oxygen atoms may also assist P–O bond rupture as a leaving group effect. For E. coli alkaline phosphatase therefore it is conceivable that two Zn^{2+} ions are bound to the phopshate ester and/or to the intermediate phosphorylated enzyme in order to assist their hydrolysis.

Acknowledgment. We are grateful to K. Barrow and G. Grossman of the Biochemistry Department, University of New South Wales, D. Fenn, and M. Whittaker of A.N.U. for their assistance with ^{31}P spectroscopy and to the Microanalytical Unit A.N.U. for analyses and molecular weight determinations.

Decomposition and Ligand Substitution Reaction Mechanisms for Organometallic Radicals

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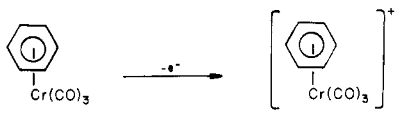
Abstract: The electrochemical oxidation of a series of (arene)chromium and (arene)tungsten tricarbonyl complexes has been examined. Studies regarding the oxidatively promoted decomposition of the chromium complexes are reported. Extension of these studies to the tungsten analogues has lead to the observation of metal coordination sphere expansion upon one-electron oxidation, an observation of fundamental significance with regards to recent reports of dramatic reaction rate enhancements in odd-electron organometallic systems. The relationship of coordination sphere expansion to these and other problems of current mechanistic organometallic chemical interest, including the oxidative instability of (arene)chromium tricarbonyl complexes, is discussed.

Introduction

The participation of odd-electron intermediates in "traditional" organometallic reactions has become a matter of growing speculation and concern.[1-7] Recent reports on the electrocatalysis of ligand substitution[8-10] and migratory insertion[6,11] reactions and on the substitution lability of stable organometallic radicals[12,13] clearly demonstrate the important role such radicals may play in organometallic reaction mechanisms. As part of an investigation of the reactivity of cationic metal carbonyl complexes with nucleophiles,[14] we have examined the electrochemical oxidation of a series of (arene)chromium tricarbonyl complexes and of a tungsten analogue. Though the oxidation chemistry of such chromium complexes has attracted considerable interest,[15-19] mechanistic details of the complex chemistry observed are lacking. At the current level of understanding,[15] initial one-electron oxidation of the chromium complex (eq 1) is followed by rapid loss of ligands and further oxidation (eq 2). The latter is presumably a multistep process of unknown mechanism. We report our observations on the one-electron oxidation chemistry of (arene)chromium tricarbonyl complexes as a contribution toward a fuller understanding of the mechanistic complexities of these systems.



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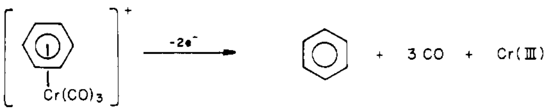

(2)

Extension of these investigations to the corresponding tungsten complexes has led not only to a better understanding of the behavior of the chromium systems but also to a finding of fundamental significance in the general area of odd-electron organometallic reaction chemistry. Thus, expanded coordination sphere complexes analogous to those currently proposed as intermediates in associative mechanisms[10,12,13] for electrocatalytic ligand substitution have been electrochemically generated *and observed*, thereby vividly demonstrating the feasibility of such intermediates. The results of these studies are summarized here.

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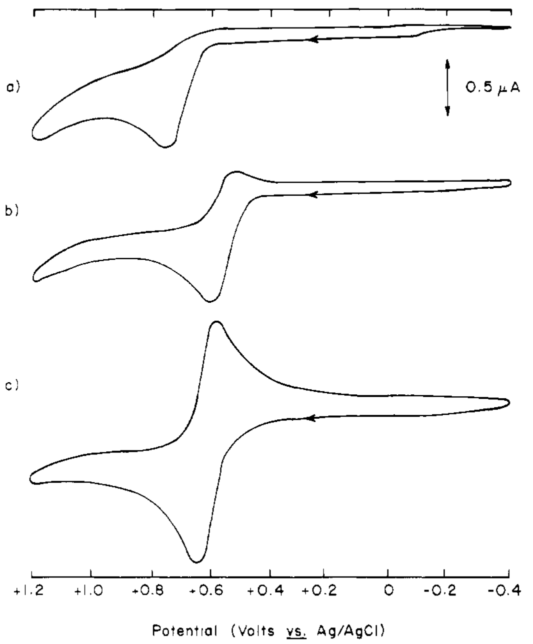
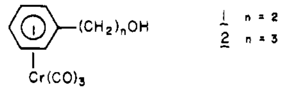


Figure 1. Cyclic voltammograms for 1 mM (arene)chromium tricarbonyl complexes in CH_3CN at platinum disk electrode (0.1 M TEAP, 200 mV/s scan rate): (a) $(C_6H_6)Cr(CO)_3$; (b) $(C_6Me_6)Cr(CO)_3$; (c) $(C_6Et_6)Cr(CO)_3$.

Results and Discussion

(Hydroxyethylbenzene)chromium tricarbonyl (**1**) and (hydroxypropylbenzene)chromium tricarbonyl (**2**) each display



electrochemical oxidations of approximately +0.7 V (vs. Ag/AgCl, Pt disk electrode, 1 mM solutions in acetonitrile, 0.1 M tetraethylammonium perchlorate (TEAP) supporting electrolyte, 25 °C) that are completely irreversible on the cyclic voltammetric time scale at scan rates up to 50 V/s. Bulk electrolysis of complex **2** at +0.8 V provides a possible explanation for the observed irreversibility—the initially yellow solution of **2** turns green (indicative of Cr(III)) and gas chromatographic analysis of the resulting solution confirms the presence of free 3-phenyl-1-propanol. Similar behavior has been noted by DeGrand et al.[15] and has been suggested to be due to initial one-electron oxidation, followed by rapid loss of ligands and the two-electron oxidation of the resulting Cr(I) species to Cr(III). Oxidation of complexes **1** and **2**, therefore, appears to result simply in rapid decomposition as in the parent systems,; no products derived from nucleophilic attack by the pendant alcohol functionality at either carbon monoxide or the arene ring are formed.

