Applying the steady-state approximation for MO_2^-, with reactions 16 and 17 the rate-determining steps, we obtain

$$\frac{d[M^-]}{dt} = \frac{k_{16} + k_{17}[H^+]}{k_{-15} + k_{16} + k_{17}[H^+]} k_{15}[M^-][O_2]$$

At low pH, $k_{17}[H^+] \gg k_{16} + k_{-15}$ and rate $= k_{15}[M^-][O_2]$, independent of H^+ concentration.

At high pH, $k_{16} \gg k_{17}[H^+]$; therefore, rate $= (k_{16}/(k_{-15} + k_{16}))k_{15}[M^-][O_2]$, again independent of H^+ concentration.

In intermediate cases, the reaction depends on H^+ concentration. As mentioned earlier, experiments at the inflection point have shown the order, with respect to H^+, to be 1.1 ± 0.4 for the 18-tungstodiphoshate.

Thus, the inflection point, as in the case of reoxidation by dioxygen of many Cu^+ complexes, is attributed to a kinetic phenomenon and does not reflect the pK_a of the dioxygen adducts.

Limited work with H_2O_2 has shown that it behaves differently. As mentioned earlier, hydrogen peroxide is less effective with tungstates but more effective with molybdates (Table III).

A different kind of mechanism ought to operate here. Similar behavior seems to have been observed with Cu^+ complexes.[19] H_2O_2 is effective oxidant even for complexes with high redox potential (reaction 11). It has been found that Cu^+ complexes with low potential react rapidly with dioxygen to form preferentially H_2O_2, whereas the slowly reacting ones, i.e., those with high potential, give complete reduction to water.[19]

Experiments with one-electron-reduced 18-tungstodiphosphate have shown that the rate of reoxidation by dioxygen monitored by following the consumption of $P_2W_{18}^{7-}$ is 2 times faster than the rate determined when the consumption of dioxygen was followed, suggesting that dioxygen participates as a two-electron oxidant and that H_2O_2 ought to be the product. This is also enhanced by the considerably slower reaction of hydrogen peroxide relative to dioxygen with $P_2W_{18}^{7-}$ (Table III).

However, no hydrogen peroxide could be detected with the experimental method used, which, nevertheless, could only detect concentrations higher than those anticipated here. Similarly, in many cases with Cu^+ complexes, in which hydrogen peroxide has been claimed to be the product, the latter could not be detected.[19,21]

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Registry No. $P_2W_{18}O_{62}^{6-}$, 90751-95-4; $SiW_{12}O_{40}^{4-}$, 12363-31-4; $H_2W_{12}O_{40}^{6-}$, 12207-61-3; $P_2Mo_{18}O_{62}^{10-}$, 137626-08-5; $P_2Mo_{18}O_{62}^{8-}$, 92844-04-7; $P_2W_{18}O_{62}^{7-}$, 12504-08-4; $P_2W_{18}O_{62}^{8-}$, 117404-39-4; $P_2Mo_{18}O_{62}^{6-}$, 57609-49-1; O_2, 7782-44-7; H^+, 12408-02-5; H_2O_2, 7722-84-1.

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(21) One may also consider a slightly modified mechanism that involves an acid-base equilibrium, reaction 15a, and dissociation of the MO_2H adduct, reaction 18, rather than attack by H^+ on MO_2, reaction 17. In this case, the pK_as of the dioxygen adducts ought to be involved:

$$M^- + O_2 \rightleftharpoons MO_2^- \tag{15}$$

$$MO_2^- + H^+ \rightleftharpoons MO_2H \tag{15a}$$

$$MO_2^- \rightarrow M + O_2^- \tag{16}$$

$$MO_2H \rightarrow M + HO_2 \tag{18}$$

We will defer discussion on this mechanism, until more data are available to support or refute it.

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Mechanistic Studies of the Oxidative Cleavage of the Molybdenum-Mercury Bonds in $[CpMo(CO)_2(PPh_3)]_2Hg$

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Chemical or electrochemical oxidation of the trimetallic complex $[CpMo(CO)_2(PPh_3)]_2Hg$ ($Cp = \eta^5\text{-}C_5H_5$) occurs in two one-electron steps. The first electron transfer generates a transient cation which undergoes Mo-Hg bond cleavage to generate a 16-electron species, $[CpMo(CO)_2(PPh_3)]^+$, and a mercury-centered radical, $CpMo(CO)_2(PPh_3)Hg^\bullet$. To account for the products, it is proposed that the radical dimerizes and then reacts with half of the available 16-electron cation to form an observable pentametallic intermediate. The second electron transfer generates $[CpMo(CO)_2(PPh_3)Hg]^+$ and returns the 0.5 mol of $[CpMo(CO)_2(PPh_3)]^+$ which was incorporated into the intermediate. The mercury-containing cation subsequently eliminates metallic mercury to yield a second mole of $[CpMo(CO)_2(PPh_3)]^+$. The 16-electron cation coordinates solvent or other available neutral or anionic ligands to yield 18-electron complexes.

