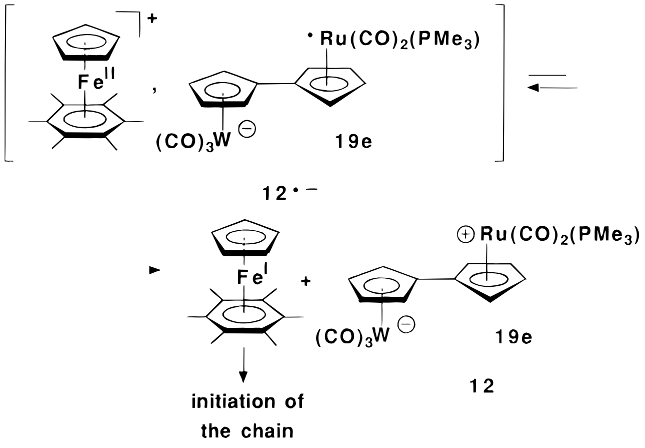


which is possibly lower than the first one.[67] From our electrocatalytic experiments, it appears that the order of the K_{disp} values is as follows:

$$\text{RuRu} \gg \text{WW} > \text{MoMo} > 1 > \text{RuMo and RuW} > \text{FeW}$$

Overall Electrocatalytic Mechanism. In the general case, one carbonyl is replaced by two PMe_3 or two $P(OMe)_3$ ligands on the same metal center. In the single case where a $P(OMe)_3$ was already ligated to the iron center, $P(OMe)_3$ was replaced selectively (rather than the carbonyl) by two PMe_3 ligands. In only one electrocatalytic synthesis could we isolate selectively the monophosphine zwitterionic adduct if the initiator was chosen to be not strong enough to induce the carbonyl substitution by the second phosphine. However, this case is of great mechanistic interest. Since this addition of PMe_3 is one of the simplest organometallic reactions,[72] let us start with its electrocatalytic mechanism (Scheme 8). The difference between the structure of the radical anion of eq 1 and the reaction product is only one electron, which serves to propagate the electrocatalytic chain.

Scheme 9. Mediation of the Cross-Electron-Transfer Step of the Propagation Chain by the Fe^{II}/Fe^I Electron-Reservoir System for the Electrocatalytic Synthesis of 12



It appears in Scheme 8 that all the electron transfers are nearly isoergonic (given experimental errors). Thus, the electron-transfer steps are equilibrated and displaced by the irreversible steps. One particularly important step is the cross-electron-transfer step in the propagation cycle. It is even slightly unfavorable if only the E_p values are considered. An important additional feature, however, is the insolubility of the zwitterion **12**, which must drive the reaction. The essential role of the solubility is clearly shown by the difference in the electrocatalytic reactions of **11** in THF and CH_3CN. When the zwitterion **12** is insoluble (THF), the reaction stops at this stage if the initiator [$Fe^ICp(C_6Me_6)$] is used, whereas it goes to **13** when **12** is soluble (CH_3CN) using the same initiator. This precipitation must be equivalent to 0.1−0.2 V, which is enough to displace the overall system. Moreover, if this is the case, it means that the same reasoning suggests that the initiator is not a

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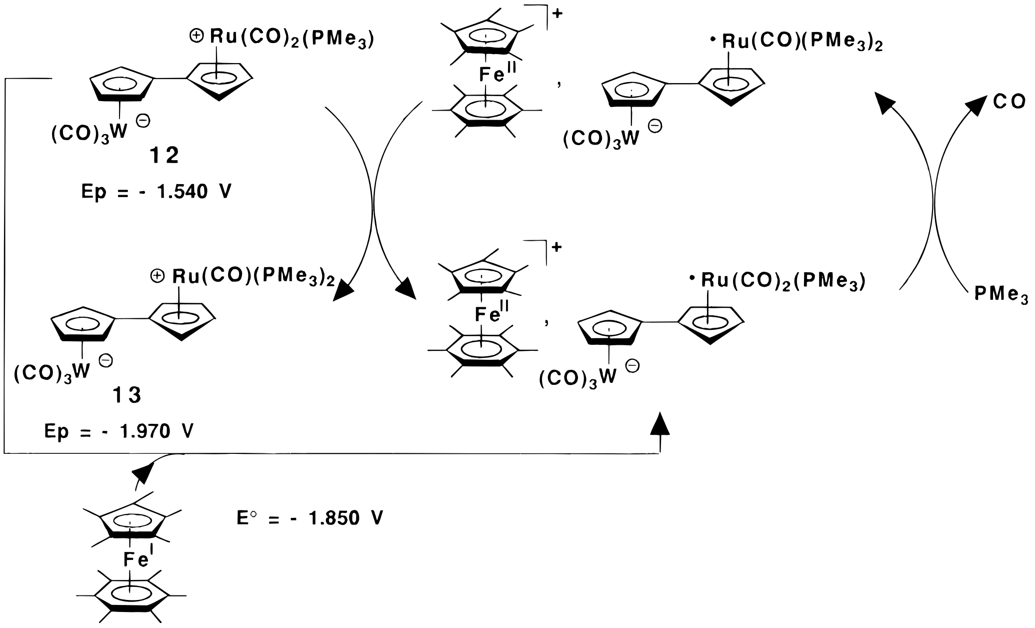
[72] Although it is commonly involved in catalytic processes with mononuclear complexes, the simple reaction $L_nM_2 + PMe_3 \rightarrow L_nM_2(PMe_3)$ has not been characterized to our knowledge; see: (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994. (b) Elschenbroich, Ch.; Salzer, A. *Organometallics: A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992. (c) Collman, J.-P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

