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A Directed Synthesis of Heterobimetallic Fulvalene Complexes via Electrochemical Reduction of C₅-Substituted Ferrocenes

Roger D. Moulton and Allen J. Bard*

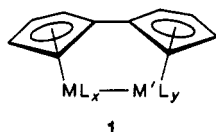
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The synthesis of fulvalene-bridged heterobimetallic complexes following electrochemical reduction of diacetylferrocene (4) is discussed. The cyclic voltammetry of 4 follows an E_qC_i mechanism with reduction to generate a mixture of pinacols and cyclopentadienides. The mixture was treated with W(CO)₃(PrCN)₃ and CH₃I to form ((1'-acetylferrocenyl)Cp)W(CO)₃CH₃ (6). The reduction of 6 shows two waves. The first reduction is followed by cleavage of the W-CH₃ bond; the second involves reduction of the ferrocene unit. (Fulvalene)FeW(CO)₅²⁻ was formed following reduction of 6 under a CO atmosphere. Studies of the synthesis and electrochemical behavior of other C₅-substituted ferrocenes is also discussed.

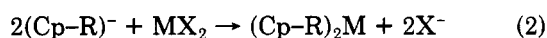
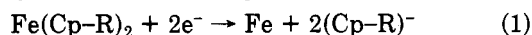
Introduction

The redox behavior of a series of bimetallic complexes containing the fulvalene ligand (1) (M = M' = Ru, Cr, Mo, W; M = Ru, M' = Mo; L = CO) was recently described.¹



The synthesis of these compounds, and particularly the formation of heterobimetallic complexes (M ≠ M'), is difficult. Approaches that have thus far appeared include reaction of dihydrofulvalene with a mixture of metal carbonyls,² partial decomplexation of homobimetallic fulvalene complexes,³ and cyclization of an acylated cyclopentadienide to form a masked C₅ ring attached to an existing CpM system.³ The first approach suffers from a reliance on statistics to form a heterobimetallic complex, which leads to low yields of the hetero form when the metal carbonyls do not react at similar rates. The latter two approaches are of more general scope but involve multiple steps and require careful manipulations under inert atmosphere conditions. We report here a new synthesis that involves the stepwise electrochemical reductive cleavage of the Fe-ring bonds of a biferrocene. Each Fe atom can be removed independently and replaced with another metal, thus leading to the direct formation of new heterobimetallic fulvalene complexes.

There have been several previous reports of reduction of ferrocenes. Ferrocene was reduced by solvated electrons in ethylamine to form Fe and cyclopentadienide.⁴ More recent reports describe the electrochemical reduction of ferrocenes Fe(Cp-R)₂ (R = alkyl, acyl, CO₂R) to generate Fe and (Cp-R)⁻.⁵ Both methods appear to generate the decomplexed cyclopentadienide in near quantitative yield. Reaction of the cyclopentadienide with a new metal provides a simple synthesis of functionalized metallocenes not available by other methods (eq 1 and 2).^{5,6}



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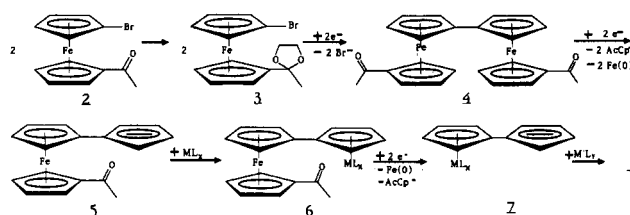
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Scheme I



The original interest in this reaction stemmed from the usefulness of the R group in the final product (metallocene (Cp-R)₂M). However, an application of this procedure toward the construction of a bimetallic system has not been explored. Our plan was to use this reduction scheme on a biferrocene unit to form the desired fulvalene compound, 1 (Scheme I).

Each ferrocene unit of the biferrocene 4 should be reducible (assuming only moderate interaction exists between them). The dianion would then decompose to 5 and Fe(0) as major products. Alternatively, a single reduction to the anion radical could be followed by cleavage of the Fe-ring bonds. The product 5 is more electron-rich than 4, and it should be resistant to further reduction. Reaction of 5 with a reactive metal complex can produce 6, and reduction of 6 followed by reaction with another metal complex may afford the desired heterobimetallic, 1.

Experimental Section

All reactions were carried out under an N₂ atmosphere with purified solvents, except as noted below. Tetrahydrofuran (THF) was purified by distillation under vacuum from sodium benzophenone ketyl. Dimethylformamide (DMF) was distilled from alumina and anhydrous CuSO₄ under vacuum (distillation temperature 63 °C). Chromatographic separations were performed by using an alumina (Fischer, activity 1) column. Carbon monoxide (Big 3 Industries) was used without further purification. Ferrocene (Aldrich) was recrystallized from hot heptane before use. 2-Cyclopenten-1-one (Fischer) was vacuum distilled from alumina before use. Acetylferrocene,⁷ 1,1'-dithioferrocene-2(TMEDA) (TMEDA = tetramethylethylenediamine),⁸ 1-bromo-1'-acetylferrocene,⁹⁻¹¹ and W(CO)₃(PrCN)₃¹² were prepared by literature methods. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) (Southwestern Chemicals) was recrystallized

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from MeOH slowly and again from THF/ether rapidly (to remove trapped solvent molecules). Other chemicals were used without further purification.

Electrochemical measurements were made in a glass cell following the procedures previously described.¹ The supporting electrolyte and the cell were dried under vacuum overnight prior to an electrochemical experiment. For voltammetry experiments, a silver wire was used as a quasi-reference electrode, a Pt mesh as the auxiliary electrode, and a Pt disk as the working electrode. Electrode potentials were referenced to the oxidation of ferrocene as previously described¹ and then converted to the normal hydrogen electrode (taking the potential of the ferrocene/ferrocenium couple as 0.548 V vs NHE in all solvents).¹³

A Pt flag ($A = 2 \text{ cm}^2$) was used for bulk electrolysis experiments. During the course of the reduction in concentrated THF solutions, the solution in the auxiliary compartment became viscous and eventually solidified. This solid material (which may arise from oxidative degradation of the solvent) is very difficult to remove from the cell, especially from the glass frits. Consequently, large-scale electrolysis was done with a mercury pool auxiliary electrode with some TBA iodide added to that compartment. Scanning of the solution before and after electrolysis showed that contamination of the working compartment by iodide or mercury salts never occurred by using this procedure, and it allowed for effective cleaning of the cell after the experiment was complete.

