Redox properties of the 17-electron sandwich $(\eta^5\text{-}C_5H_5)Mo(\eta^6\text{-}C_6Ph_6)$: electrochemical characterization of the 16 e$^-$ Lewis acid monocation and its PF_6^- adduct

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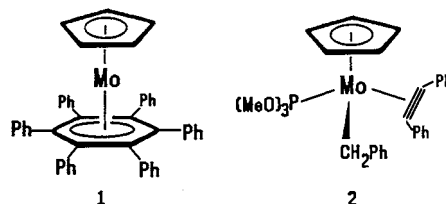[b] *Department of Chemistry, University of Vermont, Burlingtion VT 05405, USA*

Abstract

Thermolysis of $CpMo(CH_2C_6H_5)(\eta^2\text{-}PhC_2Ph)[P(OMe)_3]$ $[Cp = (\eta^5\text{-}C_5H_5)]$ unexpectedly gives the mixed-sandwich 17-electron metallocene $CpMo(\eta^6\text{-}C_6Ph_6)$, **1**. The title compound undergoes reversible one-electron oxidation ($E_{1/2} = -0.25$ V vs. ferrocene) and reduction ($E_{1/2} = -2.02$ V) reactions which were characterized by voltammetry and coulometry. When the oxidation of **1** is accomplished in $CH_2Cl_2/[Bu_4N][PF_6]$ electrolyte, the 16 e$^-$ Mo(II) complex **1**$^+$ is in equilibrium with a thermodynamically-favored product formulated as the $[PF_6]^-$ adduct, **1**-FPF$_5$, **3**. Adduct **3** remains intact upon further one-electron oxidation to the Mo(III) complex **3**$^+$, but it rapidly releases $[PF_6]^-$ when reduced to the Mo(I) species **3**$^-$. Other counterions such as $[BF_4]^-$ and $[ClO_4]^-$ do not show the same degree of interaction with the 16 e$^-$ Mo(II) cation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the course of pursuing studies of the roles of α-hydrogen elimination reactions [1] and alkyne bonding modes [2] in the synthesis of molybdenum π-complexes, the complex **2** has been found to react with diphenylacetylene to form the 17-electron mixed sandwich metallocene, $CpMo(\eta^6\text{-}C_6Ph_6)$, **1**, where $Cp = (\eta^5\text{-}C_5H_5)$, a complex that had been prepared earlier by different routes [3]. Since paramagnetic organometallic complexes, especially isolable ones, are of interest from a variety of viewpoints [4], we have investigated the electrochemical oxidation and reduction of **1** in non-aqueous solvents. We find that the 16-electron complex **1**$^+$ is a strong Lewis acid which forms an adduct with the $[PF_6]^-$ anion of the supporting electrolyte. Voltammetry measurements give information about the integrity of this adduct in three different Mo oxidation states [(I), (II), (III)] and the enthalpy of its formation in the Mo(II) complex. The existence of the 18-electron anion **1**$^-$ was also confirmed.

Table 1
Potentials (vs. Fc) of $CpMo(\eta^6-C_6Ph_6)$, **1**, and its $[PF_6]^-$ adduct, **3**

Mo(II) complex	Electrolyte[a], T (K)	$E_{1/2}$ (V)		
		Mo(III)/(II)	Mo(II)/(I)	Mo(I)/(0)
$CpMo(C_6Ph_6)$, **1**	$CH_2Cl_2/[Bu_4N][PF_6]$, 298	+0.92[b]	−0.25	−1.94[c]
$CpMo(C_6Ph_6)$, **1**	$THF/[Bu_4N][PF_6]$, 298	[d]	−0.24	−2.02
$CpMo(C_6Ph_6)$, **1**	$CH_2Cl_2/[Bu_4N][ClO_4]$, 293	[e]	−0.20	−2.0[a]
$[CpMo(C_6Ph_6)]–PF_6$, **3**	$CH_2Cl_2/[Bu_4N][PF_6]$, 273	+0.35	−1.5[b]	

[a] Electrolyte concentration, 0.1 M.
[b] Irreversible. Peak potential with $v = 0.20$ V s^{-1} reported.
[c] $T = 233$ K.
[d] Wave not observed owing to limited positive potential window of this solvent.
[e] Process not assigned. Irreversible anodic peaks at +0.78 and +1.00 V were observed.

