with the spectra of the authentic complexes independently prepared and characterized as described below.

Dihydridobis(acetone)bis(tris(p-fluorophenyl)phosphine)iridium(III) Hexafluoroantimonate. [Ir(cod)Cl]$_2$ (1.0 g, 1.5 mmol) and P(p-FC$_6$H$_4$)$_3$ (1.883 g, 5.95 mmol) were stirred with NaSbF$_6$ (1.6 g, 6.18 mmol) in MeOH (25 mL) for 24 h at room temperature. The solvent was then removed in vacuo, CH$_2$Cl$_2$ (30 mL) added, and the solution filtered to remove inorganic salts. The volume of the filtrate was reduced to 5 mL and Et$_2$O added to precipitate [Ir(cod)((p-FC$_6$H$_4$)$_3$P)$_2$]SbF$_6$ (3.02 g, 96%). ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.04–2.4, complex, cod CH$_2$; 4.40, c, cod CH; 7.2, c, ortho to P; 7.63, c, ortho to F. This complex was hydrogenated in 500-mg batches as follows. [Ir(cod)L$_2$]SbF$_6$ (500 mg, 0.43 mmol) in acetone (7 mL) was cooled to 0 °C and H$_2$ bubbled through the vigorously stirred solution for 20 min. The solvent was reduced to ca. 5 mL in vacuo, and Et$_2$O (70 mL) and pentane (20 mL) were added to precipitate the cream-colored title complex. Recrystallization from CH$_2$Cl$_2$ (5 mL)–Me$_2$CO (0.5 mL) under H$_2$ with Et$_2$O (3.0 mL)–pentanes (15 mL) gave colorless crystals (418 mg, 91%). Anal. Calcd for C$_{42}$H$_{38}$O$_2$P$_2$F$_{12}$IrSb: C, 42.8; H, 3.22. Found: C, 42.78; H, 3.05. ^{1}H NMR (CD$_2$Cl$_2$): δ –27.6, t (16), Ir–H; 1.86, s, Me$_2$CO; 7.28 and 7.61, c, Ar. The triphenylphosphine complex has been described and tri-p-tolylphosphine analogue was prepared in the same way as described above. L = (p-MeC$_6$H$_4$)$_3$: ^{1}H NMR (in (CD$_3$)$_2$CO except for the coordinated Me$_2$CO resonance, which appears only in CD$_2$Cl$_2$) δ –27.9, t (16), Ir–H; 1.78, s, Me$_2$CO; 2.39, s, MeAr; 7.29–7.35, c, Ar. Anal. Calcd for C$_{48}$H$_{56}$P$_2$O$_2$IrF$_6$Sb: C, 49.94; H, 4.85. Found: C, 50.20; H, 4.80.

Hydrido(alkylcyclopentadienyl)bis(triphenylphosphine)iridium(III) Hexafluoroantimonate. [IrH$_2$(acetone)(PPh$_3$)$_2$]SbF$_6$ (100 mg, 0.0934 mmol) was refluxed with the 1-alkylcyclopentene (or 3-alkylcyclopentene) (1 mL; R = Me or Et) in 1,2-C$_2$H$_4$Cl$_2$ (10 mL) for 6 h. The solution was cooled, the solvents were removed in vacuo, and the products were recrystallized from CH$_2$Cl$_2$–Et$_2$O (R = Me, 82 mg, 85%; R = Et, 76 mg, 78%). A mixture of isomers of alkylcyclopentadienes gave the same products after only 30 min at 40 °C in CH$_2$Cl$_2$ (yield

95–97%). Anal. Calcd for C$_{42}$H$_{38}$P$_2$F$_6$SbIr: C, 48.86; H, 3.68. Found: C, 48.74; H, 3.75. Calcd for C$_{43}$H$_{40}$P$_2$F$_6$SbIr: C, 49.35; H, 3.82. Found: C, 49.09; H, 3.94. ^{1}H NMR (R = Me): δ –14.66, t (28), Ir–H; 1.86, s, Me; 5.11, 5.32, br, CH. ^{1}H NMR (R = Et): δ –14.56, t (28), Ir–H; 1.19, t (7), Me; 2.23, q (7), CH$_2$; 4.44 and 5.24, br, CH. The tris(p-fluorophenyl)phosphine complexes were prepared in the same way (yield 80%).[10]

(η⁶-Benzene)bis(tris(p-fluorophenyl)phosphine)iridium-(I) hexafluoroantimonate was prepared by the method described in ref 10, for [(C$_6$H$_6$)Ir(PPh$_3$)$_2$]SbF$_6$, but with tris(p-fluorophenyl)phosphine; yield 80%. ^{1}H NMR (CD$_2$Cl$_2$): δ 6.1, s, C$_6$H$_6$; 7.2–7.6, c, PAr$_3$. The toluene complex was made in the same way (yield 75%). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.6, d (4), 1- and 5-H; 5.8, t (6), 2- and 4-H; 2.4, s, Me; 7.2–7.6, c, PAr$_3$.

Electrochemical and Chemical Generation of Novel Dianions from (η⁶:η⁶-Conjugated arene)bis(tricarbonylchromium) Complexes. Isolation and Spectroscopic Evidence for (η⁵:η⁵-Biphenyl)bis(tricarbonylchromium) Dianion

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Received August 5, 1986

Bis(tricarbonylchromium) complexes of arene compounds with two conjugated phenyl rings reduce electrochemically or chemically in a two-electron process to yield very stable dianions. The reduction process is proposed to proceed via an ECE mechanism generating a bis(η⁵-cyclohexadienyl)bis(tricarbonylchromium) complex. Infrared spectroscopy, ^{1}H NMR, and ^{13}C NMR data support the proposed structure for the dianion produced from (η⁶:η⁶-biphenyl)bis(tricarbonylchromium). The electrochemical properties of the bis(tricarbonylchromium) complex of bimesityl provides an explanation for electrochemical reductive properties of all (η⁶-benzene)tricarbonylchromium complexes. Finally, the oxidative electrochemical properties of the mono and bis complexes are discussed.

