

Reactivity of 17-, 18-, and 19-Electron Cationic Complexes Generated by the Electrochemical Oxidation of Tricarbonyl(mesitylene)tungsten

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Abstract: The electrochemical oxidation of (mesitylene)W(CO)₃ (W) in MeCN produces the 17-electron complex W⁺, which reacts very rapidly with solvent (S) or tri-*n*-butyl phosphite (P) to give 19-electron species (WS⁺, WP⁺) that undergo spontaneous further oxidation to the 18-electron analogues (WS²⁺, WP²⁺). The identities of WS²⁺ and WP²⁺ were established by voltammetric, IR spectroelectrochemical, and NMR experiments. Although the 17-electron \rightleftharpoons 19-electron transformation is not directly observable, digital simulation techniques allowed selection of a probable mechanism and semiquantitative determination of the rate and equilibrium parameters describing the interconversion of the 17-, 18-, and 19-electron species: W⁺ + S \rightleftharpoons WS⁺, $k \approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}} \approx 10^{-1} \text{ M}^{-1}$; W⁺ + P \rightleftharpoons WP⁺, $k \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}} \approx 3 \times 10^3 \text{ M}^{-1}$ at 298 K. The related 18-electron complex WS²⁺ is quite reactive, but orders of magnitude less so than W⁺ and WS⁺. Experiments with (mesitylene)Cr(CO)₃ (Cr) suggest that associative attack by MeCN at the 17-electron Cr⁺ is 10⁴ times slower than attack at the W⁺ analogue. This study illustrates the power of digital simulation techniques for interpreting complex mechanistic schemes and characterizing important but unobservable reaction intermediates. Electrochemical oxidation of (arene)W(CO)₃ occurs without loss of arene or CO ligands, suggesting that the electroactivation of these complexes may have useful synthetic applications; this contrasts sharply with (arene)Cr(CO)₃ analogues, which decompose with loss of arene and CO ligands upon oxidation in MeCN.

Organometallic radicals, both 17-electron and 19-electron complexes, have recently received considerable attention because of the demonstrated importance of such species in catalytic and stoichiometric transformations.¹⁻⁴ Synthetic procedures involving the initial oxidation or reduction of an 18-electron organometallic complex are becoming common and often provide a route to otherwise inaccessible molecules.⁴ This chemistry hinges on the enormous increase in reactivity that accompanies the oxidation/reduction. The enhanced reactivity of organometallic radicals with respect to ligand substitution, migratory insertion, homolytic M-C bond cleavage, atom abstraction, and reductive elimination reactions has now been amply demonstrated; examples are provided in reviews¹⁻⁴ and in other, very recent reports.⁵⁻⁸ Due to their reactive nature, the presence of 17-electron and, especially, 19-electron complexes is often inferred rather than directly observed; this is particularly true of catalytic transformations. Nevertheless, there exist numerous published studies of 17-electron complexes, which show that ligand substitution³ and probably migratory insertion as well⁵ occur via an associative mechanism.

We have been interested in using electroactivation as a means to enhance the reactivity of coordinated π -hydrocarbons. For example, the arene ring in (arene)M(CO)₃ (M = Cr, W) is only weakly electrophilic; it seems likely that oxidation would increase the reactivity of the coordinated arene and hence the ease of arene functionalization. To be able to effect such chemistry, it is necessary that the oxidized organometallic not undergo rapid decomposition or ligand loss. We^{9,10} and others¹¹⁻²⁰ have studied the electrochemical oxidation of (arene)Cr(CO)₃ complexes. With sufficient arene alkylation and/or in a nonnucleophilic solvent, the (arene)Cr(CO)₃⁺ radical cation is persistent enough to be observed. Under these conditions, phosphine nucleophiles rapidly substitute for a CO ligand to give⁹ (arene)Cr(CO)₂L⁺. In the nucleophilic solvent MeCN, the (arene)Cr(CO)₃⁺ radical is very rapidly attacked by MeCN with loss of arene and CO ligands, followed by spontaneous further oxidation to a Cr(II) species. Thus, in MeCN (and other nucleophilic solvents) the electrochemical oxidation of (arene)Cr(CO)₃ is a chemically irreversible 2-electron process that is uninteresting in a synthetic sense because the oxidation results in complete destruction, i.e., the dissociation of all initial ligands.

The electrochemical oxidation of (arene)W(CO)₃ differs from that of the chromium analogues in a number of ways. We previously found⁹ that (mesitylene)W(CO)₃ (**1**) in MeCN (with tetrabutylammonium perchlorate, TBAP) gives a chemically irreversible 2-electron oxidation wave even at a scan rate of 100 V/s. This is similar to that reported¹⁷ for (C₆Me₆)W(CO)₃ (**2**) in MeCN (although in this case the oxidation was erroneously identified as a 1-electron process). This behavior mimics that seen with the chromium analogues, but unlike the case of (mesitylene)Cr(CO)₃ (**3**) or (C₆Me₆)Cr(CO)₃, the cathodic scans following oxidation of **1** and **2** exhibit reduction waves at potentials 0.5 V or more negative of the oxidation, depending on the nucleophile present (MeCN or added alkyl phosphite). Furthermore, the oxidation of **1** in CH₂Cl₂ (with tetrabutylammonium hexafluorophosphate, TBAPF₆) remains a 2-electron, chemically irreversible process (as in MeCN) even though in CH₂Cl₂/TBAPF₆

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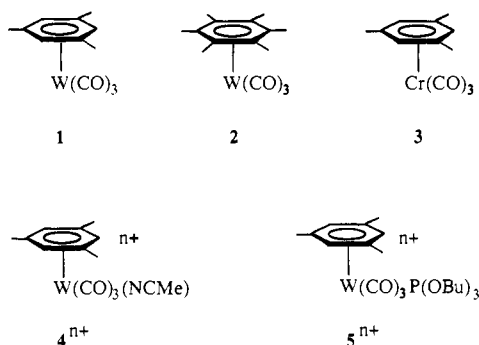
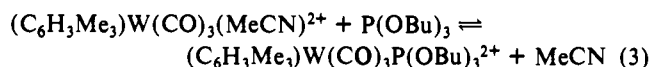
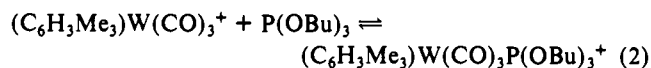
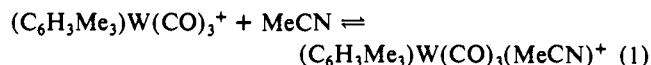


Figure 1. Numbering code for the complexes in this study.

the oxidation of **3** is a chemically reversible 1-electron process. These differences between chromium and tungsten suggested⁹ to us that the arene and CO ligands remain coordinated when **1** and **2** are oxidized. This in turn means that the electroactivated tungsten complexes may have useful synthetic applications. Figure 1 summarizes the numbering scheme for complexes relevant to the present study.