The parent complex (benzene)chromium tricarbonyl displays electrochemical behavior quite similar to that of complexes **1** and **2** (Figure 1). This electrochemical irreversibility of the oxidation of simple (arene)chromium tricarbonyl derivatives due to rapid irreversible follow-up chemical reactions has been previously noted.[15,18] Until recently,[15,16] however, conclusive evidence that decomposition of the oxidation product involves decomplexation of the arene was not presented.[20]

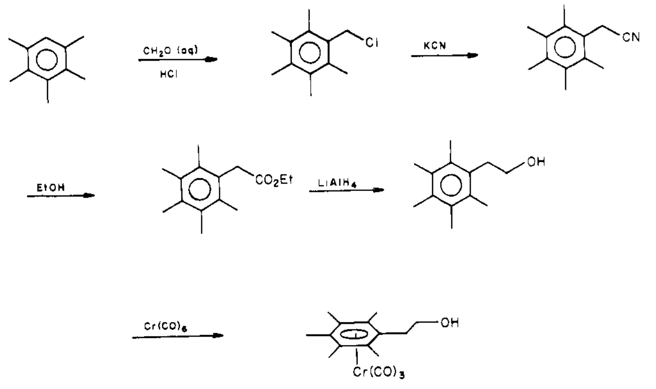
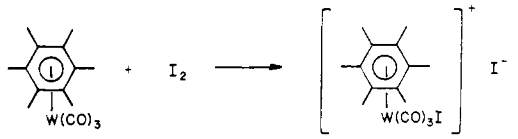


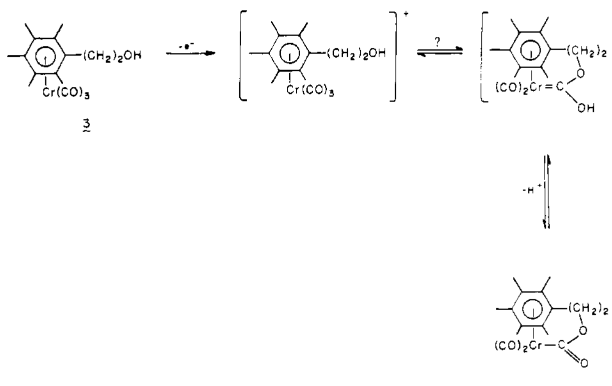
Figure 2. Synthesis of (2-(2,3,4,5,6-pentamethylphenyl)ethanol)chromium tricarbonyl (**3**).

The few reports available on the chemical[23-25] and electrochemical[16-18,26] generation of relatively stable cations from (arene)metal tricarbonyl complexes suggest that polyalkylation of the arene ring results in increased stability; thus, chemical oxidation of (hexamethylbenzene)tungsten tricarbonyl yielded a crystalline product (eq 3)[23] whereas the analgous product from (benzene)tungsten tricarbonyl proved too unstable to isolate. It has been suggested,[16,17] though not conclusively proven, that this stabilization is due to steric inhibition of intermolecular decomposition routes. Indeed, (hexamethylbenzene)chromium tricarbonyl displays a much more reversible (relative to (benzene)chromium tricarbonyl) one-electron electrochemical oxidation, and the hexaethylbenzene derivative gives rise to a still more stable cation radical (Figure 1). These results suggest that steric effects are in fact responsible for the stabilization of cation radicals of polyalkylated arene complexes; electronically, little difference would be expected between the hexamethylbenzene and hexaethylbenzene complexes (a fact mirrored by the similarity of the oxidation potentials of the two complexes).



(3)

Given these encouraging observations on cation radical stabilization, the chromium tricarbonyl complex of 2-(2,3,4,5,6-pentamethylphenyl)ethanol was prepared in the hopes of generating a cation of sufficient lifetime to permit intramolecular attack at carbon monoxide by the pendant alcohol (eq 4). Chloromethylation of pentamethylbenzene followed by displacement of chloride by cyanide to give 2,3,4,5,6-pentamethylphenylacetonitrile has been reported.[27] Ethanolysis of this nitrile to ethyl



(4)

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(20) Release of arenes from similar complexes following multielectron chemical oxidation is well documented.[21,22]

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2,3,4,5,6-pentamethylphenyl-acetate was carried out as reported for the 2,4,6-trimethyl analogoue.[28] Lithium aluminum hydride reduction of this ester afforded the desired alcohol, and formation of the chromium tricarbonyl complex[3] (Figure 2) proved to be routine. In contrast to the (hexamethylbenzene)chromium tricarbonyl complex, **3** displays an irreversible cyclic voltammetric response at scan rates below 2 V/s. Only at higher scan rates is a reduction wave for the cation radical observed. For comparison, cyclic voltamograms for a 1 mM solution of (hexamethylbenzene)chromium tricarbonyl show no qualitative changes at scan rates as low as 0.02 V/s, even in the presence of 0.285 M ethanol. Thus, intramolecular delivery of the alcohol functionality gives rise to a tremendous difference in cation radical reactivity. Bulk electrolysis of **3** results in a multielectron oxidation, and gas chromatographic analysis of the resulting solution demonstrates the nearly quantitative decomplexation of the arene. The source of this apparently intramolecular quenching of the cation radical by the pendant alcohol functionality is unknown, though it may possibly be due to an entropically driven (but otherwise sterically inhibited) nucleophilic attack by the alcohol at the metal center (vide infra).

