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Electrochemical Generation of Stable Bis(fulvalene)dimetal Anions $[(\eta^5:\eta^{5'}\text{-}C_{10}H_8)_2MCo]^-$ (M = Fe, Ru, Co)

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Electrochemical reduction of $[(\eta^5:\eta^{5'}\text{-}C_{10}H_8)_2MCo]^{n+}$ (n = 1, 2; M = Fe, Ru, Co) in a 0.1 M solution of $Bu_4N^+PF_6^-$ in CH_3CN at 20 °C yields stable anions $[(\eta^5:\eta^{5'}\text{-}C_{10}H_8)_2MCo]^-$ (M = Fe, Ru, Co). In the case of M = Co, formation of a dianion $[(\eta^5:\eta^{5'}\text{-}C_{10}H_8)_2Co_2]^{2-}$ is indicated by cyclic voltammetry. The influence of comproportionation equilibria on the number of possible reduction steps is discussed.

Introduction

Currently there is considerable interest in the properties of compounds with multiple redoxcenters, and in particular, those producing mixed-valence complexes. The increasing interest stems from attempts to produce high-temperature superconducting materials and new semiconducting materials and to understand biologically relevant mixed-valence compounds.

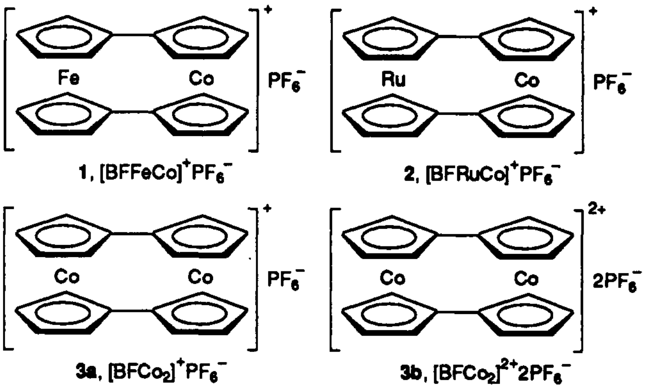
Bimetallocenes and bis(fulvalene)dimetals, for example, were synthesized with a variety of different metals[1-3] and electrochemical methods were used to produce metals in different oxidation states, in order to get more insight into the electronic structure of mixed-valence compounds, the factors affecting electron transfer between interacting sites, as well as the extent of delocalization of the valence electrons. Electrochemical data for a number of these mixed-valence compounds have been collected.[2,4-6] In general two successive one-electron oxidations/reductions were reported for the most commonly studied bimetallocenes and bis(fulvalene)dimetals, due to the reduction from the highest possible oxidation state to the neutral compound:

$$[MM]^{2+} \overset{e^-}{\rightleftharpoons} [MM]^{+} \overset{e^-}{\rightleftharpoons} [MM] \qquad (1)$$

While most of the simple metallocenes can be reduced to $[Cp_2M]^-$ anions, no comparable reduction products were reported in the case of bimetallocenes or bis(fulvalene)dimetals. Bimetallocenes and bis(fulvalene)dimetal complexes containing two different types of metals are more complicated to prepare. This appears to be the reason that they have been studied only in a few cases.[7-9]

We were able to work out a new synthesis for heterobimetal complexes[10] and in order to study the range of valence states that can be achieved in bis(fulvalene)dimetal complexes, we investigated the electrochemical behavior of 1 and 2 in comparison to **3a**,**b** (Chart I).

Chart I



1, $[BFFeCo]^+PF_6^-$

2, $[BFRuCo]^+PF_6^-$

3a, $[BFCo_2]^+PF_6^-$

3b, $[BFCo_2]^{2+}2PF_6^-$

Results and Discussion

The cyclic voltammogram of $[BFFeCo]^+PF_6^-$ (Figure 1) exhibits three waves in the potential range from +1.2 to −2.0 V versus a silver/silver chloride electrode, due to stepwise oxidation–reduction of the complex in three discrete one-electron steps according to the reaction sequence

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

The peak-to-peak separations of all three waves indicate electrochemical reversibility. The somewhat larger than theoretical value likely arises from uncompensated solution resistance.