Herein we report the results of voltammetric, IR spectroelectrochemical, bulk electrolysis, and NMR studies which show that **1** is oxidized in MeCN *without ligand loss* to give (mesitylene)W(CO)₃(MeCN)²⁺ (**4²⁺**), or (mesitylene)W(CO)₃P(OBu)₃²⁺ (**5²⁺**) when P(OBu)₃ is present. Lifetimes for these species were determined by IR experiments. Digital simulations of the voltammograms allowed the determination of rate and equilibrium parameters connecting **4²⁺** and **5²⁺** as well as their reactive and unobservable odd-electron companions (**1⁺**, **4⁺**, **5⁺**), eqs 1–3. As



may be expected, the analysis suggests that the 17-electron \rightleftharpoons 19-electron interconversions (eqs 1 and 2) are very rapid. By invoking a reasonable assumption (vide infra), it is shown that associative attack by MeCN occurs 10⁴ times more rapidly at the 17-electron tungsten complex **1⁺** than at the 17-electron chromium analogue (**3⁺**).

Experimental Section

Materials. (Mesitylene)Cr(CO)₃ and (mesitylene)W(CO)₃ were used as received from Aldrich; IR spectra established them as pure materials. Trimethyl phosphite and tri-*n*-butyl phosphite were distilled under nitrogen at reduced pressure. Dichloromethane and acetonitrile were freshly distilled under nitrogen from calcium hydride. TBAP was synthesized by metathesis of TBABr and HClO₄, recrystallized from ethyl acetate/pentane, and dried over P₂O₅ in vacuo. TBAPF₆ was made from TBABr and HPF₆, recrystallized from CH₂Cl₂/hexane, and dried over P₂O₅. Tetramethylammonium hexafluorophosphate, TMAPF₆, was similarly synthesized from TMABr and HPF₆ and recrystallized from MeCN/Et₂O.

Instrumentation and Procedures. Voltammetric experiments were done under a blanket of argon or nitrogen that was saturated with solvent, MeCN. The electrolyte was 0.10 M TBAP or TBAPF₆. Work at low temperatures utilized a simple slush bath or a FTS Multi-Cool unit. An Omega Type T thermocouple probe was inserted directly into the electrochemical cell to monitor the temperature. Cyclic voltammetry was done with EG&G 173 or BAS CV27 potentiostats in a three-electrode configuration. The voltage ramp was generated internally or fed in from an EG&G 175 programmer. The current/voltage output was recorded with a Nicolet 3091 digital oscilloscope and stored on floppy disks. The working electrode was a platinum or gold disk (diameter 1.6 mm) or a glassy carbon disk (diameter 3.0 mm) and the counter electrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with CH₂Cl₂/0.10 M TBAP and saturated with LiCl; this was separated

from the test solution by a salt bridge containing MeCN and 0.10 M TBAP or TBAPF₆.

Bulk electrolysis of 1.0 mM **1** in MeCN/0.10 M TBAPF₆ was done with an EG&G 173 potentiostat and a Model 179 digital coulometer. The working electrode was a platinum basket and the counter electrode was platinum mesh separated from the working electrode by a salt bridge. For ¹H NMR experiments, bulk electrolysis of 3.0 mM **1** to produce **4²⁺** was performed in CD₃CN with a coiled gold wire working electrode (electrode fouling occurred at low temperatures, vide infra). The electrolyte was 0.050 M TMAPF₆ and the Ag/AgCl reference electrode salt bridge contained CD₃CN/0.050 M TMAPF₆. The progress of the low-temperature electrolyses was monitored by IR. IR spectra of **4²⁺** produced in this manner were recorded before and after ¹H NMR (400 MHz) experiments with the final infrared spectrum being that of the actual sample used for NMR.

IR spectroelectrochemistry was performed with an optically transparent thin-layer electrode (IR-OTTLE), the construction and use of which has been reported.^{21,22} Experiments at low temperatures utilized a cooling procedure described in detail elsewhere.²³ The IR-OTTLE cell contained a volume of 0.35 mL. Spectra were recorded and stored on a Mattson Alpha Centauri FTIR with a routine consisting of 16 scans and a resolution of 4 cm⁻¹. All solutions were prepared and loaded into the OTTLE cell in a glovebox. The potential was applied with a EG&G 173/179 potentiostat/coulometer.

Digital simulation of proposed electrochemical mechanisms was done with a general purpose program designed to simulate voltammograms for any mechanism formulated as a combination of heterogeneous charge transfer and homogeneous reactions.²⁴ The input for the simulations of Schemes 1 and II consisted of an E⁰ for each electrode process and forward and reverse rate constants for each homogeneous reaction. The electron-transfer steps were assumed to be nonsternian. The progress of the homogeneous steps was calculated from the rate constants; equilibrium was not explicitly assumed in any of the simulations. Both the expanding space grid method of Joslin and Pletcher²⁵ and the expanding space/time grid method of Seeber and Stefani²⁶ are available in our digital simulation program, but, for reasons discussed in ref 24, the latter method can lead to serious errors when an intermediate is involved, as is the case in the present work. Accordingly, the Joslin-Pletcher algorithm was employed in all simulations described here. The number of time increments was chosen such that $k_{\text{max}}\delta t \leq 1.0$, where k_{max} is the largest rate constant used in the simulation. For a very fast homogeneous step and relatively long experimental times, this leads to time-consuming simulations; some of the results presented consumed tens of minutes of main-frame computer time.

