Confirmation of a Radical Mechanism in the Alkyne-Linkage Reduction Reaction of the $[(\eta^5\text{-}C_5H_5)Mo(C_2Me_2)_2(NCMe)]^+$ Cation

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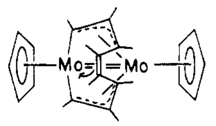
Reduction of the bis(alkyne) complex $[CpMo(C_2Me_2)_2(NCMe)]^+$ (1) by electrolysis or by potassium has been studied in nonaqueous solvents. The results have confirmed that the metallacyclononatetraene complex 2, $Cp_2Mo_2(\mu\text{-}C_8Me_8)$, is formed from 1 by one-electron reduction, through a radical mechanism. The reduction of 1 proceeds by rapid heterogeneous charge transfer from a Pt electrode, followed within a maximum of 50 ms by loss of acetonitrile. The resulting 17-electron radical $CpMo(C_2Me_2)_2$ then couples to give the metallacyclic complex in about 60% yield. A secondary product, which may be the metal–metal bonded dimer $[CpMo(C_2Me_2)_2]_2$ (3), has been partly characterized.

Introduction

The metal-initiated oligomerization of alkynes has produced some remarkable chemical transformations.[1] One such example is the linking of two, three, or four alkyne molecules to form mono- and dimetallacyclic complexes of Mo and Cr.[2–6] This alkyne oligomerization has in some cases been achieved through redox chemistry. In reactions 1 and 2, treatment of $[(\eta^5\text{-}C_mH_n)Mo(\eta^2\text{-}C_2Me_2)_2(NCMe)]^+$ (C_mH_n = Cp or indenyl) with $Na[CpFe(CO)_2]$ leads to formation of complexes with linkages of either six carbons (indenyl complex)[6] or eight carbons (cyclopentadienyl complex)[4] in the hydrocarbon chain. In these reactions the anion $CpFe(CO)_2^-$ was assumed to act as a one-electron reductant since the dinuclear complex $[CpFe(CO)_2]_2$ was isolated from the reaction mixture. Other reducing agents such as Mg or Na/Hg also accomplished this reaction, maximum isolated yields of the dimolybdenum complexes being 20–25%.[6]

$[CpMo(C_2Me_2)_2(NCMe)]^+ + [CpFe(CO)_2]^- \longrightarrow$

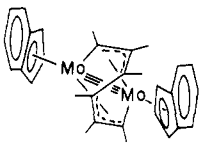
1



(1)

2

$[(\eta^5\text{-}C_9H_7)Mo(C_2Me_2)_2L]^+ + [CpFe(CO)_2]^- \longrightarrow$



(2)

Since mechanistic aspects of this reaction are still under study,[7] we thought that it would be useful to investigate by electrochemical methods the apparent first step in the reaction, namely, the one-electron reduction of the bis(alkyne) complex $[CpMo(C_2Me_2)_2(NCMe)]^+$ (1). Our results give support to the hypothesis of Green and coworkers[4–6] that the alkyne coupling reaction is radical initiated. We find that 1 reduces by a rapid one-electron transfer at a Pt electrode and that the initially formed 19-electron species $CpMo(C_2Me_2)_2(NCMe)$ undergoes rapid loss of acetonitrile. The resulting 17-electron neutral radical couples rapidly to give a good yield (ca. 65%) of the metallacyclononatetraene complex 2 and a smaller amount of a secondary product. The structure of the secondary product is not unequivocally established, but spectroscopic results suggest a simple dimer formed by metal–metal bonding of the 17-electron radical $CpMo(C_2Me_2)_2$.

Experimental Section

All electrochemical and preparative procedures were conducted under an atmosphere of dinitrogen using drybox or Schlenk procedures. Solvents were dried and distilled by conventional procedures. Electrochemical experiments were conducted as in previous studies.[8] The reference electrode was the aqueous saturated calomel electrode (SCE). The potentials given in this paper may be converted to the Cp_2Fe/Cp_2Fe^+ reference by addition of *minus* 0.56 V for THF solutions and *minus* 0.40 V for MeCN solutions. In all cases the supporting electrolyte was 0.1 M $[Bu_4N][PF_6]$. NMR spectra were obtained on a Bruker 250 MHz instrument and calibrated against TMS. Mass spectra were obtained through electron-impact ionization at 50–70 eV using a Finnigan MAT 4500 Series system with a direct probe. The starting materials $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$ were obtained from the Strem Chemical Co. $Na[CpFe(CO)_2]$ was prepared by the Na/Hg reduction of $[CpFe(CO)_2]_2$. The title cation, $[CpMo(C_2Me_2)_2(NCMe)]^+$,[9] and the dinuclear complex $Cp_2Mo_2(\mu\text{-}C_8Me_8)$[5] were prepared by the literature methods.