Introduction

Since Dessy's original report on some of the redox properties of (η⁶-benzene)tricarbonylchromium[2,3] our group[4–9] and others[10–15] have been interested in the electrochemical properties of this important class of compounds. Dessy's report on (η⁶-benzene)tricarbonyl-

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chromium[2,3] and more extensive studies on a wide variety of substituted (η^6-benzene)tricarbonylchromium complexes[7] clearly showed they all exhibited the same general type of reductive electrochemistry. The reductions generated dianions that were highly reactive on the cyclic voltammetric time scale. In contrast, (η^6-naphthalene)-tricarbonylchromium[7,8,16] yielded a stable dianion on reduction. All of these complexes were characterized as having reductions that involved two electrons per Cr(CO)$_3$ group. Recently, we reported that electrochemical reduction of (η^6:η^6-conjugated arene)bis(tricarbonyl-chromium) complexes yielded a new class of stable dianions.[6] This class of bis complexes is reduced with one electron per Cr(CO)$_3$ group in contrast to the benzene or naphthalene complexes. We proposed[6] an ECE reduction process to yield a bis(η^5-cyclohexadienyl)bis(tricarbonyl-chromium) complex. This paper expands on our studies of this new class of dianions. Redox properties of compounds 1–10 will be presented. In a recent report, the
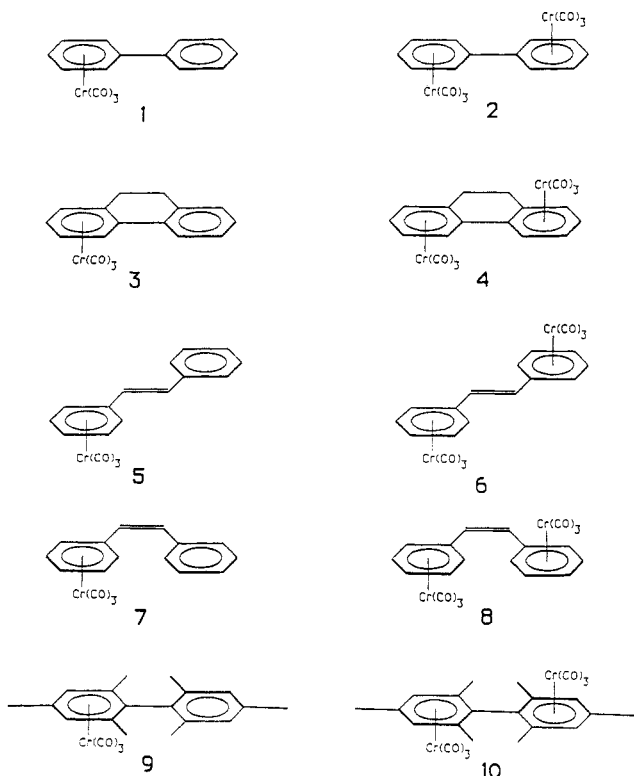
oxidative characteristics of dimethylbis[(η^6-arene)tri-carbonylchromium] E, where E is C, Si, Ge, Sn, or Pb, were reported.[4,5] Oxidation of these complexes occurs by one electron per chromium atom to form persistent cations, and the redox centers are noninteracting according to the Bard–Anson–Saveant Model.[17] This paper will also con-
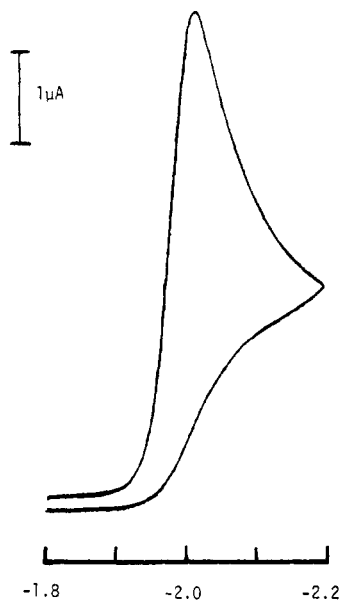
Figure 1. A cyclic voltammogram of (η^6-9,10-dihydro-phenanthrene)tricarbonylchromium in THF (0.2 M TBAP, 25 °C, 200 mV/s, HMDE).

trast the oxidative properties of compounds 1–10 to those of the dimethylbis[(η^6-arene)tricarbonylchromium]tin complexes.

Infrared, ^{1}H NMR, and ^{13}C NMR studies of the dianion formed by reduction of **10** provide strong evidence for the proposed bis(η^5-cyclohexadienyl)bis(tricarbonylchromium) complex **11**. Finally the results of this study offer a possible explanation for the high reactivity of the electrochemically generated dianions of (η^6-benzene)tri-carbonylchromium complexes.