Results and Discussion

Oxidation of (Mesitylene)W(CO)₃ in MeCN. The oxidation of **1** was studied in MeCN at temperatures from 298 to 228 K with 0.10 M TBAP or TBAPF₆ electrolyte. On the CV time scale the electrolyte chosen did not affect the results. Platinum, gold, and glassy carbon electrodes all led to similar voltammograms, although reproducibility was generally best with gold and worst with platinum electrodes, especially at low temperatures. The CV's of **1** at 298 and 228 K were very similar except for modest shifts in the peak potentials; Figure 2 illustrates a room temperature result. Qualitatively, it can be seen by reference to Figure 2 that **1** is oxidized (wave A) in a chemically irreversible manner to generate a product that is reduced at wave B, which is also chemically irreversible. By comparison of the oxidation currents of **1** and (mesitylene)Cr(CO)₃, which is known⁹ to suffer a 2-electron oxidation in MeCN, it was established that **1** also undergoes a 2-electron oxidation (wave A); this was confirmed several other ways (vide infra). The general shape of the CV in Figure 2 was maintained at both 298 and 228 K up to the largest scan rate used with conventional electrodes (100 V/s). The oxidation current i_A was proportional to the square root of the scan rate ($v^{1/2}$) up to at least 10 V/s; beyond this scan rate, iR drop and

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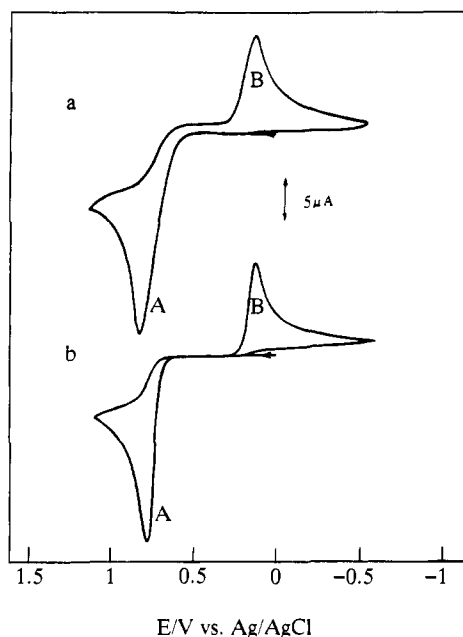


Figure 2. Observed (a) and simulated (b) cyclic voltammograms of 1.0 mM **1** in MeCN/0.10 M TBAPF₆ at 298 K. For (a) the working electrode was a platinum disk and the scan rate was 0.40 V/s. The parameters for (b) are given in Scheme 1 and Table 1; the indicated voltammogram was obtained for any scan rate up to 100 V/s.

charging current distortions became significant. Hence, wave A corresponds to a full two electrons up to at least 10 V/s, and probably much higher. An experiment with a 10 μm diameter platinum microdisk electrode showed that waves A and B in the CV of **1** are chemically irreversible at 10 000 V/s.

Bulk electrolysis of **1** in MeCN/TBAPF₆ at 298 K with a platinum electrode produced a color change from light yellow to deeper yellow. However, on this time scale, electrode fouling and decomposition of the electrogenerated complex precluded its clean synthesis in this manner.

IR spectroelectrochemical experiments with an OTTLE cell containing a gold mesh electrode were used for the rapid bulk oxidation of **1**. Figure 3 shows the results at -35 °C. With an oxidizing potential the ν_{CO} bands of **1** at 1955, 1870 cm⁻¹ were cleanly replaced over a period of ca. 5 min with ν_{CO} bands at 2113, 2044 cm⁻¹. Application of a reducing potential regenerated the starting material, showing that neither mesitylene nor CO ligands are lost when **1** is oxidized. From the volume of the OTTLE cell and the charge passed to generate the spectrum in Figure 3c, it was determined that the oxidation involves two electrons, in agreement with the CV results (vide supra).

Assuming **1** is initially oxidized by one electron to **1**⁺, one would not expect a spontaneous second oxidation unless **1**⁺ undergoes a homogeneous reaction to form a more electron-rich species. Since the CV results were independent of electrolyte (TBAP or TBAPF₆), the likely nucleophilic species is the solvent, MeCN. IR spectra show that a CO ligand is not attacked and ¹H NMR was used to rule out attack at the mesitylene ring as follows. In CD₃CN/0.050 M TMAPF₆ the ¹H NMR of 3.0 mM **1** at -30 °C had resonances at δ 5.44, 2.38. This solution was then electrolyzed at -30 °C using a coiled gold wire working electrode. After IR showed that **1** had been oxidized by two electrons to the putative (mesitylene)W(CO)₃(CD₃CN)²⁺ (Figure 3c), the ¹H NMR spectrum recorded at -30 °C had resonances at δ 6.96, 2.55, which are assigned to the coordinated mesitylene ring in the oxidized product. An IR spectrum of the NMR sample was then run to verify that decomposition had not occurred.

OTTLE experiments with **1** in MeCN at room temperature showed that the oxidized product formed cleanly, but decomposed with a *t*_{1/2} ≈ 10 min to a new species having ν_{CO} = 2087, 2010 cm⁻¹. Upon reduction, these bands shifted to 1910, 1791 cm⁻¹, which were identified with (MeCN)₃W(CO)₃ by comparison to

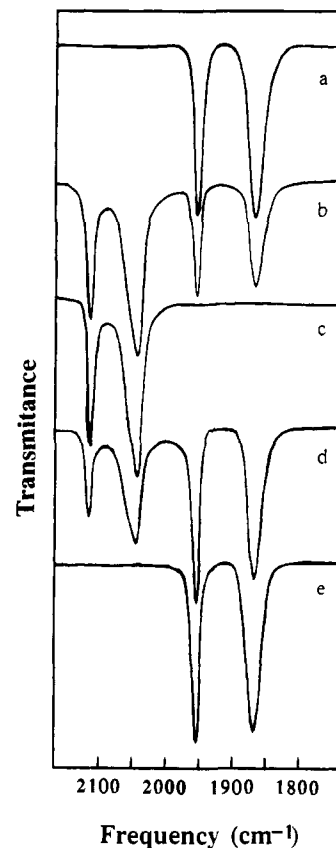
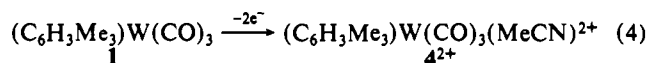


