

One-Step, Two-Electron Oxidation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$: Unexpected Formation of Stable Tungsten(IV) Dications

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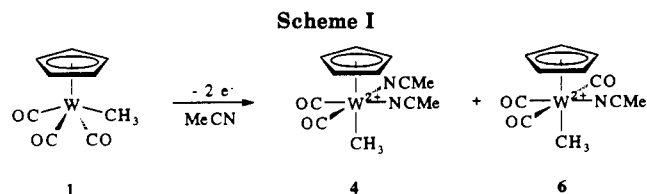
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The methyltungsten complex $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$ (1) undergoes a chemically irreversible two-electron-oxidation process at +0.55 V vs the ferrocene/ferrocenium (FC) couple in acetonitrile. Chemical oxidation with acetylferrocenium tetrafluoroborate as the oxidizing agent ($E_{\text{red}} = +0.248$ V vs FC) provides high combined yields of tungsten(IV) complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCMe})_2\text{CH}_3^{2+}$ (4) and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{NCMe})\text{CH}_3^{2+}$ (6), the 4:6 ratio being strongly dependent on the reaction conditions. Ferrocenium oxidation of 1 yields only 4. Reduction of 4 and 6 with 2 equiv of cobaltocene quantitatively generates $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCMe})\text{CH}_3$ and 1, respectively. Formation of the dicationic products 4 and 6 is proposed to take place via readily oxidizable, cationic 19-electron intermediates.

Introduction

The one-electron oxidation of stable 18-electron organotransition-metal complexes is a convenient method for the generation of reactive 17-electron species. A variety of reactions at 17-electron metal centers are commonly considered to proceed via 19-electron intermediates and/or transition states.¹⁻³ Oxidation of metal alkyl complexes often leads to rapid follow-up reactions such as CO insertion³ and metal-carbon bond cleavage.^{4,5} Organic and organometallic products formed from the oxidatively induced reactions of metal alkyls in several instances suggest the formation of alkyl radicals in these reactions.^{4,5} We recently provided experimental evidence that 19-electron complexes could be involved in the oxidatively induced metal-carbon bond homolysis reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PR}_3)\text{CH}_3$ (R = Ph, Cy (cyclohexyl))^{6a} and $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})(\text{PPh}_3)\text{CH}_3$ ^{6b} in acetonitrile. The evidence included reaction rate laws that were first order with respect to added acetonitrile when the reactions were performed in dichloromethane^{6a,b} and rate enhancements by factors of at least 50 ($(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})(\text{PCy}_3)\text{CH}_3$ ^{6a}) and 2000 ($(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{CO})(\text{PPh}_3)\text{CH}_3$ ^{6b}) as a result of changing the solvent from dichloromethane to acetonitrile.

As part of our ongoing studies of the redox chemistry of organotransition-metal compounds, we report here that $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$ (1) quite surprisingly undergoes a



two-electron-oxidation process. The reaction is accompanied by ligand addition and substitution and provides stable, diamagnetic tungsten(IV) dications without the anticipated⁵ rupture of the tungsten-methyl bond.

Results

The initial electrochemical investigation of the oxidation chemistry of 1 was carried out by the use of derivative cyclic voltammetry (DCV).⁶ DCV in many cases offers significant advantages over conventional cyclic voltammetry, including better resolution with respect to fine details in the voltammograms and more accurate readings of cyclic voltammetry peak potentials, especially for broad waves. The DCV analysis showed methyl complex 1 to undergo oxidation at $E_{\text{ox}} = +0.55$ V vs the ferrocene/ferrocenium (FC) couple. Figure 1a shows a DCV trace for the oxidation of 1 (2.0 mM substrate in acetonitrile/0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$) at a Pt microelectrode ($d = 0.4$ mm) at 20 °C and a voltage sweep rate $v = 1.0$ V/s. The cyclic voltammetric peak potential corresponds to the position where the rapidly descending curve crosses the base line after the first peak, labeled I. The low intensity of the reverse-scan DCV peak (II) indicates that the electrode-generated intermediate undergoes complete reaction on the time scale of the measurement.⁷ This situation persisted at scan rates as high as 1000 V/s. The cation $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{NCMe})^+$ (2), which would result from the anticipated^{5a,b} solvent-assisted W-CH₃ homolysis of 1⁺, is not a decomposition product under the reaction conditions. A separate DCV analysis of 2 in the form of its tetrafluoroborate salt showed this cation to undergo oxidation at +1.20 V vs FC. The DCV trace for this oxidation (conditions and concentrations as for the oxidation of 1) is displayed in Figure 1b.

