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Oxidation of the molybdenum hydride $CpMo(CO)_2(PPh_3)H$. Synthesis of *cis*- and *trans*-$CpMo(CO)_2(PPh_3)(NCMe)^+$ and the kinetics of their interconversion

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Abstract

The oxidation chemistry of $CpMo(CO)_2(PPh_3)H$ (**1**) has been investigated by electrochemical and other methods. The molybdenum hydride **1** undergoes oxidation at +0.26 V *vs.* the ferrocene/ferricinium couple in acetonitrile solution, forming *cis*-$CpMo(CO)_2(PPh_3)(NCMe)^+$ (*cis*-**2**). Hydride abstraction from **1** by the substituted trityl reagent (p-$MeOC_6H_4)Ph_2C^+ BF_4^-$ generates *trans*-**2**. The stereochemical outcome of this reaction implies a non-electron-transfer pathway for the hydride abstraction. The thermal isomerization of *trans*-**2** to the more stable *cis*-**2** in acetonitrile-d_3 proceeds without concomitant ligand exchange with the solvent. The kinetics of the isomerization have been investigated, and give the activation parameters $\Delta H^{\#} = 24.2 \pm 0.4$ kcal/mol and $\Delta S^{\#} = -3.4 \pm 1.4$ cal/K·mol. The near-zero entropy of activation is in accord with an intramolecular non-dissociative isomerization process. In contrast, treatment of *trans*-**2** with a catalytic amount of cobaltocene results in fast partial isomerization to *cis*-**2**, accompanied by ligand exchange with the solvent. This behavior is compared with the non-dissociative nature of the previously reported electrocatalytic isomerization of *cis*-$CpW(CO)_2(PMe_3)(NCMe)^+$, and suggests that the intermediate 19-electron radicals are more loosely bound for molybdenum than for tungsten.

Introduction

The one-electron oxidation or reduction of stable, 18-electron organo-transition metal complexes provides a convenient and widely applicable method for generation of reactive 17- and 19-electron species. The chemistry of odd-electron compounds has received considerable attention recently, prompted in particular by the higher reactivity in these odd-electron systems compared to their 18-electron counterparts [1]. For example, important reactions such as ligand substitution and CO migratory insertion are greatly accelerated as a result of the removal of an electron from closed-shell, 18-electron precursors [2*]. There is a large body of

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* Reference number with asterisk indicates a note in the list of references.

evidence that both of these reactions proceed *via* 19-electron intermediates or transition states. We and others have recently demonstrated that the oxidation of a number of 18-electron hydrides M–H provides a new approach to the generation of neutral 17-electron radicals [3]; this is because the incipient transient 17-electron cation radicals $M–H^{\cdot +}$, the acidities of which are higher than those of the neutral parents by about 20 pK_a units [3b], undergo heterolytic M^-H cleavage (deprotonation) as a primary reaction [3]. The ultimate fate of the primary products strongly depends on the substrate and on the reaction conditions. We present below details of the behavior of $CpMo(CO)_2(PPh_3)H$ under oxidative conditions.

Results

Electrochemical oxidation of $CpMo(CO)_2(PPh_3)H$ (1)

Figure 1a shows a derivative cyclic voltammetry (DCV) [4] trace for the oxidation of **1** (1.0 m*M* substrate in acetonitrile/0.1 *M* $Bu_4N^+PF_6^-$, 0.6 mm Pt disk electrode, voltage sweep rate $v = 1.0$ V/s, 20°C). The cyclic voltammetry peak potential for the substrate oxidation may be taken as the point at which the rapidly descending DCV curve crosses the base line after the first derivative peak (O1),