Results and Discussion

Compounds 1–8 represent molecules that have little restriction to coplanarity and thus may obtain good overlap of the conjugated phenyl rings. Compounds **9** and **10**, on the other hand, represent molecules in which there is a severe restriction to conjugation between the phenyl rings because of the steric interaction of the ortho methyl groups. The mono complexes 1, 3, 5, and 7 exhibit reductive characteristics that are analogous to the substituted (η^6-benzene)tricarbonylchromium complexes. They generally reduce at about the same potential as (η^6-benzene)tricarbonylchromium with some allowance for extra conjugation. The reductions are characterized by two electrons per Cr(CO)$_3$ group, and the reduction products are quite reactive, also similar to the substituted (η^6-benzene)tricarbonylchromium complexes. The cyclic voltammograms are irreversible until scan rates in excess of 1 V/s, at which a very small anodic peak begins to appear. A typical cyclic voltammogram of the mono complex **3** is shown in Figure 1. The redox properties of the bis(tricarbonylchromium) complexes **2, 4, 6**, and **8** stand in marked contrast to their mono complex counterparts. Each of the bis complexes is reduced approximately 300 mV positive of its corresponding mono complex (see Table I). This significant decrease in reduction potential suggests coupling between the tricarbonylchromium moieties in the same way that extended conjugation in an organic molecule generally lowers the reduction potential. Significantly, the bis complexes reduce in a reversible two-electron wave, or one electron per tricarbonylchromium group (see Figure 2 for a typical cyclic voltammogram, that of bis complex **4**). The value of $E_{3/4} - E_{1/4}$ was in each case approximately 30 mV (see Table I). The two-electron

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Table I. Electrochemical Results

compd no.	compd[a]	$E_{1/2}$,[b] V	$E_{3/4} - E_{1/4}$,[c] mV	i_d, A
1	(η^6-biphenyl)Cr(CO)$_3$	−1.948	40	2.72
2	(η^6:η^6-biphenyl)[Cr(CO)$_3$]$_2$	−1.606	30	2.68
3	(η^6-9,10-dihydrophenanthrene)Cr(CO)$_3$	−1.982	33	2.52
4	(η^6:η^6-9,10-dihydrophenanthrene)[Cr(CO)$_3$]$_2$	−1.663	31	2.76
5	(η^6-*trans*-stilbene)Cr(CO)$_3$	−1.656	37	1.83
6	(η^6:η^6-*trans*-stilbene)[Cr(CO)$_3$]$_2$	−1.385	26	2.82
7	(η^6-*cis*-stilbene)Cr(CO)$_3$	−1.673	24	2.48
8	(η^6:η^6-*cis*-stilbene)[Cr(CO)$_3$]$_2$	−1.395	17[d]	2.78
9	(η^6-bimesityl)Cr(CO)$_3$	−2.228	45	3.21
10	(η^6:η^6-bimesityl)[Cr(CO)$_3$]$_2$	−2.039	31	2.70

[a] Approximately 1 mM in THF, 0.2 M TBAP, 0 °C, on the DME. [b] Vs. the Ag/AgCl, saturated NaCl(aq) reference electrode, ±0.005 V. [c] Values for $E_{3/4} - E_{1/4}$ on the order of 30 mV are indicative of a two-electron process. Coulometric experiments on the bis complexes also indicate two electrons. The reasons for the somewhat small values of $E_{3/4} - E_{1/4}$ measured for compounds 6–8 are unknown at this time. There may be slight adsorption on the DME causing the waves to be sharper than expected. [d] The slope of the log plot is 23 mV.
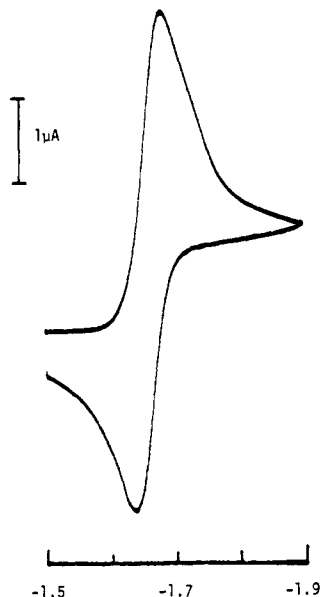

Figure 2. A cyclic voltammogram of (η^6:η^6-9,10-dihydrophenanthrene)bis(tricarbonylchromium) in THF (0.2 M TBAP, 0 °C, 50 mV/s, HMDE).

nature of the cathodic wave was further demonstrated by coulometric studies. Additional evidence of the conjugative interaction of the two complexed phenyl rings comes from a comparison of the reductive electrochemistry of dimethylbis[(η^6-phenyl)tricarbonylchromium]tin. This complex has two isolated complexed rings, reduces at the same potential as (η^6-benzene)tricarbonylchromium, and is totally irreversible even at scan rates of several volts per second.

The conjugative interaction of the two complexed phenyl rings not only results in a lower reduction potential but significantly increases the half-life of the resulting dianions. An anodic to cathodic current ratio of unity in the cyclic voltammograms is observed for the bis complexes even with scan rates as low as 20 mV/s (see Figure 2). They also appear to have half-lives on the order of several hours when bulk coulometric studies are performed. Bulk reduction followed by bulk oxidation regenerates the starting bis complex in high yields.

Polarographic, voltammetric, and coulometric studies all indicate that the reduction process for bis complexes of arene ligands with conjugated phenyl rings involves a total of two electrons.[18] This one electron per tricarbonylchromium group distinguishes this class of compounds from the benzene and naphthalene complexes.

Due to the long lifetimes of the dianions, carbonyl IR stretching frequencies were easily obtained. The two sharp bands noted for (η^6:η^6-biphenyl)bis(tricarbonylchromium) at 1963 and 1899 cm^{-1} disappeared upon exhaustive reduction, and new bands appeared at 1881, 1788, and 1765 cm^{-1}. The shift in carbonyl stretching frequencies to lower wavenumbers is consistant with a more negatively charged ligand being attached to the Cr(CO)$_3$ group. The increase in IR-active carbonyl bands from two to three suggests a lowering of symmetry at the chromium atom and is consistent with the proposed η^6 to η^5 rearrangement.