Constant-current coulometry with DCV monitoring of the disappearance of the substrate⁸ indicated the con-

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(7) The shape of a "normal" cyclic voltammogram causes the derivative cyclic voltammogram to show a peak during the reverse scan, even when the electrode-generated intermediate undergoes "complete reaction" on the time scale of the measurement.

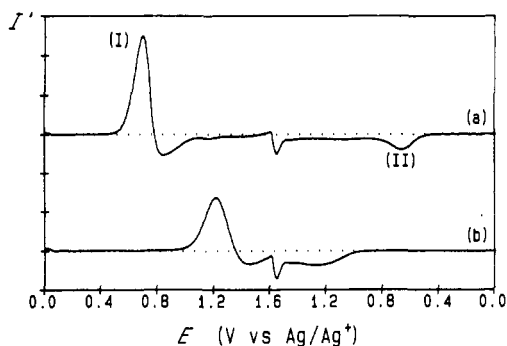


Figure 1. Derivative cyclic voltammograms for the oxidation of (a) $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$ (1; 2.0 mM) and (b) $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{NCMe})^+\text{PF}_6^-$ ($2(\text{PF}_6^-)$; 2.0 mM) in acetonitrile/0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ at a Pt microelectrode ($d = 0.4$ mm) at 20 °C and a voltage sweep rate $\nu = 1.0$ V/s.

sumption of 2.1 ± 0.1 faraday/mol of charge during the oxidation of 1. Oxidation of a dilute acetonitrile solution (ca. 6 mM; see Experimental Section for details) of 1 by dropwise addition of a solution of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{COME})\text{Fe}^+\text{BF}_4^-$ (3)⁹ ($E_{\text{red}} = +0.248$ V vs FC^{10}) provided the dicationic product $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCMe})_2\text{CH}_3^{2+}$ (4) as its bis(tetrafluoroborate) salt, isolated in 74% yield. The structural assignment is corroborated by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and IR spectroscopic data as well as by elemental analysis. The ^1H NMR spectrum of 4 (acetonitrile- d_3) displays a singlet for the methyl group at δ 1.49 (to be compared with δ 0.38 for 1), coordinated acetonitrile at δ 2.58, and a cyclopentadienyl singlet at δ 6.40 (cf. δ 5.49 in 1). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displayed resonances for the methyl group (δ 28.9), coordinated acetonitrile (δ 5.5, 135.3), cyclopentadienyl (δ 98.9), and CO (δ 196.3). The IR spectrum displayed two approximately equally intense CO bands at 2110 and 2070 cm^{-1} (to be contrasted with 2020 and 1915 cm^{-1} for 1). The high-frequency IR absorptions as well as the low-field ^1H NMR resonances strongly suggest that the product is a doubly charged species. The most electron-deficient singly charged species that may be relevant for the purpose of comparison appears to be $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_4^{+11}$ (^1H NMR (acetone- d_6) δ 6.65; IR (Nujol) 2121, 2020 cm^{-1}).

Assuming pseudo-octahedral coordination geometry at the W center and rigidity of the structure on the NMR time scale, the coordination geometry indicated in Scheme I is consistent with the spectroscopic data for 4. This ligand arrangement places the donor acetonitrile ligands trans to the acceptor carbonyl ligands. An alternative formulation in which the CO ligands have a mutual trans orientation would lead to the same number of NMR signals for symmetry reasons. However, the trans geometry is inconsistent with the presence of two equally strong IR bands. All attempts thus far at obtaining X-ray quality crystals of 4 with various counterions (BF_4^- , PF_6^- , BPh_4^-) have only resulted in needles or fine powders unsuitable for the purpose.