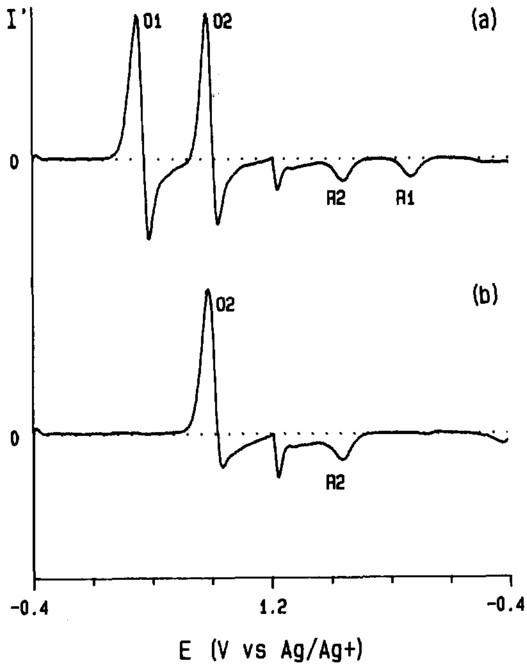


Fig. 1. Derivative cyclic voltammetry (DCV) traces for the oxidation of (a) 1.0 m*M* $CpMo(CO)_2(PPh_3)H$ (**1**), and (b) 1.0 m*M* *cis*-$CpMo(CO)_2(PPh_3)(NCMe)^+PF_6^-$ (*cis*-**2**·PF_6), in acetonitrile/0.1 *M* $Bu_4N^+PF_6^-$ at a 0.6 mm Pt disk electrode with a voltage sweep rate $v = 1.0$ V/s and at a temperature of 20°C. The ferrocene/ferricinium (FC) couple was located at +0.09 V *vs*. the Ag/Ag$^+$ reference. For explanation of labels, see text.

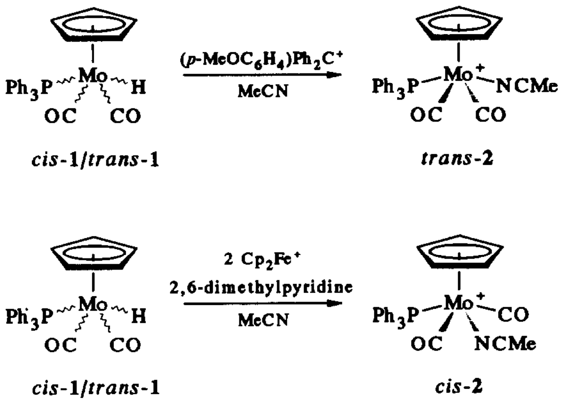
and is located at $E_p = +0.35$ V *vs.* the Ag/Ag$^+$ reference electrode. For the reference electrode used this corresponded to +0.26 V *vs.* the ferrocene/ferricinium (FC) couple. The low intensity of the derivative peak that would correspond to the reduction of **1**$^{\cdot+}$ (R1) suggests that a rapid subsequent reaction consumes **1**$^{\cdot+}$ once it is generated [5*]. The intensity of this peak was found to be similarly insignificant when the scan was reversed at 0.6 V rather than at 1.2 V *vs.* Ag/Ag$^+$, and also at voltage sweep rates exceeding 100 V/s. These observations establish that the second oxidation peak (O2), along with a corresponding low-intensity reduction peak (R2) indicating a chemically irreversible oxidation at 0.81 V *vs.* Ag/Ag$^+$ (0.72 V *vs.* FC), is due to the oxidation of a product formed from the chemical reaction that consumes **1**$^{\cdot+}$, rather than to the oxidation of **1**$^{\cdot+}$ to the dication. Addition of a little *cis*-CpMo(CO)$_2$(PPh$_3$)(NCMe)$^+$PF$_6^-$ (*cis*-**2** · **PF$_6$**; see below) caused this peak to increase in intensity. Figure 1b shows a separate DCV trace for the oxidation of *cis*-**2** · **PF$_6$** under identical conditions, and indicates that *cis*-**2** · **PF$_6$** is generated from **1**$^{\cdot+}$ on the cyclic voltammetry time scale.

Constant-current coulometry of solutions of **1** with DCV monitoring of the disappearance of the substrate indicated the passage of 1.94 ± 0.08 faraday/mol (four measurements) for the complete consumption of **1**, in excellent agreement with an overall two-electron oxidation process. A two-electron preparative-scale oxidation of **1** in acetonitrile/0.05 *M* Me$_4$N$^+$BF$_4^-$ allowed the isolation of *cis*-**2** · **BF$_4$**, only slightly contaminated with the *trans* isomer, in 27% yield after work-up (see Experimental section). Losses during work-up are believed to be part of the reason for the rather modest yield. The synthesis and characterization of each of the two isomers of **2** are described below.