The assignment of these waves to the oxidation–reduction of a particular metal center was accomplished by comparison with the redox potentials of bis(fulvalene)diiron,[4] bis(fulvalene)dicobalt,[1] Cp_2Fe, and Cp_2Co.[11] Thus the first reduction step at 0.83 V is assigned to the Fe^{III}/Fe^{II} couple and the second wave at −0.81 V to the Co^{III}/Co^{II} couple. Although it is reported that ferrocene can be reduced to the ferrocene anion $[Cp_2Fe]^-$,[12-15] it

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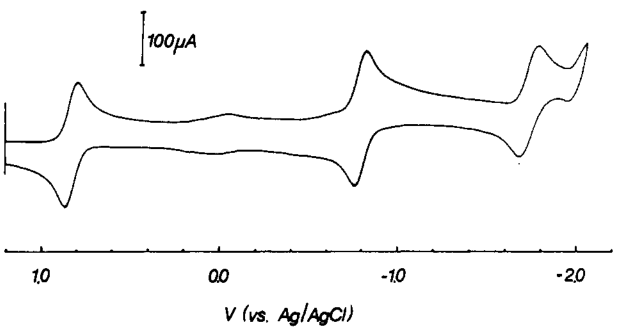

Figure 1. Cyclic voltammogram of 1 in acetonitrile/0.1 M TBAH, at a scan rate of 100 mV/s.

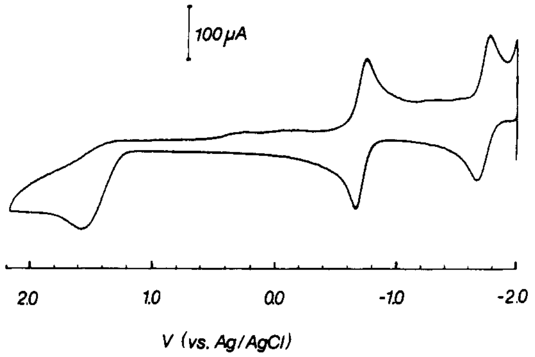

Figure 2. Cyclic voltammogram of 2 in acetonitrile/0.1 M TBAH, at a scan rate of 100 mV/s.

seemed more plausible to assign the third wave at −1.77 V to the $\mathrm{Co^{II}/Co^{I}}$ reduction. The main reason for this interpretation is that the potential lies very close to the reduction potential found for $[\mathrm{Cp_2Co}]/[\mathrm{Cp_2Co}]^-$.[11]

The cyclic voltammogram of $[\mathrm{BFRuCo}]^+\mathrm{PF_6}^-$ is shown in Figure 2. One irreversible oxidation peak at 1.45 V and two reversible oxidation–reduction waves at −0.77 and −1.75 V are observed. The waves at negative potential can readily be assigned to subsequent reduction of the cobalt atom, leading to $[\mathrm{BFRuCo}]^-$:

$$[\mathrm{Ru^{II}Co^{III}}]^+ \underset{-0.77}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Ru^{II}Co^{II}}] \underset{-1.75}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Ru^{II}Co^{I}}]^- \qquad (3)$$

The oxidation step at the anodic peak potential, E_{pa}, of 1.45 V, is attributed to the oxidation of the ruthenium atom. However, comparing the oxidation potential with that reported for ruthenocene,[16–19] there is a considerable difference and doubts exist as to the number of electrons involved.

There are controversial reports dealing with the oxidation of ruthenocene, as some confusion exists about the nature of the oxidation product. It is now firmly established, however, by studies in widely varying media,[19] that the electrochemically irreversible oxidation of ruthenocene involves the removal of two electrons, leading to a dication.

We reinvestigated the redox behavior of $\mathrm{Cp_2Ru}$ under the same conditions as 2, in order to obtain comparable electrochemical data. The cyclic voltammogram of $\mathrm{Cp_2Ru}$ shows an anodic oxidation peak at 1.04 V and a corresponding reduction peak at approximately 0.25 V. The peak heights i_{pa} and i_{pc} depend on the scan rate, with $i_{\mathrm{pa}}/i_{\mathrm{pc}}$ ratios ranging from 3.8 for v = 50 mV/s to 1.0 for v = 700 mV/s. This indicates a more complex electrode mechanism than a simple electrochemically irreversible two-electron transfer, with quantitative interpretation of the electrochemical data affording digital simulations.[20] The redox behavior of the ruthenium atom in $[\mathrm{BFRuCo}]^+\mathrm{PF_6}^-$ appears to be quite different. First of all the $i_{\mathrm{pa}}/v^{1/2}$ ratio remains constant over a range of sweep rates from 10 to 1000 mV/s. This implies that within this time scale the oxidation of the ruthenium atom is not complicated by chemical reactions.[21] A further proof is the fact that the reversible waves at −0.77 and −1.75 V remain unchanged even when scanning from +2.00 to −2.00 V. This is not expected in the case of a homogenous chemical reaction following the ruthenium oxidation at 1.45 V.