Though cations of (arene)chromium tricarbonyl that are quite stable on the cyclic voltammetric time scale have been generated, isolation of these cations has not proved possible. Available chemical evidence[23-25] suggests that cations derived from the corresponding molybdenum and tungsten complexes are more stable than their chromium counterparts. Unfortunately, all attempts to prepare the molybdenum and tungsten analogues of complexes **1** and **2** have failed. Pittman has reported a similar inability to prepare the molybdenum tricarbonyl complex of phenylethanol,[29] and Nesmeyanov has commented on the high thermal instability of the molybdenum and tungsten tricarbonyl complexes of the methyl ether of this alcohol.[30] Despite these difficulties in obtaining functionalized (arene)molybdenum and tungsten tricarbonyl complexes, the electrochemical oxidation of the known hexamethylbenzene complexes of molybdenum[31] and tungsten[25] tricarbonyl was investigated in the hopes of generating isolable cation radicals.

(Hexamethylbenzene)molybdenum tricarbonyl appears to be unstable in acetonitrile solution containing 0.1 M tetraethylammonium perchlorate; the initially yellow solution rapidly bleaches, giving a colorless solution displaying a reversible oxidation at +0.3 V. Bulk electrolysis at +0.4 V gives a deep blue solution (characteristic of high-valent molybdenum oxides) but yields an *n* value of only 0.35; apparently some type of catalyzed decomposition occurs. Qualitatively similar behavior is observed for the (1,3,5-trimethylbenzene)molybdenum tricarbonyl complex.[32]

(Hexamethylbenzene)tungsten tricarbonyl, **4**, is relatively stable in acetonitrile/0.1 M TEAP at room temperature, decomposing only slowly over the course of several hours to generate an unidentified material having a reversible oxidation near 0 V. The cyclic voltammetric behavior of **4**, however, differs remarkably from that of its chromium counterpart. Complex **4** displays a one-electron oxidation wave (established by bulk electrolysis) at +0.64 V (near the observed for the chromium analogue), but the coupled reduction wave is shifted to near 0 V (Figure 3a). This splitting is observed even at 0.01 mM concentration, suggesting that adsorption effects are not the cause.[33] Similar behavior is observed in dimethylformamide (DMF) solvent, though here the reduction wave is shifted nearly 0.6 V more negative than in acetonitrile, and is separated from the oxidation wave by greater than 1.3 V (Figure 3b). Nicholson's analysis of the effects of slow electron transfer on cyclic voltammetric behavior[35] demonstrates that, in cases of very large peak potential separation (ΔE_p), this separation is linearly dependent on (scan rate)$^{-1/2}$. The dependence of ΔE_p on scan rate (ν) was determined in both DMF and acetonitrile; in each case, plots of ΔE_{+} vs $\nu^{-1/2}$ deviate markedly from linearity (Figure 4), suggesting that some phenomenon other than simple slow electron transfer is responsible for the observed behavior.[34,35] Thus, it appears that the initially formed cation radical of **4** undergoes some type of follow-up chemical reaction; given the dramatic solvent dependence observed and the rapid rate of this follow-up reaction (no reduction wave is observed at the potential expected for a simple electrochemically reversible redox process even when scanning at 500 V/s), we propose that the reaction involves some type of ligation of the cation radical by solvent. Thus, oxidation of **4** gives rise to a species incorporating a donor solvent molecule, and this species is more difficult to reduce than the unligated cation, resulting in the observed splitting of oxidation and reduction peak potentials (eq 5). The experi-

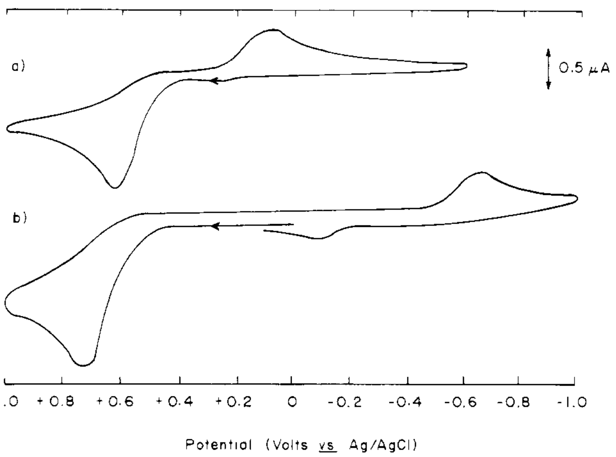

Figure 3. Cyclic voltammograms for 1 mM $(C_6Me_6)W(CO)_3$ (**4**) at platinum disk electrode (0.1 M TEAP, 200 mV/s scan rate). Solvent: (a) CH_3CN; (b) DMF.

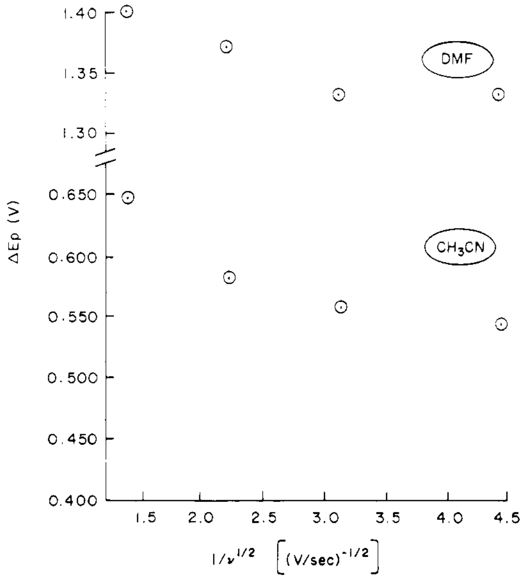

Figure 4. Dependence of peak potential separation (ΔE_p) on scan rate (ν) in cyclic voltammetry of $(C_6Me_6)W(CO)_3$ (**4**) at platinum disk electrode.