Synthesis and characterization of trans-CpMo(CO)$_2$(PPh$_3$)(NCMe)$^+$BF$_4^-$ (trans-2 · BF$_4$)

The removal of H$^-$ from transition-metal hydrides by the use of trityl cations in the presence of 2-electron donor ligands is a well-established and generally applicable procedure for the synthesis of a variety of cationic complexes [3b,6]. For complexes such as **1**, which are known to exist as rapidly equilibrating *cis* and *trans* isomers in solution [7], mixtures of *cis* and *trans* products might be expected. However, we recently reported [3b] that hydride abstraction from CpW(CO)$_2$(PMe$_3$)H (also present as *cis* and *trans* isomers) in acetonitrile resulted in the essentially exclusive high-yield generation of *trans*-CpW(CO)$_2$(PMe$_3$)(NCMe)$^+$ owing to the preference of the trityl reagent for reaction with the *trans* isomer of the hydride, presumably for steric reasons. In accord with our expectations, the reaction between **1** (as the rapidly equilibrating mixture of *cis* and *trans* isomers) and the tetrafluoroborate salt of the substituted trityl cation (p-MeOC$_6$H$_4$)Ph$_2$C$^+$ in acetonitrile proceeded analogously and gave *trans*-CpMo(CO)$_2$(PPh$_3$)(NCMe)$^+$BF$_4^-$ (*trans*-**2** · **BF$_4$**) in 68% yield (Scheme 1, top).

The structural and stereochemical assignment of **2** follows readily from ^{1}H NMR and IR spectroscopic data. The *cis* and *trans* isomers of four-legged piano-stool complexes of the type CpM(CO)$_2$(PR$_3$)X can easily be distinguished spectroscopically [7a]. In the ^{1}H NMR spectra, it is found that the *cis* isomers give rise to a Cp singlet whereas the *trans* isomers exhibit observable couplings from the phosphorus nucleus to the Cp ring protons, resulting in a Cp doublet with *J*(Cp–P) = *ca.* 1–2 Hz. In the infrared spectra the *cis* isomers show two CO



Scheme 1.

stretching bands, with the higher-energy band more intense. For the *trans* isomers, it is the lower-energy band that has the highest intensity.

In accord with this, the ^{1}H NMR spectrum (acetonitrile-d_3) of the isolated product from the trityl reaction exhibited a Cp doublet at δ 5.35 (J = 1.8 Hz) and a singlet for the coordinated acetonitrile ligand at δ 2.48. The IR spectrum (acetonitrile) showed two CO absorptions at 2000 (s) and 1915 (vs) cm^{-1}. The ^{1}H NMR spectrum showed that < 2% of the *cis* isomer was present in the product. However, the proportion of the *cis* isomer increased with time.

*Synthesis and characterization of cis-CpMo(CO)$_2$(PPh$_3$)(NCMe)$^+$PF$_6^-$ (cis-**2** · PF$_6$)*

Oxidation of **1** with Cp$_2$Fe$^+$PF$_6^-$ in acetonitrile in the presence of 2,6-dimethylpyridine led to the generation of *cis*-**2** · PF$_6$, which was isolated in 65% yield (Scheme 1, bottom). As expected for the *cis* isomer, the ^{1}H NMR spectrum (acetonitrile-d_3) displayed a Cp singlet (δ 5.65) as well as a coordinated acetonitrile doublet (δ 1.71, J = 2.5 Hz). The ^{1}H NMR spectrum indicated that less than 2% of the *trans* isomer was present in the product, and the amount did not increase with time. The IR spectrum (acetonitrile) showed two absorption bands at 1990 (vs) and 1910 (s) cm^{-1}.

Thermal isomerization of trans-2 to cis-2

When acetonitrile-d_3 solutions of *trans*-**2** were left for several hours at ambient temperature, a slow and quantitative (internal standard) isomerization reaction occurred to give *cis*-**2**, which is thus obviously the thermodynamically more stable isomer (Scheme 2, top). Compared to the rate of isomerization, exchange of coordinated acetonitrile with the solvent was rather slow, the coordinated acetonitrile doublet of *cis*-**2** gradually emerging as the reaction progressed. The kinetics of the isomerization process could be conveniently monitored by ^{1}H NMR spectroscopy. Thus, the reaction was followed for 3.5 half-lives or more at 30, 40, 50, and 60°C. Figure 2 shows a plot of ln(fraction *trans*-**2**) *vs.* time for a typical run at 30°C. The linearity was excellent for *ca.* 4 half-lives, in accord with a clean first-order isomerization process, and a first-order rate constant of 4.4 × 10^{-6} s^{-1}