Figure 3. IR spectra obtained with the OTTLE cell containing 1.0 mM **1** in MeCN/0.20 M TBAPF₆ at 238 K. The applied potential was (a) none, (b and c) oxidizing, and (d and e), reducing. The sequence a-e required ca. 10 min.

an authentic sample.²⁷ It is known²⁸ that the first oxidation of (MeCN)₃W(CO)₃ is chemically reversible and the second irreversible in MeCN on the CV time scale. A separate OTTLE study with (MeCN)₃W(CO)₃ gave ν_{CO} bands (after oxidation) at 2018, 1900 cm⁻¹, which upon further oxidation converted to 2087, 2010 cm⁻¹ (probably (MeCN)₃W(CO)₃(MeCN)²⁺); the latter set matches that formed from the decomposition of oxidized **1**.

The chemical oxidation of (C₆Me₆)W(CO)₃ by I₂ has been shown²⁹ to yield (C₆Me₆)W(CO)₃I⁺, which decomposes rapidly in donor solvents. We synthesized (mesitylene)W(CO)₃I⁺ by the reported²⁹ procedure and found that it dissolves in MeCN (ν_{CO} = 2071, 2002 cm⁻¹) but within a few minutes decomposes to liberate mesitylene and form a species having ν_{CO} = 2025, 1942 cm⁻¹, which most likely is (MeCN)₃W(CO)₃I⁺. A consideration of these results along with the OTTLE, voltammetric, and NMR data strongly suggest that the electrochemical, just as the chemical, oxidation of **1** involves conversion of W(0) to W(II) and coordination of a ligand to maintain the 18-electron count. Reaction 4 to give **4**²⁺ is proposed to occur in the absence of a ligand stronger



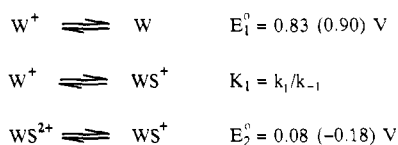
than the MeCN solvent. The presence of an alkyl phosphite greatly alters both the voltammetric response and the increase in ν_{CO} upon oxidation, thus supporting the assertion that ligand coordination occurs in conjunction with the 2-electron oxidation of **1** (as in eq 4).

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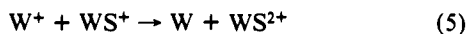
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Scheme I



A model to explain the 298 K cyclic voltammogram shown in Figure 2a must be consistent with a number of experimental observations. (1) The oxidation current i_A corresponds to two electrons at scan rates up to at least 10 V/s and probably 100 V/s, even at 228 K. (2) Both of the observed waves (A and B) are chemically irreversible at scan rates up to 10 000 V/s. (3) At an anodic switching potential of 1.1 V, the B/A current ratio is 0.50 and is essentially independent of scan rate. (4) The B/A ratio increases as the anodic switching potential is made more positive. A model that can accommodate all of these requirements is shown in Scheme I, with W and S representing **1** and MeCN, respectively. The potentials in parentheses refer to 228 K. In this simple mechanism, as the potential is swept positive, W is oxidized by 1 electron to the 17-electron species W^+ , which reacts rapidly with solvent S in a pseudo-first-order manner to give the 19-electron WS^+ . At this potential WS^+ is spontaneously oxidized to the 18-electron WS^{2+} (4^{2+}), thus accounting for the overall 2-electron nature of wave A in Figure 2. On the negative scan WS^{2+} is reduced at E_2^0 (wave B) to WS^+ , which is further reduced to W after dissociation via the k_{-1} step. Digital simulations²⁴ of this model were performed over a wide range of variables (scan rate, K_1 , k_1 , and k_{-1}) with the assumption that both charge transfers are electrochemically reversible. To satisfy the four criteria listed above, it was found that $0.1 < K_1 < 10$. If K_1 is outside this range, an unrealistic value of the rate constant k_1 is required for an acceptable simulation. For example, a K_1 of 100 or 0.01 requires $k_1 > 10^9 \text{ s}^{-1}$, even at 228 K. While 17-electron complexes are usually very reactive, previous quantitative studies³ of 17-electron species, including highly unstable ones, show that a rate constant this large is unlikely. Additionally, as will be shown below, a k_1 of 10^9 s^{-1} means that the second-order reaction of W^+ with $P(OBu)_3$ must have a rate constant exceeding the encounter controlled limit. An equilibrium constant K_1 of 10 or 0.10 implies a k_1 of at least 10^7 s^{-1} , which is probably too large as well, but not impossible. It is much more likely that K_1 is near unity for this requires only that $k_1 \geq 10^5 \text{ s}^{-1}$. Setting $K_1 = 1$ led to successful simulations of Scheme I and of the proposed mechanism for the more complex competitive reaction of W^+ with MeCN and $P(OBu)_3$ (vide infra).

Within the context of Scheme I, the homogeneous electron transfer steps given in eqs 5 and 6 can be shown to have very large equilibrium constants and, therefore, may be expected to contribute



to the overall reaction mechanism. However, simulations showed that inclusion of eqs 5 and 6 in Scheme I changes the peak currents of waves A and B by at most a few percent, even when the rate of eqs 5 and 6 is on the order of ten times faster than that of the homogeneous reaction of W^+ and S to give WS^+ (k_1 step in Scheme I); rates larger than this for eqs 5 and 6 would exceed the encounter-controlled limit. These results are consistent with earlier studies of ECE processes, which show that homogeneous electron transfer steps that short-circuit electrode processes have relatively little effect on peak currents; the effects are mostly in the interpeak region.³⁰ Homogeneous electron transfer undoubtedly does occur in our system, but we feel justified in ignoring these processes since our analysis is based on the absolute and relative magnitudes of the peak currents.