The possibility of metal–metal interaction upon reduction is a question that must be addressed. To that end, the mono- and bis(tricarbonylchromium) complexes of 9,10-dihydrophenanthrene (3 and 4) were obtained. The ethane bridge in (η^6:η^6-9,10-dihydrophenanthrene)bis(tricarbonylchromium) prevents rotation around the coannular bond between the rings. A crystal structure of 2 has revealed[19,20] the two rings to be coplaner and the tricarbonylchromium moieties to be trans to each other. It is reasonable to assume that in 4 the two tricarbonylchromium groups are also trans to each other and thus are incapable of interacting directly. As the electrochemical properties of 2 and 4 are identical, except for a slight shift of reduction potentials (less than 60 mV), it can be reasonably assumed that twisting of the phenyl rings and some sort of metal–metal interaction can by ruled out as the reason for the high stability of the dianions of 2 and 4. This view is further supported by the redox properties of 6 in which the two Cr(CO)$_3$ units are clearly too far apart to propose any metal–metal interaction.

The reversible two-electron reductions of the bis complexes are proposed to involved an ECE mechanism, shown in Scheme I. Initial electron transfer is followed by the chemical step that involves the change in bonding of the arene rings from η^6 to η^5. Transfer of a second electron leaves each Cr(CO)$_3$ group bound to a η^5-hexadienyl anion.

The proposed η^5 bonding of a cyclohexadienyl ring to the Cr(CO)$_3$ group is well-known. Recent studies have proposed a similar structure in the protonation of the dianion of (η^6-naphthalene)tricarbonylchromium.[8] Semmelhack and co-workers[21,22] have proven the structure of (η^5-cyclohexadienyl)tricarbonylchromium in work on nucleophillic substitution of (η^6-benzene)tricarbonylchromium. An analogous structure has been postulated

(18) Polarographic and voltammetric experiments were performed by using iR feedback compensation.

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Table II. Spectroscopic Data for Isoelectronic (η^5-Cyclohexadienyl)tricarbonylmetal Complexes 11,[a]
(η^5-Naphthalene)tricarbonylchromium Anion,[b] (η^5-Cyclohexadienyl)tricarbonylmanganese,[c]
[η^5-2-(Trimethylsilyl)-1,3-cyclohexadienyl]tricarbonyliron Cation,[d] and
[η^5-6-(Bis(phenylthio)methyl)cyclohexadienyl]tricarbonylchromium Anion[e]

compd	ν_{CO}, cm^{-1}	^{1}H NMR shifts for η^5-cyclo-hexadienyl ring, ppm			^{13}C NMR shifts for η^5-cyclohexadienyl ring, ppm ($^1J_{CH}$, Hz)			
		H$_2$	H$_3$	H$_4$	C$_1$	C$_2$	C$_3$	C$_4$
(naphthalene bis-Cr(CO)$_3$ complex)	1828, 1805, 1730	2.88	4.29	4.67	102.17 (s)	67.19 (d, 154)	98.02 (d, 158)	69.58 (d, 167)
(Cr(CO)$_3$ complex)	1895, 1800, 1745	2.37	4.57	5.42	32.0 (dd, 118–128)	44.8 (d, 162)	97.8 (d, 168)	
(Mn(CO)$_3$ complex)	2020, 1942	2.35	4.16	5.20	24.2 (dd, 135)	50.1 (d, 168)	98.0 (d, 168)	79.7 (d, 177)
(Me$_3$Si Fe(CO)$_3$ cation)	2100, 2050	4.17	5.45		23.93	68.36	104.71	98.87
(CH(SPH)$_2$ Cr(CO)$_3$ complex)	1901, 1802, 1712	2.80	4.41	4.92				

[a] See Experimental Section for conditions and full spectra. [b] Reference 8. [c] Reference 24. [d] Reference 23. [e] Reference 20.

by Weber and Weivers[23] for substituted (η^5-thiacyclohex-adienyl 1-oxide)tricarbonylchromium. Other isoelectronic (η^5-cyclohexadienyl)tricarbonylmetal compounds of iron[24] and manganese[25] are well-characterized.

In order to gain additional definitive information on 11, ^{1}H and ^{13}C NMR studies were carried out on the dianion. As relatively large quantities of 11 were required for the studies, conditions to generate 11 by chemical reduction were determined. Reduction of 2 with 2 mol of lithium anthracenide in THF yielded a brown powdery precipitate that was found to be pyrophric in the solid state. Spectroscopic evidence led to the identification of the brown solid as the dilithium salt of 11, coordinated by four molecules of THF. The four molecules of THF per molecule of 11 were confirmed by ^{1}H NMR integration as well as GLC analysis of THF released upon decomposition of the dilithium salt.

Infrared spectroscopy, ^{1}H NMR, and ^{13}C NMR studies of the dianion formed by reduction of 2 provide strong support for the proposed (η^5:η^5-biphenyl)bis(tricarbonyl-chromium) complex, 11.[26] Table II gives a summary of

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(26) Elemental analysis of samples of (η^5:η^5-biphenyl)bis(tricarbonyl-chromium) have not been satisfactory. Semmelhack et al.[21] and Rieke and Henry[8] have also reported difficulty in obtaining good elemental analysis for (η^5-cyclohexadienyl)tricarbonylchromium anions.