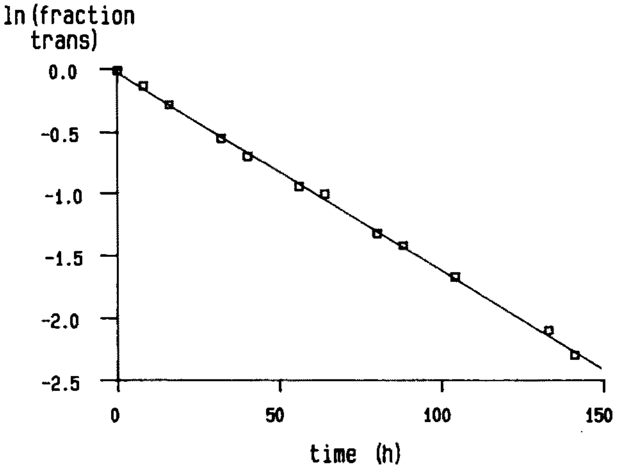


Fig. 2. Plot of ln(fraction *trans*-**2**) *vs.* time for the first-order isomerization of *trans*-**2** to *cis*-**2** in acetonitrile-d_3 at 30.0°C.

was obtained by linear regression. Use of hexamethylbenzene as an internal standard confirmed that the conversion was quantitative.

Kinetic data for the isomerization at various temperatures are given in Table 1. Figure 3 shows an Arrhenius plot of ln k *vs.* $1/T$. Linear regression yields a value for the activation energy E_a of 24.8 ± 0.4 kcal/mol. The Eyring equation yields a value of $\Delta H^{\#}$ of 24.2 ± 0.4 kcal/mol and that of $\Delta S^{\#}$ of -3.4 ± 1.4 cal/(K · mol).

Reductively induced isomerization of trans-2 to cis-2

By use of derivative cyclic voltammetry it was shown that trans-**2** · $\mathbf{BF_4}$ underwent a chemically irreversible reduction at −1.56 V *vs.* FC (1 mM substrate in acetonitrile/0.1 M $Bu_4N^+PF_6^-$, 0.6 mm Pt disk electrode, 20°C, $v = 1.0$ V/s). Under similar conditions, *cis*-**2** · $\mathbf{PF_6}$ underwent reduction at −1.57 V. The two oxidation potentials are identical within the limits of reproducibility of the measurements. Both reduction processes remained chemically irreversible at voltage sweep rates as high as 2000 V/s (25 μm electrode).

When *trans*-**2** was treated with *ca.* 10 mol-% of cobaltocene ($E^{0\prime} = -1.25$ V *vs.* FC [8]) in acetonitrile-d_3, partial and immediate isomerization to *cis*-**2** took place.

Table 1

Rate constants for the thermal isomerization of *trans*-**2** to *cis*-**2** in acetonitrile-d_3, as determined by ^{1}H NMR spectroscopy

T (°C) [a]	$10^6 \times k$ (s^{-1}) [b]
30.0	4.41 ± 0.05
40.0	15.1 ± 0.1
50.0	53.4 ± 2.4
60.0	178 ± 2

[a] Temperatures were stable to ±0.1°C. [b] Slope of ln(fraction *trans*) *vs.* time and one standard deviation obtained from linear regression analysis.

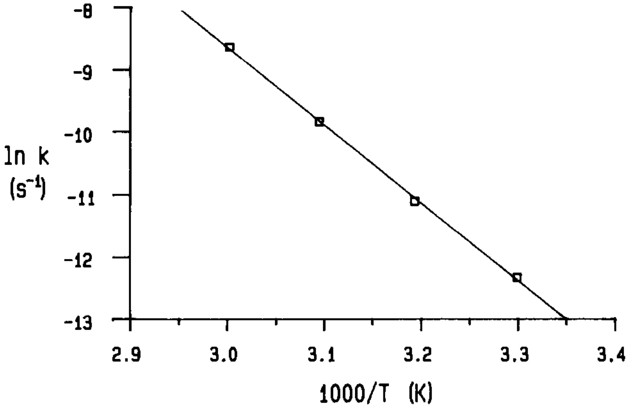
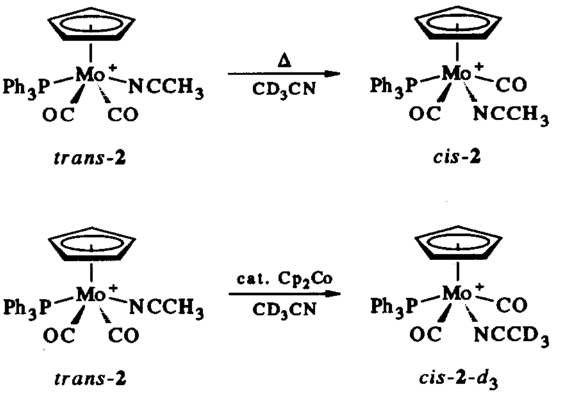