Treatment of 1 with 2 equiv of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^+\text{PF}_6^-$ (5) generated $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCCD}_3)_2\text{CH}_3^{2+}$ ($4\text{-}d_6$) during the course of several days (^1H NMR, acetonitrile- d_3 , ca. 40 mM substrate, ambient temperature). Due to a slow decomposition of the product while the reaction proceeded

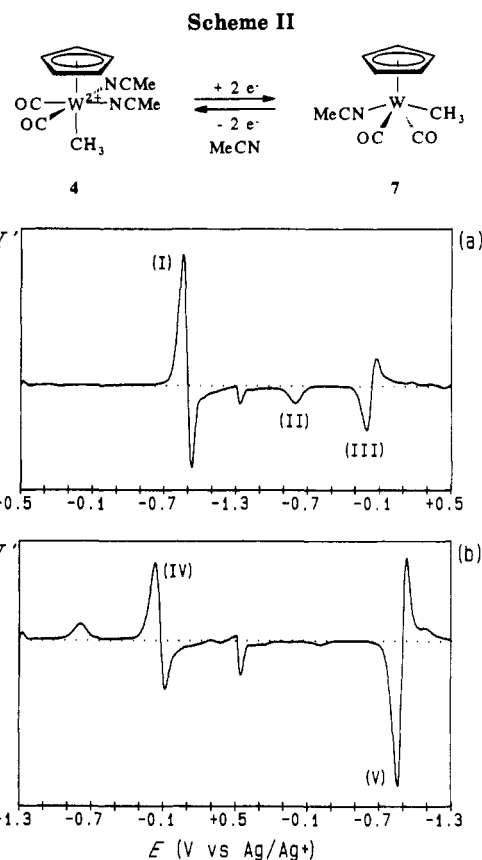


Figure 2. (a) Derivative cyclic voltammogram for the reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCMe})_2\text{CH}_3^{2+}](\text{BF}_4^-)_2$ ($4(\text{BF}_4^-)_2$). (b) Derivative cyclic voltammogram for the oxidation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCMe})\text{CH}_3$ (7), generated by steady-state reduction of $4(\text{BF}_4^-)_2$ at -1.3 V vs the Ag/Ag^+ reference. Concentrations and conditions are identical with those given in Figure 1.

to completion, this is not a practical method for the synthesis of 4. Rapid addition of 2 equiv of oxidant 3 to a concentrated solution of 1 (ca. 50 mM) in acetonitrile quantitatively (^1H NMR, internal standard) generated a mixture of the dications 4 and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{NCMe})\text{CH}_3^{2+}$ (6), the relative yields of 4 and 6 being in the range 1:1 to 4:1 for different runs. On a preparative scale (see Experimental Section for details), a 4:1 mixture of 4 and 6 was isolated in 64% combined yield. Attempts at isolating product 6 from the reaction mixture have not met with success. Therefore, 6 has been characterized only by ^1H NMR spectroscopy of a mixture of 4 and 6 (δ 1.53 (s, 3 H), 2.58 (s, 3 H), 6.60 (s, 5 H)). The IR spectrum of 6 apparently overlapped with that of 4, since no additional absorptions were observed for this mixture. The proposed structures of 4 and 6 are further corroborated by chemical evidence (vide infra). Scheme I summarizes the outcome of the reactions between 1 and oxidant 3.

Treatment of 4 with 2 equiv of cobaltocene ($E_{\text{ox}} = -1.25$ V vs FC^{12}) in acetonitrile- d_3 provided a quantitative yield (^1H NMR, hexamethylbenzene internal standard) of the known¹³ neutral methyl compound $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCCD}_3)\text{CH}_3$ ($7\text{-}d_3$). The IR spectrum of the reaction mixture displayed bands at 1815 and 1915 cm^{-1} , in close agreement with the previously reported values. Attempts at isolating $7\text{-}d_3$ were unsuccessful, in accord with previous observations.¹³ The transformation of 4 to 7 could be reversed by the addition of 2 equiv of 5, as indicated in Scheme II. The interconversions between 4 and 7 lend

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further support to the structure assigned to product 4. The chemical reversibility of these reactions furthermore suggests that no ligand coupling reactions involving the acetonitrile ligands have taken place.

