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Chemical and Electrochemical Oxidation of Group 6 Cyclopentadienylmetal Hydrides. First Estimates of 17-Electron Metal Hydride Cation Radical Thermodynamic Acidities and Their Decomposition to 17-Electron Neutral Radicals

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Abstract: The oxidation chemistry of the organometallic hydride complexes $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, **1**; Mo, **2**; W, **3**), $(\eta^5\text{-}C_5Me_5)Mo(CO)_3H$ (**4**), and $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$ (**5**) has been investigated in acetonitrile solution by electrochemical and other methods. The thermodynamic acidities of the cation radicals of **1–5** have been estimated by the use of a thermochemical cycle based on the oxidation potentials of **1–5** and their conjugate bases (anions) as well as the solution pK_a values of **1–5**. The metal hydride cation radical pK_a estimates fall in the range −10 to +5, which makes these complexes the most acidic hydrides for which pK_a values have been determined. Coulometric measurements show that **1–5** undergo overall two-electron oxidations. For compounds **2–5**, cationic acetonitrile complexes were isolated in good yields after two-electron preparative electrolyses. Chemical oxidation of **5** gives a 1:1 mixture of dihydride $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H_2^+$ (**13**) and $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)^+$ (**10**), the latter as a mixture of cis and trans isomers in the thermodynamic 95:5 ratio. Hydride abstraction from **5** using a substituted trityl cation also yields **10** but with a cis:trans ratio of 10:90. Addition of a catalytic amount of cobaltocene causes the conversion of *trans*-**10** into the thermodynamic isomer mixture without ligand dissociation. The products generated upon oxidation of the hydrides are proposed to be formed by initial deprotonation of the metal hydride cation radicals. Subsequent nucleophilic attack by acetonitrile followed by a one-electron oxidation of 19-electron adducts then generates the products. The electrocatalytic isomerization of *trans*-**10** demonstrates that the 19-electron radical derived from reduction of **10** has a finite lifetime and thus supports the notion that 19-electron species are competent intermediates, not only transition states, in ligand substitution processes of 17-electron organometallic radicals.

Transition-metal hydrides are of fundamental importance in organometallic chemistry,[2,3] particularly because of their involvement as catalysts or proposed intermediates in many catalytic processes.[2b,c] In spite of the great efforts made at understanding the properties and chemical reactivities of metal hydrides, the chemistry of electron-deficient, 17-electron hydrides resulting from the oxidation of the corresponding 18-electron neutral species remains relatively unexplored.[4-8]

Cationic 17-electron metal hydrides most commonly are generated by the oxidation of neutral precursors. Only in few cases has it been possible to isolate the paramagnetic cations.[4] Decomposition pathways that have been implied for the less stable 17-electron cations include deprotonation,[5] reductive elimination of H_2,[5b,6a] and disproportionation[4d,6] reactions. In some instances, 17-electron metal hydride cation radicals have been postulated as intermediates, resulting from electron transfer from metal hydride to alkyne, during the trans addition of metal hydrides to electron-poor alkynes.[8a,b] Recently, a two-electron oxidation of a hydrido alkene complex has been observed to induce a chemically reversible insertion of the alkene into the metal–hydrogen bond.[8c]

Metal hydride acid–base properties have been the focus of considerable attention,[9] and a substantial amount of metal hydride thermodynamic[3a,9a–c,e] and kinetic[9a,b,d] acidity data in solution has accumulated. The mononuclear systems that have thus far been investigated are all electronically saturated, mostly neutral, 18-electron complexes. No quantitative information is available about the acidity of corresponding 17-electron cation radicals, but such species would be expected to be more acidic in both the thermodynamic and the kinetic sense by virtue of the positive charge present. The increase in acidity of carbon, oxygen, nitrogen, and sulfur acids upon one-electron oxidation is substantial and well documented and has been quantified for a wide range of compounds.[10,11]

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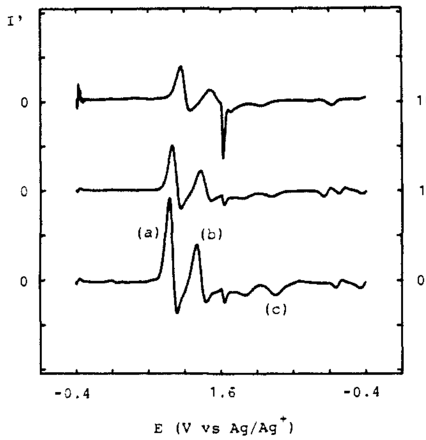

Figure 1. Derivative cyclic voltammograms of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (**2**) (1.0 mM) in acetonitrile/$Bu_4N^+PF_6^-$ (0.1 M) at a Pt microelectrode (d = 0.4 mm) at 25 °C and voltage sweep rates v of 0.1, 1.0, and 100 V/s. The traces are not drawn to the same scale.

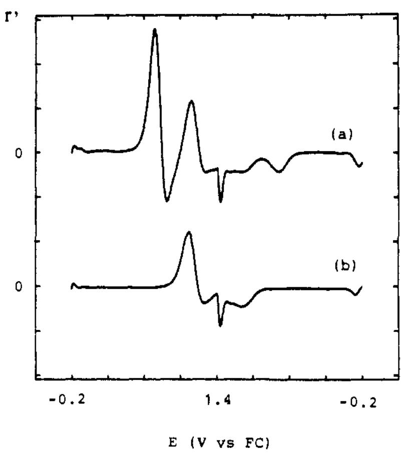

Figure 2. Derivative cyclic voltammograms of (a) $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (**2**) and (b) $(\eta^5\text{-}C_5H_5)Mo(CO)_3(NCMe)^+BF_4^-$ (**7**) at v = 1.0 V/s. Conditions are as in Figure 1.

In this paper we report the first quantitative estimates of group 6 metal hydride cation radical acidities in acetonitrile. It was anticipated that their primary mode of decomposition would entail deprotonation, a potentially useful method for the generation of neutral 17-electron radicals. In the course of this investigation, the combination of electrochemical and other methodology enabled us to explore the nature of the decomposition of some of these radicals to stable cationic products.

Results

Electrochemical Oxidation of Metal Hydrides. The initial investigation of the oxidation processes of complexes **1**–**5** was carried out by using derivative cyclic voltammetry (DCV).[12] Figure 1 shows DCV traces for the oxidation of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (**2**) (Pt disk electrode, d = 0.4 mm, 293 K, acetonitrile/0.1 M $Bu_4N^+PF_6^-$) at voltage sweep rates v of 0.1, 1.0 and 100 V/s. The cyclic voltammetry peak potential (E_p) for the oxidation of **2** may be obtained with high precision as the point where the rapidly descending DCV curve crosses the base line after the first derivative peak, labeled a. At v = 1.0 V/s, this potential was found to be +0.800 V vs the ferrocene/ferricinium (FC) couple.[13] The derivative peak that would correspond to the reduction of $2^{•+}$ back to **2** on the reverse scan, labeled c, is seen to be very small, even at high sweep rates.[15] This observation suggests the presence of a rapid homogeneous follow-up reaction that efficiently consumes electrode-generated hydride cation radical $2^{•+}$. The absence of a DCV base line crossing on the reverse scan (i.e., a real peak in a normal cyclic voltammogram) precludes the measurement of the peak potential separation between anodic and cathodic peaks for evaluation of the reversibility of the electron-transfer process. However, the "broadness" of the derivative peak, defined as the peak width at half-height, henceforth to be abbreviated as $\Delta E_{p/2}$, may give an indication about the reversibility of the process.[16] For the oxidation of **2** at v = 1.0 V/s, $\Delta E_{p/2}$ was found to be 120 mV, indicative of quasi-reversible electron transfer.[17] Under similar conditions, the oxidation of ferrocene yielded $\Delta E_{p/2}$ = 69 mV.