Fig. 3. Arrhenius plot of ln *k* (s^{-1}) *vs.* 1000/*T* (K) for the isomerization of *trans*-**2** to *cis*-**2** in acetonitrile-d_3.

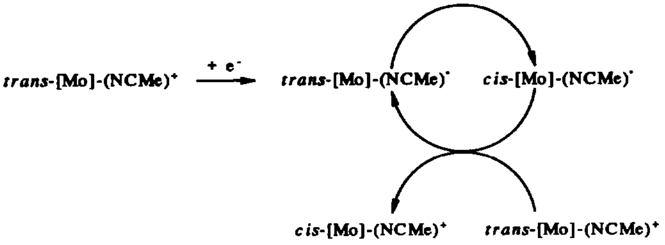


Scheme 2.

The Cp resonances in the ^{1}H NMR spectrum indicated a 59:41 mixture of *cis*-**2** and *trans*-**2** (Scheme 2, bottom). Minor amounts of *trans*-$CpMo(CO)_2(PPh_3)_2^+$ (δ 5.06 (t, $J = 1.2$ Hz)) (its identity verified by comparison with an authentic sample [9]) were also present. Traces of a red precipitate, indicating partial decomposition were also apparent. Significantly the expected resonance due to coordinated acetonitrile in the product *cis*-**2** was absent, indicating that ligand exchange with the solvent had occurred. In accord with this, a signal arising from free acetonitrile was superimposed on the residual proton resonances from the solvent. When the mixture was kept at ambient temperature, a slow, uncatalyzed thermal *trans–cis* isomerization took place, as described in the preceding subsection.

Discussion

As mentioned previously, the hydride **1** exists as a rapidly equilibrating, *ca.* 1:1 mixture of the *cis* and *trans* isomers in solution. We recently showed [3b] that



Scheme 3.

hydride abstraction from $CpW(CO)_2(PMe_3)H$ by the substituted trityl reagent $(p\text{-}MeOC_6H_4)Ph_2C^+BF_4^-$ in acetonitrile gave almost exclusively the *trans* isomer of $CpW(CO)_2(PMe_3)(NCMe)^+$. A similar stereochemical outcome was expected for the reaction between **1** ($E_{ox} = +0.26$ V *vs.* FC) and $(p\text{-}MeOC_6H_4)Ph_2C^+$ ($E_{red} = -0.32$ V *vs.* FC), and was indeed observed. Presumably, the trityl cation attack takes place preferentially at the hydride ligand of the *trans* isomer in the equilibrium mixture of *cis* and *trans* hydrides and product formation takes place under sterically-directed kinetic control. The different stereochemical outcome of the oxidation with Cp_2Fe^+, an outer-sphere one-electron oxidant, clearly indicates that the trityl reaction probably takes place not *via* a multistep electron-transfer route but rather by direct trityl cation attack on the hydride ligand.