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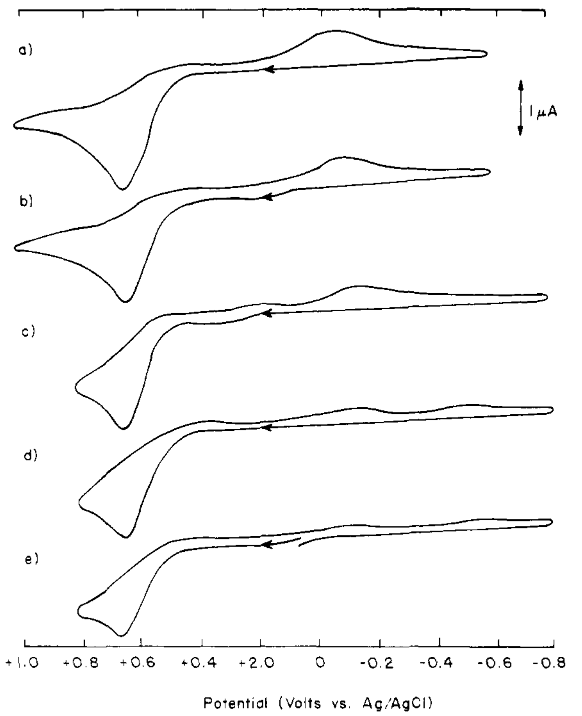
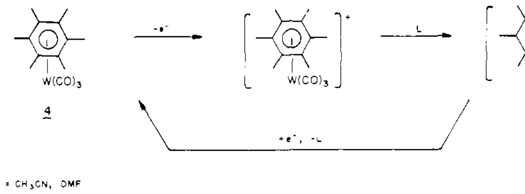


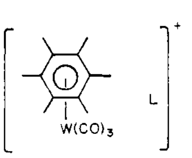
Figure 5. Cyclic voltammograms for 1 mV $(C_6Me_6)W(CO)_3$ (**4**) in CH_3CN at platinum disk electrode (0.1 M TEAP, 200 mV/s scan rate) containing (a) no added ligand, (b) 20 mM $P(OPh)_3$, (c) 10 mM PH_3, (d) 10 mM $P(O\text{-}n\text{-}Bu)_3$, and (e) 10 mM $P\text{-}n\text{-}Bu_3$.

mental determination of the structure of this ligated cation is discussed below.



(5)

This proposal suggests that addition of other donor ligands to solutions of **4** should give competitive ligation by solvent and by added ligand and that the observed reduction potentials of the ligated cations should be directly related to the donor ability of the ligands. While the results from triphenyl phosphite and triphenylphosphine addition are not conclusive, the shift in reduction potential observed for the oxidized species (Figure 5) is consistent with complex formation; thus, the apparent triphenylphosphine complex **5a** (bearing a better donor ligand) is more difficult to reduce than the corresponding triphenyl phosphite complex **5b** (bearing a poorer donor ligand). Addition of tributyl phosphite generates two reduction waves; one is due to the acetonitrile adduct of the cation radical of **4**, while the other is apparently due to the tributyl phosphite complex **5c**. Tributylphosphine addition gives similar electrochemical behavior, and here again, the resulting phosphine complex **5d** is, as expected, more difficult to reduce than the corresponding phosphite complex **5c** (Figure 5). The low reduction currents observed in all cases appear to be due to instability of the cationic complexes.



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5a, PPh_3
b, $P(OPh)_3$
c, $P(O^nBu)_3$
d, $P(^nBu)_3$

The results of the incremental titration of **4** with tributylphosphine are presented in Figure 6; the observed behavior is consistent with the proposed rapid intermolecular reaction of the cation radical of **4** with solvent or added ligands. Significantly, in these titration experiments, a new (irreversible) oxidation wave was observed to develop at approximately +0.1 V (Figure 6). Simple cyclic voltammetric blank experiments demonstrate that the new anodic wave at ca. +0.1 does not appear unless the cycle is carried through the reduction wave at ca. −0.5 V; i.e., the new anodic wave corresponds to the oxidation of a product of this reduction. The possibility existed that this wave could arise from oxidation of the phosphine-substituted complex $(C_6Me_6)W(CO)_2(PBu_3)$. Such phosphine-substituted complexes, though common for chromium,[36-38] are rare for tungsten; in fact, only one such complex, $(mesitylene)W(CO)_2(PMe_2Ph)$, has been reported.[39] Attempts to prepare $(C_6Me_6)W(CO)_2(PBu_3)$ for comparison were unsuccessful; however, the mesitylene analgoue $(mesitylene)W(CO)_2(PBu_3)$ was readily generated, albeit in quite low yield, by the procedure reported by Flood.[39] (Mesitylene)tungsten tricarbonyl displays electrochemical phosphine titration behavior similar to that of **4**; the new oxidation wave at approximately +0.1 V, though not as prominent as in the case of **4**, is clearly present. Indeed, $(mesitylene)W(CO)_2(PBu_3)$ displays an irreversible electrochemical oxidation at *exactly* the same potential as this new oxidation wave. Thus, oxidation of (arene)tungsten tricarbonyl complexes in the presence of added phosphine, followed by reduction (all on the cyclic voltammetric time scale), leads to formation of the phosphine-substituted complexes (eq 6). This exceptional facility of ligand substitution in group 6B metal arene tricarbonyl derivatives is unprecendented and strongly implicates direct metal–ligand bonding in the cation radical–ligand adducts **5** discussed above. Thus, it seems apparent that these ligand adducts actually represent coordination sphere expansion of the metal in the cationic complexes. Loss of CO from the cation radical to form $[(mesitylene)W(CO)_2(PBu_3)]^+$ is ruled out by the observation that the reduction wave in cyclic