Results and Discussion

I. Electrochemical Reduction of $[CpMo(C_2Me_2)_2(NCMe)]^+$ (1). It was reported earlier[10] that this complex

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[1] Winter, M. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.: Wiley; New York, 1985; Vol. 3, p 259.

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[10] See footnotes in ref 4 and 6.

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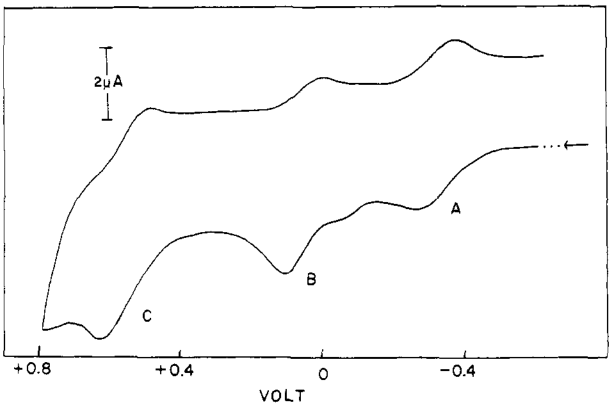

Figure 1. Cyclic voltammogram of 5×10^{-4} M **1** in THF/0.1 M $[Bu_4N][PF_6]$ at a Pt electrode (v = 0.3 V/s; T = 300 K). The scan was initiated at −1.6 V, negative of the reduction of **1**. Shown are the three waves detected for the reduction products of **1**, namely, waves B and C (arising from **2**) and wave A (arising from the secondary product).

undergoes an irreversible reduction, but only a cursory investigation was made.[11] The present systematic study has confirmed that **1** undergoes a one-electron reduction at ca. −1.40 V in THF and that the process is chemically irreversible at scan rates up to several volts per second at 253 K, or up to 20 V/s at ambient temperatures. More will be said later in section IV about the chemical and electrochemical sources of the irreversibility. This is meaningful from a mechanistic point of view since we can tell whether the reaction after electron transfer is first- or second-order only if the initial heterogeneous electron transfer is fast. For now, however, we wish to concentrate on the stoichiometry of the reaction and on the products formed in the electrochemical reduction.

The reduction of **1** in THF is a diffusion-controlled one-electron process[12] on the time scales of both cyclic voltammetry and bulk (preparative) coulometry. We compared the cathodic current function (peak current divided by square root of CV scan rate) of **1** to that of the cobaltocenium ion. The Cp_2Co^+/Cp_2Co couple was used as an internal one-electron standard because one would expect that the diffusion coefficient of Cp_2Co^+ would closely approximate that of **1**. This assumption is based on the similar size and identical charge of **1** and the standard. The ratio of the current functions of **1**:Cp_2Co^+ was 0.90 in THF and 1.04 in CH_3CN. Since the cobaltocenium reduction is firmly established as a one-electron wave under these conditions,[13] we may safely assume that **1** also reduces by one electron.

The products of this one-electron reduction may be monitored by CV scans in which the initial potential is held negative of the reduction wave of **1**. In this manner, electroactive reaction products become evident. Such a scan is shown in Figure 1. The initial potential was −1.6 V, and only the region of the scan showing electroactive products is reproduced in the figure. Three major anodic features are seen. Peak A is due to a secondary species postulated as the dimer $[CpMo(C_2Me_2)_2]_2$. Peaks B and C fall at the same potentials as the oxidation waves of the dinuclear complex $Cp_2Mo_2(\mu\text{-}C_8Me_8)$ (**2**). Potentials for the couples $\mathbf{2}/\mathbf{2}^+$ and $\mathbf{2}^+/\mathbf{2}^{2+}$, previously reported for dichloromethane solutions,[14] were remeasured in THF (Table I). Experiments of the type shown in the figure suggest that within about 5–10 s after reduction of **1**, roughly equal amounts of the dinuclear complex **2** and a second product are formed. A description of our attempts to identify the latter, which has an $E°$ potential of −0.34 V, is deferred until section III.