The result of the ferricinium oxidation is best explained in terms of initial formation of $\mathbf{1}^{\cdot+}$, which after deprotonation gives the 17-electron radical $CpMo(CO)_2(PPh_3)^{\cdot}$. A second oxidation step, presumably occurring after prior acetonitrile ligation and *via* the intermediacy of 19-electron, highly reducing [10*] $CpMo(CO)_2(PPh_3)(NCMe)^{\cdot}$, would generate **2**. Generation of the thermodynamically-preferred product under these conditions is a consequence of facile *cis/trans* equilibration at the radical stage. This view is supported by the observed reductively-induced isomerization that was initiated by catalytic amounts of cobaltocene. The catalytic cycle shown in Scheme 3 ($[Mo] = CpMo(CO)_2(PPh_3)$) describes a plausible mechanism for the reductively-induced transformation, and is analogous to that proposed previously for the *trans/cis* isomerization of $CpW(CO)_2(PMe_3)(NCMe)^+$ [3b]. However, the reductive process of **2** differs from that of $CpW(CO)_2(PMe_3)(NCMe)^+$ in some respects. First, the electrocatalytic process was much more efficient for $CpW(CO)_2(PMe_3)(NCMe)^+$, proceeding to completion rather than stopping at only 60% conversion as observed for **2**. Second, the *trans/cis* isomerization of $CpW(CO)_2(PMe_3)(NCMe)^+$ proceeded *without* exchange of solvent acetonitrile-d_3 for coordinated acetonitrile, proving that isomerization does indeed take place at the 19-electron stage. For **2**, complete ligand exchange was observed during isomerization. While this does not rule out the possibility that the *trans/cis* interconversion occurs at the 19-electron stage, these significant differences at least imply that the presumed intermediate $CpMo(CO)_2(PPh_3)(NCMe)^{\cdot}$ is considerably less stable than $CpW(CO)_2(PMe_3)(NCMe)^{\cdot}$ with respect to acetonitrile dissociation. This difference in relative stabilities of 19-electron species may be a result of the greater bulk of the PPh_3 than of the PMe_3 ligand. This view is consistent with the observation of traces of *trans*-$CpMo(CO)_2(PPh_3)_2^+$, which shows that there is also PPh_3 loss from the radicals. The differences in stabilities of the 19-electron intermediates may also be explained in terms of more metal-specific properties. Several recent reports have provided evidence that third-row metal complexes show a pronounced tendency to undergo coordination-sphere expansion [11], especially relative to their first- and second-row counterparts. The 19-electron species may therefore be more tightly bound for third-row than for second-row metal complexes.

The thermal *trans/cis* isomerization of **2** proceeded *without* concomitant exchange of acetonitrile ligand, in contrast with the outcome of the reductively induced process. For the corresponding reaction of $CpW(CO)_2(PMe_3)(NCMe)^+$, ligand exchange occurred apparently at the same rate as the isomerization itself [3b]. This observation is not necessarily in conflict with the results of the present study. The results for the tungsten complex may indicate the operation of a dissociative isomerization process, or (in agreement with the present work) that rapid ligand exchange takes place *after* isomerization. Kinetic data are not available to distinguish between these alternatives for the tungsten compound. The near-zero activation entropy for the *trans/cis* isomerization of **2** is consistent with a non-dissociative pathway for the reaction, and agrees well with activation entropies for analogous processes in neutral $CpM(CO)_2(PR_3)X$ complexes [7c]. It is the higher activation enthalpy that makes the isomerization of **2** slower than the analogous processes for the neutral hydrides, and this facilitates the independent synthesis and isolation of the stable isomers *trans*-**2** and *cis*-**2**.

Experimental section

General procedures

All handling of organometallic complexes took place under an inert atmosphere by the use of standard vacuum line, Schlenk, syringe, or dry-box techniques. Acetonitrile was distilled from P_2O_5, and acetonitrile-d_3 was distilled from CaH_2. The ^1H NMR spectra were recorded on a Varian Gemini-200 instrument. Chemical shifts are reported downfield from tetramethylsilane, residual solvent proton resonances being used as internal standards (δ 1.93 for acetonitrile). Melting points were determined 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 have been previously described [12]. Electrolytes that were employed for electrochemical experiments were 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 electrochemical experiments were carried out under a blanket of solvent-saturated argon gas. Preparative electrochemical oxidations and coulometry experiments were performed at a Pt-gauze working electrode in an H-shaped cell, the compartments of which were separated by a fritted-glass junction.