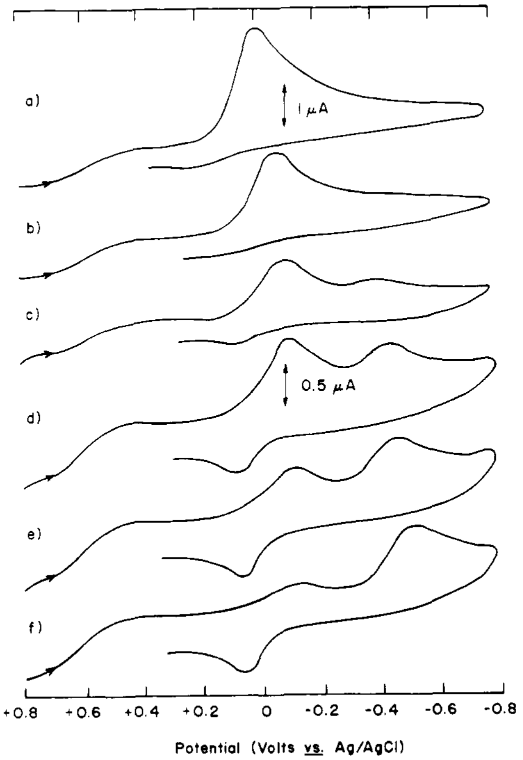

Figure 6. Cyclic voltammograms for 1 mM $(C_6Me_6)W(CO)_3$ (**4**) in CH_3CN at platinum disk electrode (0.1 M TEAP) containing (a) no added PBu_3, (b) 0.33 mM PBu_3, (c) 0.67 mM PBu_3, (d) 1.00 mM PBu_3, (e) 1.34 mM PBu_3, and (f) 1.67 mM PBu_3 (held 15 s at +0.8 V and then scanned at 500 mV/s).

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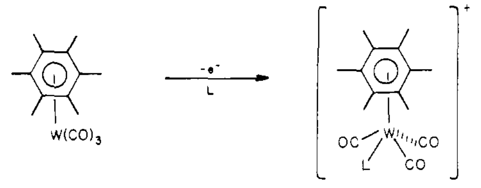

(6)

L = CH_3CN, DMF, PR_3, $P(OR)_3$

voltammograms of (mestiylene)$W(CO)_2(PBu_3)$ occurs at a significantly different potential than that for (mesitylene)$W(CO)_3$ in the presence of PBu_3. Though the difference in wave shapes for the oxidation and reduction processes (Figure 3) make current ratios difficult to evaluate, some loss of current due to decomposition of the cation radicals to electrochemically inactive products is apparent, particularly at lower scan rates. Addition of phosphines and phosphites appears to accelerate this decomposition.

This coordination sphere expansion of an electrochemically generated cation radical has direct relevance to recent reports on the electrochemical oxidation of organometallic carbonyl complexes. Thus, the electrocatalytic ligand substitutions observed by Kochi,[10] as well as the thermal substitutions in stable organometallic radicals studied by Brown[12] and Trogler,[13] may well proceed via intermediate formation of complexes with increased coordination number (i.e., the associative mechanism favored by Kochi,[10] Brown,[12] and Trogler[13] and supported by recently reported[12,13] kinetic investigations) (eq 7). The electrochemically

$$\mathrm{LM(CO)_5} \xrightarrow{-e^-} [\mathrm{LM(CO)_5}]^+ \xrightarrow[\text{fast}]{L'} [\mathrm{LL'M(CO)_5}]^+ \xrightarrow[e^-]{-L} \mathrm{L'M(CO)_5} \quad (7)$$

driven migratory insertion reaction (eq 8) studied by Giering[6,11] may also have its roots in such a phenomenon; in this case, steric crowding in the expanded coordination sphere intermediate may be relieved by rapid insertion of carbon monoxide into the iron–methyl bond (eq 9). The electrochemical decomposition of simple

$$\mathrm{CpFe(CO)_2CH_3} \xrightarrow[\mathrm{CH_3CN}]{-e^-,+e^-} \mathrm{Cp(CO)(CH_3CN)FeC({=}O)CH_3} \quad (8)$$

$$\mathrm{CpFe(CO)_2CH_3} \xrightarrow{-e^-} [\mathrm{CpFe(Co)_2CH_3}]^+ \xrightarrow[\text{fast}]{\mathrm{CH_3CN}} [\mathrm{CpFe(CO)_2(CH_3CN)CH_3}]^+ \xrightarrow{\text{fast}} [\mathrm{Cp(CO)(CH_3CN)FeC({=}O)CH_3}]^+ \xrightarrow{+e^-} \mathrm{Cp(CO)(CH_3CN)FeC({=}O)CH_3} \quad (9)$$

(arene)chromium tricarbonyl complexes (vide supra) may also prove to be related; perhaps decomposition is induced by nucleophilic attack at the metal center by solvent[40] (or by the pendant alcohol in complex **3**), and peralkylation of the arene sterically inhibits this attack. In this light, it would be interesting to examine the relative rates of the electrochemically driven migratory insertion reaction in $CpFe(CO)_2CH_3$ and its permethylated analogue $(C_5Me_5)Fe(CO)_2CH_3$. If attack by solvent is sterically inhibited in the methylated analogue, the rate of insertion should be slowed relative to the unsubstituted complex. Finally, both the chemical oxidations[21,22] and the photochemical substitution reactions[36-39] of (arene)metal tricarbonyl complexes may ultimately be mechanistically related to intermediate coordination sphere expansion as well; in the latter case, charge-transfer excitation from the metal to the arene could generate local positive charge at the metal and induce associative ligand substitution processes.