Scheme I
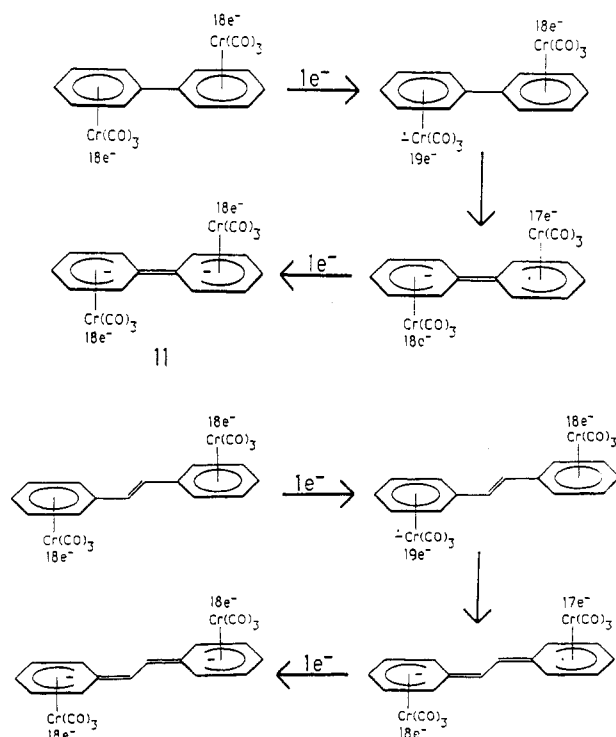
^{1}H and ^{13}C NMR data along with the IR carbonyl stretching frequencies for 11 and several other η^5-hexa-

Scheme II
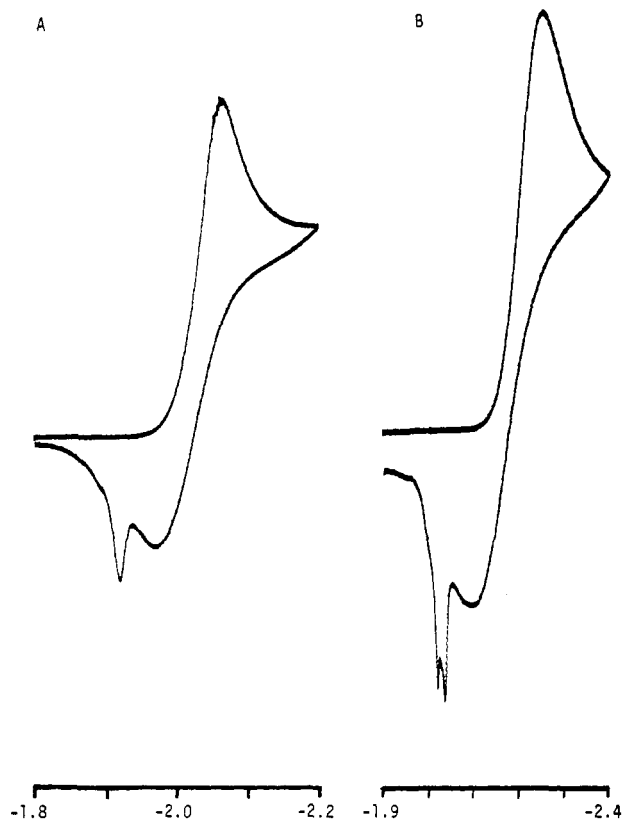
Figure 3. (A) Cyclic voltammogram of (η^6:η^6-bimesityl)bis(tricarbonylchromium) (1 mM in THF, 0 °C, 0.2 M TBAP, 20 mV/s, HMDE). (B) Cyclic voltammogram of (η^6-bimesityl)tricarbonylchromium (1 mM in THF, 0 °C; 0.2 M TBAP, 50 mV/s, HMDE).

dienyl species. The characteristic pattern of chemical shifts for the ^{1}H NMR spectra is very similar to the other η^5-hexadienyl species with the protons on carbons 2 being shifted markedly upfield compared to the others. The ^{13}C NMR chemical shifts of carbons 2, 3, and 4 as well as the one bond C–H coupling constants also match well with the known structures. Three-bond C–H coupling constants are observable and are quite useful in verifying the ^{13}C assignments.[27,28] One carbonyl signal is observed in the ^{13}C NMR spectra of the dianion approximately 9 ppm downfield from the carbonyl signal of the neutral bis complex of biphenyl.

In order to further demonstrate the importance of overlap between the arene rings in the reduction mechanism, we synthesized the mono- and bis(tricarbonylchromium) complexes of bimesityl (2,2',4,4',6,6'-hexamethylbiphenyl), compounds **9** and **10**, respectively. Because of the steric interactions of the ortho methyl groups, coplanarity of the rings and overlap along the coannular bond will be greatly reduced.[29]
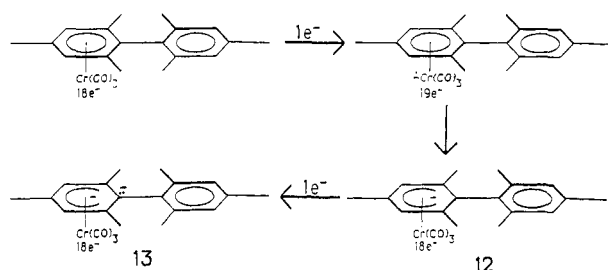
With regard to reduction potential, the mono- and bis(tricarbonylchromium) complexes of bimesityl fit the pattern of the other conjugated diphenyl complexes. The reduction potential of the bis complex of bimesityl is nearly 200 mV positive of the mono complex, similar to the other bis complexes in Table I. In both complexes of bimesityl,

the reduction potential is considerably negative of the other diphenyl complexes. In fact, the reduction potential of (η^6:η^6-bimesityl)bis(tricarbonylchromium) is slightly negative of the reduction potential of (η^6-biphenyl)tricarbonylchromium. The most obvious reasons for the more negative reduction potentials are the electron donation of the methyl groups themselves[30] and the fact that the nearly orthogonal orientation of the arene rings prevents much of the extended conjugation allowed in the other systems.