Scheme 10. Mechanism of the Electrocatalytic Substitution of CO by PMe_3 in the Zwitterion 12 Initiated by the Electron Reservoir $[Fe^I(Cp^*)(C_6Me_6)]$



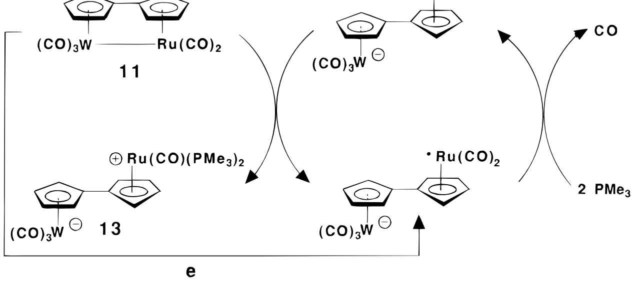
strong enough reducing agent in THF to reduce **12** back to its radical anion involved in the propagation cycle. In contrast, the initiator can serve as a mediator (redox-catalytic relay)[73] to transfer the electron in this cross-electron-transfer step. This is especially true because the cationic (oxidized) form of the mediator serves as the countercation of the radical anion in the propagation chain (Scheme 9).

Indeed, the structural rearrangement required for the starting material to accept the electron is larger, because of the bond breaking and internal rotation,[73d,74] than for the mediator whose sandwich framework remains unchanged.[75] Thus, it is likely that electron transfer is faster within the ion-pair cage containing the mediator than with the starting material (given the similar potential values of these three species).

Let us now consider the situation where a stronger reducing initiator is used. In the case of $[Fe^ICp^*(C_6Me_6)]$, the $E°$ value is -1.85 V, i.e. 0.3 V more negative than for $[Fe^ICp(C_6Me_6)]$.[75−77] This stronger initiator can reduce **12**, even in THF, back to its radical anion **12**$^{\bullet-}$ in order to maintain and eventually prolong the propagation chain. We know that the radical anion **12**$^{\bullet-}$ can undergo substitution of CO by PMe_3 at its 17-electron ruthenium center to give the radical anion **13**$^{\bullet-}$ of the final zwitterion **13**. This simply means that the stronger initiator can undergo a second propagation cycle, represented in Scheme 10.

The electron transfer between the initiator and **12** is presumably equilibrated due to the insolubility of **12** in THF, which almost compensates for the difference in potential. Thus, both formulations of the two previously mentioned cycles and of a unique cycle involving PMe_3 addition and substitution of CO by PMe_3 as the "chemical" step of the propagation cycle could be thought of as suitable to explain the electrocatalytic process (Scheme 11). In fact, the overall cycle is preferred, since it avoids involving the formation of **12**, whose insolubility in THF inhibits further electrocatalytic reactions (electrocatalytic reaction of **11** in THF does lead to **13** if a strong enough initiator is used).

Scheme 11. Mechanism of the Electrocatalytic Synthesis of 13 Using a Cathodic Initiation in DMF or Initiation Using the Complex $[Fe^ICp(C_6Me_6)]$ in CH_3CN or the Complex $[Fe^ICp^*(C_6Me_6)]$ in THF



In the case of the cathodically induced electrocatalysis, the situation is somewhat different. The more polar solvent DMF (dielectric constant $\epsilon = 36.7$) was used, and **12** was soluble. Similarly, when acetonitrile ($\epsilon = 36$) was used in the electrocatalytic synthesis, **12** was soluble. In these cases, no insolubility of **12** drives the first electrocatalytic cycle toward its formation. It is now appropriate to write equilibria which take into account the similarity of the potential values. These equilibria are shifted toward the irreversible chemistry of the radical anion **12**$^{\bullet-}$ of the cycle, since **12** does not react with anything else. The electron transfer involving **12** is very slightly endergonic and is thus not expected to be fast. On the other hand, the substitution of CO by PMe_3 can now kinetically compete with this electron transfer. Not only is **12** not formed, as noted

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(73) See: (a) Reference 4, Chapter 7. (b) Savéant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Savéant, J.-M. In Mechanisms and Processes in Molecular Chemistry. Astruc, D., Ed. *New J. Chem.* **1992**, *16*, 131. (d) Reference 4, Chapter 1.