Chemical analysis was done by Galbraith Laboratories (Knoxville, TN). Melting point measurements were performed in unsealed glass capillaries.

1-Bromo-1'-(1-methyl-2,5-dioxacyclopentyl)ferrocene (3) from 1-Bromo-1'-acetylferrocene. Ethylene glycol (10 mL) and 100 mL of benzene were refluxed overnight in a flask and condenser fitted with a Dean-Stark trap and a CaCl_2 drying tube. 1-Bromo-1'-acetylferrocene (4.140 g, 13.48 mmol) was dissolved in 50 mL of benzene and added to the ethylene glycol mixture along with a small lump of *p*-toluenesulfonic acid, and the mixture was refluxed. After 18 h, a small quantity of water had collected in the trap. The solution was then shaken with aqueous NaHCO_3 , and the aqueous fraction was discarded. The benzene fraction was washed with water three times, dried over MgSO_4 , and evaporated. The residue was adsorbed onto an alumina column and eluted with Skelly B/benzene (1:1). A fast moving yellow band was observed and collected. The fraction was concentrated to 25 mL and cooled in the freezer. Upon standing overnight, yellow crystals had formed. These were collected by decanting, washed with cold Skelly B, and dried in air: total yield 3.10 g (66%); mp 46–48 °C; $^1\text{H NMR}$ (acetone- d_6) δ 2.05 (s, 3 H, CH_3), 3.97 (s, 4 H, CH_2CH_2), 4.21 (m, 6 H, 3,4,2',3',4',5'), 4.45 (t, $J = 2 \text{ Hz}$, 2 H, 2,5); mass spectrum: m/e 350. Microanal. Calcd: C, 47.90; H, 4.31. Found: C, 47.90; H, 4.23. Elution of the column with benzene gave an orange byproduct (200 mg; mp 63–64 °C) whose $^1\text{H NMR}$ and mass spectra are consistent with those of a condensation product of acetone with the starting material.

1',1''-Diacylbiferrocene (4) from Ketal 3. Ketal 3 (1.729 g, 4.925 mmol) was dissolved in 40 mL of THF, and 0.772 g of Mg was added. As the solution was stirred; 0.44 mL of ethylene dibromide¹⁴ was added (5.16 mmol) by syringe. After 20 min of stirring, a noticeable evolution of gas occurred and the solution began to darken. Finely divided $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.778 g, 3.27 mmol) was placed in a 50-mL flask and heated at 150 °C under vacuum until all of the material had turned blue. After 3 h, the THF solution was cooled to 0 °C and transferred to the CoCl_2 and stirred.¹⁵ The solution immediately became green but soon precipitated a white powder while the solution turned yellow. After 18 h of stirring, the THF solution was added to 50 mL of water to which a few drops of sulfuric acid had been added. This mixture was stirred overnight, and a red solid precipitated. This was collected by filtration, and the filtrate was extracted with ether, evaporated, and the extracts were combined with the precipitate. The mixture was then dissolved in hot toluene and recrystallized to yield 0.480 g of 4 (43%), mp 192–194 °C (lit.¹⁶

mp 191–192 °C). A 25% yield of acetylferrocene was obtained by chromatography of the mother liquors.

Synthesis of ((1'-Acetylferrocenyl)- η^5 -cyclopentadienyl)tungsten Methyl Tricarbonyl (6). Diacylbiferrocene (4) (98 mg, 0.216 mmol) was added to THF/0.2 M TBAPF₆ in the cell and reduced at a potential midway between the two reduction waves (–2.27 V vs NHE). As the electrolysis proceeded, the orange solution became red. After the electrolysis was complete, the solution was transferred by cannulus to a 50-mL Schlenk flask and was refluxed 3 h with $\text{W}(\text{CO})_3(\text{PrCN})_3$ (225 mg, 0.47 mmol). The mixture was cooled, CH_3I (0.20 mL) was then added by syringe, and the mixture was stirred for 30 min. The solution was extracted with Skelly B/water, dried over MgSO_4 , and evaporated. The resulting solid was chromatographed. Elution with CH_2Cl_2 removed an orange band. The orange band was evaporated to dryness and recrystallized from Skelly B/toluene (4:1) to obtain 27 mg of 6 (26% yield) as orange needles. Elution with acetone removed some 4 (15 mg) and a yellow compound, possibly $(\text{acetylCp})\text{W}(\text{CO})_3\text{CH}_3$.

In a similar experiment 0.400 g of 4 (0.88 mmol) was suspended with partial dissolution in THF/0.2 M TBAPF₆. Bulk electrolysis was done as described above, except the potential was maintained at the second CV reduction peak potential. After 60 C were passed, the solution was removed from the cell and some undissolved 4 (0.112 g) was recovered. Reaction with $\text{W}(\text{CO})_3(\text{PrCN})_3$ and CH_3I was performed as described above, followed by the usual workup and separation methods. Unreacted $\text{W}(\text{CO})_3(\text{PrCN})_3$ was recovered from the column, as was 6 (0.046 g, 21%) and some 4 (0.122 g): $^1\text{H NMR}$ δ 0.11 (s, 3 H, WCH_3), 2.23 (s, 3 H, COCH_3), 4.34 (t, $J = 2 \text{ Hz}$, 2 H, 3,4-ferrocenyl), 4.45 (t, $J = 2 \text{ Hz}$, 2 H, 3',4'-ferrocenyl), 4.59 (t, $J = 2 \text{ Hz}$, 2 H, 2,5-ferrocenyl), 4.70 (t, $J = 2 \text{ Hz}$, 2 H, 2',5'-ferrocenyl), 5.51 (t, $J = 2 \text{ Hz}$, 2 H, 3,4-CpW), 5.87 (t, $J = 2 \text{ Hz}$, 2 H, 2,5-CpW); mass spectrum: m/e 574. Microanal. Calcd: C, 45.20; H, 3.25. Found: C, 44.64; H, 3.33.