Features of the electrochemical reduction of (η^6:η^6-bimesityl)bis(tricarbonylchromium) such as $E_{3/4} - E_{1/4}$, indicate a two-electron reduction similar to the other bis complexes. In addition, cyclic voltammetric experiments demonstrate the resulting dianion to be persistent on that time scale (see Figure 3A). However, there is a large separation between cathodic and anodic peaks. The dependence of this separation upon scan rate suggests considerable bond reorganization is taking place during reduction. This reorganization could well involve a change in bonding of the $Cr(CO)_3$ groups as well as a twisting of the two benzene rings that try to become coplaner.

Coulometric examinations also indicate a two-electron reduction but point out the fact that the dianion of (η^6:η^6-bimesityl)bis(tricarbonylchromium) is much less persistent than the dianions of the other bis complexes in Table I. A significant amount of the mono complex is observed in polarograms following reoxidation with a corresponding loss of the bis complex. The reduced persistence of this dianion in comparison with the others further supports the importance of coplanarity in the stability of the dianions formed from the bis complexes.

The electrochemical behavior of (η^6-bimesityl)tricarbonylchromium, **9**, reveals it to be unique among the mono $Cr(CO)_3$ complexes. This complex is similar to the other mono complexes in that it is more difficult to reduce than its corresponding bis complex. (η^6-Bimesityl)tricarbonylchromium differs from the other mono complexes in that it alone exhibits a reoxidation peak of the reduced species in cyclic voltammetry (see Figure 3B). Like the corresponding bis complex, the E_p for (η^6-bimesityl)tricarbonylchromium is quite large, suggesting significant bond reorganization occurs during reduction.

The mechanism proposed for the two-electron reduction of (η^6-bimesityl)tricarbonylchromium is similar to the ECE process suggested for the conjugated arene bis(tricarbonylchromium) complexes. Upon addition of the first electron, the $Cr(CO)_3$ group rearranges from η^6 to η^5 bonding yielding the radical ion **12** that now may add a second electron to produce the dianion **13** (Scheme II). The unusual stability of **13** compared to dianions of other

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(30) A similar shift to more negative potentials with more methyl groups is observed in the series (η^6-benzene)tricarbonylchromium ($E_{1/2}$ = -2.159 V), (η^6-toluene)tricarbonylchromium ($E_{1/2}$ = -2.195 V), and (η^6-mesitylene)tricarbonylchromium ($E_{1/2}$ = -2.317 V); all in propylene carbonate, reference Ag/AgCl, saturated NaCl(aq). Milligan, S. N.; Rieke, R. D., unpublished results.
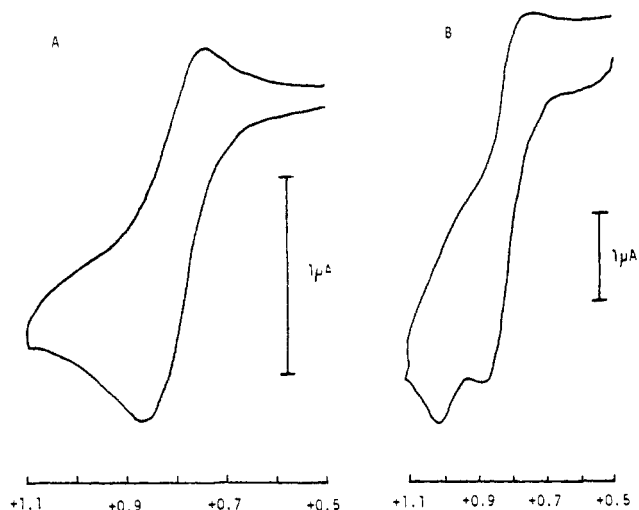
Figure 4. (A) Cyclic voltammogram of dimethylbis(η^6-phenyltricarbonylchromium)tin (1 mM, propylene carbonate, 0.25 M TEAP, 0 °C, 50 mV/s, Pt disk). (B) Cyclic voltammogram of (η^6:η^6-biphenyl)bis(tricarbonylchromium) (1 mM, propylene carbonate, 0.25 M TEAP, 0 °C, 500 mV/s, Pt disk).

mono complexes is most likely due to steric bulk protecting the phenyl anion type species from attack. The expected highly reactive carbon 1 of **13** is protected by a cage of four methyl groups.

The results of this study provide a likely explanation for the reductive electrochemical properties of all (η^6-benzene)tricarbonylchromium complexes. The observed two-electron reductions would presumably occur via a similar ECE process, yielding a dianion similar to **13** but not as sterically protected. Reaction of this dianion with solvent, electrolyte, or spurious water would explain the high degree of chemical irreversibility of these dianions. The reaction of a phenyl anion type of species like **13**, but unprotected by steric bulk, with a proton source is expected to be rapid for several reasons. Not only does it have a high degree of anion character at carbon one, but also upon protonation it would yield a relatively stable (η^5-hexadienyl)tricarbonylchromium species. Studies are underway to verify these proposals for the (η^6-benzene)-tricarbonylchromium complexes.