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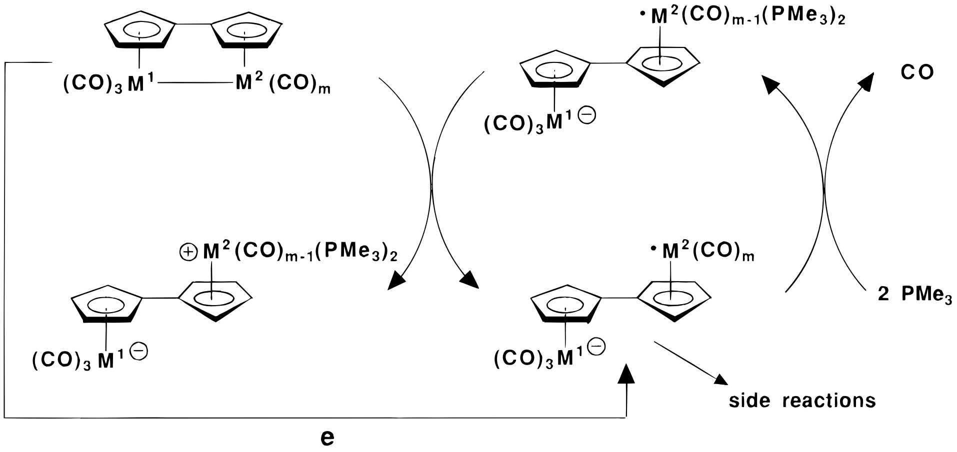
Scheme 12. General Mechanism for the Cathodically Induced Electrocatalytic Syntheses of the Zwitterions Using Electron-Reservoir Fe^I Complexes as Initiators in CH_3CN[a]



[a] M^1 = Mo, W; M^2 = Mo, W, m = 3; M^2 = Fe, Ru, m = 2; R = Me, OMe. Potential side reactions of the 17e radical anions (slower than the chain propagation reactions): (1) dimerization to tetranuclear dianion; (2) monoelectronic reduction by the initiator to the dinuclear dianion; (3) formation of a monoanionic dinuclear M_2 hydride by H-atom abstraction from the medium.

in the electrochemical experiment, but it is also likely that it is not even involved as an intermediate, since its formation is neither thermodynamically nor kinetically favorable. This distinction between the electron-reservoir initiation in THF and both the initiation in CH_3CN and the electrochemically induced electrocatalysis in DMF is of interest for obvious reasons of selectivity in the synthesis as well as for the light it sheds on the mechanism. The overall diagram is then appropriate to take into account the cathodically induced electrocatalytic process of Scheme 12. We now understand the role of the reducing power of the initiator as well as the distinction between the electron-reservoir initiation in THF and the cathodic one in DMF. This was made possible not only by the variety of initiators of the same [Fe^{I}Cp(arene)] family but also by the fact that the zwitterion **12** had a reduction potential not more negative than that of the starting material and that **12** was very insoluble in THF. In CH_3CN, the electron-reservoir initiator [Fe^{I}Cp(C_6Me_6)] can lead, although very slowly, to the bis(phosphine) adduct, whereas it cannot in THF. This stresses the role of the driving force of precipitation in THF. The large difference in rate between the two initiators is due to the fact that, with [Fe^{I}Cp*(C_6Me_6)], the electron-transfer initiation is largely exergonic and thus fast, whereas it is not with [Fe^{I}Cp(C_6Me_6)]. It is likely that the similarity between the potential of the starting material and that of the monophosphine adduct would hold as well in the other cases. However, in order to synthesize the monophosphine zwitterions, one would have to use an initiator whose redox potential is also the same as that of the starting material in each case. Thus, it is logical that only the bis(phosphine) zwitterions were obtained, since their reduction potentials, on the order of −2 V vs SCE, are even more negative than that of [Fe^{I}Cp*(C_6Me_6)]. We believe that the best way to take into account the formation of all the bis(phosphine) zwitterions is to use the overall scheme in which both chemical steps, PMe_3 addition and CO substitution by PMe_3, occur before the back electron transfer (Scheme 12).