Summary and Conclusions

Considerable light has been shed on the mechanism of cation radical stabilization in (arene)chromium tricarbonyl complexes. The cation radical of (hexaethylbenzene)chromium tricarbonyl decays much more slowly than that of the mexamethylbenzene complex, rather clearly suggesting steric effects as the primary means of stabilization. In addition, a dramatic effect of intramolecular delivery of an alcohol nucleophile to the electrochemically generated cation radical of an (arene)chromium tricarbonyl complex has been documented, though the source of the observed destabilization of the cation radical is at present only a matter of conjecture.

The electrochemical oxidation of (hexamethylbenzene)tungsten tricarbonyl, **4**, has yielded surprising results that bear direct relevance to current reports on the oxidation of metal carbonyl complexes.[6,8-11] Oxidation of **4** is followed by rapid complexation of either solvent or added ligands (phosphines or phosphites) to generate expanded coordination sphere intermediates that, when reduced, regenerate **4** or give rise to the ligand-substituted complex. This coordination sphere expansion upon oxidation has far-reaching implications, ranging from support for the proposed associative mechanism for the electrocatalytic substitution of ligands in metal carbonyl complexes[10] and a plausible mechanism for the recently observed oxidatively promoted migratory insertion of carbon monoxide into a metal–carbon bond[6,11] to the mechanistically unexplored chemical oxidations of (arene)metal tricarbonyl complexes and sources of the stabilization of the products of these oxidations. Investigation of the one-electron chemistry of organometallic complexes appears to offer tremendous promise for suggestive and intriguing results of fundamental importance in the field of mechanistic organometallic chemistry and should prove to be an area of vigorous future research endeavors.

Experimental Section

Materials. Organometallic complexes were treated as air sensitive, using standard techniques, until isolated as crystalline solids. Tetrahydrofuran (THF), toluene, and hexane were dried over sodium benzophenone ketyl and vacuum transferred before use. Dichloromethane was dried over CaH_2 and vacuum transferred. Butyl ether was refluxed over $LiAlH_4$ and distilled under argon, onto Linde 4A molecular sieves. $Cr(CO)_6$, $W(CO)_6$, and $(C_6H_6)Cr(CO)_3$ were obtained from Pressure Chemical Co. (Pittsburgh, PA). Other reagents were purchased from standard commercial sources. E. Merck 70-230 mesh silica gel was used for chromatographic purifications. (Hexamethylbenzene)molybdenum tricarbonyl,[41] (mesitylene)molybdenum tricarbonyl,[32] and (2,3,4,5,6-pentamethylphenyl)acetonitrile[27] were prepared as described. (Arene)chromium tricarbonyl complexes were prepared by using the general procedure described by Mahaffy and Pauson.[42] (Mesitylene)tungsten dicarbonyl tributylphosphine was prepared as reported by Flood.[39] ^1H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane as an internal standard.

(Hydroxyethylbenzene)chromium Tricarbonyl,[43] 1. An argon-flushed, 250-mL three-neck round-bottom flask, equipped with an argon inlet, reflux condenser, and oil bubbler vented in a fume hood (CO evolved!), was charged with 4.0 g of $Cr(CO)_6$ (18.2 mmol), 2.17 mL of 2-phenethyl alcohol ($d = 1.023$, 18.2 mmol), 120 mL of ether, and 10 mL of THF. The colorless suspension was heated to reflux. Reflux was maintained for 72 h, giving a bright yellow solution containing tracers of a green solid. The solution was cooled under argon and filtered through a 1 in. × 2 in. pad of silica; adhering material was washed through with a few small portions of THF, leaving a green band on the silica. Removal of solvent in vacuo, with gentle heating, gave an orange oil that solidified to a crystalline mass. Recrystallization from toluene/hexane at 0 °C gave long yellow needles: yield 3.1 g (66%); mp 49.7–51.3 °C (lit.[43] 51–52 °C); ^1H NMR (acetone-d_6) δ 2.55 (t, 2 H, $PhCH_2$), 3.78 (t, 2 H, CH_2OH), 3.98 (s, 1 H, OH), 5.3–5.7 (m, 5 H, Ph); ^{13}C NMR (acetone-d_6) δ 38.9, 62.8 (CH_2CH_2), 92.6, 95.4, 95.8, 113.0 (Ph), 234.7 (CO); IR (THF) ν_{CO} 1880, 1956 cm^{-1}.

(Hydroxypropylbenzene)chromium Tricarbonyl, 2. This complex was prepared as described above, substituting 2.46 mL of 3-phenyl-1-propanol ($d = 1.008$, 18.2 mmol) for phenethyl alcohol. Reflux was continued for 39 h. Crystallization from 35 mL of toluene at −50 °C afforded 2.95 g (60%) of yellow needles: mp 74.9–76.1 °C; ^1H NMR (acetone-d_6) δ 1.8 (m, 2 H, $CH_2CH_2CH_2$), 2.5 (m, 2 H, $PhCH_2$), 3.6 (br t, 3 H, CH_2OH), 5.6 (m, 5 H, Ph); ^{13}C NMR (acetone-d_6) δ 32.1, 34.9, 61.2 ($CH_2CH_2CH_2$), 92.4, 94.7, 95.8, 115.7 (Ph), 234.6 (CO); IR (THF) ν_{CO} 1810, 1880, 1956 cm^{-1}.

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(40) This hypothesis is strongly supported by Rieke's very recent observation of dramatically enhanced cation stability in a nonnucleophilic solvent (trifluoroacetic acid): Milligan, S. N.; Tucker, I.; Rieke, R. D. *Inorg. Chem.* **1983**, *22*, 987.

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Anal. Calcd for $C_{12}H_{12}CrO_4$: C, 52.95; H, 4.44; Cr, 19.10. Found: C, 53.23; H, 4.43; Cr, 18.77.