2. Results and discussion

2.1. Characterization of **1**

Selective attack of the Grignard reagents $CH_2=CHMgBr$ and CH_3MgI on the metal center of the cation $\{CpMo(\eta^2-PhC_2Ph)–[P(OMe)_3]_2\}[BF_4]$ has been demonstrated to afford reactive molecules which undergo novel ring-forming reactions with diphenylacetylene to give the η^3-cyclopropenyl and η^4-cyclopentadiene complexes $CpMo(\eta^3-C_3MePh_2)\{P(OMe)_3\}_2$ and $CpMoH\{\eta^4-C(Ph)C(H)–C(Ph)C(Ph)C(Ph)(H)\}P(OMe)_3$ ([1]b). Under similar conditions, the addition of two equivalents of $C_6H_5CH_2MgCl$ to a purple solution of $\{CpMo(\eta^2-PhC_2Ph)[P(OMe)_3]_2\}[BF_4]$ [5] in THF at 273 K gave an emerald-green colored mixture from which $CpMo(CH_2C_6H_5)(\eta^2-PhC_2Ph)\{P(OMe)_3\}$, **2**, was isolated as a deep green air-sensitive solid after low temperature column chromatography on alumina.

Thermolysis of **2** in benzene at 373 K with an excess of diphenylacetylene afforded a deep green/yellow solution, from which **1** was isolated as a bright yellow, extremely air-sensitive, solid. Spectroscopic analysis of the supernatant liquid from the preparation revealed the presence of trimethylphosphite, diphenylacetylene, and dibenzyl. The last compound presumably arises through coupling of benzyl radicals formed during the thermolysis. The room temperature ^1H- and $^{13}C\{^1H\}$-NMR spectra of **1** displayed resonances that were assigned to a Cp ligand and to phenyl rings. Each signal was broad, suggesting that **1** was a paramagnetic complex. This was confirmed by employing a variation of the Evans NMR method [6] which revealed a magnetic moment indicative of one unpaired electron ($\mu_{eff} = 1.58$ BM). This complex was finally confirmed as having the sandwich structure **1** by Hursthouse and Mazid using X-ray diffraction methods [7].

2.2. Electrochemistry

Complex **1** displays chemically reversible one-electron oxidation and reduction processes which establish the electron-transfer series of Eq. (1), involving the 16-electron 1^+, 17-electron **1** and 18-electron 1^-:

$$1^+ \underset{}{\overset{e^-}{\rightleftharpoons}} 1 \underset{}{\overset{e^-}{\rightleftharpoons}} 1^- \tag{1}$$

The monoanion 1^- was more persistent in THF than in CH_2Cl_2. An essentially Nernstian [8] 1 e$^-$ wave was observed in the former solvent at ambient temperatures and slow cyclic voltammetry (CV) scan rates, $E_{1/2} = -2.02$ V versus Fc (Table 1). In CH_2Cl_2, however, the reduction wave (designated as wave D in our discussion below) was reversible only at reduced temperatures (Fig. 1). Under ambient conditions, the cathodic wave lacked chemical reversibility and was several times
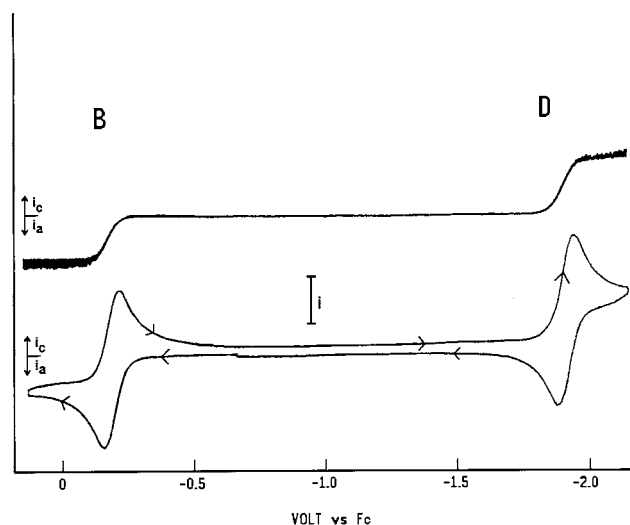

Fig. 1. Voltammetry of 0.5 mM **1** in $CH_2Cl_2/0.1$ M $[Bu_4N][PF]_6$ at 228 K at Pt electrodes. Top, rotating Pt electrode scan, $v = 2$ mV s^{-1}; bottom, CV scan, $v = 0.20$ V s^{-1}, at twice the current sensitivity. Waves B and D refer to the labels from text, processes $1^+/1^{2+}$ and $1^+/1$, respectively.
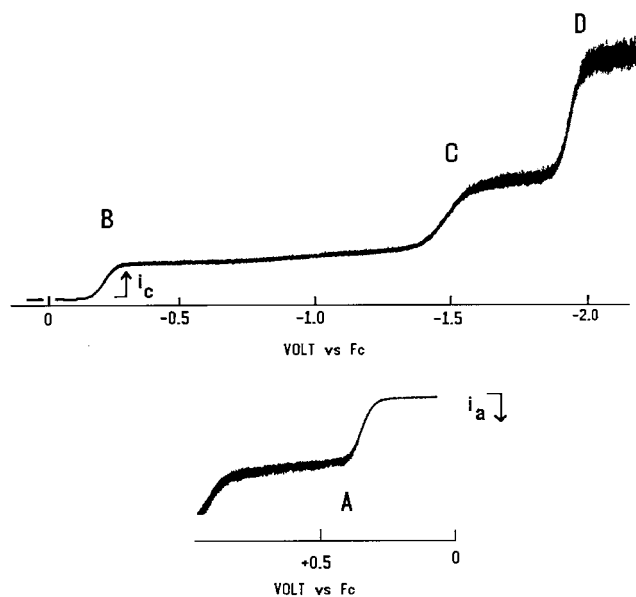
Fig. 2. Rotating Pt electrode scans of anodically electrolyzed (E_{appl} = 0 V) solution of **1** in $CH_2Cl_2/[Bu_4N][PF_6]$ (same solution as Fig. 1), in both negative (upper) and positive (lower) scan directions, T = 233 K. Waves A through D refer to labels in text.