Electrochemical Reduction of Acetylferrocene. Acetylferrocene (164 mg) was dissolved in THF/0.2 M TBAPF₆, and bulk electrolysis was done at –2.40 V vs NHE, which consumed 1.1 faradays/mol. The solution became green when the electrolysis was initiated (due to the presence of the anion radical of acetylferrocene⁶) but turned to yellow as the coulometry proceeded. The mixture was extracted with Skelly B/water, dried, and evaporated. A mass of semicrystalline material was obtained, which was redissolved in Skelly B and recrystallized to afford small yellow plates. The mass spectrum of these consisted of a parent m/e of 458 with two larger peaks at m/e 440 and 422 corresponding to successive losses of H_2O from the pinacol dimer. The crystals melted at 145–160 °C dec (lit.¹⁷ for pinacol dimer mp 140–143 °C). An attempt at purification of the material by chromatography led to the isolation of 0.080 g of acetylferrocene. A much slower moving oil was removed from the column with acetone.

A similar reduction was done in DMF/0.2 M TBAPF₆. Acetylferrocene (150 mg) was reduced at –2.4 V vs NHE, and the resulting solution showed oxidation peaks similar in size and potential to the THF solution described above. The solution was transferred to a 100-mL Schlenk flask by cannulus, and 0.500 g of $\text{W}(\text{CO})_3(\text{PrCN})_3$ was added against a counter current of N_2 . The solution was then refluxed overnight and allowed to cool, when 0.2 mL of CH_3I was added by syringe. The resulting mixture was stirred for 30 min and then extracted ($3 \times 100 \text{ mL}$) with ether/ H_2O . The resulting extracts were combined, dried over MgSO_4 , and evaporated. The yellow residue was dissolved in Skelly B (10 mL) and recrystallized to yield 27 mg of $(\text{acetylCp})\text{W}(\text{CO})_3\text{CH}_3$ (8%) (mp 71–72 °C (lit.⁶ mp 73 °C). TLC of the mother liquors showed that along with some acetylferrocene, two yellow compounds were present, possibly both $(\text{R-Cp})\text{W}(\text{CO})_3\text{CH}_3$ (R = H, acetyl) products.

Reduction of 6 under CO Atmosphere. 6 (98 mg) was dissolved in THF/0.2 M TBAPF₆, and electrolysis was done at the level of the first reduction (–2.30 V). The electrolysis was discontinued when 19 C had passed ($n_{\text{app}} = 1.15$ faradays/mol). The solution was then saturated with CO, and another electrolysis performed at –2.60 V (33 C, $n_{\text{app}} = 2.00$ faradays/mol). After the

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electrolysis was complete, 200 mg of I_2 was added, and the solution was extracted with ether/water. The ether fraction was washed with 10% aqueous $Na_2S_2O_3$, dried, and chromatographed. A fast moving band in toluene was obtained, which afforded a tan oil upon evaporation. A slower band was removed with CH_2Cl_2 , which was recrystallized with toluene/Skelly B (1:4) to yield (1'-acetylferrocenyl) Cp W(CO) $_3$ I (18 mg, 15%): mp 135 °C dec; 1H NMR δ 2.30 (s, 3 H, COCH $_3$), 4.43 (t, J = 2 Hz, 2 H, 3',4'-ferrocenyl), 4.53 (t, J = 2 Hz, 2 H, 3,4-ferrocenyl), 4.74 (m, 4 H, 2',5',2,5-ferrocenyl), 5.92 (t, J = 2 Hz, 2 H, 3,4-CpW), 6.23 (t, J = 2 Hz, 2 H, 2,5-CpW); mass spectrum: m/e 602 (- acetylCp). Microanal. Calcd: C, 35.02; H, 2.20. Found: C, 35.07; H, 2.33.

Synthesis of 1,1'-Bis(1-hydroxy-2-cyclopentenyl)ferrocene (11). 1,1'-Dilithioferrocene-bis(tetramethylethylenediamine) (2.34 g, 5.44 mmol) was suspended in 120 mL of diethyl ether and cooled to 0 °C. A solution of 0.97 mL of 2-cyclopenten-1-one in 25 mL of ether was transferred to the rapidly stirred ferrocene solution by cannulus. A yellow precipitate began to form immediately. After the addition was complete, the solution was allowed to stir for 1 h at room temperature. The solution was then extracted with 100 mL of water and evaporated to dryness. The semisolid residue obtained was suspended in acetone, and the insoluble material was collected by decanting. It was recrystallized from hot CH_2Cl_2 to yield 0.553 g (29%) of 11 as yellow crystals. This compound melted at 130 °C with the evolution of gas and a color change to red. 1H NMR (acetone): δ 1.52 (br s, 4 H, CH_2CH_2), 4.18 (m, 8 H, 2,3,4,5,2',3',4',5'), 4.70 (br s, 2 H, OH), 5.78 (d, J = 3 Hz, 4 H, $CH=CH$). Mass spectrum: m/e 350. Anal. Calcd: C, 68.59; H, 6.33. Found: C, 68.81; H, 6.56.

Attempted Dehydration of 11. 11 (0.47 g, 1.34 mmol) was placed in a vacuum sublimation apparatus and heated to 145 °C under vacuum. A darkening of the material and an evolution of gas were observed. A small quantity of an orange compound collected on the cold finger after 1 h. The heating bath was removed, and the material was allowed to cool under vacuum. TLC showed that both the volatile and nonvolatile residues contained a similar mixture of products. The mixture was adsorbed on a column; eluting with CH_2Cl_2 gave a reddish oil whose 1H NMR was not suggestive of the product 14 (since it lacked the cyclopentadienyl resonances expected at $5 \leq \delta \leq 6$). Dehydration of 11 with 2,4-dinitrobenzenesulfonyl chloride¹⁸ or by azeotropic distillation from benzene with *p*-toluenesulfonic acid³ gave a red oil with similar properties to those described above.