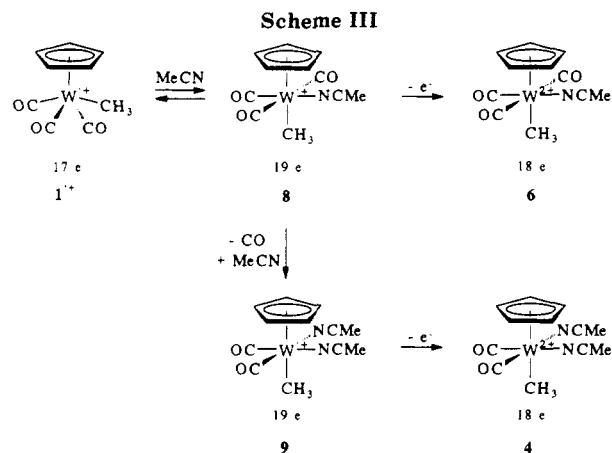
The chemically reversible interconversions between 4 ($E_{\text{red}} = -1.00$ V vs FC) and 7 ($E_{\text{ox}} = -0.18$ V vs FC) could also be observed by DCV. Figure 2a shows the DCV trace for the reduction of 4. Peak I corresponds to the reduction of 4, and the low intensity of the peak for the reverse process (II) indicates the occurrence of a rapid follow-up reaction generating a product, presumably 7, that undergoes oxidation at peak III. Figure 2b shows the DCV trace for the oxidation of 7, generated by steady-state reduction of 4 at an electrode rest potential of -1.3 V vs the Ag/Ag⁺ reference. This reduction generates 4, observed as peak IV. During the reverse sweep, 7 is regenerated (reduction peak V).

Reduction of a 3:1 mixture of 4 and 6 with 2 equiv of cobaltocene quantitatively generated a 3:1 mixture of 7-*d*₃ and 1 (¹H NMR, acetonitrile-*d*₃, internal standard). This reaction provides strong support for the structural assignment of 6, which, as has already been mentioned, could not be successfully isolated.

Discussion

From the oxidation potential measured for 1, a highly unfavorable equilibrium constant of 5×10^{-10} (25 °C) is calculated for the transfer of an electron from 1 to the ferrocenium cation. It appears extremely unlikely that this weak oxidant should be able to oxidize 1^{•+} even further to the dication stage before coordination of acetonitrile to yield the 18-electron dication 4. Instead, we propose that the 19-electron species ($\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3(\text{NCMe})\text{CH}_3^{\bullet+}$) (8) is an intermediate in the process. Despite its being a cation, 8 possesses excess electron density that tends to lower its oxidation potential well below that of neutral 1. The electrode potential difference for these two oxidation processes may be estimated to be at least 1.35 V. A DCV analysis of a mixture of 4 and 6 displays two reduction peaks, one located at -1.00 V vs FC (attributed to 4) and the other at -0.80 V vs FC, which we attribute to 6. The difference between the peak potentials for oxidation of 1 and reduction of 6, amounting to 1.35 V, provides a *minimum* value for the difference in oxidation potentials of 8 and 1. Taking into account the unknown kinetic potential shifts arising from the chemical irreversibility of both electrode processes will serve to increase this gap. Neutral 17-electron systems, generated by photochemical^{14a-g} or other means,^{14h} have previously been found to be capable of reducing suitable substrates, presumably via the intermediacy of neutral 19-electron adducts.¹⁴ In accord with this, it has recently been suggested^{15a} that fast, reversible one-step two-electron redox processes normally take place via rapid, intervening structural rearrangements (in this case solvent ligation) that render the second electron-transfer step more facile than the first.^{15b}

Scheme III shows a possible reaction mechanism that explains the formation of both dicationic products during



the oxidation of 1. The 19-electron intermediate 8 plays a crucial role here. In the presence of relatively high concentrations of oxidant 3, direct oxidation of 8 to yield product 6 is possible. However, under dilute conditions or in the presence of the weaker oxidant 5, the second-order electron-transfer reaction cannot compete with the pseudo-first-order ligand substitution process with the solvent acetonitrile to generate the new 19-electron intermediate ($\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2(\text{NCMe})_2\text{CH}_3^{\bullet+}$) (9).² Just as 7 was much easier to oxidize than 1, intermediate 9 should be oxidized more readily than 8, leading to dicationic product 4 even when the weak oxidant 5 is employed.