larger in height than a one-electron value. It is probable that **1**$^-$ decomposes in CH_2Cl_2 by slow reduction of the solvent [9], and the reductive process was not studied in detail.

Reduction of **1** to **1**$^-$ allows the sandwich complex to attain the 18-electron configuration. The oxidation of **1** to **1**$^+$, involving formation of a 16-electron complex, is more novel and is therefore emphasized below.

2.3. Oxidation of **1** in $CH_2Cl_2/[Bu_4N][PF_6]$: cyclic voltammetry

Two oxidation waves are observed in CV scans in $CH_2Cl_2/[Bu_4N][PF_6]$. The first ($E_{1/2}$ = − 0.25 V) is a chemically reversible and diffusion-controlled [10] 1 e$^-$ reaction (Eq. (2)) involving formation of the 16 e$^-$ monocation, **1**$^+$:

$$1 \rightleftharpoons 1^+ + e^- \tag{2}$$

The fact that a unity value of i_c/i_a persisted for this wave down to a low sweep rate, v, of 0.05 V s^{-1} established a minimum half-life for **1**$^+$ of 20 s. In subsequent discussions and Figs. 1–3, this wave at $E_{1/2}$ = − 0.25 V is wave B.

A second anodic wave (later, wave E) at E_p = + 0.92 V was diffusion controlled but chemically irreversible, having twice the height of **1**/**1**$^+$ over a range of v and T. The ultimate electrode products of wave E are unknown. Noting, however, that the oxidation of **1**$^+$ is involved, we may use the potential of + 0.9 V as an approximation of the formal potential of the couple

1$^+$/**1**$^{2+}$, even though the dication decomposes on the CV time scale (Eq. (3)):

$$1^+ - e^- \rightleftharpoons 1^{2+} \rightarrow decomp \tag{3}$$

2.4. Oxidation of **1** in $CH_2Cl_2/[Bu_4N][PF_6]$: bulk electrolysis and evidence for adduct formation

Exhaustive electrolysis of **1** in $CH_2Cl_2/[Bu_4N][PF_6]$ with E_{appl} = 0 V (positive of wave B) resulted in a color change from yellow to red with release of ca. 0.9 F/eq. Judging from CV and rotating Pt electrode (RPE) scans, only two products were formed. One was the expected 16 e$^-$ monocation, **1**$^+$, which was slightly dominant at 293 K. Referring to Fig. 2, waves B ($E_{1/2}$ = − 0.25 V) and D ($E_{1/2}$ = 1.9 V) after electrolysis are those of **1**/**1**$^+$and **1**/**1**$^-$ (Eq. (1)), respectively. The height of the cathodic wave D is much larger than that of B, an anomaly explained below. The two additional waves (anodic wave A (Fig. 2, inset) and cathodic wave C) arise from a second (final) product. We reiterate that this second product is formed only on the longer time scale (ca. 20 min) of bulk electrolysis, rather than in CV scans of **1**, the slowest of which requires ca. 20 s.

A CV scan of the electrolyzed solution at 260 K (Fig. 3) shows that wave A is chemically reversible ($E_{1/2}$ = + 0.35 V) and that wave C (E_{pc} = − 1.5 V) is irreversible. Also appearing in Fig. 3 is wave E (the second oxidation wave of **1** (Eq. (3)) because the scan extends to a sufficiently positive potential.