(Hexamethylbenzene)chromium Tricarbonyl.[44] This complex was prepared as described above, substituting 2.95 g of hexamethylbenzene (18.2 mmol) for phenethyl alcohol. Reflux was continued for 45 h. The yellow solid that precipitated upon cooling was washed through the pad of silica with THF. Removal of solvents in vacuo afforded a mixture of yellow and white solids. This mixture was washed repeatedly with pentane (6 × 5 mL) to remove unreacted hexamethylbenzene, yielding a bright yellow crystalline solid: 0.95 g (18%); ^1H NMR (CCl_4) δ 2.20 (s); IR (CCl_4) ν_{CO} 1890, 1960 cm^{-1}.

(Hexaethylbenzene)chromium Tricarbonyl.[41] This complex was prepared as described above, substituting 4.48 g of hexaethylbenzene (18.2 mmol) for phenethyl alcohol. Reflux was continued for 72 h. Methylene chloride (3 × 10 mL) was used to rinse the silica pad. The volume of the filtrate was reduced to approximately 25 mL in vacuo, with gentle heating. The resulting suspension was filtered, and the solid was washed well with pentane (2 × 10 mL, 5 × 5 mL), affording a bright yellow crystalline solid, yield 1.54 g (22%): IR (THF) ν_{CO} 1870, 1949 cm^{-1}.

Ethyl (2,3,4,5,6-Pentamethylphenyl)acetate. A 250-mL round-bottom flask with a magnetic stirrer was charged with 26 mL of absolute ethanol, 1.4 mL of H_2O, and 8.2 mL of concentrated H_2SO_4. With good stirring, 2,3,4,5,6-pentamethylphenylacetonitrile[27] (17.8 g, 0.095 mol) was slowly added, giving a thick suspension. The flask was fitted with a reflux condenser, and the mixture was carefully heated to reflux. Reflux was continued for 20 h, and then an additional 0.3 mL of H_2O was added to the hot solution (total H_2O 1.7 mL, 0.094 mol). The mixture was cooled, giving a solid tan mass. This was dissolved/suspended in 40 mL of $CHCl_3$, washed 2 × 150 mL of saturated $NaHCO_3$ and 2 × 200 mL of H_2O, and dried over Na_2SO_4. Solvent was removed on a rotary evaporator, giving an off-white solid. This was extracted with 300 mL of CCl_4; undissolved solid was removed by filtration. Solvent was removed on a rotary evaporator, and the residue was taken up in 125 mL of ethanol and 20 mL of H_2O. The mixture was heated and filtered while hot to remove undissolved solids. Finally, the filtrate was heated to boiling, 50 mL of H_2O and 30 mL of ethanol were added, and the solution was cooled to room tempeature, giving white needles: yield 15.92 g (71%); mp 79.0–80.0 °C; ^1H NMR (CCl_4) δ 1.24 (t, 3 H, CH_2CH_3), 2.19 (s, 15 H, $C_6(CH_3)_5$), 3.60 (s, 2 H, $ArCH_2$), 4.06 (q, 2 H, CH_2CH_3); IR (KBr) ν_{CO} 1735 cm^{-1}, ν 2860–3000 (s, br), 1430–1470 (s, br), 1370 (m), 1340 (s), 1305 (m), 1260 (m), 1215 (s), 1180 (s), 1038 (m), 880 (w), 820 (w) cm^{-1}.

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.10, 77.02; H, 9.43, 9.56.

2-(2,3,4,5,6-Pentamethylphenyl)ethanol. Lithium aluminum hydride (2.3 g, 0.074 mol) was suspended in 100 mL of anhydrous ether. Ethyl 2,3,4,5,6-pentamethylphenylacetate (11.32 g, 0.048 mol) dissolved in 75 mL of ether was added quickly; residues were rinsed in with 2 × 25 mL of ether. The suspension was stirred for 15 min, and then an additional 0.5 g of $LiAlH_4$ (0.016 mol) was added. After the solution was stirred for an additional 2 h at room temperature, 100 mL of ether was added, and the mixture was carefully quenched with 100 mL of ethyl acetate. Filtration on a coarse sintered glass frit afforded a gray solid that was washed with 50 mL of ether, 25 mL of $CHCl_3$, and 25 mL of acetone and then dried in air. This solid was carefully added to 200 mL of ice-cold 20% H_2SO_4. The resulting solution was extracted with 2 × 250 mL of $CHCl_3$ and then 3 × 100 mL of $CHCl_3$. The combined organic layers were dried over Na_2SO_4 and K_2CO_3. Solvent was removed on a rotary evaporator, affording a white crystalline solid: 6.36 g (68%); mp 106.6–108.0 °C; ^1H NMR (CCl_4) δ 1.4 (br s, 1 H OH), 2.2 (s, 9 H, CH_3), 2.23 (s, 6 H, CH_3), 2.94 (t, 2 H, $ArCH_2$), 3.66 (t, 2 H, CH_2OH); IR (KBr) ν 3200–3400 (s, br), 2880–3000 (s, br), 1400–1500 (s, br), 1040 (s) cm^{-1}.

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.88, 80.93; H, 10.28, 10.17.