Attempted Reaction of Ketal 3 with 2-Cyclopenten-1-one. 3 (0.102 g, 0.291 mmol) was dissolved in 15 mL of ether and cooled to -78 °C. BuLi (0.20 mL, 1.494 M in hexane, 0.299 mmol) was added by syringe, and the solution was allowed to come to room temperature. The yellow solution gradually turned orange, and after 15 min, an orange powder began to precipitate. To the rapidly stirred suspension of the lithiated ferrocene was added 0.30 mL (3.58 mmol) of 2-cyclopenten-1-one by syringe. The orange precipitate immediately disappeared, and a white precipitate appeared. The slurry was stirred for 1 h at room temperature. It was then added to 50 mL of water and extracted with hexane, dried over $MgSO_4$, and evaporated. The residue was dissolved in acetone and stirred with water overnight to hydrolyze the ketal. Extraction of the mixture followed by chromatography yielded acetylferrocene and debrominated 3 from the product mixture.

Results

Synthesis of Diacetylferrocene 4. A two-step synthesis of diacetylferrocene has previously been described.^{16,19} An approach involving Grignard coupling of a bromoferrocene was used in this study, since it was hoped the Grignard reagent would be a starting point for the synthesis of other C_5 -substituted ferrocenes (see discussion). 1-Bromo-1'-acetylferrocene was made as previously described,⁹⁻¹¹ then the ketone was protected with ethylene

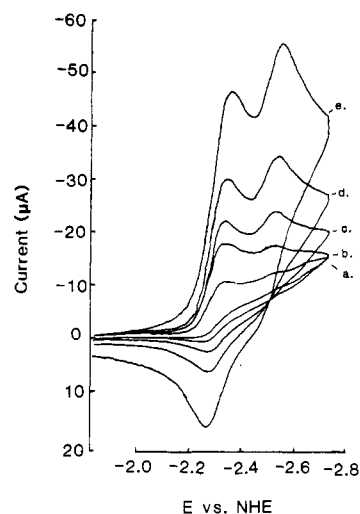


Figure 1. Cyclic voltammetry of 4.5 mM 4 in THF/0.2 M $TBAPF_6$ as a function of scan rate (mV/s): a, 20; b, 50; c, 100; d, 200; e, 500.

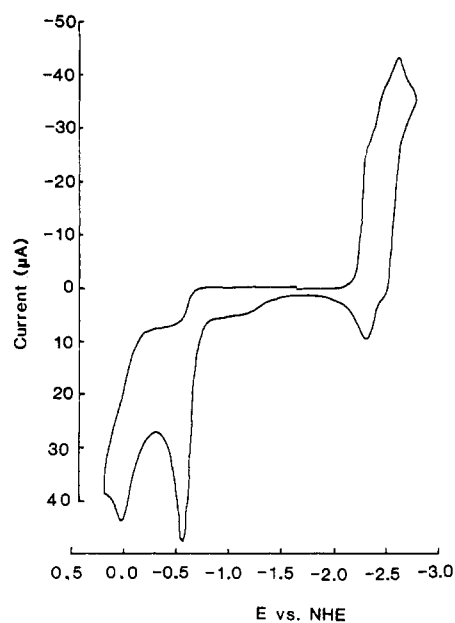


Figure 2. Cyclic voltammetry of 33 mM 4 in THF/0.2 M $TBAPF_6$ following exhaustive reduction at -2.28 V (scan rate = 200 mV/s).

glycol to form 3. The molecule condensed readily with acetone, since traces of acetone present in the glycol solution reacted to form 1-bromo-1'-(1-oxo-3-methyl-2-butenyl)ferrocene as a byproduct.

Grignard coupling of 3 was done as described for bromoferrocene,¹⁴ and hydrolysis of the ketal during the workup afforded the product 4 in 43% yield. In agreement with previous results,¹⁴ a 25% yield of the debrominated material (acetylferrocene) was also obtained, presumably by abstraction of a proton from the solvent by either the Grignard reagent or the ferrocene radical before coupling occurs.

Synthesis of 6. Cyclic voltammetry of 4 in THF/0.4 M $TBAPF_6$ shows two well-resolved reduction waves (Figure 1). At higher scan rates (above 1 V/s) evidence for reversibility is seen in both waves, which leads to the determination of the reversible reduction potentials: $E_{1/2}^1 = -2.18$ V; $E_{1/2}^2 = -2.37$ V vs NHE. The separation between the reduction potentials of 4 can be interpreted to result from a weak interaction between the reducible centers in the molecule, making the addition of the second

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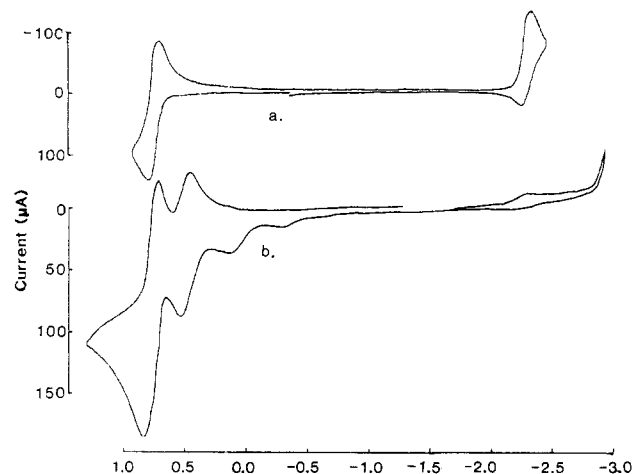


Figure 3. Cyclic voltammetry of 50 mM acetylferrocene in THF/0.2 M TBAPF₆ (a) before and (b) after bulk electrolysis at -2.4 V ($\nu = 200$ mV/s). Note different current scales.

electron to the molecules slightly more difficult than the first. Bulk electrolysis of the solution (either at the potential of the first reduction or the second) consumed between 1 and 2 faradays/mol and generated a dark red solution. The solution after reduction (Figure 2) showed a new reversible reduction peak ($E_{1/2} = -2.65$ V). In addition, an irreversible oxidation peak at -0.60 V and another at 0.00 V were seen. These are attributed to **5** and acetylCp⁻, respectively, by comparison to the reduction products of acetylferrocene (see below), and the expected electron-donating effect the ferrocene unit has on the oxidation potential of Cp⁻. Several more positive reversible oxidation waves (suggestive of compounds with a ferrocene structure) were also observed. Reaction of the red solution with W(CO)₃(PrCN)₃ followed by CH₃I afforded **6** in 26% yield. If the reduction was carried out at the level of the second reduction a yield of 21% for **6** was obtained.