The combined RPE plateau currents of A and B were exactly equal to the height of the anodic current for **1** prior to electrolysis, suggesting quantitative conversion of the starting material to the mixture of **1**$^+$ and the second product. As is justified below, the second product (**3**) is assigned a structure in which $[PF_6]^-$ is coordinated to **1**$^+$, most likely through donation of a lone pair from the fluorine atom to the electron-deficient metal, as in **3a**. A strong ion pair (**3b**) cannot be ruled out.
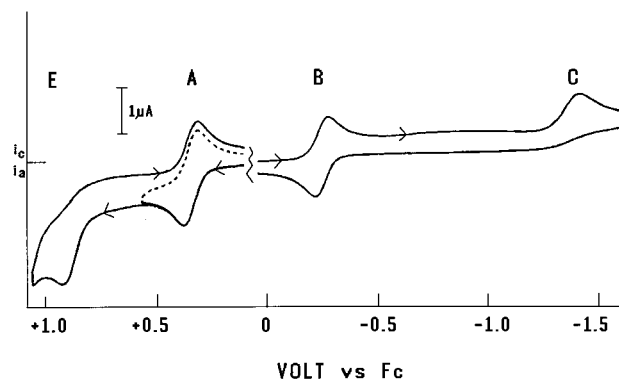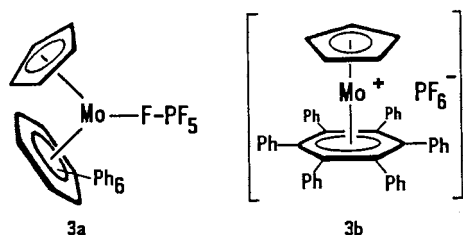

Fig. 3. CV scan v = 0.20 V s^{-1}, of same solution as Fig. 2, T = 260 K. scan The potential scan window is different from that of Fig. 2, thus showing wave E, Eq. (3).

Table 2
Ratios of [**3**]/[**1**$^+$] as measured by voltammetry at various temperatures in CH_2Cl_2/0.1 M [Bu_4N][PF_6]

[**3**]/[**1**$^+$]	K_{eq}[a]	Temperature (K)
0.72	7.2	293
0.85	8.5	282
1.15	11.5	272
1.35	13.5	260
1.74	17.4	248
2.14	21.4	233

[a] $K_{eq} = $[**3**]$/$[**1**$^+$][$PF_6^-$].

3a   **3b**

The electrolysis products **1**$^+$ and **3** are in equilibrium in CH_2Cl_2/0.1 M [Bu_4N][PF_6], as shown by the effect of temperature variations on the relative heights of waves A and B in electrolyzed solutions. Table 2 gives the measured ratios of [**3**]/[**1**$^+$] and the corresponding equilibrium constants (defined as in Eq. (4)), and Fig. 4 gives the plot of K_{eq} as a function of temperature. The adduct **3** is thermodynamically favored over **1**$^+$, with $\Delta H = -2.9$ kcal mol^{-1}.

$$\mathbf{1}^+ + [PF_6]^- \rightleftharpoons \mathbf{3} \tag{4}$$

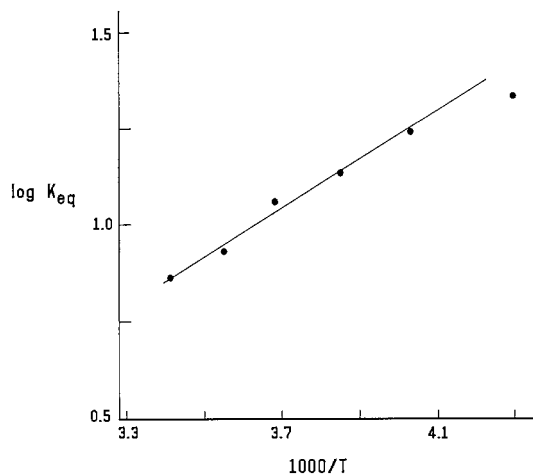$$K_{eq} = [\mathbf{3}]/[\mathbf{1}^+][PF_6^-]$$

Fig. 4. Plot of log K_{eq} (= [**3**] [{PF_6}$^-$]/[**1**$^+$]) as function of $1/T$ for solution of Fig. 2. The lowest temperature sample may not have achieved equilibration. Linear regression including all points gives $\Delta H° = -2.51$ kcal mol^{-1}; that excluding the lowest temperature point gives $\Delta H°$ -2.86 kcal mol^{-1}.
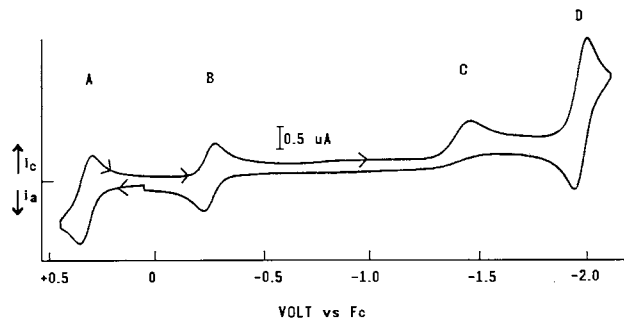

Fig. 5. CV scan, $v = 0.20$ V s^{-1}, of electrolyzed **1** in CH_2Cl_2/Bu_4NPF_6, same solution as Fig. 2, $T = 253$ K. Arrows indicate direction of potential sweep.