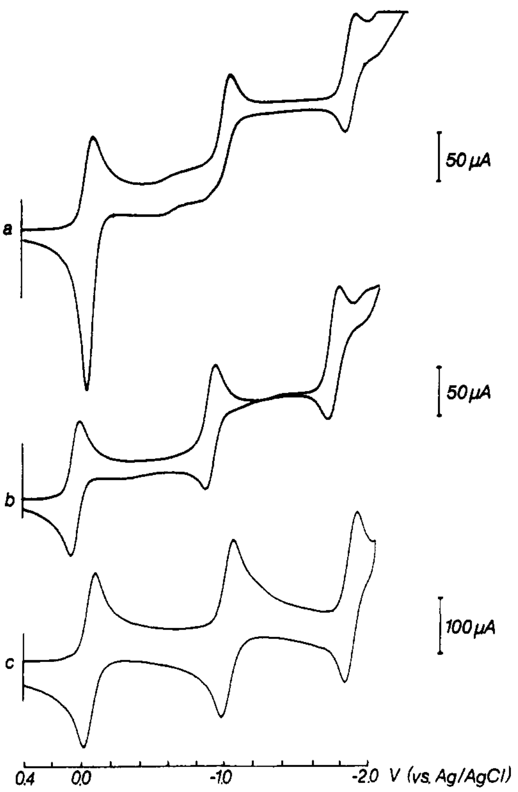

Figure 3. Cyclic voltammogram of **3a** and **3b** in acetonitrile/0.1 M TBAH (C(**3a**) = C(**3b**) = 1 mM) at different scan rates: (a) **3b** at 10 mV/s; (b) **3a** at 10 mV/s; (c) **3a** or **3b** at 100 mV/s.

The $\mathrm{Co^{III}/Co^{II}}$ couple at −0.77 V can be used as an internal standard for a reversible one-electron transfer. Comparing the $i_p/v^{1/2}C$ value of this couple with the current function of the irreversible oxidation wave at 1.45 V, we noticed that the latter was slightly larger, but still much smaller than the theoretically expected value for an irreversible two-electron transfer.[21] Thus, while the oxidation of $\mathrm{Cp_2Ru}$ clearly involves two electrons, the oxidation of the ruthenium atom in 2 is most likely a one-electron oxidation leading to a $\mathrm{Ru^{3+}}$ species.

Possibly the charge effect arising from the proximity of the cobalt(III) center as well as stabilization of the mixed-valence ion by electron delocalization over the metal centers, renders an abstraction of a further electron more difficult.

$[\mathrm{BFCo_2}]^{2+}$ (**3b**) can be reduced in $\mathrm{CH_3CN}$ in two successive reversible one-electron steps at −0.07 and −0.95 V versus SCE,[1,2,25] yielding the neutral compound. The possibility of anion formation at more negative potentials

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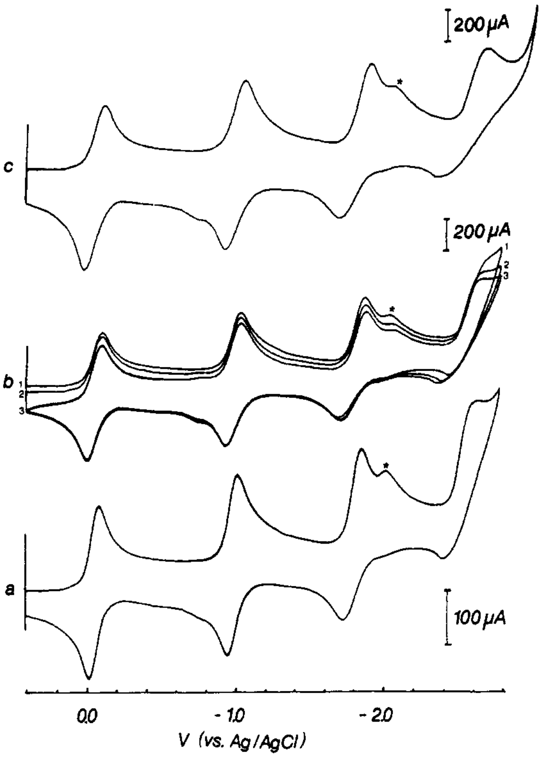

Figure 4. Cyclic voltammogram of **3a** in acetonitrile/0.1 M TBAH at different scan rates: (a) 100 mV/s; (b) 500 mV/s (multiscan); (c) 700 mV/s; Asterisk indicates solvent impurity.

has never been taken into account.