Conclusion

(1) A general synthesis of the bimetallic zwitterions $[(CO)_3M^1FvM^2(CO)_{m-1}(PR_3)_2]$ (R = Me, OMe; M^1 = Mo, W; M^2 = Mo, W (m = 2); M^2 = Fe, Ru (m = 1)) has been found to occur in a few minutes at ambient temperature by an electrocatalytic reaction of $[(CO)_3M^1FvM^2(CO)_m]$ with PR_3 using the electron-reservoir complexes [Fe^{I}Cp(C_6R_6)] (R = H or Me) as the initiator in THF or CH_3CN.

(2) In THF, with $[(CO)_3\overline{WFvRu}(CO_2)]$ as starting material, the choice of the Fe^I electron-reservoir complex used as initiator, [Fe^{I}Cp(C_6Me_6)] or [Fe^{I}Cp*(C_6Me_6)], selectively leads to the monophosphine zwitterion $[(CO)_3W^-FvRu^+(CO)_2PMe_3]$ (**12**) or to the bis(phosphine) zwitterion $[(CO)_3W^-FvRu^+(CO)(PMe_3)_2]$ (**13**), respectively. This selectivity is rationalized on the basis of redox and peak potentials and on solubilities. It shows the great flexibility of the family of electron-reservoir [Fe^{I}Cp(arene)] complexes as efficient and selective electrocatalysts.

(3) The CV's of the starting materials and of the zwitterionic products show that the electrocatalytic synthesis is slower than the electrochemical time scale for the *homo*bimetallic complexes and faster than the electrochemical time scale for the *hetero*bimetallic complexes (with PMe_3), confirming the thermodynamic *instability* of the homobimetallic primary radical anions and the thermodynamic *stability* of the heterobimetallic radical anions.

(4) The concentration and nature of the phosphorus donor strongly influences the rate of the reaction, consistent with an associative mechanism of ligand addition/substitution involving “19-electron” radical centers. However, it is likely that the HOMO of such 19-electron radicals is delocalized onto the fulvalene framework, which serves as an electron sink that facilitates the electrocatalytic process by preventing side reactions.

Experimental Section

Unless specifically stated otherwise, all manipulations (column chromatography, recrystallizations, etc.) were performed under an atmosphere of purified argon or nitrogen, in either a Vacuum Atmospheres or Braun drybox or using standard Schlenk and vacuum-line techniques. Diethyl ether (Et_2O), dimethoxyethane (DME), tetrahydrofuran (THF), THF-d_8, and toluene were distilled under nitrogen from sodium or potassium benzophenone ketyl before use. Acetonitrile (CH_3CN), CD_3CN, and hexane were distilled from CaH_2. Dimethylformamide (DMF) was dried over CaH_2 and then distilled under Ar and stored over 3 Å molecular sieves. Acetone and acetone-d_6 were distilled from K_2CO_3 and degassed by three freeze−pump−thaw cycles. The compounds [$Fe^ICp(C_6Me_6$],[78,79] [$Fe^ICp^*(C_6Me_6)$],[78,79] [$Fe^ICp(C_6H_6)$],[78–80] [WFe(fulvalene)$(CO)_5$] (**5**),[27] [WRu(fulvalene)$(CO)_5$] (**11**),[27] [Mo_2(fulvalene)$(CO)_6$] (**1**),[81] [W_2(fulvalene)$(CO)_6$] (**3**),[81] and [MoRu(fulvalene)$(CO)_5$] (**9**)[9,82] were prepared according to literature procedures. All other reagents were obtained from commercial suppliers and used without further purification.