The peak labeled b in Figure 1 (E_p = +1.21 V vs FC, $\Delta E_{p/2}$ = 165 mV) appeared to be due to the oxidation of a product arising from the rapid decomposition of $2^{•+}$. The relative size of this peak, compared with the substrate oxidation peak, was independent of the voltage sweep rate up to 100 V/s, further emphasizing that the decomposition of $2^{•+}$ is indeed rapid. Seeding the solution with $(\eta^5\text{-}C_5H_5)Mo(CO)_3(NCMe)^+BF_4^-$ (**7**) caused this peak to increase in intensity. A separate DCV analysis of the oxidation of **7** gave E_p = +1.21 V vs FC and $\Delta E_{p/2}$ = 172 mV at v = 1.0 V/s. Figure 2 shows DCV curves for the oxidation of 1.0 mM solutions of **2** (a) and **7** (b). The position of the peak due to **7** completely matches the position of the decomposition product peak in the top trace and suggests that **7** is indeed the decomposition product. The intensities of the two peaks furthermore indicate that **7** is formed in a quantitative yield upon oxidation of **2** under the DCV conditions.

Constant-current coulometry with DCV monitoring of the disappearance of substrate[18] required the passage of 2.1 ± 0.1 F/mol for the substrate oxidation peak to disappear completely. Exhaustive preparative electrolysis of **2** (concentration 5–10 mM) followed by isolation of the product (see Experimental Section for details) provided **7**, identified by comparison of its ^1H NMR and IR (ν_{CO}) spectra with those of an authentic sample, in 75% isolated yield. This result contrasts sharply with the findings in a previous study of the electrochemical oxidation of **2**.[5a] In the earlier report, it was found that the constant-potential oxidation of **2** (concentration 48 mM, acetonitrile, 0.1 M $Et_4N^+ClO_4^-$) at +0.50 V vs SCE required 1.08 ± 0.05 F/mol and proceeded to give the dimer $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ in 60% isolated yield. The reported peak potential for the oxidation of **2** was +0.360 V vs SCE, corresponding to +0.048 V vs FC.[14] Comparison with our results reveals significant differences in oxidation potential, the number of electrons transferred, and even the nature of the isolated product.

These discrepancies remain puzzling to us. We have repeated our measurements in acetonitrile/0.1 M $Et_4N^+ClO_4^-$ but this did not alter the results in any qualitative or quantitative ways. DCV measurements performed on freshly sublimed **2** as well as on **2** generated in situ by the addition of $HBF_4{\cdot}Et_2O$ to a solution of the PPN^+ salt[19] of the anion $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ also gave

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(15) During the use of *derivative* cyclic voltammetry, a small peak is to be expected during the reverse scan even in cases when the electrode-generated species undergoes "complete" reaction on the time scale of the measurement. This is in contrast with the absence of a corresponding peak in the normal cyclic voltammogram.

(16) This method is similar to the use of the difference peak potential and half-peak potential as a diagnostic for Nernstian waves in cyclic voltammetry.[14] Digital simulation gives $\Delta E_{p/2}$ = 70.3 mV for a Nernstian one-electron transfer: Lerflaten, O. Thesis for the sivilingeniør degree, Norwegian Institute of Technology, Trondheim, 1980.

(17) For comparison, the separation between the peak and half-peak potentials in the normal cyclic voltammogram of **3** was 95 mV under these conditions.

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Table I. Electrochemical Data and Product Yields for the Oxidation of Metal Hydrides **1–5**

compd	$E_{ox}(MH)^a$	$\Delta E_{p/2}{}^b$	$n_{ox}{}^c$	oxidation product	yield,[d] %
$(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ (**1**)	+0.668	80	2.1 (0.1)	$(\eta^5\text{-}C_5H_5)Cr(CO)_3(NCMe)^+$ (**6**)	*e*
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ (**2**)	+0.800	117	1.9 (0.1)	$(\eta^5\text{-}C_5H_5)Mo(CO)_3(NCMe)^+$ (**7**)	77
$(\eta^5\text{-}C_5H_5)W(CO)_3H$ (**3**)	+0.758	108	2.2 (0.3)	$(\eta^5\text{-}C_5H_5)W(CO)_3(NCMe)^+$ (**8**)	78
$(\eta^5\text{-}C_5Me_5)Mo(CO)_3H$ (**4**)	+0.561	102	2.5 (0.1)	$(\eta^5\text{-}C_5Me_5)Mo(CO)_3(NCMe)^+$ (**9**)	58
$(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$ (**5**)	+0.195	78	1.9 (0.1)	$(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)^+$ (**10**)[f]	59

[a] Peak potential for the oxidation of metal hydride, V vs ferrocene/ferricinium, as measured by DCV. Acetonitrile/0.1 M $Bu_4N^+PF_6^-$, 293 K, v = 1.0 V/s, Pt disk electrode (d = 0.4 mm), 1.0 mM substrate. [b] Derivative current peak width at half-height. [c] Number of electrons per molecule as determined by constant-current coulometry. Standard deviations (three measurements) in parentheses. [d] Isolated yields of oxidation products. [e] Not isolated. [f] Obtained as a mixture of cis and trans isomers in a 95:5 ratio.

identical results. Addition of excess acid caused no further changes. Constant-potential oxidation of **2** (concentration 50 mM) at a potential 140 mV anodic of the peak potential that we measured for **3** also did not produce the dimer. Furthermore, a DCV analysis of the oxidation of the dimer $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ revealed that this complex is oxidized at +0.55 V vs FC, i.e., at a potential 0.25 V *less anodic* than the potential required for the oxidation of **2**. The oxidation of **2** thus would not be expected to give significant amounts of the dimer, since the dimer is more readily oxidized than is the hydride. This trend is in accord with the fact that, using oxidation state formalisms, **2** is a Mo(II) complex whereas the dimer is a Mo(I) complex. The oxidation peak potential that we find for the dimer compares reasonably well with 0.97 V vs SCE or 0.66 V vs FC (unspecified substrate concentration and temperature, v = 0.2 V/s, acetonitrile/0.1 M $Bu_4N^+ClO_4^-$) reported previously.[20]

In a qualitative manner, hydrides **1**, **3**, **4**, and **5** behaved very much like **2** electrochemically. These complexes all appeared to undergo two-electron oxidations by coulometry. DCV analyses indicated the generation of the corresponding cationic acetonitrile complexes **6**, **8**, **9**, and **10** by comparison with authentic samples. Finally, preparative electrolyses provided these cationic complexes in moderate to good yields (except **6**). Judging from the DCV traces, the instantaneous product yields from **1** and **5** were only about 35 and 25%, respectively, whereas the yields from **3** and **4** appeared to be quantitative. The pertinent electrochemical and isolated yield data for the oxidation of hydride complexes **1–5** are summarized in Table I. The chromium cation **6** was not isolated, since it appeared to undergo decomposition during the CH_2Cl_2 extraction step of the workup procedure, leading to a bluish green solution. No attempt was made at identifying the secondary products formed here. However, the IR spectrum of the crude reaction mixture indicated **6** to be a major CO-containing compound in solution (ν_{CO} 2073, 2010, 1998 cm^{-1}).