The compounds $CpMo(CO)_2(PPh_3)H$ [7b], $Cp_2Fe^+PF_6^-$ [13a], and $(p\text{-}MeOC_6H_4)Ph_2C^+BF_4^-$ [13b] were prepared by published procedures. All other reagents were obtained commercially and used as received.

cis-$CpMo(CO)_2(PPh_3)(NCMe)^+PF_6^-$ *(cis-***2** $\cdot$ PF_6*).* A solution of **1** (168 mg, 0.356 mmol) and 2,6-dimethylpyridine (80 μL, 0.69 mmol) in acetonitrile (40 mL) was treated with $Cp_2Fe^+PF_6^-$ (228 mg, 0.69 mmol) at −20°C and stirred for 1 h. The solvent was removed by rotary evaporation and the residue washed with ether. The solid residue was dissolved in dichloromethane (10 mL) and the red solution was washed with water (2 × 10 mL), dried ($MgSO_4$), filtered, and concentrated to *ca.* 2 mL. The product was precipitated by slow addition of ether (151 mg, 65%); Orange solid, m.p. 220–223°C; ^1H NMR δ 1.71 (d, $J = 2.5$ Hz, 3H), 5.65 (s, 5H), 7.2–7.4 (m, 6H), 7.5–7.7 (m, 9H); IR (acetonitrile) 1990 (vs), 1910 (s) cm^{-1}. Anal. Found: C, 48.40; H, 3.57; N, 2.33. $C_{27}H_{23}F_6MoNO_2P_2$ calcd.: C, 48.74; H, 3.48; N, 2.11%.

*trans-$CpMo(CO)_2(PPh_3)(NCMe)^+BF_4^-$ (trans-**2** · **BF_4**).* A solution of **1** (152 mg, 0.317 mmol) in acetonitrile (20 mL) was treated with (p-$MeOC_6H_4$) $Ph_2C^+BF_4^-$ (110 mg, 0.305 mmol), whereupon the mixture turned from red to orange. The solvent was removed by rotary evaporation and the residue was washed with ether on a glass frit filter and dissolved in dichloromethane. The product was crystallized by the slow addition of ether and dried *in vacuo* (132 mg, 68%): Orange crystals, mp 223–226°C; ^1H NMR (acetonitrile-d_3) δ 2.48 (s, 3H), 5.35 (d, $J = 1.8$ Hz, 5H), 7.5–7.6 (m, 15H); IR (acetonitrile) 2000 (s), 1915 (vs) cm^{-1}.

*Kinetics of the thermal isomerization of trans-**2** to cis-**2** in acetonitrile-d_3.* In a typical experiment, *trans*-**2** · **BF_4** (10 mg, 0.016 mmol) and hexamethylbenzene (HMB; *ca.* 1 mg, 0.006 mmol; internal standard for quantification purposes) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile-d_3 (0.5 mL) was added by vacuum transfer and the tube sealed under vacuum. The ^1H-NMR spectrum was recorded immediately and the tube was then immersed in a constant-temperature water bath. Further NMR spectra were recorded at intervals up to at least 3.5 half-lives. The resonances due to *trans*-**2** (δ 2.48 (s), 5.35 (d)) were replaced by those of *cis*-**2** (δ 1.71 (d), 5.65 (s)). The coordinated acetonitrile doublet of *cis*-**2** at δ 1.71 then gradually vanished as a result of a much slower exchange with the solvent. Comparison of the combined integrated Cp resonance intensities with the signal of the HMB internal standard showed the reaction to be quantitative within the limits of experimental accuracy. Since the starting material and the equilibrium mixtures were both at least 98% isomerically pure by ^1H NMR, we reasoned that no correction for the initial contents of the *cis* isomer or for the final content of the *trans* isomer was needed for the kinetic analysis. The data were therefore treated as for a simple chemically irreversible first-order reaction, and a plot of ln(fraction *trans*-**2**) *vs.* time yielded a straight line. A representative plot for one run is shown in Fig. 2.

*Cobaltocene-induced isomerization of trans-**2** to cis-**2** in acetonitrile-d_3.* An NMR tube equipped with a ground-glass joint was charged with *trans*-**2** · **BF_4** (5 mg, 0.008 mmol; *ca.* 98% isomerically pure by ^1H NMR) and cobaltocene (*ca.* 0.2 mg, 0.001 mmol). Acetonitrile-d_3 (0.6 mL) was added by vacuum transfer at liquid-nitrogen temperature. The sample was warmed to ambient temperature and shaken well and the ^1H NMR spectrum was recorded immediately. The Cp region of the spectrum revealed the presence of a 59 : 41 mixture of *cis*-**2** and *trans*-**2**. The coordinated acetonitrile resonance of unconsumed *trans*-**2** was still present, and the expected resonance due to coordinated acetonitrile in *cis*-**2** was absent, demonstrating the occurrence of ligand exchange with the solvent. A triplet at δ 5.06 ($J = 1.2$ Hz) signalled the presence of traces of *trans*-$CpMo(CO)_2(PPh_3)_2^+$.