The dependence of the product distribution on the reaction conditions is in agreement with this interpretation. Dilute conditions yielded 4 as the only product. At high concentrations, 4 as well as 6 was obtained in all runs. However, the relative amounts of 4 and 6 did vary from one run to the next, although precautions were taken to perform the experiments in a reproducible manner. It is likely that the observed variation may be explained by irreproducible mixing of the reactants. The high-concentration, rapid-mixing procedure is likely to result in uneven mixing of oxidizing agent and substrate, giving rise to uneven concentrations of the two reactants throughout the solution.

In view of our previous investigations of the oxidative behavior of some ruthenium complexes,^{5a,b} we are somewhat surprised to see that the oxidation of 1 proceeds with retention of the W-CH₃ bond. However, it is known that third-row and second-row metals are more prone to coordination-sphere expansion than to rupture of metal-carbon bonds. For example, the oxidation of (arene)M(CO)₃ complexes leads to strikingly different behavior for M = Cr than for M = W.¹⁶ These observations may be viewed in the context of generally higher metal-carbon bond dissociation energies for third-row and second-row metals than for first-row metals.¹⁷

We anticipate that the discovery of the dicationic species 4 with its crowded coordination sphere will lead to new and interesting chemistry. It may potentially act as a precursor to new, higher oxidation state complexes.

Experimental Section

General Procedures. All reactions involving organometallic complexes were performed under an inert atmosphere with use of standard vacuum-line, Schlenk, syringe, or drybox techniques. Acetonitrile and acetonitrile-*d*₃ were distilled from P₂O₅ and CaH₂, respectively. ¹H and ¹³C[¹H] NMR spectra were recorded on

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Varian XL-300 or Varian Gemini-200 instruments. Chemical shifts are reported downfield from tetramethylsilane with use of the residual solvent proton resonances as internal standards. Infrared spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer. Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany. The electrochemical cells, data-handling procedures, and electrodes were as previously described.^{6a,18} Acetonitrile containing 0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ was used as solvent for electrochemical experiments and was passed through a column of active neutral alumina before use in order to remove water and protic impurities. The electrolyte was freed of air by purging with purified argon, and all measurements were carried out under a blanket of solvent-saturated argon gas.

Compounds 1,^{18a} 2,¹¹ 3,⁹ 5,^{19b} and cobaltocene^{19c} were prepared according to published procedures. All other chemicals were obtained commercially and used as received.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NCMe})_2\text{CH}_3^{2+}](\text{BF}_4^-)_2$ ($4(\text{BF}_4)_2$). A solution of 3 (180 mg, 0.56 mmol) in acetonitrile (2 mL) was added dropwise, at such a rate that the blue color of the oxidizing agent never persisted, to a stirred solution of 1 (100 mg, 0.28 mmol) in acetonitrile (50 mL) at 0 °C. The product was precipitated by the addition of ether at -20 °C. The solvent was decanted, and the residue was washed with ether. Recrystallization from acetonitrile/ether at 0 °C gave 4 (121 mg, 74%): yellow powder, mp 150–155 °C; ¹H NMR (200 MHz, acetonitrile-*d*₃) δ 1.49 (s, 3 H), 2.58 (s, 6 H), 6.40 (s, 5 H); ¹³C{¹H} NMR (50 MHz, acetonitrile-*d*₃) δ 5.5, 28.9, 98.9, 135.3, 196.3; IR (acetonitrile) ν_{CO} 2110, 2070 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{B}_2\text{F}_8\text{N}_2\text{O}_2\text{W}$: C, 25.02; H, 2.45; N, 4.86. Found: C, 25.35; H, 2.91; N, 5.45.

Preparation of a Mixture of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{NCMe})\text{CH}_3^{2+}](\text{BF}_4^-)_2$ ($6(\text{BF}_4)_2$) and $4(\text{BF}_4)_2$. A solution of 1 (50 mg, 0.14 mmol) in acetonitrile (20 mL) was added to a vigorously stirred solution of 3 (88 mg, 0.28 mmol) in acetonitrile (5 mL) at 0 °C by rapid injection with a syringe. The solution rapidly turned orange. The ionic products were precipitated by the addition of ether (30 mL) at -20 °C. The solvent was decanted, and the residue was washed with ether. Drying in vacuo left a 1:4 mixture, as determined by ¹H NMR spectroscopy, of $6(\text{BF}_4)_2$ and $4(\text{BF}_4)_2$ (55 mg, 64%). ¹H NMR for $6(\text{BF}_4)_2$ (acetonitrile-*d*₃): δ 1.53 (s, 3 H), 2.58 (s, 3 H), 6.60 (s, 5 H).