The low yield of product from these reactions is surprising, since previous reports^{5,6} claimed essentially quantitative formation of metallocenes following reduction of disubstituted ferrocenes. We therefore undertook a study of the reduction of acetylferrocene, a simpler analogue of **4**.

Electrochemical Reduction of Acetylferrocene.

Literature reports concerning the reduction of acetylferrocene are contradictory; El Murr⁵ et al. reported that reduction of the molecule occurred in an ECE process which generated Fe (as a finely divided metallic powder) and a pair of cyclopentadienide molecules. However, Lacan and Ibrasagic reported¹⁷ the formation of a pinacol-type dimer. In light of this apparent disagreement, the following two reduction experiments were performed. In the first, exhaustive electrolysis of acetylferrocene ($E_{1/2} = -2.25$ V; $E_{app} = -2.40$ V) in THF/0.2 M TBAPF₆ was performed ($n_{app} = 1.1$ faradays/mol). Cyclic voltammetry of the solution after reduction is shown in Figure 3. Two small peaks corresponding to the oxidation of Cp⁻ and acetylCp⁻ were seen. The oxidation of acetylCp⁻ is seen at 0.0 V, which confirms the assignment of the second oxidation wave observed following reduction of **4** to this product. A larger reversible oxidation wave located less positive than the original acetylferrocene/ferrocenium. The potential of the latter peak is in agreement with the expected oxidation potential of pinacol dimer. The solution was extracted (to remove electrolyte) and slowly evaporated. The yellow crystals obtained exhibited a mass spectrum and melting point consistent with those of the pinacol structure. In the second experiment, the electro-

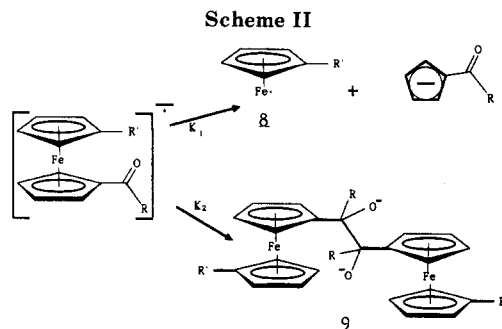


Table I. Cyclic Voltammetric Behavior of the Reduction Peaks of **4**^a

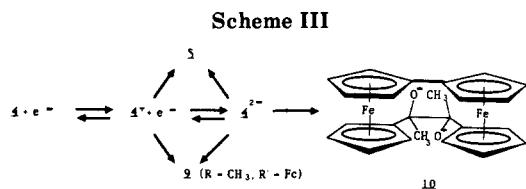
ν	i_p	E_{pc}^{1b}	$E_p - E_{p/2}^c$	ΔE_p	$\psi \nu^{1/2d}$	i_{pa}/i_{pc}	k_f^e	E_{pc}^{2b}
0.02	2.05	-2.210	75					
0.05	2.95	-2.212	72					-2.405
0.10	4.00	-2.215	75	88	0.28	0.523	1.4	-2.408
0.20	5.40	-2.221	84	92	0.34	0.648	1.6	-2.416
0.50	8.20	-2.228	78	108	0.33	0.915	0.7	-2.430
1.00	11.15	-2.239	99	125	0.33	0.924	1.2	-2.446

^a 3.4 mM **4** in THF/0.2 M TBAPF₆. Scan rates are in V/s; potentials are in V vs. NHE. Currents in μ A. $E_{\lambda} = -2.28$ V in all cases. ^b E_p^1 and E_p^2 refer to the first and second reductions, respectively. ^c Separation of peak and half-peak potentials in mV. ^d ψ was obtained from ΔE_p values.²⁰ ^e Derived by method described in ref 20 from i_{pa}/i_{pc} . k_f is the rate constant for the decomposition of **4**⁻, in s⁻¹.

lysis was performed as described above, and then the solution was refluxed with W(CO)₃(PrCN)₃ followed by CH₃I. Workup of the solution afforded a small amount (8%) of (AcCp)W(CO)₃CH₃. At no point during these experiments was any insoluble material (such as Fe) produced. On the basis of these results, we suggest that the reduction of an acylated ferrocene to its radical anion is followed by two possible reaction pathways (Scheme II). It may decompose in a first-order process to the half-sandwich radical **8** (pathway 1), or it may dimerize to a pinacol, **9** (pathway 2). In the case of acetylferrocene, roughly 90% of the anion radical reacts via pathway 2. A ferrocene dianion is reported^{5,6} to react predominantly via pathway 1, but this can only be observed with substituted ferrocenes containing two electron-withdrawing groups. By this method compounds such as (acetylCp)W(CO)₃CH₃⁵ and 1,1'-diacetylcobaltocene⁶ have been made in high yield from 1,1'-diacetylferrocene.

Analysis of Voltammetry of **4.** The voltammetric characteristics of the peaks are summarized in Table I. The peak currents increased linearly with $\nu^{1/2}$ and concentration. The splitting of the anodic and cathodic peak potentials (ΔE_p) increased with scan rate. Uncompensated resistance in solution was not responsible for the increase in ΔE_p , since the oxidation peaks of **4** ($E_{1/2}^1 = 0.70$ V, $E_{1/2}^2 = 0.95$ V) showed near Nernstian behavior, with $\Delta E_p =$ ca. 65 mV, independent of ν . We therefore assign the peak splitting to some sluggishness in the heterogeneous kinetics. The peak splitting of the first reduction peak can be related to the dimensionless parameter ψ , which changes inversely with $\nu^{1/2}$.²⁰ Examination of the values in Table I show that the agreement is quite good.