Oxidation Studies

The oxidative characteristics of the series of conjugated diphenyl complexes **1–10** were also studied. These complexes have oxidation processes distinctively different from the bis complexes of dimethyldiaryltin. Reference to Figure 4 shows clearly the differences in the cyclic voltammetric behavior of the conjugated systems compared to those having a dimethyltin moiety separating the rings. Two peaks are seen in the oxidative cyclic voltammogram of **2**. The second process is rather dependent on scan rate, merging with the first peak at slow scan rates (20 mV/s) but having a separation between the two processes at higher scan rates (greater than 50 mV/s) of about 100 mV. At the slow scan rates, the current function for the first peak begins to drop and approach the one-electron limit. Although the close proximity of the two oxidative processes makes the current function of the second peak somewhat speculative, it would appear that the sum total of both processes involves two electrons. Thus, it appears that the oxidation processes at all scan rates total two electrons. It should be pointed out that the mono complexes do not exhibit this oddity. Instead, the mono complexes oxidize with only one peak on the cyclic voltammogram whose current function is a one electron value.

Secondly, the biphenyl and 9,10-dihydrophenanthrene bis complexes do not fit the Bard–Anson–Saveant model.[17] Calculations for n_{bis} are quite poor.

Finally, the cations produced from the conjugated diaryl bis complexes exhibit less chemical reversibility in comparison to the dimethyldiphenyltin bis complex. Even at 0 °C and fast scan rates (500 mV/s) the oxidation processes exhibit only an extremely small cathodic peak on the return scan. The close proximity of the waves make it unclear as to whether both waves have a coupled reduction or if only the first oxidation is chemically reversible. Regardless of the number of couples that show chemical reversibility at high scan rates, the fact remains that the persistence is much lower in these directly conjugating systems than those with an intervening group between phenyl rings. In contrast, the mono complexes **1**, **3**, **5**, **7**, and **9** show chemical reversibility much like the dimethyldiaryltin and other substituted benzene complexes.

These three major differences in the electrochemical behavior of these respective complexes point to conjugative interaction between the phenyltricarbonylchromium moieties in complexes **2**, **4**, **6**, **8**, and **10**. The very observation of two oxidation processes, each of one electron, being separated by only 100 mV would support the conclusion that some conjugative interaction is occurring between the separate phenyltricarbonylchromium portions.[31,32] This interaction is also reflected in the poor results of the n_{bis} calculations from the Bard–Anson–Saveant model.

Thus, despite the opportunity for orbital overlap and interaction, the cations of the bis complexes are much less persistent than those of the dimethylbis[(η^6-arene)tricarbonylchromium]tin complexes as judged by cyclic voltammetry.

Conclusions

The redox properties of the mono- and bis(tricarbonylchromium) complexes of conjugated diphenyl compounds are reported. The bis complexes are found to reduce in a reversible two-electron process, one electron per $Cr(CO)_3$ group, to yield stable dianions with half-lives of an hour or more at ambient temperatures. These conjugated bis complexes are in unique contrast to all benzene and naphthalene complexes that reduce via two electrons per $Cr(CO)_3$ group. The mono complexes of the conjugated diphenyl compounds are reduced via a highly irreversible two-electron process similar to all (η^6-benzene)tricarbonylchromium complexes.

The two-electron reduction mechanism of the bis complexes is proposed to involve an ECE mechanism in which the chemical step involves a change in bonding between the arene and $Cr(CO)_3$ groups from η^6 to η^5. The resulting conjugated bis(η^5-cyclohexadienyl)bis(tricarbonylchromium) dianions are quite stable. NMR studies on the dianion are consistent with the proposed structure.

When the conjugative interaction between the two (η^6-arene)tricarbonylchromium moieties is reduced, such as by forcing the two benzene rings to be nearly orthogonal (as is the case in the (η^6:η^6-bimesityl)bis(tricarbonylchromium) complex), new electrochemical properties result. The bis complex of bimesityl still reduces in a reversible two-electron process. However, the reduction potential is now much more cathodic, and the resulting dianion is much less stable. Of greater interest is (η^6-bimesityl)tri-

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carbonylchromium that also reduces in a two-electron process. This dianion, however, is quite stable on the cyclic voltammetric time scale. Steric bulk of the methyl groups is suggested as the major force in stabilizing this dianion. Results of this study are used to rationalize the reductive electrochemical behavior of all (η^6-benzene)tricarbonyl-chromium complexes. Finally, the oxidative electrochemical properties of the mono and bis complexes of the conjugated diphenyl molecules are presented.

Experimental Section

All manipulations of air-sensitive materials were conducted in a VAC argon drybox or under argon in Schlenk apparatus connected to a double manifold providing vacuum and dry argon. THF was freshly distilled from Na/K alloy under argon. DMF-d_7 was dried over activated Al_2O_3 and stored in the drybox. Electrochemical equipment and techniques have been described in detail elsewhere.[5] ^{1}H NMR and ^{13}C NMR spectra were obtained on either a Varian EM-390 or a Varian XL-300 superconducting NMR spectrometer and referenced to either Me$_4$Si or the deuteriated solvent as appropriate. Infrared spectra were obtained on a Perkin-Elmer 283 IR spectrophotometer by dissolving the sample in THF, cannulating it into NaCl IR solution cells capped with septa that were previously flushed with argon, and then quickly scanning the 2000–1600 cm^{-1} region. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. GLC was performed on a Hewlett-Packard 5890A gas chromatograph (interfaced with a Perkin-Elmer LC-100 integrator) equipped with a 5.5 ft × $^1/_8$ in. column of SP 2100 column packing on Supelco support. Elemental analyses were performed by Galbraith Labs, Knoxville, TN. High-resolution mass spectra were obtained from the Midwest Regional Center for Mass Spectrometry, University of Nebraska—Lincoln.