2.5. Proof of chemical reversibility of 3 and 1

When the anodically prepared solutions containing a mixture of **3** and **1** (e.g. Fig. 2) are exhaustively reduced at potentials slightly negative of wave C (ca. -1.6 V), waves B and D of the regenerated starting material **1** are formed in amounts equal to those measured prior to the original oxidation. Therefore both **1**$^+$ and **3** are reduced by one electron to give **1**. The fact that the conversion of **3** to **1** (Eq. (5)) is not only quantitative but extremely rapid is shown by the following analysis of CV data on solutions containing **1**$^+$ and **3**.

$$\mathbf{3} + e^- \rightarrow \mathbf{1} + [PF_6]^- \tag{5}$$

Consider Fig. 5, a CV scan at 253 K, $v = 0.20$ V s^{-1}, of an anodically prepared solution of **1**$^+$ and **3**. The initial positive-going scan through wave A ($E_{1/2} = +0.35$ V) involves the Mo(II)/Mo(III) oxidation of **3** to **3**$^+$ (Eq. (6)). Wave B is that arising from reduction of **1**$^+$ to **1** (reverse of Eq. (2), Mo(II)/Mo(I)).

$$\mathbf{3} \rightleftharpoons \mathbf{3}^+ + e^- \tag{6}$$

Wave C is the irreversible cathodic process of Mo(II)–PF_6 going to Mo(I), Eq. (5). Finally, wave D is the reduction of Mo(I) to Mo(0), **1** to **1**$^-$. In this scenario, the height of wave D reflects the amount of **1** produced at the electrode from both waves B and C. Once the irreversibility of wave C is taken into account, the heights of the three waves are completely consistent with this model. Irreversible wave C has a lower peak height when compared to a reversible system; Eq. (7) is required if i_p(C) is to be directly compared with the reversible peaks i_p(B) and i_p(D) in Fig. 5 [11].

$$i_p(\text{irrev}) = 1.1 \, [i_p(\text{rev})] \, [\alpha^{1/2}] \tag{7}$$

This relationship predicts a peak height of approximately $0.77 \times i_p$(rev) for an irreversible system with a charge transfer coefficient, α, of 0.5 (this value of α is justified by analysis of the shape of wave C) [12]. The predicted height of wave D (see Eq. (8)) is 1.8 µA, close to the value of 2.0 µÅ measured experimentally.

$$i_p(B) + i_p(C)/0.77 = i_p(D) \qquad (8)$$

This analysis and the aforementioned analysis of RPE plateau currents demonstrate that the 17 e$^-$ complex **1** is generated immediately and quantitatively in the one-electron reduction of **3** (Eq. (5)). Taken together, these data support Schemes 1 and 2 for interconversion of the various redox forms with and without [PF$_6$]$^-$ attachment:
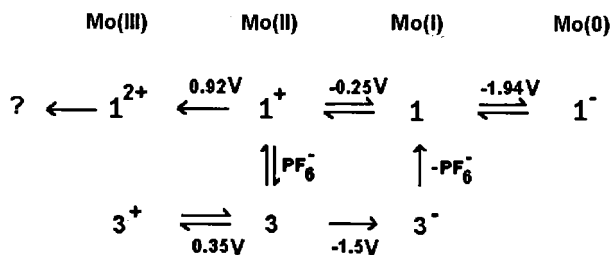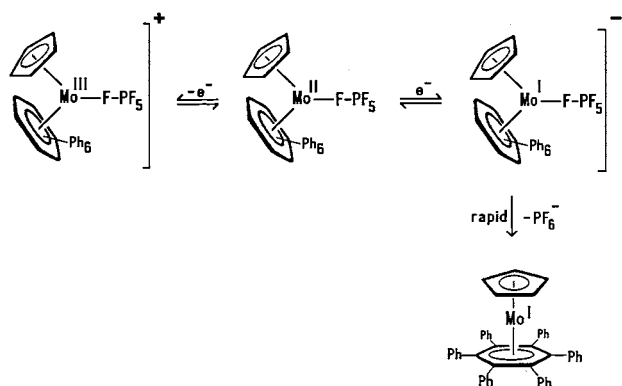
Scheme 1.

2.6. Deduction of the identity of 3

The above electrochemical experiments do not in themselves establish that the second product involves association of **1**$^+$ with a [PF$_6^-$] counterion. Rather, this deduction is made from observations of the changes engendered by alterations in the solvent and supporting electrolyte. The assumption that underlies our conclusion is that **3** must be related to **1**$^+$ in one of three ways: as an isomer, as a solvent adduct, or as a counterion adduct (or ion pair).