(2-(2,3,4,5,6-Pentamethylphenyl)ethanol)chromium Tricarbonyl, 3. This complex was prepared as described above, using 2.0 g of $Cr(CO)_6$ (9.1 mmol) and substituting 2-(2,3,4,5,6-pentamethylphenyl)ethanol (1.75 g, 9.1 mmol) for phenethyl alcohol. Reflux was continued for 72 h. The silica pad was washed with THF. The volume of the bright yellow filtrate was reduced to approximately 10 mL in vacuo, with gentle heating, giving a yellow solid and a nearly colorless solution. The mixture was filtered, and the solid was washed well with pentane, giving a greenish yellow solid. This material was chromatographed (in air, collecting in a foil-wrapped receiver) on a $^3/_4$ in. × 5 in. column of silica gel slurried in benzene, eluting with benzene/2% acetone. A green band remained on the column; the faster moving bright yellow band was eluted and immediately brought to dryness in vacuo, affording a bright yellow powder: 2.17 g (73%); mp 113.6–115.5 °C dec; ^1H NMR (C_6D_6) δ 0.76 (s, 1 H, OH), 1.59 (s, 6 H, CH_3), 1.63 (s, 3 H, CH_3), 1.73 (s, 6 H, CH_3), 2.36 (t, 2 H, $ArCH_2$), 3.18 (t, 2 H, CH_2OH); IR (KBr) ν_{CO} 1860, 1950 cm^{-1}, ν 3260 (s, br), 2850–3000 (m), 1450 (m), 1390 (s), 1050 (s), 680 (s), 640 (s) cm^{-1}.

Anal. Calcd for $C_{16}H_{20}CrO_4$: C, 58.53; H, 6.14. Found: C, 58.28; H, 6.14.

(Hexamethylbenzene)tungsten Tricarbonyl,[25] **4.** A 50-mL Schlenk tube was charged with 15 mL of *n*-decane. The tube was evacuated and then filled with argon. Under an argon flush, 2.146 g of $W(CO)_6$ (6.1 mmol) and 0.892 g of hexamethylbenzene (5.5 mmol) were added. The tube was then fitted with an argon-flushed reflux condenser open to a mercury bubbler. The mixture was slowly heated to reflux, with no cooling water flowing; a yellow color developed rapidly. Sublimed $W(CO)_6$ was periodically returned to the solution by shaking the tube. Gentle reflux was continued for 20 h—a tungsten mirror formed, and some $W(CO)_6$ remained; the solution was yellow. The mixture was cooled and filtered through a 1 in × 1 in. pad of silica under argon, washing with 4 × 10 mL of CH_2Cl_2; a black band was left on the silica. Methylene chloride was removed from the bright yellow filtrate in vacuo, giving bright yellow crystals and a colorless supernatant (decane). The mixture was filtered under argon, and the solid was washed with 4 × 10 mL of pentane and then dried in vacuo: yield 0.67 g (28%); IR (THF) ν_{CO} 1862, 1943 cm^{-1}.

Apparatus and Procedures. Electrochemical measurements were performed by using PAR instruments (EG & G Instrument Co., Princeton, N.J.) and a Houston Instruments x-y recorder or a Tektronix storage oscilloscope. Cyclic voltammetry was carried out in a conventional two-compartment cell in a Vacuum Atmospheres inert atmosphere drybox, using a platinum disk working electrode, at ambient temperature (25 ± 3 °C). Potentials were measured and are quoted with respect to a Ag/AgCl reference electrode. Bulk electrolyses were carried out in the same cell by using either a platinum foil or a platinum gauze electrode. Solutions were 1 mM in metal complexes and 0.1 M in tetraethylammonium perchlorate. The platinum disk electrode used for cyclic voltammetry was polished on a paper towel after each scan to avoid coating problems, which were especially noticeable with the less substituted chromium complexes. All solvents and reagents were thoroughly dried and degassed before use.

Bulk Electrolysis of (Hydroxypropylbenzene)chromium Tricarbonyl, 2. Fifteen milliliters of a 1.09 mM solution of **2** in acetonitrile containing 0.1 M tetraethylammonium perchlorate was electrolyzed at +0.8 V at a platinum gauze electrode. Gas chromatographic analysis of the solution after electrolysis was completed (8-ft 3% SE-52 on Chrom G AWDMCS, 60–200 °C at 15 C/min, injector 210 °C, detector 230 °C, 35 mL/min flow rate, N_2 carrier) revealed the presence of an approximately stoichiometric amount of 3-phenyl-1-propanol. A solution of complex **2** under analogous chromatographic conditions does not generate free arene before electrolysis.

Bulk Electrolysis of (2-(2,3,4,5,6-Pentamethylphenyl)ethanol)chromium Tricarbonyl, 3. Electrolysis of **3**, as above, followed by gas chromatographic analysis (6-ft 3% Carbowax 20 M, 200 °C, injector 260 °C, detector 270 °C, 35 mL/min flow rate, N_2 carrier) revealed the presence of an approximately stoichiometric amount of 2-(2,3,4,5,6-pentamethylphenyl)ethanol and a trace (1–2%) of the corresponding formate (prepared for comparison from the alcohol by overnight reflux in 98% HCO_2H).

Acknowledgment. This work was supported by the Department of Energy. K.M.D. thanks the Fannie and John Hertz Foundation for fellowship support. The assistance of Dr. Brian Willett with electrochemical experiments and the helpful comments of H. B. Gray and W. P. Giering are gratefully acknowledged.

Registry No. 1, 38959-95-4; **2**, 92204-71-2; **3**, 92641-71-9; **4**, 33505-53-2; **5a**, 92669-20-0; **5b**, 92669-21-1; **5c**, 92669-22-2; **5d**, 92669-23-3; $(C_6Me_6)Mo(CO)_3$, 12216-16-9; (mesitylene)$W(CO)_2(PBu_3)$, 92669-24-4; $Cr(CO)_6$, 13007-92-6; $(C_6Me_6)Cr(CO)_3$, 12088-11-8; $(C_6Et_6)Cr(CO)_3$, 47378-46-1; $W(CO)_6$, 14040-11-0; $(C_6H_6)Cr(CO)_3$, 12082-08-5; ethyl (2,3,4,5,6-pentamethylphenyl)acetate, 92622-89-4; 2,3,4,5,6-pentamethylphenylacetonitrile, 34688-70-5; 2-(2,3,4,5,6-pentamethylphenyl)ethanol, 92622-90-7.

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