The rate of the reactions following the reductions were estimated from the i_{pa}/i_{pc} values by fitting the ratios to the working curve of k_f/τ ($\tau = (E_{1/2} - E_{\lambda})/\nu$) given by Nicholson and Shain²⁰ with the assumption that the following reaction was a first-order one. Small values of i_{pa} were difficult to measure, so only data at the faster scan



rates was used. Despite the relatively large random errors, consistent values for the rate constant over the range of scan rates studied was obtained (see Table I). An average of these values gives $k = 1.2 \pm 0.4 \text{ s}^{-1}$ for the reaction following the first reduction. From a voltammogram of 4 at 1 V/s (the highest scan rate employed), a similar treatment based on the i_{pa}/i_{pc} ratio for the second peak gave a value of $10 \pm 3 \text{ s}^{-1}$ for the rate of the reaction following the second reduction. Thus the reduction of 4 can be best described as an E_qC_i mechanism (KG zone by Saveant's analysis²¹), in which a quasi-reversible electron-transfer reaction is followed by a moderately slow irreversible reaction.

We suggest that the electrochemical reduction of 4 follows Scheme III. When the reduction occurs at the first wave, the formation of the anion radical of 4 is accompanied by decomplexation, since 5 was observed electrochemically and since 6 was isolated from the product mixture. There is also evidence that some pinacolization occurs: the voltammetry of reduced 4 and reduced acetylferrocene are similar, and 4 was recovered following chromatography of the reaction mixture after workup, even though the mixture was exhaustively reduced. The recovery of 4 may result from autoxidation of the pinacol, analogous to the behavior of acetylferrocene.¹⁷ The rate constant of 1.2 s^{-1} for the following reaction is therefore probably a combination of first- and second-order terms, since both decomplexation and pinacolization seem to be occurring.

The dianion of 4 is less stable, and a faster reaction follows reduction. If we take the separation of the two reduction waves as an indication that only a modest interaction exists between the orbitals of each ferrocene unit, the introduction of a second electron into a previously reduced biferrrocene should not greatly affect the rates of the reactions that form 5 and 9. However, a doubly reduced molecule of 4 has available to it the additional reaction that forms 10, an intramolecular pinacolization. We suggest the increased following reaction rate associated with the second reduction is an indication the reaction that forms 10 is occurring. The decreased yield of 6 observed when the electrolysis is performed at this potential (21% vs 26%) is consistent with an additional side reaction.

Voltammetry of 6 ($ML_x = W(CO)_3^-$). Cyclic voltammetry of 6 shows two reduction waves (Figure 4). The first (-2.19 V) is irreversible and generates a product oxidized at -0.20 V. By comparison, the reduction of (acetylCp)W(CO)₃CH₃ is reported⁶ to occur at -1.8 V (vs SCE) and cleaves the W-CH₃ bond. The oxidation of the (acetylCp)W(CO)₃⁻ thus produced is reported at 0.20 V. On the basis of the agreement of the relative position of the peaks of 6 and (acetylCp)W(CO)₃CH₃ (the inductive effects of ring substituents of the CpW(CO)₃ system is negligible⁶), we propose that the reduction of 6 at the level of the first reduction generates (CpR)W(CO)₃⁻ (R = 1'-acetylferrocene).

The second reduction wave ($E_{1/2} = -2.40 \text{ V}$) is reversible on the time scale of a typical CV experiment ($\nu = 200 \text{ mV/s}$). The peak splitting for this reduction ($\Delta E_p = 65$

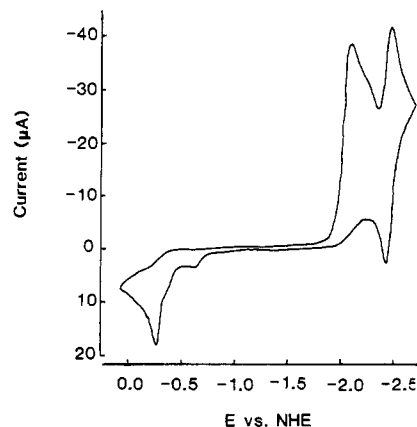


Figure 4. Cyclic voltammetry of 5.2 mM 6 in THF/0.2 M TBAPF₆ ($\nu = 200 \text{ mV/s}$).

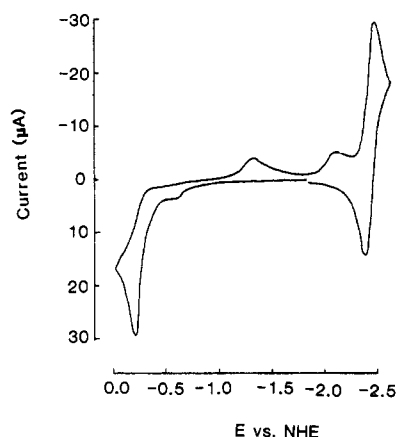
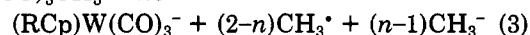


Figure 5. Cyclic voltammetry of 5.2 mM solution of (CpR)W(CO)₃⁻ (R = 1'-acetylferrocenyl), generated by reduction of 6 at -2.30 V ($\nu = 200 \text{ mV/s}$).

mV) suggests faster heterogeneous kinetics than in the reduction of 4.

Bulk Electrolysis of 6. The bulk electrolysis of 6 at the level of the first reduction ($E_{app} = -2.30 \text{ V}$) generates the solution shown in Figure 5. The reduction consumes 1.15 faradays/mol; therefore, both methyl anion and radicals may be produced (eq 3). Methyl anions would react



rapidly with proton sources in solution and be evolved as methane; no evidence for the presence of methyl anion can be seen by scanning after the electrolysis.