^1H NMR spectra were recorded on a University of California at Berkeley 300 MHz instrument equipped with a Nicolet Model 1280 data collection system and a Cryomagnets, Inc., magnet or on Bruker AMX-300 or AMX-400 instruments. ^1H NMR spectra are reported as follows: chemical shift in ppm downfield of tetramethylsilane using the residual proton resonances of the deuterated solvent as an internal standard (multiplicity, coupling constant in hertz, number of protons). The AA′XX′ patterns of symmetrical fulvalene ligands are reported as triplets with a coupling constant equal to half the frequency difference between the outer two lines. Satellites due to coupling to the ^{183}W nucleus (14% natural abundance) are reported as $^2J_{WH}$. $^{13}C\{^1H\}$ NMR spectra were recorded on the Bruker AMX-400 instrument operating at 100 MHz. $^{13}C\{^1H\}$ NMR chemical shifts are reported relative to tetramethylsilane using the deuterated solvent resonances as internal standards. The resonances due to the carbons in[$Fe\{P(OMe)_3\}_2$] and [$Fe(PMe_3)_2$] fragments are reported as triplets with coupling constants equal to the frequency difference between the outer two lines, representing the sum of $^1J_{PC}$ and $^3J_{PC}$. $^{31}P\{^1H\}$ NMR spectra were recorded on the University of California at Berkeley 300 MHz instrument operating at 121.5 MHz. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4 in CD_3CN or THF-d_8. Infrared spectra were recorded on a Perkin-Elmer Model 681 spectrophotometer equipped with a 580 B data station or on a Perkin-Elmer System 2000 FTIR spectrophotometer; only the most intense peaks in the spectra are reported. Mass spectra were acquired by the University California at Berkeley Mass Spectrometry Laboratory on AEI-MS12, Finnigan 4000, or Kratos MS50 instruments. The natural isotopic distribution of the transition metals produced broad peak envelopes; only the most intense peak of each fragment is reported. Elemental analyses were performed by the University of California at Berkeley Microanalytical Laboratory. Melting points were measured on a Büchi melting point or Thomas-Hoover Unimelt apparatus in glass capillary tubes sealed under argon and are uncorrected. Cyclic voltammograms (CV) and chronoamperograms were recorded on a PAR 273 potentiostat−galvanostat with a compensation system for ohmic drop. The electrolyte nBu_4NBF_4 was used at a concentration of 0.1 M. The working electrode (Pt) was treated with a 0.1 M HNO_3 solution followed by a saturated aqueous solution of [$Fe(NH_4)_2(SO_4)_2$]·$6H_2O$. A Pt wire was used as the auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). The CV scan rate was 0.400 V s^{-1}.

1. Preparation of the Standard [$Fe Cp^I(C_6Me_6)$] Solution.[78,79] In the drybox, a Schlenk flask was charged with [$Fe^{II}Cp(C_6Me_6)$]PF_6[78,79,83,84] (43 mg, 0.10 mmol) and DME or THF (5 mL). Na/Hg amalgam (0.7%, 1.5 g) was added and the mixture stirred for 1 h (DME) or 3 h (THF), during which time it became dark green. The reduction was assumed to be quantitative, and aliquots of solutions prepared in this manner were used in the electrocatalysis experiments.

2. (fulvalene)[$W(CO)_3^-$][$Fe(CO)\{P(OMe)_3\}_2^+$] (6). Method A. In the drybox, a Schlenk flask was charged with [(fulvalene)WFe$(CO)_5$] (**5**; 51 mg, 0.10 mmol) and THF (10 mL). $P(OMe)_3$ (100 μL, 0.80 mmol) was added *via* syringe, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.01 mmol) in DME. The reaction mixture became reddish purple, and a precipitate began to form within 5 min. After 15 min, TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the drybox, dissolved in CH_3CN, and filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum and the residue recrystallized from acetone/hexane at −78 °C to give a red powder (51 mg, 70%): mp 128−129 °C; ^1H NMR (400 MHz, CD_3CN) δ 5.63 (t, J = 2.4 Hz, 2H), 5.14 (t, J = 2.4 Hz, 2H), 5.12 (m, 2H), 4.96 (t, J = 1.9 Hz, 2H), 3.98 (m, 18H); $^{13}C\{^1H\}$ NMR 9100 MHz, CD_3CN) δ 225.86, 90.75, 86.55, 86.32, 83.92, 79.48, 54.45 (t, J_{PC} = 3.7 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN) δ 167.97; IR (CH_3CN) 1985, 1895, 1783 cm^{-1}; MS m/z (relative intensity) 700 (M^+ − CO, 10), 672 (M^+ − 2CO, 26.2) 616 (M^+ − 4CO, 36.8), 520 (M^+ − $P(OMe)_3$ − 3CO, 18.1), 492 (M^+ − $P(OMe)_3$ − 4CO, 34.4). Anal. Calcd for $C_{20}H_{26}FeO_{10}P_2W$: C, 32.99; H, 3.61. Found C, 33.07; H, 3.59.

Method B. In the drybox, a Schlenk flask was charged with [(fulvalene)WFe$(CO)_5$] (**5**; 51 mg, 0.10 mmol) and THF (10 mL). A second flask was charged with [$Fe^{II}Cp(C_6Me_6)$]PF_6 (33 mg, 0.01 mmol) and DME (5 mL). To this flask was added a 0.7% Na/Hg amalgam (1.5 g), and the mixture was stirred for 1 h at −20 °C. To the first flask was added $P(OMe)_3$ (100 μL, 0.80 mmol), followed by an aliquot of the [$Fe^ICp(C_6Me_6)$] solution (0.01 mL). The reaction mixture quickly became dark red, and a precipitate formed. After 15 min, TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum and the residue recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give red crystals (52 mg, 72%). ^1H NMR and X-ray diffraction analysis performed by R. Boese[54] confirmed that the product was **6**.