The first of these is eliminated in part on the basis that two isomers would be unlikely to differ as greatly in redox potentials as is observed in the Mo(II)/Mo(III) couples of the systems under study (0.35 V for **3**, ca. 0.9 V for **1**$^+$) [13]. The stabilization of the Mo(III) oxidation state for **3** (ca. 12 kcal mol^{-1}) implies that the metal center is significantly more electron rich in **3** compared to **1**$^+$. Since the two π ligands in **1**$^+$ have no additional ligation sites, the added electron density in **3**

Scheme 2.

must come from an outside source, either the solvent or the supporting electrolyte anion.

When CH$_2$Cl$_2$ is used with a perchlorate electrolyte anion (as either [Et$_4$N][ClO$_4$] or [Bu$_4$N][ClO$_4$]), the wave for **1/1**$^+$ is observed in CV experiments, but exhaustive anodic electrolysis of **1** gave neither a wave for **3** nor any other recognizable product wave. Instead, a series of small cathodic waves most likely arising from decomposition products remained after electrolysis. These control experiments show that the presence of [PF$_6$]$^-$ is necessary for the formation of **3**.

Electrochemical results in THF/[Bu$_4$N][PF$_6$], however, mimicked those obtained in CH$_2$Cl$_2$/[Bu$_4$N][PF$_6$]. The couples **1/1**$^+$ (wave B) and **1/1**$^-$ (wave D) were apparent after anodic electrolysis. There is also electroactivity in the range of -1.5 V (wave C), and the height of wave D is again roughly that expected from the combined products of waves B and C. There is also a broad anodic wave near $+0.4$ V (Figure in Supplementary Material) and an irreversible cathodic wave at -0.95 V. The broad wave is also observed in CV scans of the fresh solution of **1** prior to electrolysis, and appears to arise from two or more overlapping anodic processes. These results suggest that **3** forms in THF/[PF$_6$]$^-$ media as well as in CH$_2$Cl$_2$/[PF$_6$]$^-$ media, albeit not as cleanly in the former. The other waves in the THF electrolysis solutions arise from decomposition products or from a structure in which THF is metal-coordinated.

3. Discussion

Reversible redox reactions involving 16 e$^-$/17 e$^-$/18 e$^-$ couples have been described for a number of metal sandwich compounds [14], including those to the left of iron in the periodic table. The latter include [Cp$_2^*$Mn]$^{+/0/-}$ [15] (Cp* = η^5-C$_5$Me$_5$), [(C$_6$Me$_6$)$_2$Cr]$^{2+/+/0}$ [16], [(C$_6$Me$_6$)CrCp*]$^{+/0/-}$, [16] [(C$_6$H$_6$)$_2$V]$^{+/0/-}$, [16] [(C$_7$H$_7$)VCp]$^{+/0/-}$, [16,18] and [(C$_7$H$_7$)NbCp]$^{+/0/-}$ [19]. Also relevant are the 15 e$^-$/16 e$^-$/17 e$^-$ couples of [Cp$_2$Cr]$^{+/0/-}$ and its analogues [20]. There is clearly ample precedent for reversible redox processes involving both oxidation and reduction of 17 e$^-$ metal sandwich compounds of the early transition metals. The difference in $E_{1/2}$ values between the **1**$^+$/**1** and **1/1**$^-$ couples (1.78 V in THF) is very similar to those reported for [(C$_6$Me$_6$)CrCp]*$^{+/0/-}$ (1.8 V in THF) [17] and [Cp$_2^*$Mn]$^{+/0/-}$ (1.94 V in CH$_3$CN) [15]. In this context, the electron-transfer series **1**$^+$/**1**/**1**$^-$ is unremarkable.

It is the equilibration of the 16 e$^-$ complex **1**$^+$ with **3** that makes this system of more than routine interest. Metal complexes which incorporate the anion [PF$_6$]$^-$ into their coordination spheres are known [21]. For that matter, studies have been reported in which the coordi-

nation of halocarbons to metals was demonstrated [22]. The new complex **3** was most prominent in CH_2Cl_2/[Bu$_4$N][PF$_6$] media, in which it is thermodynamically favored over **1**$^+$. The facts that **1**$^+$ undergoes irreversible decomposition in CH_2Cl_2 when [ClO$_4$]$^-$ is substituted for [PF$_6$]$^-$, and that evidence was found for **3** in THF/[PF$_6$]$^-$ media is suggestive that the Lewis base in the adduct **3** is the hexafluorophosphate anion, rather than CH_2Cl_2.

A troublesome aspect of this conclusion relates to the fact that the perchlorate anion is normally considered to have a coordination tendency superior to that of hexafluorophosphate [21,23]. In this light, one must ask why electrolysis in CH_2Cl_2/[R$_4$N][ClO$_4$] did not yield a stable adduct. A possible answer is that the 'normal' coordination tendency might be reversed for molybdenum. The majority of isolated perchlorate complexes have contained the later transition metals [24], although this circumstance may not arise from inherent stability factors. It is also pertinent to note that the anion [PF$_6$]$^-$ stabilizes the Cr(I) radical cation [(arene)Cr(CO)$_3$]$^+$ in CH_2Cl_2, whereas others such as [ClO$_4$]$^-$ and [BF$_4$]$^-$ fail to do so. Thus, only when [PF$_6$]$^-$ is present is the one-electron oxidation of (C$_6$H$_6$)Cr(CO)$_3$ chemically reversible by cyclic voltammetry [25].