The conclusion from the studies of **1** in MeCN is that oxidation produces a 17-electron radical W^+ that reacts rapidly and re-

versibly with solvent to give WS^+ . Voltammetric, spectroelectrochemical, and NMR experiments show, however, that the observed species is the 18-electron complex WS^{2+} . The insensitivity of the voltammetric results on the CV time scale to the nature of the electrolyte strongly suggests that solvent and not electrolyte anion (ClO_4^- , PF_6^-) reacts with W^+ . This follows from the demonstrated¹⁰ greater nucleophilicity of ClO_4^- compared to PF_6^- . The power of digital simulation techniques to extract rate and equilibrium parameters for important intermediates that are not experimentally observable has been illustrated. The assumptions inherent in our analysis are quite reasonable ones: (1) the oxidation of **1** occurs initially by one electron and (2) the subsequent spontaneous 1-electron oxidation of W^+ implies a homogeneous reaction of W^+ to generate a more electron-rich species (WS^+). The assumption that this species is WS^+ is consistent with the known associative behavior of 17-electron complexes. Although the equilibrium constant for $W^+ \rightleftharpoons WS^+$ is rather small (near unity), the spontaneous second oxidation means that the electroactive species is entirely converted to WS^{2+} .

As noted above, the oxidation of $(C_6Me_6)W(CO)_3$ in MeCN has been previously reported,¹⁷ with the observed CV being very similar to that in Figure 2a. In this study¹⁷ the species responsible for wave B (and hence observed) was assigned as the 19-electron complex WS^+ . While consistent with the qualitative shape of the CV, this hypothesis can be dismissed in view of our observation that wave A involves a 2-electron change. Similarly, the large increase (ca. 165 cm^{-1}) in ν_{CO} upon oxidation of **1**, as well as the NMR spectrum of the product, is consistent^{29,31} only with a $W(II)$ (i.e., 18-electron) species.

It is interesting to compare the behavior of (mesitylene)Cr(CO)₃ (**3**) and (mesitylene)W(CO)₃ (**1**) when oxidized in MeCN. Although both **1** and **3** undergo a net 2-electron oxidation at a similar potential, the chemistry involved is entirely different for the two complexes. With 3^+ , attack by solvent leads to rapid loss of arene and CO ligands, followed by further oxidation. In contrast, 1^+ (W^+) merely adds the solvent, retaining the arene and CO groups, and then is further oxidized. It is known³² that the metal-ligand bond strengths are greater in **1** than in **3**, apparently by a substantial amount, and so it is perhaps not surprising that 1^+ is more reluctant than 3^+ to dissociate arene and CO ligands. Whatever the reason, the important point is that (arene)W(CO)₃ complexes can be electroactivated without decomposition, which means that it may be possible to utilize the oxidatively induced enhanced electrophilic character of the arene and CO ligands in synthetic procedures.

A comparison of the relative reactivity of the 17-electron complexes 1^+ and 3^+ toward associative attack by MeCN is possible provided the reasonable assumption is made⁹ that this step is rate limiting in the overall decomposition of 3^+ in MeCN. It was found that the oxidation of **3** displayed some chemical reversibility at a platinum electrode at sweep rates greater than 10 V/s. Assuming an ECE mechanism, the rate of reaction of the 17-electron radical 3^+ with MeCN was calculated by both analytical and digital simulation procedures as previously described.⁹ Correcting for the solvent concentration, the second-order rate constant at 298 K was computed to be $10 \text{ M}^{-1} \text{ s}^{-1}$. This rate constant is circa 10^4 times smaller than that for the reaction of 1^+ with MeCN to give 4^+ (vide infra). This conclusion, that the 17-electron tungsten complex is much more reactive than the chromium analogue with respect to attack by MeCN, parallels closely the reaction of the 18-electron complexes (arene)M(CO)₃⁺ (M = Mn, Re) with MeCN, for which the third-row metal (Re) was found³³ to be ca. 10^4 times more reactive than the first-row metal (Mn). These rate orders, $W \gg Cr$ and $Re \gg Mn$ may reflect less steric congestion for nucleophilic attack at the third-row metal center. In contrast to our results, recent work with the

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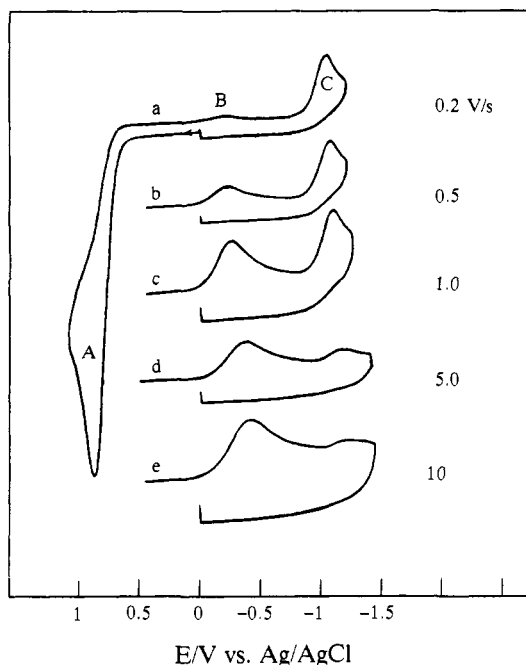


Figure 4. Cyclic voltammograms of 1.0 mM **1** and 3.7 mM $\text{P}(\text{OBU})_3$ in $\text{MeCN}/0.10 \text{ M TBAP}$ at 228 K. The working electrode was a glassy carbon disk. The relative current sensitivity is 10.8 (a), 5.4 (b), 5.4 (c), 1.0 (d), and 1.0 (e).

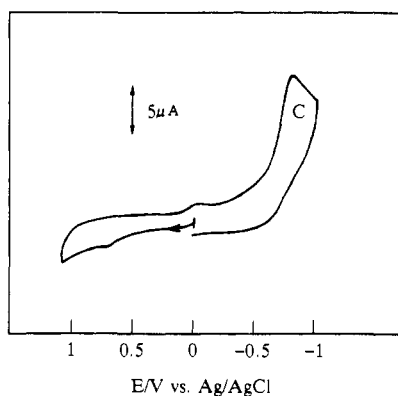


Figure 5. Cyclic voltammogram at 298 K, obtained after bulk electrolysis with a platinum basket electrode of 0.50 mM **1** and 0.50 mM $\text{P}(\text{OBU})_3$ in $\text{MeCN}/0.10 \text{ M TBAPF}_6$ at 298 K. The working electrode for the CV was a glassy carbon disk and the scan rate was 0.20 V/s.