3. (fulvalene)[$W(CO)_3^-$][$Fe(CO)(PMe_3)_2^+$] (12). In the drybox, a Schlenk flask was charged with [(fulvalene)WFe$(CO)_5$] (**5**; 51 mg, 0.10 mmol) and THF (10 mL). PMe_3 (105 μL, 1.0 mmol) was added, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.005 mmol) in DME. The reaction mixture immediately became orange, and a precipitate began to form. After 10 min, TLC analysis (silica gel, 1:1 THF/hexanes) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum. The residue was recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give orange-red crystals (50 mg, 79%): mp >250 °C (decomposes without melting); ^1H NMR (400 MHz, CD_3CN) δ 5.57 (t, J = 2.3 Hz, 2H), 5.12 (t, J = 2.3 Hz, 2H), 4.87 (t, J = 2.0 Hz, 2H), 4.81 (t, J = 2.3 Hz, 2H), 1.48

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(m, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 226.16, 86.26, 85.87, 84.93, 78.27, 21.28, 54.45 (t, J_{PC} = 16.2 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN) δ 25.33; IR (CH_3CN) 1958, 1895, 1785 cm^{-1}; FAB-MS (nitrobenzyl alcohol) *m/z* (relative intensity) 632 (M^+). Anal. Calcd for $C_{20}H_{26}FeO_4P_2W$: C, 37.99; H, 4.15. Found: C, 37.69; H, 4.12.

4. (fulvalene)[$WFe(CO)_4(P\{OMe\}_3)$] (7). In the drybox, a Schlenk flask was charged with [(fulvalene)$WFe(CO)_5$] (**5**; 102 mg, 0.20 mmol). THF (25 mL) was added, followed by $P(OMe)_3$ (100 μL, 0.80 mmol). The mixture was irradiated at 300 nm for 40 min and the solvent removed under vacuum. The residue was dissolved in THF (4 mL) and transferred *via* cannula to a Schlenk column containing silica gel (230−400 mesh, 2 × 15 cm). Elution with Et_2O/hexane (1/1) gave a brownish black band, which was collected, and the solvent was removed under vacuum. The residue was taken into the drybox and recrystallized from THF/hexane at −30 °C to give purple-black crystals (80 mg, 66%): mp 141−142 °C; ^1H NMR (400 MHz, CD_3CN) δ 5.29 (t, J = 2.3 Hz, 2H), 4.84 (t, J = 2.3 Hz, 2H), 4.67 (q, J = 2.4 Hz, 2H), 3.95 (q, J = 2.1 Hz, 2H), 3.61 (d, J = 5.6 Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8) δ 220.08, 218.39, 217.63, 91.94, 86.87, 84.88, 84.04, 82.26, 72.50, 52.94 (d, J_{PC} = 5.40 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN) δ 194.83; IR (THF) 1971, 1921, 1880, 1866 cm^{-1}; MS *m/z* (relative intensity) 604 (M^+, 100), 576 ($M^+ -$ CO, 10.4), 548 ($M^+ -$ 2CO, 5.3), 480 ($M^+ - P(OMe)_3$, 9.5), 452 ($M^+ - P(OMe)_3$ − CO, 29.9), 424 ($M^+ - P(OMe)_3$ − 2CO, 38.6), 396 ($M^+ - P(OMe)_3$ − 3CO, 30.9), 368 ($M^+ - P(OMe)_3$ − 4CO, 49.8). Anal. Calcd for $C_{17}H_{17}FeO_7PW$: C, 33.80; H, 2.84. Found: C, 33.65; H, 3.17.

5. Preparation of 6 from 7. In the drybox, a Schlenk flask was charged with **7** (32 mg, 0.053 mmol) and THF (10 mL). $P(OMe)_3$ (50 μL, 0.40 mmol) was added, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.01 mmol) in DME. The reaction mixture immediately became deep red. After 10 min, TLC analysis (silica gel, 1:1 THF/hexane) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum. The ^1H NMR spectrum showed only **6**, and the yield was 35 mg (91%).