The electronic effect of coordination of [PF$_6$]$^-$ to Mo(II) can be quantified by comparison of the redox potentials of **3** and **1** in the various oxidation state changes. To do this we must first assume that the peak potentials of the irreversible processes of Eqs. (3) and (5) (waves E and C, respectively) are reasonable approximations of the formal potentials of the couples **1**$^+$/**1**$^{2+}$ and **3**/**3**$^-$, respectively (Table 1). With these values in hand we can then compare the potentials of the Mo(II)/Mo(III) and Mo(II)/Mo(I) couples with and without [PF$_6$]$^-$ coordination.

Comparison of the potentials for waves A ($E_{1/2}$ = + 0.35 V) and E (E_p = + 0.9 V) shows that [PF$_6$]$^-$-coordination strongly stabilizes the Mo(III) oxidation state relative to Mo(II). Similarly, the negative shift of wave C compared to B argues for stabilization of Mo(II) relative to Mo(I) by [PF$_6$]$^-$-coordination. Thus, in the Mo(I)/Mo(II)/Mo(III) sequence, addition of a single weakly basic ligand continuously stabilizes the next higher oxidation state. Since the difference in $E_{1/2}$ potentials between the Mo(III)/Mo(II) and Mo(II)/Mo(I) couples is considerably greater (ca. 1.9 V)in the [PF$_6$]$^-$-bound complex than in the unbound complex (ca. 1.2 V), it can also be stated that Lewis-base coordination of PF$_6^-$ stabilizes the Mo(II) oxidation state with respect to disproportionation into Mo(III) and Mo(I).

Finally we note that although we favor the Lewis acid/base pair **3a** as the structure of the adduct, we cannot rule out other means of association between **1**$^+$ and [PF$_6$]$^-$. A non-solvent-separated ion pair, **3b**, is

also a reasonable candidate. Thermodynamic studies have been used to characterize equilibria between covalently-bonded and tight ion-paired species such as **3a** and **3b** [26]. Thermodynamic data on the present system do not, however, have the accuracy necessary for analysis of the entropic trends that are diagnostic of the various association modes [27].

In a broader sense, the present results are important in demonstrating another class of electron-deficient sandwich complexes of the early transition metals may interact reversibly with weak anionic ligands. Interactions of this nature are known to influence the activities of metallocene catalysts in olefin polymerizations [28], and could, in principle, form a basis for selective analytical detection of the anions.

4. Experimental

Standard Schlenck procedures were employed to assure dry- and oxygen-free preparative procedures. Electrochemical experiments were conducted with samples within a controlled-atmosphere enclosure using methods previously detailed [29]. The complex {CpMo(η^2-PhC$_2$Ph)[P(OMe)$_3$]$_2$}[BF$_4$] was prepared as described in Ref. [5].

4.1. Preparation of complexes CpMo(CH$_2$C$_6$H$_5$)(η^2-PhC$_2$Ph)[P(OMe)$_3$](2)

To a purple solution of {CpMo(η^2-PhC$_2$Ph)-[P(OMe)$_3$]$_2$}[BF$_4$] (0.49 g, 0.73 mmol) in THF (10 ml) at 273 K was added C$_6$H$_5$CH$_2$MgCl (2 M in THF, two equivalents). The solution was stirred at this temperature for 10 min and turned emerald green. The solvent was removed at 273 K and the residue subjected to column chromatography on alumina at 243 K. Elution with Et$_2$O/hexane gave a green band from which CpMo(CH$_2$C$_6$H$_5$)(η^2-PhC$_2$Ph)[P(OMe)$_3$] was obtained as a deep green, air-sensitive, solid (0.34 g, 84%). ^{1}H-NMR (C$_6$D$_6$, 293 K) δ 7.7–6.8 (m, 15H, Ph), 4.84 (s, 5H, C$_5$H$_5$), 3.15 (d, 9H, $^3J_{HP}$ = 10.7, P(OCH$_3$)$_3$), 2.80 (qt, 1H, $^3J_{HP}$ = 6.6, $^2J_{HHgem}$ = 11.4, CHHC$_6$H$_5$), 2.41 (qt, 1H, $^3J_{HP}$ = 6.6, $^2J_{HHgem}$ = 11.4, CHHC$_6$H$_5$; ^{13}C{^{1}H}-NMR (C$_6$D$_6$, 293 K) δ 200.9 (d, $^2J_{CP}$ = 16.3, ≡CPh), 200.7 (d, $^2J_{CP}$ = 47.5, ≡CPh), 139–121 (Ph), 92.3 (C$_5$H$_5$), 51.6 [d, $^2J_{CP}$, P(OCH$_3$)$_3$], 21.7 (d, $^2J_{CP}$ = 13.5, CH$_2$C$_6$H$_5$); ^{31}P{^{1}H}-NMR (C$_6$D$_6$, 293 K) δ 197.0 (s).