17-electron complexes $\text{M}(\text{CO})_3(\text{PR}_3)_2^+$ ($\text{M} = \text{Fe}, \text{Os}$) suggests³⁴ that associative attack in this case is faster with iron compared to osmium by a factor of about six.

Effect of $\text{P}(\text{OBU})_3$ on the Oxidation of (Mesitylene) $\text{W}(\text{CO})_3$ in MeCN. Cyclic voltammetry of **1** in MeCN in the presence of $\text{P}(\text{OBU})_3$ is illustrated by data at 228 K (-45°C) in Figure 4. As can be seen, two reduction waves (B and C) are present, the relative magnitudes of which are scan rate dependent. Similar results were obtained at 298 K, except that a scan rate approximately ten times that shown for each CV in Figure 4 was required to produce CV's with analogous B/C current ratios. Reduction wave B corresponds to that in MeCN without $\text{P}(\text{OBU})_3$, as shown in Figure 2a. (The difference in potentials for wave B in Figures 2 and 4 is due solely to the temperature—Scheme I.) It was found that the current i_A did not change when $\text{P}(\text{OBU})_3$ was added to **1** in MeCN, meaning that wave A corresponds to two electrons with or without $\text{P}(\text{OBU})_3$. Room temperature bulk electrolysis of 0.50 mM **1**, 0.50 mM $\text{P}(\text{OBU})_3$, and 0.10 M TBAPF_6 in MeCN

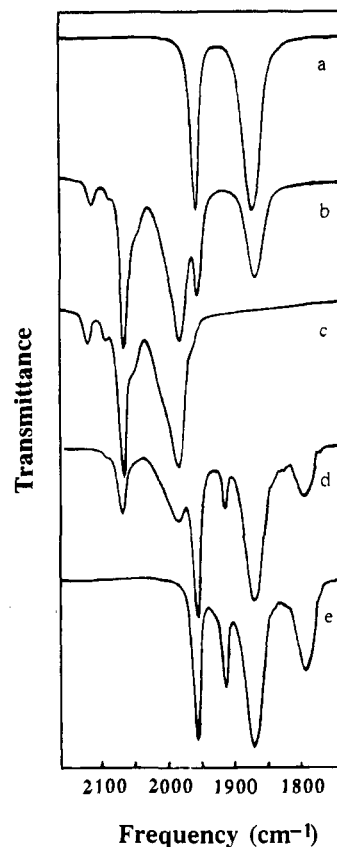


Figure 6. IR spectra obtained with the OTTLE cell containing 1.0 mM **1** and 1.1 mM $\text{P}(\text{OBU})_3$ in $\text{MeCN}/0.20 \text{ M TBAPF}_6$ at 298 K. The applied potential was (a) none, (b and c) oxidizing, and (d and e) reducing. The sequence a–e required ca. 8 min.

with a platinum basket working electrode gave a color change from light yellow to a deeper yellow and a charge corresponding to 2.0 electrons. A CV of the solution after electrolysis is shown in Figure 5; note that the only prominent feature is wave C at -0.74 V (-0.97 V at 228 K). As discussed below, the species reduced at wave C is very likely (mesitylene) $\text{W}(\text{CO})_3\text{P}(\text{OBU})_3^{2+}$ (5^{2+}), which is formed in competition with 4^{2+} .

A room temperature OTTLE experiment in the presence of $\text{P}(\text{OBU})_3$ is shown in Figure 6. Oxidation of **1** produced a new species having ν_{CO} bands at 2064, 1980 cm^{-1} . There were also weak ν_{CO} bands at 2113 and 2086 cm^{-1} (Figure 6c), which are readily assigned from the analysis given above as due to 4^{2+} ($\nu_{\text{CO}} = 2113, 2044 \text{ cm}^{-1}$) and the oxidation product of $(\text{MeCN})_3\text{W}(\text{CO})_3$ (probably $(\text{MeCN})_3\text{W}(\text{CO})_3(\text{MeCN})^{2+}$, $\nu_{\text{CO}} = 2087, 2010 \text{ cm}^{-1}$), respectively. Reduction of this solution produced the spectrum in Figure 6e, which corresponds to mostly **1**, along with a substantial amount of $(\text{MeCN})_3\text{W}(\text{CO})_3$ ($\nu_{\text{CO}} = 1911, 1791 \text{ cm}^{-1}$). The OTTLE and CV experiments strongly suggest that the species having $\nu_{\text{CO}} = 2064, 1980 \text{ cm}^{-1}$ and responsible for wave C in Figures 4 and 5 is 5^{2+} . The low ν_{CO} frequencies of 5^{2+} compared to 4^{2+} are consistent with the stronger σ -donor character of $\text{P}(\text{OBU})_3$ compared to MeCN. A separate OTTLE experiment showed that 5^{2+} decomposes with a $t_{1/2} \approx 30 \text{ min}$ at room temperature, showing that 5^{2+} is slightly more stable than 4^{2+} ($t_{1/2} \approx 10 \text{ min}$). Both 4^{2+} and 5^{2+} decompose with loss of the arene, as was shown by the appearance of $(\text{MeCN})_3\text{W}(\text{CO})_3$ as the principal product of reduction of solutions of 4^{2+} and 5^{2+} that were ca. 2 half-lives old. It may be noted that the symmetry of 4^{2+} and 5^{2+} is sufficiently low that one might expect to observe three ν_{CO} bands. While only two bands are seen, note that the lower frequency band is broad and that two ν_{CO} bands are observed for complexes of similar symmetry, e.g., $(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3\text{I}$.³⁵

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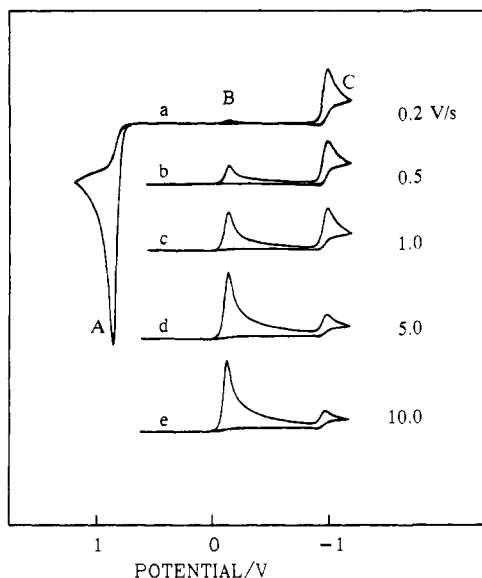


Figure 7. Simulated cyclic voltammograms, based on Scheme II at 228 K, of a solution containing a 1:3.7 molar ratio of 1:P(OBu)₃. The input parameters are given in Scheme II and Table I; the current axis is normalized by dividing the current by (scan rate)^{1/2}. Comparisons may be made to experimental voltammograms in Figure 4.