Syntheses. The mono- and bis(tricarbonylchromium) complexes of biphenyl and 9,10-dihydrophenanthrene (compounds 1–4) were prepared by standard methods and described in detail elsewhere.[5] The mono- and bis(tricarbonylchromium) complexes of *cis*- and *trans*-stilbene (compounds 5–8) were supplied by Dr. Bennett R. Willeford of Bucknell University. The preparation of dimethylbis((η^6-arene)tricarbonylchromium)tin and related complexes has also been described.[5]

(η^6-Bimesityl)tricarbonylchromium (9). Bimesityl was prepared from mesitylene via a standard method[33] and recrystallized from ethanol before use. Bimesityl (0.498 g, 2.09 mmol) and (η^6-benzene)tricarbonylchromium[34] (1.816 g, 8.48 mmol) were placed in a 100-mL Schlenk tube. The tube was evacuated, refilled five times with argon, and heated to 160 °C for 16 h in a hot-melt reaction similar to that reported for the complexation of biphenyl.[19] The melt was allowed to cool, and the solids were broken up with a glass rod. Unreacted bimesityl and (η^6-benzene)tricarbonylchromium were removed from the mixture by insertion of a cold finger and sublimation at 70 °C (0.02 torr) for 3 days. (η^6-Bimesityl)tricarbonylchromium was then separated from the reaction mixture in 30% yield (0.233 g, 0.622 mmol) by sublimation

at 100 °C (0.02 torr) for 2 days. Recrystallization from hexanes gave bright yellow crystals of excellent purity: mp 155–157 °C; IR (THF) 1956, 1880 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) δ 6.97 (sb, 1 H), 6.91 (s, 1 H), 5.19 (s, 2 H), 2.61 (s, 3 H), 1.82 (s, 6 H), 1.77 (s, 3 H); mass spectrum calcd for C$_{21}$H$_{22}$O$_3$Cr 374.0974, found 374.0977. Anal. Calcd for C$_{21}$H$_{22}$O$_3$Cr: C, 67.37; H, 5.92; Cr, 13.89; O, 12.82. Found: C, 67.16; H, 5.79; Cr, 14.06; O (by difference), 12.99.

(η^6:η^6-Bimesityl)bis(tricarbonylchromium) (10). The unsublimed material remaining from the above preparation of (η^6-bimesityl)tricarbonylchromium above gives (η^6:η^6-bimesityl)bis(tricarbonylchromium) in crude yield of 40% (0.415 g, 0.813 mmol). (η^6:η^6-Bimesityl)bis(tricarbonylchromium) was further purified by filtration and recrystallization from a 1:1 mixture of heptane and acetone by using standard Schlenkware techniques to give bright orange crystals: mp 248 °C dec; IR (THF) 1970, 1958, 1889 cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$) 5.33 (m, 2 H), 5.27 (m, 2 H), 2.47 (s, 6 H), 2.29 (s, 6 H), 1.81 (s, 6 H); mass spectrum calcd for C$_{24}$H$_{22}$O$_6$Cr$_2$ 510.0226, found 510.0211. Anal. Calcd for C$_{24}$H$_{22}$O$_6$Cr$_2$: C, 56.48; H, 4.34; Cr, 20.37; O, 18.81. Found: C, 56.27; H, 4.26; Cr, 20.58; O (by difference), 18.89.

(η^5:η^5-Biphenyl)bis(tricarbonylchromium) Dianion (11). Standard methods were used to prepare (η^6:η^6-biphenyl)bis(tricarbonylchromium) in gram quantities.[35] (η^6:η^6-Biphenyl)bis(tricarbonylchromium) (2.91 g, 6.88 mmol) was dissolved in 40 mL of THF by using standard Schlenkware techniques. Lithium anthracenide (2 equiv) were formed by stirring anthracene (2.85 g, 16.0 mmol) with lithium metal (0.105 g, 15.1 mmol) in 40 mL of THF for 3 h. The dark blue lithium anthracenide solution was then cannulated into the solution containing the (η^6:η^6-biphenyl)bis(tricarbonylchromium) and stirred for 15 min. A fine dark brown powder, which precipitated as the mixture was stirred, was filtered off on a medium Schlenkware frit, washed with three 20-mL portions of THF, and blown dry by passing argon over the solid overnight. The apparatus was removed to a VAC argon drybox where the brown solid (3.55 g, 4.60 mmol, 68% yield for C$_{34}$H$_{42}$O$_{10}$Cr$_2$Li$_2$) was removed from the frit and stored in a ground glass stoppered Erlenmeyer flask for future use. The dianion was decomposed to biphenyl and THF for quantitative GLC studies by adding I$_2$ in glyme at −78 °C. Note: Thin residual films of the brown dianion solid coating the apparatus instantly turn bright yellow upon exposure to air. Small solid samples removed from the drybox and exposed to air have been found to smoulder and burst into flame: IR (THF) 1828, 1805, 1730 cm^{-1} (lithium counterion, lithium anthracenide prep); IR (THF) 1881, 1788, 1765 cm^{-1} (tetrabutylammonium counterion, electrochemical prep); ^{1}H NMR (DMF-d_7) δ 4.67 (t, 2 H, J_{HH} = 5.2 Hz), 4.30 (dd, 4 H, J_{HH} = 7.0 and 5.5 Hz), 3.61 (m, 16 H, THF), 2.88 (d, 4 H, J_{HH} = 7.0 Hz), 1.77 (m, 16 H, THF); ^{13}C NMR (DMF-d_7) 242.96 (s), 102.17 (s), 98.02 (dd, $^1J_{CH}$ = 158.9 Hz, $^3J_{CH}$ = 7.3 Hz), 69.58 (dt, $^1J_{CH}$ = 167.9 Hz, $^3J_{CH}$ = 6.8 Hz), 69.19 (dt, $^1J_{CH}$ = 157.9 Hz, $^3J_{CH}$ = 5.3 Hz).

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