Encouraged by the results for 1 and 2, we investigated the electrochemical behavior of **3a** and **3b**. As we expected both compounds can be reduced to anions in a reversible one-electron step at −1.83 V (Figure 3c). For **3a** in extremely dry acetonitrile even a fourth reduction wave at −2.55 V is detected, with a peak separation of 200 mV indicating electrochemical quasireversibility (Figure 4a). This last reduction peak is attributed to the formation of the dianion $[BFCo_2]^{2-}$, which is isoelectronic with $[BFNi_2]$. Thus **3a** shows the complete reduction series only known for the simple metallocenes:

$$[BFCo_2]^{2+} \xrightleftharpoons[-0.06]{e^-} [BFCo_2]^+ \xrightleftharpoons[-0.99]{e^-} [BFCo_2] \xrightleftharpoons[-1.83]{e^-}$$
$$[BFCo_2]^- \xrightleftharpoons[-2.55]{e^-} [BFCo_2]^{2-} \quad (4)$$

The reason for the quasireversibility of the fourth reduction/oxidation step could not be determined unambiguously. Changes in sweep rate from 100 to 1000 mV/s resulted in a larger peak-to-peak separation and a small shift of the peak potential E_{pc} to a more negative value. This seems to indicate a quasireversibility due to a smaller heterogeneous charge transfer constant. Probably the increased electron number in the molecule renders further reduction more difficult.

However, plots of $i_{pc}/v^{1/2}C$ values versus scan rate indicate homogeneous chemical complications for the charge transfers at −1.83 and −2.55 V. While the current functions for the reductions at −0.06 and −0.99 V remain almost constant with increasing scan rate, the $i_{pc}/v^{1/2}C$ values of peak 3 and 4 are higher and decrease slightly at low scan rates reaching a limiting value at higher sweep rates. Most probably comproportionation equilibria as discussed below in case of **3b** are responsible for these deviations of the current function from the reversible behavior. Further studies, however, are limited by the relatively low solubility of **3a** in CH_3CN and the scan range available by our present instrumentation. Within the concentration range (C = 0.5–1.2 mM) and scan range studied the cyclic voltammograms of **3a** appear almost diffusion controlled (Figure 4) and no further evidence for a redox mechanism complicated by a following chemical reaction can be given.

The different reduction behavior of $[BFCo_2]^+$ and $[BFCo_2]^{2+}$ was already indicated by the number of possible reduction steps and even more striking when the scan rate was changed from 100 to 10 mV/s. While the cyclic voltammogram for the monocation remains almost unchanged, the cyclic voltammogram for the dication changes drastically (Figure 3a and 3b). The anodic counterpeak at −0.99 V is missing and the i_{pa}/i_{pc} ratio for the first reduction wave at −0.06 V rises to 2.0. This means that the electrochemical reduction of the dication is no longer diffusion controlled but complicated by a homogenous chemical reaction.

Comproportionation equilibria are frequently discussed[6,22-24] in connection with mixed-valence compounds:

$$[MM]^{2+} + [MM] \rightleftharpoons 2[MM]^+ \qquad (5)$$

The stability of the mixed-valent state relative to the isovalent is reflected in the equilibrium quotient, K_c, for the comproportionation reaction. K_c can be determined electrochemically when the $E°$ values governing the two stages of reduction are well separated:[22,24]

$$MM^{2+} \rightleftharpoons MM^+ \qquad E_1°$$
$$MM^+ \rightleftharpoons MM \qquad E_2° \qquad (6)$$
$$\ln K_c = nF/RT(E_1° - E_2°)$$

The free energy of the comproportionation reaction, $\Delta G_c°$, is related to the potential difference by the equation[24,25]

$$\Delta G_c° = -0.5[F\Delta E°(-R)T \ln 4] \qquad (7)$$

Thus the potential difference $\Delta E° = E_1° - E_2°$ provides a measure for the stability of the mixed-valence species with respect to the corresponding fully oxidized and reduced states.