With the above information in hand, one can readily interpret the qualitative features of the CV's in Figure 4. As W⁺ is formed at wave A, reaction can occur with MeCN to give WS⁺ (4⁺) or with P(OBu)₃ to give WP⁺ (5⁺). These species are oxidized spontaneously to WS²⁺ and WP²⁺ (4²⁺ and 5²⁺), respectively. The relative amount of WS²⁺ and WP²⁺ formed depends on the relative rates and equilibria of formation of WS⁺ and WP⁺. If the scan rate is slow enough, equilibrium conditions obtain and the WS⁺ formed from the reduction of WS²⁺ at wave B will be converted to WP⁺ and then be spontaneously oxidized to WP²⁺. Thus, wave B will vanish. If the scan rate is large enough to preclude the attainment of equilibrium conditions, some of the WS⁺ produced at wave B will be further reduced to W (plus S) before it can be converted to WP²⁺, and hence wave B will be observed. That faster scan rates are required at 298 K compared to 228 K in order to get the same CV profiles seen in Figure 4 simply reflects larger rate constants at the higher temperature. The interpretation of the CV's in Figure 4 can be put on a sound quantitative basis by digital simulation of models incorporating the qualitative observations just presented.

Before discussing digital simulations, it should be noted that cyclic voltammetry of **2** in the presence of PBU₃ in MeCN has been previously described.¹⁷ These authors reported CV's similar to those in Figure 4 and the interpretation given was that wave C corresponds to the reduction of WPBu₃⁺. Our voltammetric and OTTLE results with **1** in the presence of P(OBu)₃ clearly show that wave C is due to WP²⁺ and not WP⁺, and hence the elusive 19-electron WP⁺ species is not experimentally observed.

A model to rationalize the voltammetric data must satisfy a number of criteria. (1) The processes represented by waves A, B, and C in Figure 4 are all chemically irreversible. (2) Wave A corresponds to two electrons. (3) The current ratio B/C is very dependent on scan rate. (4) Any model must be consistent with Scheme I in the limit of zero P(OBu)₃ concentration. These criteria place stringent limitations on proposed heterogeneous electron-transfer and homogeneous reactions. The CV's of **1** in MeCN without P(OBu)₃ were successfully reproduced by the model in Scheme I. From this we concluded that $k_1 \geq 10^5 \text{ s}^{-1}$ and $K_1 \approx 1$. The value of 10^5 s^{-1} for k_1 applies to CV's at 228 K as well as 298 K. Since k_1 must be larger at the higher temperature, we conclude that $k_1 \geq 10^6 \text{ s}^{-1}$ at 298 K. For reasons explained below, it is unlikely that k_1 is in fact much larger than this number.

Digital simulations based on a variety of models were tried in an attempt to reproduce the CV's of **1** in the presence of P(OBu)₃.

Scheme II

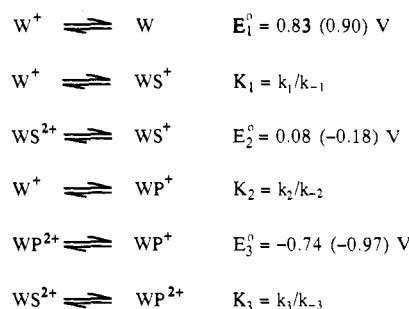


Table I. Rate and Equilibrium Parameters for Schemes I and II^a

	298 K	228 K	298 K	228 K
k_1	1 000 000	100 000	k_1/k_2	50
k_{-1}	1 000 000	100 000	K_2/K_1	10
k_2^b	20 000	2 000	k_3^b	5
k_{-2}	2 000	200	k_{-3}	0

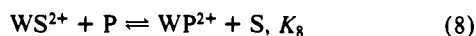
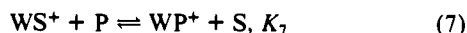
^aAll rate constants are in units of s⁻¹. ^bThe P(OBu)₃ concentration is 3.7 mM.

A successful mechanism is given in Scheme II and CV's calculated from this model (at 228 K) are presented in Figure 7, which may be compared to experimental CV's at 228 K in Figure 4. Scheme II contains three charge-transfer reactions and three homogeneous reactions and consists of Scheme I to which reactions involving possible phosphite complexes have been added. The potentials in parentheses refer to 228 K and those without parentheses refer to 298 K. According to this model, as the potential is swept positive, W is oxidized to W⁺, which reacts rapidly and reversibly with solvent or phosphite to generate WS⁺ and WP⁺, respectively. These are spontaneously oxidized to the 18-electron complexes WS²⁺ and WP²⁺, which can interconvert (k_3, k_{-3}). At E_2° , WS²⁺ is reduced to WS⁺, which can dissociate (k_{-1}) and be further reduced to W or be trapped to give WP⁺ (and thereby WP²⁺). At E_3° , WP²⁺ is reduced to WP⁺, followed by dissociation (k_{-2}) to W⁺ and further reduction to W. An alternative model in which the K_2 step is replaced by the reaction $\text{WS}^+ \rightleftharpoons \text{WP}^+$ also gave acceptable fits to experimental data, but it may be ruled out because this reaction requires that ligand substitution in these 19-electron species be associative; if dissociative, this alternative model is identical with the one in Scheme II. The experimental criteria listed above permit relatively little variation in the various rate and equilibrium parameters. Since Scheme II contains a large number of adjustable parameters, it might appear difficult to know if the fit determined is unique. However, it must be emphasized that the parameters describing the first three of the six reactions in Scheme II were obtained from simulations of Scheme I, which refers to independent experiments in which P(OBu)₃ was not present. Accordingly, the constants $k_1, k_{-1}, K_1, E_1^\circ, E_2^\circ$ from Scheme I were used as input and not allowed to vary when simulating Scheme II. With these constants in hand, the ratios k_1/k_2 and K_2/K_1 were varied until the current ratio B/C approached the experimental values while wave A remained a 2-electron change and waves A, B, and C remained irreversible. All of this was possible with Scheme II minus the K_3 step. However, at this point the scan rate dependence of the B/C ratio (Figure 4) could not be reproduced even approximately. Inclusion of step K_3 solved this problem and led to simulations that mimic the data very closely at all scan rates and at both 298 and 228 K. A summary of the rate and equilibrium parameters derived in this manner is given in Table I.