Oxidation of 1 with 3 in Acetonitrile-*d*₃. As mentioned in the Results, these reactions proceeded to give variable relative yields of $4\text{-}d_6$ and $6\text{-}d_3$. The details of a specific experiment will be presented here. A mixture of 1 (10 mg, 0.028 mmol) and hexamethylbenzene (1.0 mg, 0.006 mmol) was dissolved in ether (1 mL), and the solution was divided equally into two NMR tubes that were equipped with ground-glass joints. The solvent was carefully removed by vacuum transfer. Oxidant 3 (6.4 mg, 0.028

mmol) was added to one tube. Acetonitrile-*d*₃ (0.5 mL) was added to both tubes by vacuum transfer, and the tubes were sealed under vacuum. A rapid reaction took place in the tube containing 3, as evidenced by the color change from deep blue to intense orange. The contents of both tubes were analyzed by ¹H NMR spectroscopy. Comparison of the spectra revealed that the substrate was completely consumed and that a 3:1 mixture of $4\text{-}d_6$ and $6\text{-}d_3$ was formed in a quantitative combined yield within experimental errors.

Cobaltocene Reduction of $4(\text{BF}_4)_2$ in Acetonitrile-*d*₃. A mixture of $4(\text{BF}_4)_2$ (6.0 mg, 0.010 mmol) and hexamethylbenzene (1.0 mg, 0.006 mmol) was dissolved in acetonitrile (1 mL), and the solution was divided equally into two NMR tubes that were equipped with ground-glass joints. The solvent was carefully removed by vacuum transfer. To one of the tubes, cobaltocene (1.9 mg, 0.010 mmol) was added. Acetonitrile-*d*₃ (0.5 mL) was added to both tubes by vacuum transfer before the tubes were sealed under vacuum. A reaction took place in the cobaltocene-containing tube, as evidenced by the disappearance of the cobaltocene and formation of an orange solution. The only W-containing product detectable by ¹H NMR spectroscopy was $7\text{-}d_3$ (δ 0.14 (s, 3 H), 5.37 (s, 5 H)). The product yield was obtained by determining the cyclopentadienyl signal intensities of both samples with the hexamethylbenzene internal standard and was found to be quantitative within experimental errors, with complete consumption of the substrate. The NMR tube containing $7\text{-}d_3$ was opened, and an aliquot was analyzed by IR spectroscopy (ν_{CO} 1915, 1815 cm^{-1}). Oxidizing agent 5 (3.3 mg, 0.010 mmol) was added to the remaining solution. The ¹H NMR spectrum of this solution revealed that $4\text{-}d_6$ had formed.

Cobaltocene Reduction of a 3:1 Mixture of $4(\text{BF}_4)_2$ and $6(\text{BF}_4)_2$. A 3:1 mixture of $4(\text{BF}_4)_2$ and $6(\text{BF}_4)_2$ (10 mg, 0.017 mmol combined) and hexamethylbenzene (1.0 mg) were dissolved in acetonitrile (1 mL), and the solution was divided equally into two NMR tubes that were equipped with ground-glass joints. The solvent was carefully removed by vacuum transfer. To one of the tubes was added cobaltocene (3.4 mg, 0.018 mmol). Acetonitrile-*d*₃ (0.5 mL) was added to both tubes by vacuum transfer before the tubes were sealed under vacuum. Again, a reaction took place in the cobaltocene-containing tube. The only W-containing products detectable by ¹H NMR spectroscopy were $7\text{-}d_3$ and 1 in a 3:1 ratio. The combined product yield was found to be quantitative within experimental errors, and a complete conversion of the substrates had taken place.

Constant-Current Coulometry Experiments. Constant-current electrolyses were carried out in an H-shaped cell, the compartments of which were separated by a medium-frit glass junction. A platinum-gauze working electrode was used. Solutions of 1 (1–2 mM) in 20 mL of acetonitrile/0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ were electrolyzed with a constant current of 10 mA, while the disappearance of the substrate was monitored by DCV. Three separate measurements indicated the consumption of 2.1 ± 0.1 faraday/mol of charge.

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