The cyclic voltammogram observed for the bis(fulvalene)dicobalt dication (**3b**) at low scan rates can be explained if a comproportionation equilibrium after the second reduction step at −0.99 V is taken into account. The relations 6 and 7 yield a K_c value of 5.8×10^{15} and a $\Delta G_c°$ value of −10.3 kcal[25] for **3a** and **3b**, respectively. This means that thermodynamically the mixed-valent state of the monocation $[BFCo_2]^+$ is highly favored and that the extent of the back dissociation is negligibly small:

$$\text{E} \quad [BFCo_2]^{2+} + e^- \rightleftharpoons [BFCo_2]^+ \qquad E_1°$$
$$\text{E} \quad [BFCo_2]^+ + e^- \rightleftharpoons [BFCo_2] \qquad E_2° \qquad (8)$$
$$\text{C}' \quad [BFCo_2] + [BFCo_2]^{2+} \rightleftharpoons [BFCo_2]^+ \qquad K_c,\ k_f,\ (k_b)$$

The effect of the comproportionation equilibrium on the cyclic voltammogram can only be observed when the $[BFCo_2]^{2+}$ concentration is large and remains constant throughout the experiment. This is the case when $[BFCo_2]^{2+}(PF_6^-)_2$ (**3b**) is used as starting material for cyclic voltammetry. In case of the monocation $[BFCo_2]^+PF_6^-$ (**3a**), the dication is electrochemically generated during a

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Table I. Electrochemical Data[a] for Bis(fulvalene)dimetal Compounds and Metallocenes

compd	$E^{2+/+}$ (ΔE_p)	$E^{+/0}$ (ΔE_p)	$E^{0/-}$ (ΔE_p)	$E^{-/2-}$ (ΔE_p)	ref
$[BFFeCo]^+PF_6^-$ [b]	0.83 (64)	−0.81 (61)	−1.77 (73)		this paper
$[BFRuCo]^+PF_6^-$ [b]	1.45[c]	−0.77 (61)	−1.75 (56)		this paper
$[BFCo_2]^+PF_6^-$ [d]	−0.06 (69)	−0.99 (56)	−1.83 (64)	−2.55 (200)	this paper
	−0.07[e]	−0.95			1
$[BFFe_2]^+PF_6^-$	0.86	0.27			5
Cp_2Fe	0.41				
Cp_2Co	−0.89	−1.85			11
Cp_2Ru	1.04[f]				this paper

[a] Potentials (E) are given in volts versus Ag/AgCl and ΔE_p in mV. All measurements are in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile. [b] Scan rate = 10 mV/s. [c] E_{pa}. [d] Scan rate = 100 mV/s. [e] Versus SCE. [f] $E_{pa}{}^{2+/0}$.

scan, as long as the potential is more positive than −0.06 V. However, most probably at −0.99 V there is no $[BFCo_2]^{2+}$ left in solution.

Thus the electron transfer of the first two reduction steps of **3b** exhibits all features of a catalytic mechanism (EEC′). This is a specific type of electrode mechanism where the reactant is regenerated by a chemical reaction following the electron transfer. When the sweep rate is large or k_f small, the chemical reaction has no effect. However, for large values of k_f, or as the sweep rate is decreased, there is effectively more reactant $[BFCo_2]^+$ generated. Therefore on the back scan the oxidation peak corresponding to the redox reaction at −0.99 V becomes far less pronounced and in the limit at a scan rate of 10 mV/s dissappears completely and is replaced by a plateau (Figure 3a), independent on further decrease of the sweep rate. The oxidation peak at −0.06 V, however, is increased due to the increased concentration of $[BFCo_2]^+$ by the comproportionation reaction following the charge transfer.

When the concentration of a solution of **3b** is increased the current plateau at −0.99 V can be observed at higher sweep rates. Figure 5 shows multiple scan studies as well as the influence of increased concentration on the cyclic voltammogram of **3b**. $i_{pc}/v^{1/2}C$ values for the peaks at −0.06 and −0.99 V decrease markedly with increased scan rate and increase for the third reduction step at −1.83 V. All current functions approach a limiting value at higher scan rates. This seems to be a further proof of the postulated mechanism.