4.2. (η^5-C$_5$H$_5$)Mo(η^6-C$_6$Ph$_6$) (1)

To a green solution of CpMo(CH$_2$C$_6$H$_5$)(η^2-PhC$_2$Ph)[P(OMe)$_3$] (0.18 g, 0.32 mmol) in benzene (10 ml) was added PhC≡CPh (0.43 g, 2.4 mmol). The closed system (Young's tube) was heated at ca. 375 K for 17 h, whereupon the color changed to green–yellow. After

reduction of the solvent to 2 ml, pentane (10 ml) was added and the reaction mixture was stirred 5 min, then filtered. The yellow precipitate was washed twice with pentane (10 ml) and crystallized from THF at 243 K to afford **1** as a bright yellow, extremely air-sensitive, solid (0.11 g, 50%). ^{1}H-NMR (CD$_2$Cl$_2$, 293 K) δ 11.40 (br), 10.35 (br), 8.84 (br), 7.84 (br); ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 293 K) δ 134.8 (br), 132.4 (br), 130.9 (br), 117.6 (br); Evans NMR (CHCl$_3$), $\mu_{eff} = 1.58$ BM.

4.3. Electrochemistry

CH$_2$Cl$_2$ and THF were reagent-grade solvents twice distilled from CaH$_2$, the second time under vacuum in a bulb-to-bulb transfer. The supporting electrolytes, [Bu$_4$][NPF$_6$], [Et$_4$N][ClO$_4$], and [Bu$_4$N][ClO$_4$], were vacuum dried at 350 K before use. An Ag/AgCl wire was used as the experimental reference electrode. Ferrocene was added to the solution near completion of each experiment, and all potentials in this paper employ Fc/Fc$^+$ as the reference couple. Conversion to the aqueous SCE reference requires addition of $+0.46$ V for CH$_2$Cl$_2$ or $+0.56$ V for THF.

5. Supplementary material available

One voltammogram showing electrochemical behavior of solution of **1** after bulk oxidation in THF/0.1 M [Bu$_4$N][PF$_6$].

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[7] The crystal structure of **1** was obtained at 173 K by M.A. Mazid and M.B. Hursthouse at the University of Wales, Cardiff. The arene ring is planar to within 0.01 Å.

[8] In the context of this study, Nernstian refers to a description in which the CV peak separations of a wave are essentially equal to those of ferrocene under the same experimental conditions, including T, concentration, and scan rate, v. Typically, peak separations of 70–90 mV were observed for ferrocene$^{0/+}$ with $v = 0.05$–0.50 V s^{-1}.

[9] The anion **1**$^-$ likely reduces CH$_2$Cl$_2$ (to an unspecified product), and in the process regenerates neutral **1**, which is reduced again by the electrode. This mechanism increases the cathodic current of wave D over the 1 e$^-$ height and decreases or eliminates the anodic component of the wave. It is an example of homogeneous redox catalysis (see C.P. Andrieux, P. Hapiot, J.-M. Saveant, Chem. Rev. 90 (1990) 723).

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[12] On the basis of the relationship $E_p - E_{p/2} = 48$ mV/αn, a width of 96 mV is predicted for wave C with $n = 0.5$, close to the measured value of 98 mV. Further verification of the value is obtained from the relative height of C to the anodic branch of A, both of which arise from the same concentration of **3** at the electrode surface, assuming interconversion of **1**$^+$ and **3** which is slow on the CV time scale. It is predicted that $i_p(C)/i_p(A) = 0.77$, and the measured value is 0.68.

[13] This comparison makes use of the peak potential of the irreversible oxidation of **1**$^+$ ($E_{pa} = 0.92$ V, scan rate 200 mV s^{-1}) as an approximation of the $E_{1/2}$ of **1**$^+$/**1**$^{2+}$. There is also a less obvious assumption involved for the reversible oxidation of **3** ($E_{1/2} = 0.35$ V). The Nernstian wave demonstrates that if there is ligand ([PF$_6$]$^-$) loss and gain during the redox reaction, both processes are fast on the CV time scale. Our analysis assumes that any such process would not significantly change the $E_{1/2}$ value. For more on the implications of a Nernstian wave see W.E. Geiger, in: S.J. Lippard (Ed.), Progress in Inorganic Chemistry, vol. 33, Wiley, New York, 1985, pp. 277–281.

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