6. (fulvalene)[$Mo(CO)_3^-$][$Mo(CO)_2(PMe_3)_2^+$] (2). In the drybox, a Schlenk flask was charged with [(fulvalene)$Mo_2(CO)_6$] (**1**; 48 mg, 0.10 mmol) and THF (15 mL). PMe_3 (105 μL, 1.0 mmol) was added, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.015 mmol) in DME. The purple reaction mixture quickly became orange-yellow, and a precipitate began to form within a few minutes. After 15 min, TLC analysis (silica gel, 1:1 THF/hexane) indicated that no starting material remained. Et_2O (30 mL) was added to complete the precipitation, and the solvent was removed *via* cannula. The precipitate was dried under vacuum, taken into the drybox, and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum. The residue was recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give a yellow powder (37 mg, 60%): mp 248−250 °C; ^1H NMR (400 MHz, CD_3CN) δ 5.54 (m, 2H), 5.50 (t, J = 2.4 Hz, 2H), 5.22 (m, 2H), 5.06 (t, J = 2.4 Hz, 2H), 1.64 (d, J = 10.3 Hz, 18H). Lit.:[28] mp 242−244 °C; ^1H NMR (300 MHz, CD_3CN) δ 5.53 (m, 2H), 5.50 (t, J = 2.4 Hz, 2H), 5.22 (m, 2H), 5.06 (t, J = 2.4 Hz, 2H), 1.64 (d, J = 10.3 Hz, 18H).

7. (fulvalene)[$W(CO)_3^-$][$W(CO)_2(PMe_3)_2^+$] (4). In the drybox, a Schlenk flask was charged with [(fulvalene)$W_2(CO)_6$] (**3**; 66 mg, 0.10 mmol) and THF (15 mL). PMe_3 (210 μL, 2.0 mmol) was added, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.020 mmol) in DME. The purple reaction mixture quickly became yellow, and a precipitate began to form within a few minutes. After 15 min, TLC analysis (silica gel, 1:1 THF/hexane) indicated that no starting material remained. Et_2O (30 mL) was added to complete the precipitation, and the solvent was removed *via* cannula. The precipitate was dried under vacuum, taken into the drybox, and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum. The residue was recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give a yellow powder (55 mg, 70%); mp >300 °C; ^1H NMR (300 MHz, CD_3CN) δ 5.59 (m, 2H), 5.48 (t, J = 2.3 Hz, 2H), 5.33 (m, 2H), 5.08 (t, J = 2.2 Hz, 2H), 1.76 (d, J = 10.2 Hz, 18H). Lit.:[28] mp >300 °C; ^1H NMR (300 MHz, CD_3CN) δ 5.60 (m, 2H), 5.48 (t, J = 2.2 Hz, 2H), 5.33 (m, 2H), 5.08 (t, J = 2.2 Hz, 2H), 1.76 (d, J = 10.4 Hz, 18H).

8. (fulvalene)[$Mo(CO)_3^-$][$Ru(CO)(PMe_3)_2^+$] (10). In the drybox, a Schlenk flask was charged with [(fulvalene)$MoRu(CO)_5$] (**9**; 47 mg, 0.10 mmol) and THF (10 mL). PMe_3 (105 μL, 1.0 mmol) was added, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.010 mmol) in DME. The reaction mixture quickly became dark red. After 10 min, the reaction mixture had turned orange and a precipitate had begun to form. After 0.5 h, TLC analysis (silica gel, 1:1 THF/hexane) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum. The residue was recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give a yellow powder (37 mg, 60%): mp 284−287 °C; ^1H NMR (400 MHz, CD_3CN) δ 5.56 (t, J = 2.4 Hz, 2H), 5.36 (t, J = 2.1 Hz, 2H), 5.17 (t, J = 2.1 Hz, 2H), 5.09 (t, J = 2.4 Hz, 2H), 1.53 (d, J = 10.1 Hz, 18H). Lit.:[26] mp 280−282 °C; ^1H NMR (300 MHz, CD_3CN) δ 5.55 (t, J = 2.3 Hz, 2H), 5.36 (t, J = 2.3 Hz, 2H), 5.17 (t, J = 2.0 Hz, 2H), 5.08 (t, J = 2.3 Hz, 2H), 1.52 (d, J = 10.1 Hz, 18H).