The electrochemical data indicate that the rate constant for the comproportionation reaction must be considerably smaller than the rate constant for the heterogeneous charge transfer. Using working curves[26] and a method developed by Nicholson and Shain,[21] we obtained 1.9×10^{-4} L mol^{-1} s^{-1} for the k_f value of the comproportionation reaction. The average standard rate constant for a reversible electron transfer, however, lies in the range of $k° > 0.3v^{1/2}$ cm s^{-1}.[26]

This is to our knowledge the first time that the influence of a comproportionation equilibrium is directly monitored in a cyclic voltammetry experiment.

Comparing the electrochemical data in Table I, it is obvious that all bis(fulvalene)bimetals studied exhibit comparably large $\Delta E°$ values between successive electron transfers, indicating delocalization of the valence electrons and interaction of the two metals.[4,24] Comproportionation equilibria are supposed to exist for all compounds but they cannot be observed within the time scale generally used in cyclic voltammetry. This is possibly due to very small rate constants of the chemical reaction.

Electron delocalization as well as the rigidity of the fulvalene ligands most likely are responsible for the observed stability of the reduction products. However, further investigations concerning different types of heterobimetal compounds are still in progress in order to confirm these assumptions.

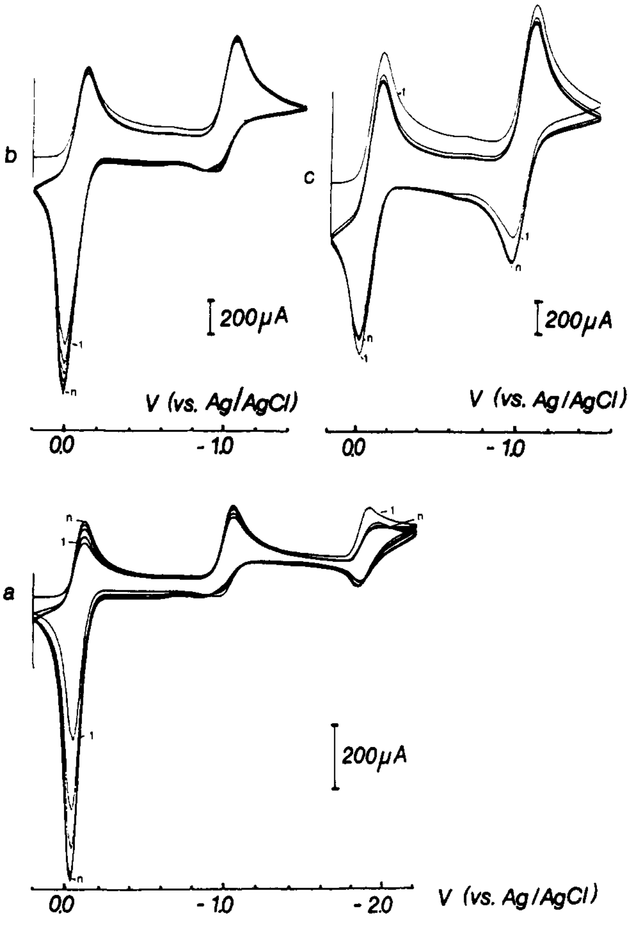

Figure 5. Cyclic voltammogram of **3b** in acetonitrile/0.1 M TBAH at different concentrations and scan rates: (a) v = 50 mV/s, C = 1.5 mM; (b) v = 200 mV/s, C = 2.7 mM; (c) v = 500 mV/s, C = 2.7 mM.

Experimental Section

Cyclic voltammetry was carried out by using a Wenking LT-78 potentiostat and a Wenking VSG 72 voltage scan generator, equipped with a Hewlett-Packard 7015 B XY recorder. Unless otherwise stated solutions were ca. 1 mM of the metal complex in acetonitrile and contained 0.1 M n-tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. For the measurements a conventional three-electrode cell with a platinring working electrode, glassy carbon counter electrode, and a silver/silver chloride reference electrode was used. Acetonitrile and TBAH were obtained from Fluka Chemicals (high purity). Acetonitrile was dried according to literature procedures and freshly distilled from CaH_2 before use. TBAH was recrystallized from methanol. All manipulations and electrochemical mea-

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surements were performed under argon, at 20 °C. The complexes 1 and 2 were synthesized according to a procedure, which is to be published.[10]

$E°$ values were taken where possible as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was judged on the basis of the peak-to-peak separation (ΔE_p) for the complementary anodic and cathodic cyclovoltammetric waves, relative to the predicted value of 59 mV for a reversible one-electron process.[21,26] IR drop due to solution resistance was not compensated and led to ΔE_p values somewhat greater than the predicted 59 mV.