Partial chemical reversibility was observed by DCV for the oxidation of **5** at v = 100 V/s, and the reversible oxidation potential for this compound, taken as the midpoint between the anodic and cathodic peak potentials, was estimated to be +0.16 V vs FC. The two-electron preparative electrolysis yielded a 95:5 mixture of the cis and trans isomers of $[(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)]^+PF_6^-$ (*cis*-**10** and *trans*-**10**), which is also the thermodynamically favored ratio of the two, as will be discussed later. The stereochemical assignments of *cis*-**10** and *trans*-**10** are based on their ^1H NMR and IR spectra. It has long been observed that the cis and trans isomers of "four-legged piano stool" complexes $(\eta^5\text{-}C_5H_5)M(CO)_2LX$ (where L is a phosphine or phosphite ligand) may be differentiated by means of their ^1H NMR and IR spectra.[21] Thus, cis isomers give rise to a singlet for the cyclopentadienyl ligand in the ^1H NMR spectra, whereas the trans complexes display a doublet with $J_{P\text{-}H} \cong 2$ Hz.[21] The two isomers each give rise to two well-separated C–O stretch bands in the infrared, pairwise at nearly the same frequencies. However, the relative intensities of the two bands differ: In the cis species, the high-frequency band is stronger, but in the trans analogue, the low-frequency band is more intense.[21a] The ^1H NMR spectrum (CD_3CN) of *cis*-**10** displayed a singlet at δ 5.77 due to the cyclopentadienyl ligand, and coordinated acetonitrile gave a doublet at δ 2.58 ($J_{P\text{-}H}$ = 2.9 Hz). The IR spectrum showed two absorptions at 1971 and 1879 cm^{-1}, the former of which was more intense. These observations support our structural assignment for *cis*-**10**. The characterization of *trans*-**10** will be discussed later.

Homogeneous Chemical Oxidation of Hydrides 2, 3, and 5. In order to see whether chemical oxidation proceeded qualitatively in the same fashion as the electrochemical oxidations, we investigated the three Mo- and W-centered hydrides **2**, **3**, and **5**. For **5**, ferricinium hexafluorophosphate (**11**) was used as the one-electron oxidant, while for **2** and **3**, $[(phen)_3Fe^{3+}](PF_6^-)_3$ (**12**), where phen = 9,10-phenanthroline, was used. $E°$ for the Fe^{3+}/Fe^{2+} couple of **12** in acetonitrile has been reported to be +1.09 V vs SCE[22] (+0.78 V vs FC).

Oxidation of **2** and **3** with 2 equiv of **12** in acetonitrile-d_3 yielded **7** and **8**, respectively, as the only cyclopentadienyl-containing products detectable by ^1H NMR. In addition, signals due to the phenanthroline ligand in diamagnetic $(phen)_3Fe^{2+}$ were observed, as well as a broad signal at ca. δ 10.5, which is attributed to acid generated by deprotonation of unstable $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$.

Treatment of **5** with 1 equiv of **11** in acetonitrile-d_3 consumed all of the substrate and yielded ferrocene and a 1:1 mixture of *cis*-**10** (accompanied by a trace of the trans isomer, the spectral characteristics of which will be discussed later) and the cationic dihydride $[(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H_2]^+PF_6^-$ (**13**). The identity of **13** was established by comparison of its ^1H NMR spectrum with that of an independently prepared sample (vide infra). Solutions of **13** in acetonitrile-d_3 only slowly decomposed to the thermodynamic 95:5 mixture of *cis*-**10** and *trans*-**10**, with a half-life of ca. 30 h at ambient temperature.

In the presence of the hindered base 2,6-lutidine, the complete oxidation of **5** required 2 equiv of ferricinium oxidizing agent. In this case, the only product derived from **5**, detectable by ^1H NMR, was the thermodynamic 95:5 mixture of *cis*-**10** and *trans*-**10**, formed in quantitative yield. On a preparative scale, a similar isomeric mixture of **10** was isolated in 77% yield.

Synthesis, Characterization, and Solution Structure Dynamics of $[(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H_2]^+BF_4^-$ (13). The addition of excess $HBF_4{\cdot}Et_2O$ to an ether solution of **5** at 0 °C caused the immediate and virtually quantitative formation of **13** as a white precipitate. Unless care was taken to use extremely dry solvents, **13** showed a pronounced tendency to undergo partial deprotonation to yield **5** in solution. The ^1H NMR spectrum of **13** was identical with the spectrum arising from one of the products obtained from the oxidation of **5** by ferricinium in acetonitrile-d_3. The room temperature ^1H NMR spectrum of **13** in CD_2Cl_2 displayed a singlet cyclopentadienyl resonance at δ 5.69, a PMe_3 doublet ($J_{P\text{-}H}$ = 10.7 Hz) at δ 1.88, and a hydride doublet, integrating for 2 protons, at δ −2.44 ($J_{P\text{-}H}$ = 40.5 Hz). Lowering the temperature caused the doublet to broaden, merge with the base line, and eventually to reappear as two doublets. No other signals were affected by the temperature changes. The 500-MHz ^1H NMR spectra of the hydride region at various temperatures are shown in Figure 3. The spectra show that a fluxional process is taking place in which the two hydride ligands are rapidly exchanging

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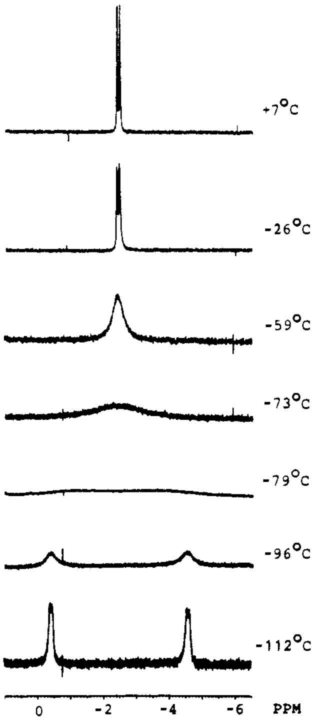

Figure 3. Hydride region of variable-temperature 500-MHz ^{1}H NMR spectra of $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H_2^+BF_4^-$ (13) in CD_2Cl_2.

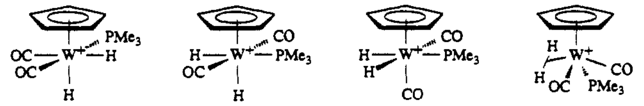

Figure 4. Possible structures for cation $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H_2^+$.

positions. At the low-temperature limit (-112 °C), the exchange process is slow enough that a static structure may be observed. The separate chemical shifts for the two hydride ligands are δ -0.61 and -4.57, both with apparent coupling constants J_{P-H} of ca. 30 Hz. However, the signals were still broad at this temperature and these are not the real coupling constants expected in a well-resolved spectrum for the static structure. The average of the two limiting J_{P-H} values should be 40.5 Hz, the observed coupling in the room temperature spectrum. The resolution was not good enough at -112 °C to observe any coupling between the two nonidentical hydrides. We were unable to obtain good spectra upon further lowering of the temperature.

With the assumption of pseudooctahedral coordination geometry at the tungsten center in **13**, only three structures (Figure 4) are possible that contain two chemically different hydride ligands. The three alternatives are denoted **13a**, **13b**, and **13c**, all of which have the hydride ligands in a mutual cis arrangement. A dihydrogen (η^2-H_2) complex[23] such as **14** may be excluded on the basis of the observation of two nonequivalent hydrogens. Rotation around the metal-(H_2) bond vector in dihydrogen complexes, rendering the two atoms of the dihydrogen ligand equivalent, appears to be so fast[24] that no nonequivalence can be observed by ^{1}H NMR in solution. The apparently quite similar P-H coupling constants observed at -112 °C suggest that both hydrides are located in a cis fashion relative to the phosphine ligand, indicating that structure **13a** best describes the static, low-temperature structure of the cationic dihydride.

From the variable-temperature ^{1}H NMR spectra of **13** we estimate the coalescence temperature for the two hydride signals to be -77 °C, which, by the use of well-known relationships,[25] gives a free energy of activation, $\Delta G^{\ddagger}$, for the exchange process of 8.0 kcal/mol. An exchange mechanism involving rotation around the W-(H_2) bond of an intermediate η^2-H_2 complex such as **14** appears especially attractive[23b] in view of the facile equilibria between dihydrides and dihydrogen compounds that have been demonstrated recently.[24b,26]

Cationic hydride **13** was also obtained, as its Cl^- salt, when **5** was treated with ca. 5 equiv of dry HCl gas in acetonitrile-d_3 at -35 °C. The ^{1}H NMR spectrum acquired at this temperature demonstrated the complete formation of **13**. No evidence was found for the presence of unprotonated **5**. Upon warming, broadened signals were observed at first, presumably due to rapid exchange of the hydride ligands of **13** with excess acid. The initially colorless solution underwent rapid decomposition to yield an orange solution, presumably containing the chloride $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)Cl$, but this reaction was not further investigated.