Preparative electrochemical synthesis of cis-2 · BF_4. A solution of **1** (55.8 mg, 0.116 mmol) in acetonitrile/0.05 *M* $Me_4N^+BF_4^-$ (20 mL) was oxidized for the time required for the passage of 2 faradays/mol at a constant current of 10 mA, during which the solution turned from pale yellow to deep orange. The solvent was removed by vacuum transfer, and the solid residue extracted with dichloromethane (10 mL). The solution was filtered and concentrated, and the product (14.3 mg, 27% yield) was crystallized twice from dichloromethane/ether.

Acknowledgments

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References

1 (a) D. Astruc, Acc. Chem. Res., 24 (1991) 36; (b) W.C. Trogler (Ed.), Organometallic Radical Processes, J. Organomet. Chem. Libr., Vol. 22, Elsevier, Amsterdam, 1990; (c) M. Chanon, M. Julliard and J.C. Poite (Eds.), Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis, Kluwer Academic, Dordrecht, 1989; (d) D. Astruc, Chem. Rev., 88 (1988) 1189; (e) M.C. Baird, Chem. Rev., 88 (1988) 1217.

2 For some recent reviews with leading references, see ref. 1.

3 (a) R.J. Klingler, J.C. Huffman and J.K. Kochi, J. Am. Chem. Soc., 102 (1980) 208; (b) O.B. Ryan, M. Tilset and V.D. Parker, J. Am. Chem. Soc., 112 (1990) 2618; (c) O.B. Ryan, M. Tilset and V.D. Parker, Organometallics, 10 (1991) 298; (d) D.E. Westerberg, L.F. Rhodes, J. Edwin, W.E. Geiger and K.G. Caulton, Inorg. Chem., 30 (1991) 1107; (e) O.B. Ryan and M. Tilset, J. Am. Chem. Soc., 113 (1991) 9554; (f) O.B. Ryan, K.-T. Smith and M. Tilset, J. Organomet. Chem., 421 (1991) 315.

4 (a) E. Ahlberg and V.D. Parker, J. Electroanal. Chem., Interfacial Electrochem., 121 (1981) 73; (b) V.D. Parker, Electroanal. Chem., 14 (1986) 1.

5 Note that in derivative cyclic voltammetry, a residual peak will be seen during the reverse scan even in the event of "complete reaction" simply due to the shape of the normal cyclic voltammogram in such cases.

6 W. Beck and K. Sünkel, Chem. Rev., 88 (1988) 1405 and references cited.

7 (a) A.R. Manning, J. Chem. Soc. A, (1967) 1984; (b) A. Bainbridge, P.J. Craig and M. Green, J. Chem. Soc. A, (1968) 2715; (c) J.W. Faller and A.S. Anderson, J. Am. Chem. Soc., 92 (1970) 5852.

8 J.C. Kotz, in A.J. Fry and W.E. Britton (Eds.), Topics in Organic Electrochemistry, Plenum, New York, 1986, Chap. 3.

9 J. Markham, K. Menard and A. Cutler, Inorg. Chem., 24 (1985) 1581.

10 −1.56 V *vs.* FC from the reduction potential of **2**. The strongly reducing properties of 19-electron species have been demonstrated: D.R. Tyler, ref. 1b, p. 338, and references cited.

11 (a) V. Skagestad and M. Tilset, Organometallics, 10 (1991) 2110; (b) Y. Zhang, D.K. Gosser, P.H. Rieger and D.A. Sweigart, J. Am. Chem. Soc., 113 (1991) 4062; (c) K.M. Doxsee, R.H. Grubbs and F.C. Anson, J. Am. Chem. Soc., 106 (1984) 7819.

12 (a) E. Ahlberg and V.D. Parker, J. Electroanal. Chem., Interfacial Electrochem., 121 (1981) 57; (b) E. Ahlberg and V.D. Parker, Acta Chem. Scand., Ser. B, 34 (1980) 97.

13 (a) I.R. Lyatifov, S.P. Solodovnikov, V.N. Babin and R.B. Materikova, Z. Naturforsch., Teil B, 34 (1979) 863; (b) H.J. Dauben, L.R. Honnen and K.M. Harmon, J. Org. Chem., 25 (1960) 1442.