The reduction of ferrocenes under CO atmosphere is reported^{5b} to afford half-sandwich Fe carbonyls (CpR)Fe(CO)₂⁻. Starting with (CpR)W(CO)₃⁻ (R = 1'-acetylferrocene), reduction under CO should produce 1 (M = W(CO)₃⁻, M' = Fe(CO)₂⁻). Therefore, after the initial electrolysis was complete, the solution was saturated with CO, and an electrolysis at the second reduction potential was performed ($E_{app} = -2.60 \text{ V}$). As the electrolysis proceeded, a small peak began to appear at -1.10 V (Figure 6). By comparison with literature values²² of the oxidation potential of (Cp)Fe(CO)₂⁻ (-1.8 V vs 1 mM Ag⁺/Ag), we suggest that the new peak corresponds to the oxidation of the Fe center in (fulvalene)FeW(CO)₅²⁻ ((acetylCp)Fe(CO)₂⁻ is oxidized at a more positive potential^{5b}). The yield of the fulvalene complex can be inferred by comparison

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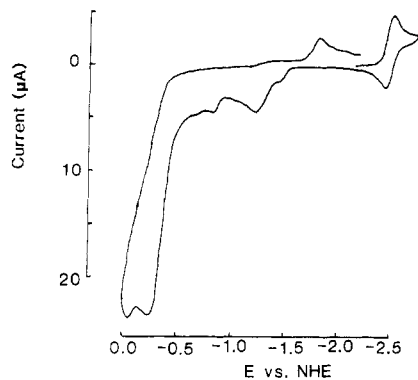


Figure 6. Cyclic voltammety of the solution shown in Figure 5, after reduction at -2.60 V under CO atmosphere. Notice the new oxidation peak at -1.1 V, corresponding to **1** ($ML_x = W(CO)_3^-$; $M'L_y = Fe(CO)_2^-$; $v = 200$ mV/s).

with the oxidation at -0.20 V, which is constant in size throughout the electrolysis. If the new compound were generated quantitatively, the two peaks would be roughly equal in size. From Figure 6, it can be seen that the new peak is only about 1/10 the size of the other. This suggests a low yield of the new product. We strongly suspect the main product of this reduction is pinacol dimer **9** ($R = (C_5H_4)W(CO)_3^-$).

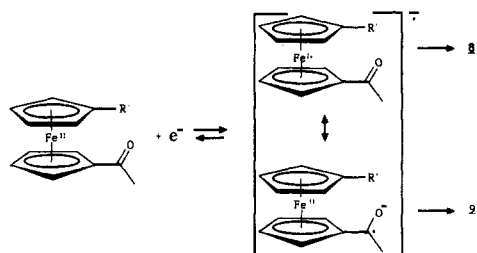
The reduced solution was worked up with excess I_2 in the expectation that (fulvalene)FeW(CO)₅I₂ would be isolated. Separation of the mixture on alumina gave a fast moving yellow band in toluene (similar R_f to (fulvalene)-Ru₂(CO)₄I₂). Unfortunately, evaporation of this band gave only a tan oil, which was not found to be analytically pure. However a sample of ((1'-acetylferrocene)Cp)W(CO)₃I was obtained in 15% yield by elution with CH₂Cl₂. This product may be formed by oxidation of the pinacol dimer **9** ($R' = C_5H_4W(CO)_3I$) by I_2 (eq 4) or by autoxidation.



Discussion

The synthesis of the fulvalene complexes from di-acetylbiferrocene is limited, due to the side reactions that form pinacols. In this study we report yields intermediate between El Murr et al. and Ibrasagic, who mention the formation of cyclopentadienides and pinacols, respectively, following the reduction of acetylferrocene. The yield of the decomplexed form is higher in the reduction of **4** than in the reduction of **6**; however, in neither case is the yield as high as was initially expected.

The electrochemical behavior of **4** and **6** is reasonable, based on their structures. The reactivity of acylated ferrocene anions can be thought of in terms of the following canonical structures:



The competition between the "Fe(1)" and "ketyl" forms has not been mentioned in previous discussions of the reduction of ferrocenes. To the extent the added electron is localized on the Fe atom (the LUMO of ferrocene is an antibonding Fe-ring orbital²³), decomplexation may occur.

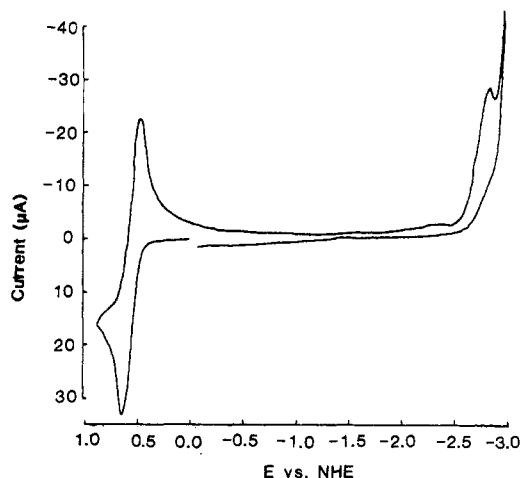
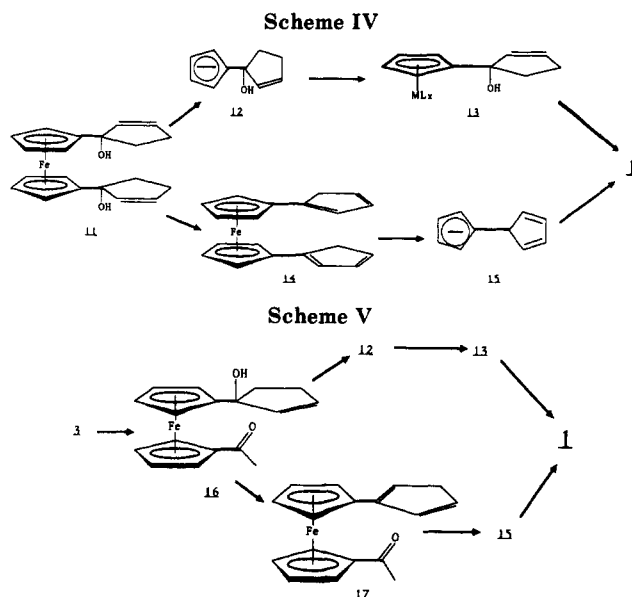


Figure 7. Cyclic voltammety of 13 mM **11** in THF/0.2M TBAPF₆ ($v = 200$ mV/s).