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Diphosphine-Bridged, Heterobimetallic Complexes Containing Iridium and Osmium. Reversible Ortho Metalation of a Bridging Bis(diphenylphosphino)methane Group at the Iridium Center Promoted by the Adjacent Osmium Center

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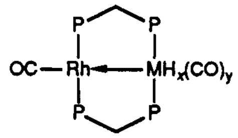
The compound (PPN)[HOs(CO)$_4$] reacts readily with [IrCl(η^2-dppm)$_2$] (PPN$^+$ = (Ph$_3$P)$_2$N$^+$, dppm = Ph$_2$PCH$_2$PPh$_2$) at ambient temperature, yielding the heterobinuclear complex [IrOs(H)$_2$(CO)$_3$(μ_2-η^3-(*o*-C$_6$H$_4$)PhPCH$_2$PPh$_2$)(dppm)] (1), in which one phenyl group is ortho-metalated at the Ir center. Treatment of 1 with the electrophile sources HBF$_4$·Et$_2$O or [AuPPh$_3$]BF$_4$ reverses the ortho metalation to give the hydrido-bridged species, [IrOs(CO)$_3$(μ-H)(μ-X)(dppm)$_2$][BF$_4$] (X = H (2), AuPPh$_3$ (3)). Deprotonation of 2 with use of NaH regenerates compound 1. The AuPPh$_3$ group in 3 is readily replaced by an iodo group in the reaction with I$_2$ to give [IrOs(CO)$_3$(μ-H)(μ-I)(dppm)$_2$][BF$_4$] (4). Under a CO atmosphere, compound 2 yields [IrOs(CO)$_5$(dppm)$_2$][BF$_4$] (5), and reaction of 5 with Me$_3$NO·2H$_2$O results in loss of one carbonyl group from the Ir center to yield [IrOs(CO)$_4$(dppm)$_2$][BF$_4$] (6). The structure of 5 has been determined by X-ray techniques. This compound crystallizes, together with 1.5 equiv of CH$_2$Cl$_2$, in the monoclinic space group $P2_1/c$, with cell parameters a = 12.063 (2) Å, b = 22.725 (3) Å, c = 22.050 (3) Å, β = 101.66 (1)°, V = 5920 Å^3, and Z = 4. The structure has refined to R = 0.043 and R_W = 0.063 on the basis of 5515 unique observations with 444 parameters varied. Compound 5 has a trans-bridging arrangement of diphosphine ligands and has two carbonyls bound to Ir and three on Os. The carbonyl and phosphine arrangement on Os suggests a trigonal bipyramidal (TBP) arrangement characteristic of Os(0), which then forms a dative Os → Ir bond to the Ir(+I) center, giving it a TBP geometry also. The Os–Ir separation of 2.9652 (4) Å is at the long end of the range expected for a normal single bond.

Introduction

Our ongoing interests in metal–metal cooperativity effects in binuclear complexes[1] have recently expanded to include complexes containing two different metals.[2-8] Most of the heterobinuclear complexes studied by us to date contain Rh as one of the metals and have been derived from the precursors, [(OC)Rh(μ-dppm)$_2$MH$_x$(CO)$_y$] (M = Co, Ir, x = 0, y = 2; M = Fe, Ru, Os, x = 1, y = 2; M = Mn, Re, x = 0, y = 3; M = Cr, W, x = 1, y = 3; dppm = Ph$_2$PCH$_2$PPh$_2$).[4] These compounds have been formulated as containing a Rh(+I) center with an accompanying M → Rh donor–acceptor bond,[4,8] as shown in the drawing below, and join the growing list of compounds for which a metal–metal dative bond appears to be present.[9] Such bonds have been shown to be relatively labile,[9b] so they may be a source of incipient coordinative unsaturation in these diphosphine-bridged complexes. We are interested in obtaining additional information about the natures of these metal–metal interactions, about the subtle electron redistributions that might occur during reactions, and about the effect of the dative M → Rh bond on the re-



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[1] See for example: (a) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1637. (b) Sutherland, B. R.; Cowie, M. *Organometallics* **1985**, *4*, 1801. (c) Cowie, M.; Vasapollo, G.; Sutherland, B. R.; Ennett, J. P. *Inorg. Chem.* **1986**, *25*, 2648. (d) Vaartstra, B. A.; Cowie, M. *Organometallics* **1990**, *9*, 1594.

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