Table I. Electrochemical Potentials (versus SCE) for Compounds in This Study

compd	solv	couple	potential, V
1	THF	0/1+^{a}	−1.40
1	CH_3CN	0/1+^{a}	−1.56
2	THF	0/1+^{b}	+0.02
		1+/2+^{a}	+0.57
2	CH_2Cl_2	0/1+^{b,c}	−0.11
		1+/2+^{b,c}	+0.64

^{a} Chemically irreversible, E_p at v = 0.1 V/s given. ^{b} Reversible, $E°$ given. ^{c} Potentials for this couple reported in ref 14 were −0.02 and +0.70 V, with $[Bu_4N][BF_4]$ as supporting electrolyte. The potentials for ref 14 and for the present study are within 30 mV when referenced to $Cp_2Fe^{0/+}$.

Exhaustive controlled-potential electrolysis of **1** at a Pt basket electrode in THF converted the cation to **2** as the dominant product. Electroyses at ambient temperature gave dark brown solutions and poor conversions to the dinuclear complex. High coulomb counts (corresponding to n_{app} of 1.8e) were indicative of significant side reactions. More efficient conversions were obtained at lower temperatures. Electrolysis of a 5 mM solution of **1** at 263 K in THF consumed 1.1 faraday. The purple-brown solution displayed only the waves due to dinuclear **2** and that of the proposed dimer **3**. Yields can be calculated for the electrolysis if it is assumed that the diffusion coefficients of the reactants and products are similar. By this procedure[15] a yield of about 60% was calculated for the electrochemical conversion of **1** to **2**.

The dinuclear complex **2** was isolated from the electrolysis solution to confirm its identity. Lowering the solution temperature to 248 K precipitated most of the $[Bu_4N][PF_6]$ electrolyte. After filtration the volume of the solution was reduced by about one-half, cooled to 273 K, and treated with a 1:1 hexane/ether mixture until the remainder of the supporting electrolyte precipitated. Filtration followed by evaporation of the remaining solvent gave 60 mg of a brown solid (56% yield) identified as reasonably pure **2** by comparison of its NMR spectrum and electrochemical properties with those of an authentic sample. Minor amounts of the secondary product were in evidence in the NMR spectra (vide infra).

These results demonstrate that the dinuclear complex **2** is produced in reasonably high yield from the one-electron electrochemical reduction of $[CpMo(C_2Me_2)_2(NCMe)]^+$.

II. Metal Reduction of $[CpMo(C_2Me_2)_2(NCMe)]^+$. The reduction of **1** by potassium was briefly investigated in order to see if chemical and electrochemical reductions gave similar results. A solution of 200 mg of **1** in 100 mL

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[11] Allen, S. R.; Green, M., unpublished work at the University of Bristol.

[12] Details of the CV and chronoamperometry measurements establishing the diffusion-controlled nature of the reduction may be found in the M.S. Thesis of D. P., University of Vermont, 1985.

[13] Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

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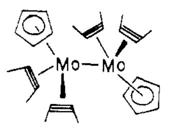
[15] At a scan rate of 500 mV/S, the original cathodic peak height of **1** was 40.5 μA. The anodic peak height observed for the first oxidation of the dinuclear product **2** after electrolysis was 12.7 μA. Taking into account the stoichiometry of the reaction, we calculate % yield = [100%][12.7 × 2/40.5] = 63%. The same procedure applied to the wave with $E°$ = −0.34 V gives a 37% yield for the secondary product. This calculation assumes that the secondary product is a dinuclear complex, requiring 2 mol of **1** for each mole of product. The apparent complete mass balance should be viewed as fortuitous, since this calculation should not be expected to have great precision. However, it is apparent that the two complexes together account for virtually all the electrode products.

of THF was brought into contact with an equimolar amount of potassium in the form of a freshly distilled mirror. In one experiment, aliquots of the reaction mixture were periodically monitored by cyclic voltammetry. The two major products were those identified above, namely, the dinuclear complex **2** and the proposed dimer **3**. The reaction was allowed to proceed to completion at 303 K. After removal of the solvent, the solid was dissolved in 1:1 hexane/ether, filtered, and evaporated. The residue was analyzed by thin-layer chromatography on silica gel (1:1 hexane/ether) and shown to contain **2** as the major product. This was confirmed by NMR spectroscopy in acetone-d_6. The ^{1}H NMR spectrum also confirmed the loss of CH_3CN and the presence of peaks apparently arising from the proposed dimer (vide infra). All indications are that the reduction of **1** proceeds by a similar route when initiated either electrochemically or by alkali metal.

III. Spectroscopic Properties of the Secondary Product. The secondary product formed in both the electrochemical and alkali-metal reductions of **1**, having $E° = -0.34$ V, was not isolated. However, it was investigated in the residues remaining after evaporation of the crude reaction mixtures of reduced **1**. The major component of these mixtures was always the dinuclear complex **2**.