Hydride Abstraction from 5 by Trityl Reagents. The use of the triphenylmethyl (trityl) cation to effect the net abstraction of H^- from a variety of ligands in transition-metal complexes is well established. Removal of H^- from neutral metal hydrides normally yield electron-deficient 16-electron cations, often bonded to weakly coordinating ligands.[27] The ease with which added ligands can be attached to these species makes this a valuable synthetic method in organometallic chemistry.[28]

We find that for many purposes the use of methoxy-substituted trityl derivative $Ph_2(p\text{-}MeOC_6H_4)C^+BF_4^-$ (**15**) is a favorable alternative to the use of $Ph_3C^+BF_4^-$. The reason for this is that **15**, readily available in large quantities,[29a] displays a much higher long-term stability than $Ph_3C^+BF_4^-$. For example, solid **15** may be stored in a refrigerator for more than a year, unprotected against air and moisture,[29b] without any signs of deterioration. As a solid, it is unaffected by atmospheric moisture and may, unlike the unsubstituted parent trityl cation, be conveniently handled in air during weighing and transfer.

Treatment of phosphine hydride **5** with 1 equiv of trityl derivative **15** in acetonitrile gave **10** in 95% isolated yield, the trans isomer (90%) dominating over the cis analogue (10%). The stereochemical assignment for *trans*-**10** is based on its ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum displayed a cyclopentadienyl doublet (δ 5.53, J = 1.8 Hz), a coordinated acetonitrile singlet (δ 2.51), and a PMe_3 doublet at δ 1.71. The IR spectrum showed two CO bands at 1978 and 1888 cm^{-1}, the latter of which was the more intense. The stereochemical outcome of the hydride abstraction reaction remained unchanged in the presence of 20 equiv of 2,6-lutidine.

A solution of *trans*-**10** in acetonitrile-d_3 very slowly ($t_{1/2} \sim$ 40 h, ambient temperature) is converted into a stable 95:5 mixture

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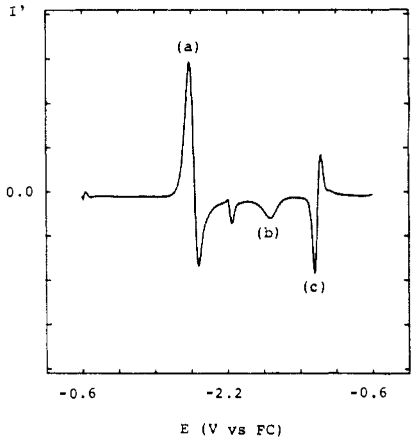

Figure 5. Derivative cyclic voltammogram of *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)^+BF_4^-$ (*trans*-**10**) at v = 1.0 V/s. Conditions are as in Figure 1.

of *cis*-**10** and *trans*-**10**, as indicated by the appearance of the cyclopentadienyl doublet of *cis*-**10**. This established that the cis complex is thermodynamically preferred and that formation of *trans*-**10** must take place under kinetic control. The cis–trans interconversion apparently takes place with acetonitrile dissociation, since ligand exchange with the solvent, which caused the disappearance of coordinated acetonitrile signals, was observed. In accord with this, a singlet due to free acetonitrile gradually appeared at δ 2.02, slightly downfield from the solvent residual proton resonances. A kinetic analysis of ^{1}H NMR data acquired during ca. 3 half-lives of this reaction showed that cis–trans interconversion and acetonitrile ligand exchange with the solvent proceeded at the same rates. Rate constants (T = 295 ± 1 K) for the trans → cis and cis → trans interconversions were estimated to be 5.0×10^{-6} and 2.5×10^{-7} s^{-1}, respectively.

Reductively Induced Isomerization of *trans*-10 to *cis*-10. It is now well established that one-electron oxidations may induce rapid cis–trans isomerization processes within the coordination sphere of otherwise conformationally stable 18-electron mononuclear organotransition-metal complexes.[30-33] Such transformations in some cases require only catalytic amounts of oxidants.[31i,k,32,33c] We suspected that the formation of the thermodynamic cis–trans mixture of **10** during the oxidation of **5** could be due to rapid equilibration at a 17- or 19-electron stage. In order to gain further insight into this, we examined the electron-transfer chemistry of the two isomers of **10**.

Scheme I

$$
\begin{array}{llll}
 & & \Delta G^\circ & \\
\text{M-H} \rightleftarrows \text{M}^- + \text{H}^+ & & 2.301RT\,\text{p}K_a(\text{M-H}) & (1) \\
\text{M}^- \rightleftarrows \text{M}\cdot + e^- & & FE^\circ_{ox}(\text{M}^-) & (2) \\
\text{M-H}^{+\cdot} + e^- \rightleftarrows \text{M-H} & & -FE^\circ_{ox}(\text{M-H}) & (3) \\
\hline
\text{M-H}^{+\cdot} \rightleftarrows \text{M}\cdot + \text{H}^+ & & 2.301RT\,\text{p}K_a(\text{M-H}^{+\cdot}) & (4)
\end{array}
$$

$$\text{p}K_a(\text{M-H}^{+\cdot}) = \text{p}K_a(\text{M-H}) + F/2.301RT\,[E^\circ_{ox}(\text{M}^-) - E^\circ_{ox}(\text{M-H})] \quad (5)$$

Table II. Metal Hydride pK_a Values, Reversible Oxidation Potentials for the Corresponding Anions, and Metal Hydride Cation Radical pK_a Estimates

metal hydride M–H	pK_a(M–H)^a	E_{ox}(M$^-$)^b	pK_a(M–H$^{\bullet+}$)^c
1	13.3	–0.688	–9.5
2	13.9	–0.385	–6.0
3	16.1	–0.379	–3.0
4	17.1	–0.603	–2.5
5	26.6	–1.119	+5.1

^{a}Reported hydride pK_a values in acetonitrile. From refs 9a and 9c. ^{b}Reversible potentials for the oxidation of metal anions, vs ferrocene/ferricinium. From ref 34. ^{c}Calculated by using eq 6.

Cations *cis*-**10** and *trans*-**10** were indistinguishable by DCV, both being reduced at –1.90 V vs FC ($\Delta E_{p/2}$ = 85 mV, v = 1.0 V/s). A DCV trace for the reduction of *trans*-**10** is shown in Figure 5. The peak labeled a corresponds to the reduction of **10**. The low intensity of the oxidation peak b during the reverse scan demonstrates that the reduction process is chemically irreversible, a situation that remained unchanged even at v = 10 000 V/s. The irreversibility appears to be due to facile loss of coordinated acetonitrile on the time scale of the measurements. An oxidation peak, labeled c, corresponding to the oxidation of $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)^-$[34] is apparent at –1.23 V vs FC during the reverse sweep, indicating preferential loss of the acetonitrile ligand upon reduction of **10**. The favored loss of acetonitrile was further demonstrated by the observation that sodium amalgam reduction of **5**, followed by methylation with iodomethane, yielded $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)Me$ in 71% isolated yield.