On the other hand, electron density on the carbonyl group (which must be significant, since the group has a pronounced effect on the reduction potential) increases the likelihood of pinacolization. Pinacols from other acylated analogues are well-characterized, although they have not been made by electrochemical methods.

The small value for the heterogeneous rate constant for the reduction of **4** can be attributed to either a small value of k^0 or to the effect of the following reactions on the peak potential, which decreases k_f^0 .^{21,24} The observed rates of the following reactions are not fast enough to perturb the reduction potential significantly, so we conclude k^0 for the reduction is small. This agrees with a previous study²⁵ of the reduction of ferrocene in DME at -45 °C, which gives large ΔE_p values for the couple $FC^{0/-}$, which were attributed to slow heterogeneous kinetics.

Other cyclopentyl-substituted ferrocenes may be considered as precursors to the fulvalene complexes. Of these, two were explored in detail (Schemes IV and V).

1,1'-Dilithioferrocene and 2-cyclopenten-1-one react to form the allylic alcohol **11**. **11** is reducible near the solvent limit (Figure 7), but the reduction does not lead to a new

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oxidation peak assignable to the cyclopentadienide, possibly because the solvent (THF) oxidizes the reduced ferrocene before it decomplexes. In contrast, 14 was expected to be more easily reducible, but the attempted dehydration of 11 (with heat, catalytic acid, or 2,4-dinitrobenzenesulfonyl chloride) in each case gave a mixture of products, none of which showed an NMR spectrum suggestive of the desired structure of 14.

The bromo ketal 3 was also tested as a precursor to a C₅-substituted ferrocene similar to 11 (Scheme V). The product would be more easily reduced, as it contains the acetyl group. However, reaction of the lithiated ketal²⁶ with 2-cyclopenten-1-one followed by hydrolysis gave only acetylferrocene, probably because the ketone acts as an acid.

Conclusions

In this paper we report electrochemical evidence for the formation of the new heterobimetallic complex 1 ($M = W(CO)_3^-$, $M' = Fe(CO)_2^-$) by reduction of 6. Decomplexation of the ferrocene unit in 6 occurs in low yield, and pinacol dimers are the major product of the reduction. The overall synthesis of 1 can be made easier (four steps) by using a more direct route to 4 starting with commercially available chloromercuriferrocene.^{16,19} One advantage of the method is that several of the intermediates are air-stable solids which allows relatively simple handling procedures.

The reaction conditions involved in the decomplexation reaction are relatively mild so that weakly coordinated or

unstable ligands could have been incorporated into the final product. A limitation of the method is that the metal to be attached first (i.e., in compound 6) must be stable to the reducing conditions required for the next step. We do not feel this is a restrictive limitation.

As described above, the yield of 1 prepared from 4 is limited by the side reactions to form pinacols. Although outside the scope of the present study, we feel that the use of a sterically demanding group such as *t*-Bu or Si(*t*-Bu)₃ attached to the ketone could be explored to block this side reaction. This would require the synthesis of the diacylated analogue of 4 for which the starting materials involved are less available. Cyano-based analogues of 4 might also be available in reasonable yield from bisferrocenyl and may behave more favorably.

If the radical anion of C₅-substituted ferrocenes can be made inert to side reactions, decoordination of the ferrocene unit may occur in reasonable yield. This would open a useful synthetic pathway to new heterobimetallic complexes containing the fulvalene molecule.

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Registry No. 2, 12088-99-2; 3, 111291-37-3; lithiated 3, 111291-42-0; debrominated 3, 42086-47-5; 4, 12203-92-8; 5, 111291-38-4; 6, 111291-39-5; H₂-9 (R = CH₃, R' = H), 55351-91-2; 11, 111291-41-9; W(CO)₃(PrCN)₃, 83732-34-7; (acetylCp)W(CO)₃CH₃, 73249-59-9; ((1'-acetylferrocenyl)Cp)W(CO)₃I, 111291-40-8; ethylene glycol, 107-21-1; ethylene dibromide, 106-93-4; acetylferrocene, 1271-55-2; 1,1'-dilithioferrocenebis(tetramethylethylenediamine), 65587-59-9; 2-cyclopenten-1-one, 930-30-3.

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Electrochemical Behavior of Thiolate-Bridged Manganese Dimers

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The oxidative behavior of thiolate-bridged manganese dimers having the general formulae Et₄N-[Mn₂(μ-SR)₃(CO)₆], Mn₂(μ-SR)₂L₂(CO)₆, and Mn₂(μ-SR)₂(μ-CO)L₂(CO)₄ where R = Me, *t*-Bu, or Ph and L = PMe₃, PPh₃, or CH₂[PPh₂]₂ (dppm) was studied. The ease of oxidation is dependent on the electron-donating ability of the R group in the thiolate bridge of the dimers. Oxidation of a recently characterized compound, Mn₂(μ-SMe)₂(μ-CO)(PMe₃)₂(CO)₄, occurs by an ECE (E = electrochemical step, C = chemical step) process. The character of the chemical step has been probed by cyclic voltammetry in solvents of varying donor ability and through ESR spectroscopy of the intermediate. The ECE mechanism has been confirmed quantitatively by digital simulation. An X-ray structure determination was carried out on Mn₂(μ-SMe)₂(μ-CO)(PMe₃)₂(CO)₄. Crystal data: monoclinic, space group P2₁/c; *a* = 9.753 (4), *b* = 14.872 (6), *c* = 16.052 (6) Å; β = 115.38 (2)°; *Z* = 4. The Mn-Mn distance is 2.581 Å, and the bridging carbonyl is symmetrically disposed with respect to the two manganese atoms.

Introduction

Studies on the oxidation and reduction chemistry of organometallic compounds have been greatly advanced by

the availability of information from electrochemical experiments. In the past few years, there has been extensive integration of chemical and electrochemical experiments using organometallic complexes. Such studies have produced, notably, information on the tendencies toward oxidation or reduction as a function of the type of com-

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