There are several other aspects of Scheme II that were probed experimentally. The pseudo-first-order rate constants k_2 and k_3 should depend on the concentration of P(OBu)₃. When [P(OBu)₃] was decreased from the nominal value of 3.7 mM to 1.1 mM, the B/C current ratio increased by a factor of two at 1.0 V/s, as predicted by Scheme II. The equilibrium between WS²⁺ and WP²⁺ is accessible since these are the species observed in the OTTLE experiments. From these we infer that $K_3 > 100$. The

simulations predict that k_3 is ca. 5 s^{-1} at 298 K. While it was not feasible to measure this directly, it was possible to determine that the reaction is over in less than 1 min, consistent with the indicated rate constant.

It is both interesting and informative to examine the parameters in Table I. The rate and equilibrium constants refer to pseudo-first-order conditions. Correcting for concentrations, the constants at 298 K become: $k_1^* \approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $K_1^* \approx 10^{-1} \text{ M}^{-1}$, $k_2^* \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $K_2^* \approx 3 \times 10^3 \text{ M}^{-1}$. When considering Scheme I above, it was stated that K_1 is limited because of the implied magnitude of k_1 . The reason for this is now apparent. For example, if $K_1 = 100$, consideration of experimental data and Scheme I requires that $k_1 > 10^9 \text{ s}^{-1}$ at 228 K. Assuming this translates into $k_1 > 10^{10} \text{ s}^{-1}$ at 298 K, Scheme II then implies that $k_2^* \geq 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This value is near the encounter-controlled limit and seems impossibly large, particularly in view of the lower rate constant ($10^7 \text{ M}^{-1} \text{ s}^{-1}$) measured for the reaction of P(OPr)_3 and the extremely unstable/reactive $\text{Mn}(\text{CO})_5$ radical.³⁶ That $K_2^* > K_1^*$ and $k_2^* > k_1^*$ is expected from the greater basic strength of P(OBu)_3 compared to MeCN. The relatively large values of k_1^* and k_2^* are in line with the normal behavior of 17-electron species in associative reactions. The 18-electron complex WS^{2+} is quite reactive ($k_3 \approx 5 \text{ s}^{-1}$), but nevertheless orders of magnitude less so than the related 17-electron (W^+) and 19-electron (WS^+) complexes. It is not known if step k_3 is associative or dissociative, although the 2+ charge would be expected to favor the former mode of activation. It is interesting to compare the equilibrium constants for reactions 7 and 8. The parameters in Table I permit these to be calculated: $K_7 = (K_2/K_1) \cdot ([\text{MeCN}]/[\text{P(OBu)}_3]) \approx 10^4$, $K_8 \approx ([\text{MeCN}]/[\text{P(OBu)}_3]) \cdot (\exp(-1/RT)[-F(0.08) + F(-0.74) - RT \ln 1 - RT \ln 10]) \approx 10^{18}$. The much greater constant for eq 8 probably reflects the 2+ charge and, especially, the half-antibond present in the 19-electron complexes.³



It is noteworthy that the phosphite complex WP^{2+} is reduced at a potential ca. 0.8 V negative of the WS^{2+} reduction. This is

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not surprising in view of the substantially lower ν_{CO} frequencies of WP^{2+} and the known^{37,38} superior σ -donating ability of P(OR)_3 compared to MeCN. However, a number of systems are known in which an acetonitrile complex is reduced at a potential *negative* of a phosphite or phosphine analogue. Two examples of this phenomenon are the $\text{MeCpMn}(\text{CO})_2\text{L}^{+/0}$ and $\text{Cr}(\text{CO})_5\text{L}^{+/0}$ couples ($\text{L} = \text{MeCN}, \text{P(OMe)}_3$, or PPh_3).^{39,40} On the other hand, the reduction of $(\text{CF}_3)_2\text{C}_2\text{Co}_2(\text{CO})_5\text{L}$ follows⁴¹ the trend observed by us for WL^{2+} , i.e., $E^\circ(\text{L} = \text{MeCN}) > E^\circ(\text{L} = \text{P(OR)}_3)$. We do not have an explanation for this contrasting behavior except to suggest that it is linked to different electronic structure requirements of the systems in question.

General Comments and Summary. The electrochemical oxidation of (mesitylene) $\text{W}(\text{CO})_3$ (W) in MeCN produces the 17-electron complex (W^+) that reacts very rapidly with solvent or phosphite to give 19-electron species (WS^+ , WP^+) that undergo spontaneous further oxidation to WS^{2+} , WP^{2+} . Although the 17-electron \rightleftharpoons 19-electron transformation is not directly observable, digital simulation techniques that model experimental voltammetric data were successfully used to determine rate and equilibrium parameters. The complex W^+ is among the most reactive 17-electron complexes reported to date and is ca. 10^4 times more reactive than the 17-electron chromium analogue (Cr^+) toward associative attack by MeCN to generate 19-electron species. In contrast to the behavior seen with (arene) $\text{Cr}(\text{CO})_3$, oxidation of (arene) $\text{W}(\text{CO})_3$ does not lead to loss of arene and CO ligands, suggesting that electroactivated (arene) $\text{W}(\text{CO})_3$ complexes may have useful synthetic applications.

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