Addition of 10–15 mol % of cobaltocene (E° = –1.25 V vs FC[30d]) to a 50–100 mM solution of the thermodynamically unstable isomer *trans*-**10** (contaminated with 5–10% of *cis*-**10**) in acetonitrile-d_3 caused the immediate (<5 min) conversion of the substrate into the thermodynamic mixture of the two isomers, demonstrating the presence of a rapid and efficient reductively induced electrocatalytic isomerization reaction. Significantly, the process took place *without* dissociation of acetonitrile: The singlet resonance due to coordinated acetonitrile in *cis*-**10** and the corresponding doublet from the trans isomer were both present, their integrated intensities being 60% of the cyclopentadienyl intensities, demonstrating that no ligand exchange with the solvent occurred. Addition of 20 mol % of cobaltocene to a dilute (2 mM) solution of *trans*-**10** did not initiate the electrocatalytic isomerization process, nor did the partial (0.2 F/mol) electrolysis of 2 mM solutions of *trans*-**10** in acetonitrile/0.1 M $Bu_4N^+PF_6^-$.

Discussion

Determination of Metal Hydride Cation Radical pK_a Values. The observation that H$^+$ is liberated upon chemical oxidation of **2** and **3** in dry acetonitrile suggests that the cation radicals undergo net deprotonation reactions, although mechanistic details about these reactions are not known. Scheme I shows a thermochemical cycle that may be used to estimate metal hydride cation radical acid strengths, independent of the mode of decomposition of these species. Similar cycles have been devised previously for the determination of pK_a values for organic cation radicals and dications as well for anion radical and dianion conjugate bases.[10,11] In

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Scheme I, pK_a(M–H) and $pK_a(\text{M–H}^{\bullet+})$ are the thermodynamic (Brønsted) acidities of the neutral and oxidized hydrides, and E°_{ox}(M–H) and $E^\circ_{ox}(\text{M}^-)$ are the reversible potentials for the oxidation of the metal hydride and its conjugate base (anion), respectively. At T = 25 °C, the hydride cation pK_a may be determined from eq 6. We have previously,[34] in connection with

$$pK_a(\text{M–H}^{\bullet+}) = pK_a(\text{M–H}) + 16.9[E^\circ_{ox}(\text{M}^-) - E^\circ_{ox}(\text{M–H})] \quad (6)$$

the determination of metal hydride bond dissociation energies in solution, reported estimates of the reversible oxidation potentials for a number of metal anions. Insertion of these oxidation data into eq 6, along with the metal hydride oxidation potentials reported in this study as well as Norton's pK_a data for the pertinent metal hydrides,[9a,c] gives pK_a estimates for the cation radicals of metal hydrides **1–5**. The results are summarized in Table II.

The $pK_a(\text{M–H}^{\bullet+})$ data in Table II constitute the first quantitative estimates of metal hydride cation radical acidities. These cation radicals by far are the most acidic metal hydride species for which quantitative acidity estimates have been reported. The most acidic metal hydride previously reported in acetonitrile solution is $HCo(CO)_4$, the reported pK_a value being 8.3.[9c]

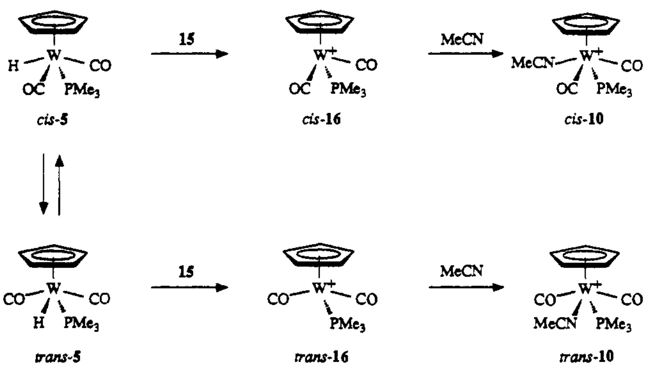
For compound **5**, as mentioned already, a good estimate of its reversible oxidation potential was obtained because the oxidation process exhibited partial chemical reversibility at v = 100 V/s. Such was not the case for hydrides **1–4**. The observed quasi-reversible nature of the electron-transfer processes will serve to shift the cyclic voltammetry peak potential somewhat in the anodic direction, away from the true reversible value. In addition, the rapid follow-up reaction will cause a potential shift in the cathodic direction. We do not know with certainty by how much these opposing effects cause the measured peak potentials to deviate from the reversible values, and this causes some uncertainties in the reported pK_a values for the cation radicals of **1–4**. However, the fact that similar behavior of all these species is observed by DCV suggests that the errors should be nearly constant, and therefore the relative acidities at least should be reliable. It is interesting to note that the neutral M–H species and their cation radicals differ in acidity by a relatively constant 20.6 ± 1.5 pK_a units, regardless of the nature of the metal or changes in the ligand environment. Thus, a correlation of pK_a(M–H) vs $pK_a(\text{M–H}^{\bullet+})$ yields a straight line with slope 0.954 (r = 0.96) (eq 7). The correlation suggests a constant difference between the pK_a's of these metal hydrides and their cation radicals.

$$pK_a(\text{M–H}) = 0.954pK_a(\text{M–H}^{\bullet+}) + 20.4 \quad (7)$$

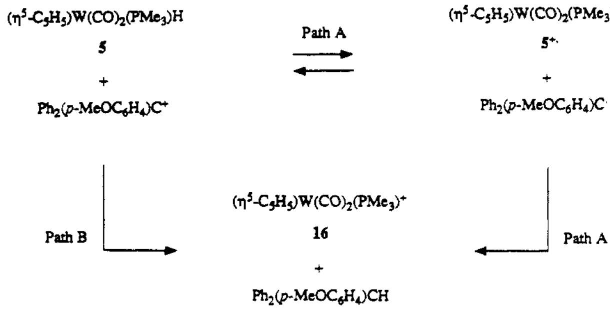
The data in Table II show that for the hydride cation radicals $(\eta^5\text{-}C_5H_5)M(CO)_3H^{\bullet+}$, acidities decrease in the order M = Cr > Mo > W, as has been observed previously for the corresponding neutral metal hydrides. Furthermore, substitution of $\eta^5\text{-}C_5Me_5$ for the $\eta^5\text{-}C_5H_5$ ligand (M = Mo, **2** and **4**) causes a decrease in the acidity by 3.5 pK_a units. In the W systems (**3** and **5**), the introduction of a PMe_3 ligand for CO causes an acidity decrease of 8 pK_a units. Substituent effects on the corresponding neutral metal hydrides also were of the same magnitude.[9c]

Mechanism of Hydride Abstraction from $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$. In solution, tungsten hydride **5** exists as a rapidly equilibrating near 1:1 mixture of cis and trans isomers (^{1}H NMR, CD_3CN, +20 to –40 °C). The highly selective and high-yield formation of *trans*-**10** upon hydride abstraction from **5** using trityl derivative **15** suggests that **15** reacts selectively with *trans*-**5** followed by capture of the "naked" cation *trans*-**16** by acetonitrile before the stereochemical integrity of **16** is lost or that *trans*-**16** (whether formed selectively from *trans*-**5** or by equilibration of *cis*-**16** and *trans*-**16**) selectively is captured by acetonitrile (Scheme II). The former alternative appears most likely, the source of this selectivity being the steric bulk of the PMe_3 ligand. The approach of the sterically demanding trityl cation toward the hydride ligand is less hindered by the bulky phosphine group in *trans*-**5** than it is in *cis*-**5**, and attack by **15** would be expected to preferentially take place on *trans*-**5**. Acetonitrile coordination to **16** presumably would be less sensitive to steric effects.

Scheme II



Scheme III



Formation of **10** from **5** presumably takes place via the coordinately unsaturated, 16-electron cation **16**, most likely weakly bonded to the BF_4^- counterion.[27] A consequence of the observed selective production of *trans*-**10** is that the interconversion between the cis and trans isomers of **16** must also be slow, at least relative to the capture of **16** by solvent acetonitrile. It has been reported that $(\eta^5\text{-}C_5H_5)W(CO)_2(P(OPh)_3)(BF_4)$ in CD_2Cl_2 undergoes relatively slow (minutes) cis–trans isomerization even at +10 °C.[28e] We note that there is already precedence that 16-electron cations, generated by hydride abstraction using the trityl cation, may capture phosphine ligands with retention of their stereochemical integrity.[35] Furthermore, Gladysz and co-workers[36a–d] have found that $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)^+$, generated from optically active $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)CH_3$, binds to aldehydes, ketones, alkenes, and other Lewis bases to yield optically active adducts, providing firm evidence that unsaturated (or weakly ligated) 16-electron cations may possess substantial conformational stabilities.