The ^{1}H NMR spectrum of the powder from either the potassium or the coulometric reduction, in acetone-d_6, gave only two peaks that could not be assigned either to **2**, solvent, or CH_3CN.[16] These peaks were singlets at δ = 5.33 and 2.52 ppm. If the former is assigned to a Cp resonance, the peaks have relative intensities of 5:12. The electron-impact mass spectrum of this mixture was also investigated. A solids probe at ambient temperatures was used, and the spectrum of pure **2** was ratioed and subtracted from that of the mixture.[16] The major feature of the difference spectrum was an intense cluster of peaks centered at approximately m/e 214. This is consistent with the presence in the fragment of a single Mo, which has seven naturally occurring isotopes with abundances between 9% and 24%. The largest peak, m/e 214, is consistent with the molecular composition (for ^{95}Mo) of $[\mathrm{CpMo(C_2Me_2)}]^+$.

The mass spectral data suggest that the minor product has at least one unlinked alkyne group. The NMR data show that there is only one type of CH_3 group in the product. Thus it is likely that the product contains two equivalent dimethylalkynes per cyclopentadienyl unit (NMR intensity ratio of 12:5). Since the species $\mathrm{CpMo(C_2Me_2)_2}$ is a 17-electron radical, it is likely that the minor product is a simple dimer of this unit, most likely bonded through the metals, as in the structure below.



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A structure of this type has been postulated by Brammer et al.[6] as an intermediate in the reduction of **1** to **2**. In spite of our detecting a species with spectral properties consistent with this metal–metal bonded dimer, we have seen no evidence that, once formed, it reacts further to give complex **2**.

IV. Formation and Fate of the 19-Electron Radical $\mathbf{CpMo(C_2Me_2)_2(NCMe)}$. Describing the reduction of **1** as an irreversible one-electron process gives only crude information about the electrodic reduction of the cation. Details about the rate-determining step in the electron-transfer reaction can often be obtained from studies of wave shapes and positions as a function of CV scan rates and/or concentration variations. Our experiments enable us to write eq 3–5 as describing the events occurring early in the cathodic reduction of **1**.

$$[\mathrm{CpMo(C_2Me)_2(NCMe)}]^+ + e^- \rightleftharpoons \mathrm{CpMo(C_2Me_2)_2(NCMe)}\ \text{(very rapid)} \quad (3)$$

$$\mathrm{CpMo(C_2Me_2)_2(NCMe)} \rightarrow \mathrm{CpMo(C_2Me_2)_2} + \mathrm{NCMe}\text{(rapid)}$$

$$2\mathrm{CpMo(C_2Me_2)_2} \rightarrow \mathbf{2} \text{ or } \mathbf{3}$$

The first reaction involves the heterogeneous electron transfer from the electrode to the 18-electron cation **1** in solution. Although CV scans show that the reduction is chemically irreversible, the shape of the cathodic wave firmly establishes that the initial charge transfer is fast (Nernstian). The appropriate diagnostic parameter is derived from the width of the wave. For a Nernstian system, the difference between the potentials at the cathodic peak (E_p) and half-peak ($E_{p/2}$) currents is 57 mV for a one-electron process.[17] On the other hand, a slow one-electron charge transfer (an electrochemically irreversible system) has $E_p - E_{p/2} = 48/\alpha$ mV. α is the charge-transfer coefficient and often has a value close to 0.5, so that $E_p - E_{p/2}$ values of about 96 mV are common for slow one-electron transfers.[18] For the reduction of **1** in acetonitrile, a value of 58 mV (±2 mV RSD) was observed over the CV scan range of v = 0.01 to 0.50 V/s, clearly consistent with a rapid heterogeneous electron transfer to **1**. The result in THF was similar. In this solvent, broadening of the peak was observed at higher scan rates (e.g., $E_p - E_{p/2} = 70$ mV at $v = 0.5$ V/s). However, the broadening was shown to be due to uncompensated resistance effects, since an identical concentration of the reversible standard $\mathrm{Cp_2Co^+}$ gave the same result.