9. (fulvalene)[$W(CO)_3^-$][$Ru(CO)(PMe_3)_2^+$] (13) (Using [$Fe^ICp^*(C_6Me_6)$]). In the drybox, a Schlenk flask was charged with [(fulvalene)$WRu(CO)_5$] (**11**; 55 mg, 0.10 mmol) and THF (10 mL). A second flask was charged with [$Fe^{II}Cp^*(C_6Me_6)$]PF_6^- (48 mg, 0.010 mmol) and DME (5 mL). To this flask was added a 0.7% Na/Hg amalgam (2 g), and the resulting mixture was stirred for 1.5 h at −20 °C to generate [$Fe^ICp^*(C_6Me_6)$]. PMe_3 (105 μL, 1.0 mmol) was added to the solution of [(fulvalene)$WRu(CO)_5$], followed by an aliquot of the solution of [$Fe^ICp^*(C_6Me_6)$] (0.020 mmol). The reaction mixture immediately became deep red. After 10 min, the mixture had become orange and a precipitate had formed. After 0.5 h, TLC analysis (silica gel, 1:1 THF/hexane) indicated that no starting material remained. The solvent was removed under vacuum. The residue was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum, and the crude product was recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give yellow-orange crystals (37 mg, 54%): mp 295−296 °C dec; ^1H NMR (400 MHz, CD_3CN) δ 5.53 (t, J = 2.3 Hz, 2H), 5.38 (t, J = 2.1 Hz, 2H), 5.18 (t, J = 2.1 Hz, 2H), 5.09 (t, J = 2.3 Hz, 2H), 1.54 (d, J = 10.2 Hz, 18H). Lit.:[26] mp 297−299 °C; ^1H NMR (300 MHz, CD_3CN) δ 5.53 (t, J = 2.3 Hz, 2H), 5.38 (t, J = 2.1 Hz, 2H), 5.18 (t, J = 2.1 Hz, 2H), 5.09 (t, J = 2.3 Hz, 2H), 1.54 (d, J = 10.1 Hz, 18H).

10. (fulvalene)[$W(CO)_3^-$][$Ru(CO)(PMe_3)_2^+$] (13) (Using [$Fe^ICp(C_6Me_6)$]). In a flame-dried and degassed Schlenk flask, [(fulvalene)$WRu(CO)_5$] (**11**; 78 mg, 0.14 mmol), PMe_3 (146 μL, 1.41 mmol), and CH_3CN (10 mL) were added, followed by [$Fe^ICp(C_6Me_6)$] (8 mg, 0.03 mmol) in CH_3CN (2 mL). The mixture was stirred at room temperature for 2.5 h. TLC analysis (silica gel, 1:1 THF/pentane) showed that no starting material remained. The solvent was removed under vacuum, and the solid residue was washed with ether (2 × 20 mL). The product **13** was obtained as a yellow-orange powder (61 mg, 64% yield) with spectroscopic data as in paragraph 9.

11. (fulvalene)[$W(CO)_3^-$][$Ru(CO)_2(PMe_3)^+$] (12). In the drybox, a Schlenk flask was charged with [(fulvalene)$WRu(CO)_5$] (**11**; 55 mg, 0.10 mmol) and THF (10 mL). PMe_3 (105 μL, 1.0 mmol) was added, followed by a solution of [$Fe^ICp(C_6Me_6)$] (0.020 mmol) in DME. The reaction mixture immediately turned dark red but quickly became orange, and a precipitate formed. After 15 min, TLC analysis (silica gel, 1:1

THF/hexane) indicated that no starting material remained. Et_2O (35 mL) was added to complete the precipitation. The solvent was removed *via* cannula and the precipitate dried under vacuum. The precipitate was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum and the residue recrystallized from CH_3CN/Et_2O at −30 °C in the drybox to give a yellow powder (45 mg, 71%): mp >300 °C (dec); ^1H NMR (400 MHz, CD_3CN) δ 5.69 (t, J = 2.1 Hz, 2H), 5.62 (t, J = 2.4 Hz, 2H), 5.57 (t, J = 2.1 Hz, 2H), 5.14 (t, J = 2.4 Hz, 2H), 1.68 (d, J = 11.5 Hz, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN) δ 245.82, 225.54, 110.44, 89.13, 86.84, 86.24, 85.63, 81.61, 20.76 (d, J_{PC} = 36.7 Hz); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN) δ 6.62; IR (CH_3CN) 2003, 1899 cm^{-1}; HRMS (FAB, nitrobenzyl alcohol) calcd for $C_{18}H_{18}O_5P^{99}Ru^{182}W$ (MH^+) 625.9433, found 625.9431.

12. Conversion of 12 to 13. In the drybox, a Schlenk flask was charged with zwitterion **12** (25 mg, 0.04 mmol) and CH_3CN (15 mL). PMe_3 (210 μL, 2.0 mmol) was added, followed by a solution of $[Fe^ICp^*(C_6Me_6)]$ (0.030 mmol). The green color of the reducing agent gradually faded, and the reaction mixture changed from orange to yellow. The mixture was stirred for 1.5 h and the solvent removed under vacuum. The residue was taken into the drybox and dissolved in CH_3CN, and this solution was filtered through a plug of Celite (1 × 4 cm). The solvent was removed under vacuum. The ^1H NMR spectrum of the resulting crude product showed **13** as the only fulvalene compound present.

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