The mechanism of hydride abstraction from metal alkyls by the trityl cation has been investigated in some detail, and it has been shown in some cases that the reaction takes place via initial electron transfer from the metal alkyl to the trityl cation, yielding the metal alkyl cation radical and the trityl radical.[37] The electron transfer is followed by hydrogen atom transfer from the cation radical to the trityl radical. A similar reaction pathway is conceivable, and kinetically feasible (as will be elaborated shortly) for the trityl/methyl hydride reactions. It has in some instances been observed that treatment of metal hydrides with Ph_3C^+ may

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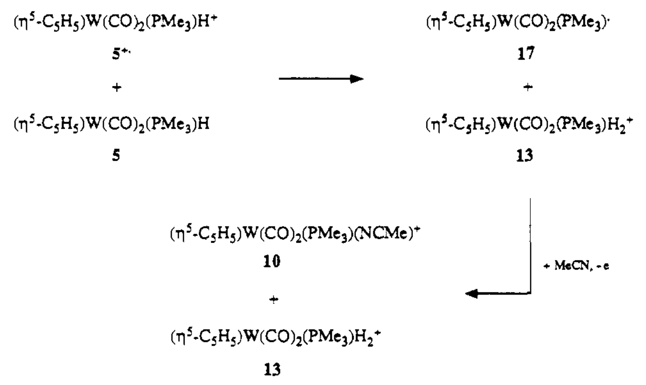
Scheme IV



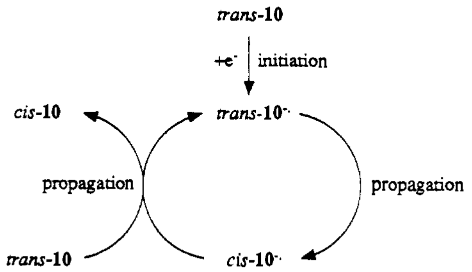
lead to stable metal hydride cations, but these have failed to undergo subsequent M–H bond cleavage.[4a,c,f] For the reaction between hydride **5** and trityl reagent **15**, the electron-transfer mechanism is illustrated in Scheme III (path A). Trityl reagent **15** undergoes a reversible reduction at –0.32 V vs FC. Thus, the electron-transfer equilibrium in path A is unfavorable by an overall 0.52 V, corresponding to a redox equilibrium constant of 1.4×10^{-9}. Assuming diffusion control ($k \cong 2 \times 10^{10}$ M^{-1} s^{-1}) for the reverse electron transfer yields a maximum possible rate constant for the two-step sequence of 28 M^{-1} s^{-1}. This value is high enough to allow for a second-order reaction (substrate concentration ca. 10 mM; see Experimental Section for details) to go to near completion within minutes. Thus, the electron-transfer pathway must be considered in spite of the unfavorable initial electron-transfer equilibrium. The alternative, a one-step removal of hydride, is also indicated in Scheme III (path B). The indirect, or electron transfer, route (A) generates the intermediate $5^{\bullet+}$. This intermediate is the same as that produced during the electrochemical or ferricinium-mediated oxidation of **5**. Our results show that in the presence of 2 equiv of 2,6-lutidine, $5^{\bullet+}$ undergoes deprotonation to yield a radical species that eventually generates *cis*-**10** as the predominant product (vide infra). During the trityl reaction, the presence of as much as 20 equiv of 2,6-lutidine did not affect the relative amounts formed of *cis*-**10** and *trans*-**10**. This difference in stereochemical outcome in the trityl and electron-transfer-mediated reactions *strongly suggests that an electron-transfer pathway is not operative during the hydride abstraction* by the trityl reagent **15**. However, we cannot conclusively rule out that the hydrogen atom transfer step in path A (possibly within the solvent cage) may take place much faster than proton transfer even in the presence of 20 equiv of 2,6-lutidine.

Deprotonation of Metal Hydride Cation Radicals. It appears plausible from the data at hand that the primary reaction of the acidic metal hydride cation radicals is loss of a proton. The observed and isolated products from the oxidation reactions then reflect the fate of the neutral 17-electron radicals generated during the deprotonation (eq 8). During the chemical oxidations in

$$\mathrm{M{-}H} \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} \mathrm{M{-}H}^{\bullet+} \xrightarrow{-\mathrm{H}^+} \mathrm{M}^{\bullet} \xrightarrow{+\mathrm{MeCN},\,-e^-} \mathrm{M}^{+}\mathrm{{-}NCMe} \qquad (8)$$

acetonitrile-d_3, the "medium"—most likely unavoidable traces of residual moisture or the PF_6^- counterions—appears to be basic enough to effect the deprotonation of $2^{\bullet+}$ and $3^{\bullet+}$. It has been pointed out that in acetonitrile solvent, minute amounts of water will have a higher proton-accepting ability than the solvent itself, due to the much higher basicity of water when compared to acetonitrile.[38] The medium also appeared to be capable of deprotonating all of the hydride cations during the coulometric experiments for all the hydrides. This behavior requires the transfer of two electrons per molecule, fully consistent with the experimental data. The sequence of events in the last step of eq 8, acetonitrile addition and electron transfer, will be addressed at the end of this discussion.

Scheme V



The chemical oxidation of **5** in dry acetonitrile-d_3 (vacuum transferred directly from CaH_2)—a medium that would be expected to be considerably less basic than the acetonitrile/0.1 M Bu_4NPF_6 electrolyte employed for electrochemical experiments—required only 1 equiv of oxidant. This result suggests that another molecule of **5**, rather than the medium, acts as the base during the deprotonation step. As shown in Scheme IV, this process would result in a 1:1 mixture of **13** and **10** after a net one-electron oxidation of the substrate. Production formation would occur via the 17-electron radical **17**, which under the oxidizing conditions present would be expected (vide infra) to yield **10** in the observed thermodynamic 95:5 cis/trans isomer ratio. The feasibility of a proton transfer from $5^{\bullet+}$ (pK_a = 5.1, this work) to **5** is further supported by the observation that ca. 5 equiv of dry HCl (pK_a = 8.9 in acetonitrile[38]) is also capable of completely protonating **5** to give **13** in acetonitrile-d_3. This observation places a lower limit to the pK_a value of dihydride **13** at ca. 9 pK_a units.