A further diagnostic concerning the electrochemical versus chemical irreversibility of the reduction concerns the way in which the cathodic peak potential, E_p, varies with scan rate. If the reduction of **1** is irreversible because the charge-transfer step (eq 3) is very slow, then E_p is predicted to shift negative by 60 mV (assuming $\alpha = 0.5$) for each tenfold increase in CV scan rate. If, however, the irreversibility arises from fast decomposition of the 19-electron radical (eq 4), then E_p shifts by only −30 mV per decade increase in v.[19] The latter behavior, diagnostic of an $\mathrm{E_{rev}C_{irrev}}$ mechanism, was found for the reduction of **1**. In order to minimize errors due to resistive loss, E_p for **1** was measured by using $\mathrm{Cp_2Co^+}$ as an internal standard, and differences between the potentials of **1** and those of the standard were plotted as a function of log scan rate over the range 0.01–1.0 V/s. Slopes of −31.7 and −31.9 mV were found for THF and CH_3CN solutions, respectively. These data confirm that the NCMe ligand is lost very rapidly from the 19-electron radical, even in acetonitrile, which might have been expected to suppress the loss of that ligand.

Finally, the cathodic wave for **1** has a potential which is independent of the concentration of **1**. This was shown to be true for THF solutions of **1** ranging in concentration from 1.2×10^{-4} to 9.1×10^{-4} M, when measured versus an internal standard of the same current height. This dem-

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onstrates that the chemical reaction following the initial electron transfer (C in the EC mechanism) is first order in the reactant **1**. It is a further confirmation that dimerization or another coupling reaction (eq 5) *follows* the rapid loss of NCMe (eq 4).

Conclusions

1. Detailed voltammetry studies have demonstrated that the title compound undergoes a one-electron reduction, irreversible up to scan rates of 20 V/s at ca. −1.4 V versus SCE.

2. **1** accepts an electron rapidly from a Pt electrode (eq 3) and then undergoes loss of NCMe (eq 4) in less than 50 ms at ambient temperatures, producing a 17-electron radical.

3. The radical produced in eq 4 couples rapidily to give in excess of 60% of the metallacyclononatetraene complex **2**, in which linking of the four alkynes has occurred.

4. The 17-electron radical also forms a secondary product which may be the metal–metal bonded dimer $[CpMo(C_2Me_2)_2]_2$ (**3**).

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Registry No. **1**, 74380-97-5; **2**, 76800-62-9; $[CpMo(C_2Me_2)_2]_2$, 118299-17-5.

Supplementary Material Available: NMR and mass spectra of mixture of **2** and the secondary reaction product and a table of chemical shifts of K reduction and bulk electrolysis products in acetone-d_4 (4 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Benzyne Derivatives of Rhenium Formed by Facile Ortho-Hydrogen Abstraction in a Homoleptic Rhenium Aryl. X-ray Structure of the Cationic Benzyne $[Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2][I_5]$

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The paramagnetic benzyne complexes $Re(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2R)_2$ (R = Me, **2a**; R = Ph, **2b**) are formed at low temperature via ligand-induced ortho-hydrogen abstraction on addition of phosphine to the homoleptic aryl $Re(2\text{-}MeC_6H_4)_4$ (**1**). Complexes **2** are oxidized under mild conditions to the benzyne cations [**2**][X] ($X = PF_6^-, BPh_4^-, OTf^-, Co(CO)_4^-, I_5^-$) with $E_{1/2} = -0.90$ V (relative to Cp_2Fe at 0.00 V). The cations are reduced by strong nucleophiles, e.g., $LiBEt_3H$, Me_3SiCH_2MgCl, in THF, back to the neutral species. NMR data for [**2**][X] are in agreement with the solid-state structure, determined for [**2a**][I_5] by X-ray crystallography. Crystals are orthorhombic, space group $Pna2_1$, with $a = 18.735$ (2), $b = 13.954$ (5), $c = 14.193$ (2) Å, $Z = 4$, $D_{calcd} = 2.23$ g cm^{-3}. The geometry of the cation can be described as distorted trigonal bipyramidal with the benzyne symmetrically η^2-bound at an equatorial site (Re–C(benzyne) = 2.02 (2) Å) and with axial phosphines (Re–P = 2.421 (5) and 2.435 (5) Å); the equatorial Re–C($2\text{-}MeC_6H_4$) distances are 2.09 (1) Å.

Interest in the chemistry of transition-metal–benzyne derivatives has increased since the first example of such a compound was structurally characterized in 1979.[1] Stable mononuclear benzyne derivatives are now known for Zr,[2] Nb,[1,3] Ta,[1,3] and Ni;[4] in addition, the intermediacy of such species has been postulated in a number of instances.[5] In all cases except Ni, benzyne formation evidently proceeds via ortho-hydrogen abstraction from a high-valent, electrophillic, d^0 metal complex, often requiring prolonged thermolysis at high temperature. The reactivity of metal–benzyne bonds has been investigated in a few cases.[1,2,4] Insertion of alkenes, alkynes, and nitriles,

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