An alternative mechanism that would also generate dihydride **13** and radical **17** is the transfer of a hydrogen atom from **5** to $5^{\bullet+}$, a possibility that cannot be ruled out at this point. Of course, the free energy change is the same regardless of which of the two mechanisms is operative. Using the lower limit pK_a estimate for **13** of ca. 9 pK_a units in acetonitrile along with the oxidation potential for **5** reported in this study yields a minimum W–H bond dissociation energy (BDE) of 76 kcal/mol for **13**, using the previously employed thermochemical cycle.[34] Interestingly, this minimum value for the W–H BDE in **13** is somewhat higher than those reported for **3** (65 kcal/mol) and **5** (62 kcal/mol). Our data seem to allow for the formation of radical **17** both via the proton transfer and via the hydrogen atom transfer routes. A similar mechanistic dichotomy arose in the recent report that acetonitrile solutions of stable (by cyclic voltammetry) cation radical $(\eta^5\text{-}C_5H_5)Re(PPh_3)_2H_2^{\bullet+}$ decomposed to yield a 1:1 mixture of $(\eta^5\text{-}C_5H_5)Re(PPh_3)_2H_3^+$ and $(\eta^5\text{-}C_5H_5)Re(PPh_3)_2(NCMe)H^+$ in a reaction that was catalyzed by dication $(\eta^5\text{-}C_5H_5)Re(PPh_3)_2H_2^{2+}$.[6b]

Electrocatalytic, Reductively Induced Cis–Trans Isomerization of $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)^+$ (10). The reductively induced isomerization of *trans*-**10** (containing 10% of the cis isomer) to the thermodynamic 95:5 mixture of the cis and trans isomers to the best of our knowledge represents the first example of *reductively* induced cis–trans isomerizations in mononuclear organometallic chemistry. Numerous examples exist of *oxidatively* induced isomerization processes,[30–33] but only in a few instances have these been proven to be electrocatalytic reactions.[31i,k,32,33c] A plausible catalytic cycle for the *trans*-**10** to *cis*-**10** catalyzed process is shown in Scheme V. A prerequisite for a successful electrocatalytic chain process, of course, is that the overall free energy change for the reaction is negative.[30e] The free energy change may be considered to be the algebraic sum of the free energy changes for each of the propagation steps.[30e] The chemical irreversibility of the DCV reduction waves for **10**, even at voltage sweep rates as high as 10 000 V/s, unfortunately precludes the evaluation of the two terms.

No catalytic process was observed on partial electrolysis of solutions of *trans*-**10**. Presumably, this is due to the high dilution (1–2 mM) conditions of the electrochemical experiments. The DCV data show that radicals **19** have extremely short lifetimes; under dilute conditions they presumably decompose by loss of acetonitrile before they have the chance to undergo the second-

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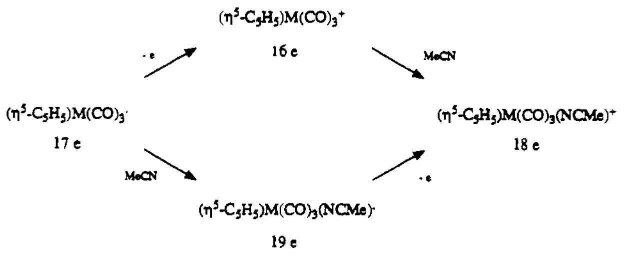
[38] Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

order cross redox reaction (propagation step, left half of cycle). Consistent with this explanation, treatment of dilute solutions of *trans*-**10** with 20 mol % of cobaltocene did *not* initiate the catalytic process. The successful reactions employing cobaltocene were carried out with concentrations of *trans*-**10** in the range 50–100 mM, which would greatly favor the second-order cross electron transfer.

The finding that *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)^+$ could be isomerized to the cis analogue *without loss of the acetonitrile donor ligand* in the presence of catalytic amounts of cobaltocene demonstrates that the $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(NCMe)^\bullet$ (**18**) radical has a considerable lifetime, relatively speaking, before it decomposes via loss of acetonitrile. The isomerization of *trans*-**18** must be fast compared to the rate of ligand (acetonitrile) loss, which itself appeared to be fast by DCV at $v = 10\,000$ V/s (time scale of measurement, ca. 10^{-4} s). An *upper limit* to the lifetime of **18** may then be estimated at ca. 10^{-5} s. The exceptionally short lifetime of electrode-generated 19-electron manganese carbonyl radicals has recently been elegantly illustrated by Kochi and co-workers.[39] For example, reduction of $Mn(CO)_6^+$ was found to be chemically irreversible at voltage sweep rates as high as 460 000 V/s,[39a] resulting in radical lifetimes shorter than 0.1 μs. Since the half-life for isomerization of *trans*-**10** is ca. 40 h, *the rate of isomerization is increased by a factor* $>10^{10}$ *upon one-electron reduction.*

Implications for the Intermediacy of 19-Electron Species in Ligand Substitution Processes of 17-Electron Radicals. There is a growing body of evidence that ligand substitution reactions in 17-electron systems take place via associative mechanisms, i.e., with 19-electron intermediates or transition states readily accessible.[40–45] Only recently has the equilibrium between 17- and 19-electron species $[Mn(CO)_2(\eta^2\text{-dppe})(\eta^1\text{-dpp})$ and *cis*-$Mn(CO)_2(\eta^2\text{-dppe})_2$, respectively, where dppe = $Ph_2PCH_2CH_2PPh_2]$ been estimated by digital simulation of cyclic voltammetry data. The equilibrium constant K_{eq} was estimated to be 10^6 in favor of the 17-electron radical.[39a] The problems with directly observing 19-electron species during the ligand substitution reactions have left considerable doubt in most cases as to whether the 19-electron species represent true intermediates or transition states along the reaction coordinate for the associative substitution processes.[30f,39a,43d,45e] In addition to the aforementioned equilibrium, which suggests that 19-electron species may have finite lifetimes and therefore be true intermediates, further support is provided by Tyler and co-workers, who have presented strong evidence that highly reducing 19-electron species can form from the $(\eta^5\text{-}C_5H_5)Mo(CO)_3^\bullet$,[41] $(\eta^5\text{-}C_5H_5)Fe(CO)_2^\bullet$,[46a–c] and $W(CO)_5^{\bullet-}$ [46d] radicals in the presence of phosphines. Transient 19-electron intermediates have reportedly been detected[45a] electrochemically during the oxidation of (arene)$W(CO)_3$ compounds in the presence of phosphines.

Scheme VI



We have conclusive evidence that 19-electron radicals **18**, in spite of their short (by DCV) lifetimes, may undergo cis–trans isomerization prior to dissociation of acetonitrile. Kochi and co-workers have demonstrated that acetonitrile is a superior leaving group, when compared to both CO and phosphines, in 19-electron radicals.[39b,40d,47] Our observation that **18** decomposes to $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)^-$ [identified by DCV; its presence also implied by the formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)Me$ following treatment of the Na/Hg reduction product of **10** with iodomethane] suggests that acetonitrile is the only ligand that dissociates from **18**. The reductively induced isomerization prior to acetonitrile loss establishes that this 19-electron radical has a finite lifetime. This provides new solid evidence that 19-electron adducts formed by ligation of two-electron donors to 17-electron species may in fact represent *intermediates* (located in a potential well along the reaction coordinate) *rather than transition states* (representing energy maxima) during ligand substitution reactions of 17-electron species. Whether some of the excess electron density may be removed from the metal center by η^4 or η^3 bonding of the cyclopentadienyl ring[48] is not clear.

Mechanism of Formation of Products from Metal Hydride Cation Radical Decomposition. We still have not explicitly addressed the question of whether the formation of acetonitrile-containing cationic products takes place via electron transfer from the 17-electron radicals, followed by acetonitrile coordination to the resulting 16-electron intermediate, or via acetonitrile coordination yielding 19-electron intermediates, followed by oxidation of the 19-electron species (Scheme VI). However, the three following observations strongly suggest that formation of 19-electron adducts takes place: (1) The thermodynamic mixture of *cis*-**10** and *trans*-**10** is obtained during chemical and electrochemical oxidation of **5**; (2) *trans*-**10** undergoes rapid electrocatalytic isomerization to the more stable isomer *cis*-**10** without ligand dissociation; (3) interconversion of *trans*-**10** and *cis*-**10** is very slow in the absence of reducing agents.

By extension, the same sequence of events appears likely for the decomposition of the other metal hydride cations included in this work. For electronic reasons, the equilibrium between 17-electron radicals $(\eta^5\text{-}C_5H_5)W(CO)_2L$ (L = CO, PMe_3) and 19-electron species $(\eta^5\text{-}C_5H_5)W(CO)_2L(NCMe)$ would be expected to be even more favorable when L = CO than when L = PMe_3 because the extra acceptor ligand CO is more able to accommodate

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some of the excess electron density in the 19-electron adduct.

This timing of events is in contradiction with a report in which it was concluded that radical $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^\bullet$ was oxidized to 16-electron $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^+$ at the potential where anion $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^-$ underwent oxidation to the radical. This conclusion was based on the observation that voltammetric oxidation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^-$ yielded both dimer $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2\text{(CO)}_6$ and acetonitrile adduct $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{(NCMe)}^+$ at a potential cathodic of that required to oxidize the dimer.[20] In our view, it would be highly surprising if oxidation of the electron-deficient radical $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^\bullet$ took place at the same potential as oxidation of the electron-rich anion $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^-$. The prior formation of 19-electron $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{(NCMe)}^\bullet$ from electrode-generated $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3^\bullet$ (lower pathway in Scheme VI) in a reaction competing with radical dimerization, followed by oxidation of the 19-electron radical, would be equally consistent with the experimental data.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out by using vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile and acetonitrile-d_3 were distilled from P_2O_5 and CaH_2, respectively, and dichloromethane-d_2 was distilled from CaH_2. The electrochemical instrumentation, cells, data-handling procedures, and electrodes have been previously described.[12a,49] 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 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 at 293 K. ^{1}H NMR spectra were recorded on JEOL FX-100, Varian XL-300, or Bruker AM-500 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, using the residual solvent proton resonance as internal standard (δ 1.93 for acetonitrile, 5.32 for dichloromethane). Infrared spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer. Melting points were measured in capillary tubes sealed under vacuum on a Büchi melting point apparatus and are uncorrected. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

Metal hydrides **1–5**,[28g,50] acetonitrile adducts **6–9**,[28a,g,51] cobaltocene,[52] ferricinium hexafluorophosphate,[53] $\text{(phen)}_3\text{Fe}^{3+}(\text{PF}_6^-)_3$,[54] and $(p\text{-MeOC}_6\text{H}_4)\text{Ph}_2\text{C}^+\text{PF}_6^-$ [29a] were prepared according to published procedures.

***trans*-[(η⁵-C₅H₅)W(CO)₂(PMe₃)(NCMe)]⁺BF₄⁻ (*trans*-10).** To a stirred solution of **5** (53 mg, 0.139 mmol) in acetonitrile (15 mL) was added $\text{Ph}_2(p\text{-MeOC}_6\text{H}_4)\text{C}^+\text{BF}_4^-$ (50 mg, 0.139 mmol) at −20 °C. Stirring was continued while the solution was heated to 0 °C over a 3-h period. The solvent was removed in vacuo, and the residual orange oil was washed with ether (3 × 10 mL), upon which the oil solidified. The orange solid was dissolved in dichlormethane (2 mL), and the solution was layered with ether. The product crystallized upon refrigeration overnight (66 mg, 93%): orange prisms, mp 130–133 °C dec; ^{1}H NMR (100 MHz, CD_3CN) δ 1.71 (d, J = 10.3 Hz, 9 H), 2.51 (s, 1 H), 5.53 (d, J = 1.8 Hz, 5 H); IR (CH_3CN) 1978 s, 1888 vs cm^{-1}. Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{BF}_4\text{NO}_2\text{PW}$: C, 28.32; H, 3.37; N, 2.75. Found: C, 28.63; H, 3.43; N, 2.90. The ^{1}H NMR spectrum displayed a small amount (ca. 10%) of the cis isomer.

***cis*-[(η⁵-C₅H₅)W(CO)₂(PMe₃)(NCMe)]⁺PF₆⁻ (*cis*-10).** To a solution of **5** (64 mg, 0.168 mmol) and 2,6-lutidine (39 μL, 0.335 mmol) in acetonitrile (20 mL) was added solid ferricinium hexafluorophosphate (110 mg, 0.332 mmol) at −20 °C. After 10 min of stirring, all of the ferricinium had been consumed as evidenced by the color change to bright orange. The solvent was removed in vacuo, and the residue was washed with ether until the filtrate was colorless. The product was dissolved in CH_2Cl_2 (10 mL), and the solution was extracted with ice-cold water (2 × 5 mL). The organic phase was dried (MgSO_4), filtered, concentrated to 2 mL, and layered with ether. The product crystallized upon cooling in the refrigerator overnight (73 mg, 77%): ^{1}H NMR (100 MHz, CD_3CN) δ 1.68 (d, J = 10.2 Hz, 9 H), 2.58 (d, J = 2.9 Hz, 3 H), 5.77 (s, 5 H); IR (CH_3CN) 1971 vs, 1879 s cm^{-1}. The ^{1}H NMR spectrum displayed a trace (ca. 5%) of the trans isomer.

[(η⁵-C₅H₅)W(CO)₂(PMe₃)H₂]⁺BF₄⁻ (13). A stirred solution of **5** (43 mg, 0.113 mmol) in ether (15 mL) was treated with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (25 μL, 0.21 mmol) at 0 °C. A white precipitate formed immediately. The solvent was decanted, and the residue was washed with ether (3 × 30 mL). Drying in vacuo yielded **13** (50 mg, 95%): white powder, mp 210–215 °C dec; ^{1}H NMR (100 MHz, CD_2Cl_2, 40 °C) δ −2.44 (d, J = 40.5 Hz, 2 H), 1.88 (d, J = 10.7 Hz, 9 H), 5.69 (s, 5 H); IR (CH_3CN) 2073, 2015 cm^{-1}. Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{BF}_4\text{O}_2\text{PW}$: C, 25.56; H, 3.43. Found: C, 25.45; H, 3.53.

(η⁵-C₅H₅)W(CO)₂(PMe₃)Me. A slurry of ***trans*-10** (20 mg, 0.039 mmol) in THF (3 mL) was stirred with excess (1% w/w). A transient purple color developed during a 5-min period but disappeared during the next 30 min. Stirring was continued for 1 h. The pale yellow solution was decanted and treated with methyl iodide (25 μL, 0.27 mmol) at −25 °C for 5 min. The volatiles were removed by vacuum transfer. The residue was extracted with ether (2 × 5 mL) and filtered through activity III alumina (0.5 × 2 cm). The filtrate was evaporated until dryness. The yellow crystalline product (11 mg, 71%) was identified as $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_2\text{(PMe}_3\text{)Me}$ by comparison of its ^{1}H NMR and IR spectra with published values.[55]

Cobaltocene-Catalyzed Isomerization of *trans*-10. A solution of ***trans*-10** (20 mg, 0.039 mmol) in acetonitrile-d_3 (0.5 mL) was treated with a solution of cobaltocene (1 mg, 0.005 mmol) in acetonitrile-d_3 (0.1 mL) while stirring. The mixture was immediately transferred to an NMR tube, and the spectrum was recorded immediately. The spectrum revealed the presence of ***cis*-10** and ***trans*-10** in a 95:5 ratio, in addition to a small amount of the cobalticinium cation.

Constant-Current Coulometry Experiments. Constant-current electrolyses with DCV monitoring of the disappearance of substrate were carried out in an H-shaped cell, the compartments of which were separated by a fritted glass junction. A Pt gauze working electrode was used. Solutions containing 0.5–1.0 mmol of the hydrides in 20 mL of acetonitrile/0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ were electrolyzed with a constant current of 20 mA. Monitoring of the electrode potential during the electrolyses related that the applied potential was well below the DCV peak potential for ca. 90% of the time required for the substrate DCV peak to disappear. The results from these experiments are summarized in Table I.

Preparative Electrolyses Experiments. The preparative electrolyses were carried out in acetonitrile/0.05 M $\text{Me}_4\text{N}^+\text{BF}_4^-$. In a typical experiment, 20 mL of a 2 mM substrate solution of the hydride was electrolyzed for the time that was required for the passage of 2.0 F/mol of charge. The solution was concentrated by rotary evaporation, and the residue was extracted with CH_2Cl_2 (5 mL). The filtered extract was concentrated, and the product was isolated after recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. The product yields obtained in these reactions are listed in Table I.

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