Introduction

There has long been widespread interest in the reductive and oxidative cleavages of metal-metal bonds in transition-metal organometallic compounds.[1-14] For binuclear species, these cleavages are often two-electron processes producing synthetically useful anionic or cationic fragments. Cationic fragments resulting from oxidations are generally coordinatively unsaturated and so

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are able to acquire another ligand, such as a solvent molecule or the anion associated with the oxidizing agent.[7-14] Thus, oxidation can lead directly to substitution or to complexes of weakly coordinating anions which are useful synthetic intermediates.[15]

We have recently reported[16] synthetic applications of the oxidative cleavage of the Mo–Hg bonds in the trimetallic complex $[CpMo(CO)_2(PPh_3)]_2Hg$ (**1**, Cp = η^5-C_5H_5). During that investigation, we discovered that the cleavage reaction proceeds through a mechanism different from that reported for the oxidative cleavage of $[CpMo(CO)_3]_2Hg$ with di-*tert*-butylquinone[17] and from that typical of dialkylmercury compounds.[18] These related oxidative cleavages involve an initial one-electron transfer, followed by cleavage of one Hg–Mo or Hg–C bond to produce a cationic mercury-containing fragment and a radical. The radical may either dimerize or be further oxidized while the cationic fragment extrudes mercury before further reaction.

In contrast with these examples, the first step in the oxidative cleavage of compound **1** produces $[CpMo(CO)_2(PPh_3)]^+$ and the mercury-centered radical $CpMo(CO)_2(PPh_3)Hg^\bullet$. It is proposed that the radical dimerizes and then reacts with half of the available $[CpMo(CO)_2(PPh_3)]^+$ to form an observable pentametallic intermediate. Further oxidation of this intermediate produces a cationic mercury-containing species which subsequently extrudes the mercury to produce a second mole of $[CpMo(CO)_2(PPh_3)]^+$. In this report, we will discuss our evidence for this mechanism, including the synthesis of the interesting mercury triphenylphosphine complex $[CpMo(CO)_2(PPh_3)HgPPh_3][BF_4]$ (**6**).

Experimental Section

General Procedures. The complexes $[CpMo(CO)_2(PPh_3)]_2Hg$ (**1**) and ferrocenium tetrafluoroborate, $FcBF_4$, were prepared according to the literature procedures.[19,20] Solvents were distilled under nitrogen before use: CH_2Cl_2 (Fisher Optima) from CaH_2; CH_3CN (Burdick and Jackson distilled in glass) from P_2O_5; tetrahydrofuran (Fisher Optima) from Na/benzophenone. All other chemicals were reagent grade or better. All reactions were carried out under an atmosphere of nitrogen or argon.

IR spectra were obtained using a Mattson Instruments Cygnus 100 FTIR instrument, and ^1H and ^{31}P NMR spectra were obtained on a Bruker AMX 360 NMR spectrometer. Chemical shifts were assigned relative to TMS internal standard for ^1H or 85% H_3PO_4 external standard for ^{31}P. Atomic absorption measurements were made with a Perkin-Elmer Model 403 AA spectrophotometer using an air/acetylene flame and a copper hollow cathode lamp. Cyclic voltammetry and controlled-potential electrolyses were performed using a Bioanalytical Systems BAS 100A electrochemical analyzer. Cyclic voltammetry was done using a 3-mm glassy-carbon or a 0.5-mm Pt-disk working electrode, a Pt-wire auxiliary electrode, and a Ag/AgCl reference electrode. Controlled-potential electrolyses were performed using a 1 × 9 cm Pt-foil working electrode, a Pt gauze counter electrode, and an SCE reference electrode in an EG&G Princeton Applied Research Model 377A coulometry cell system. All potentials are expressed relative to the formal potential of the ferrocenium/ferrocene couple (Fc^+/Fc), which we measure as approximately +0.45 V versus Ag/AgCl. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Mercury Analysis. Mercury was analyzed by an indirect atomic absorption procedure. The gray powder resulting from the oxidation of **1** in 3:1 CH_2Cl_2/CH_3CN was collected on a Buchner funnel and dried under a stream of nitrogen. Hot concentrated nitric acid (3.4 mL) was used to dissolve the mercury residue. The resulting HNO_3/Hg^{2+} solution was transferred to a 500-mL volumetric flask and diluted with deionized water, producing a nitric acid concentration of 0.1 N. A portion of the diluted HNO_3/Hg^{2+} solution (30 mL) was treated with CuI (100 mg). At the same time, 30 mL of a 0.1 N HNO_3 blank solution was also treated with 100 mg of CuI. Both the sample and blank solutions were sonicated for 30 min, during which time HgI_2 precipitated. This reaction solubilized an equivalent amount of Cu^+. The resulting solutions were filtered and aspirated into the AA spectrophotometer, and their absorbances at 327 nm were measured. Comparison with standard $CuCl_2$ solutions allowed the determination of the concentration of copper in each solution. The concentration of copper in the blank was subtracted from that in the sample, and the concentration of mercury required to give rise to the excess copper was calculated.

$[CpMo(CO)_2(PPh_3)HgPPh_3][BF_4]$ (6): Method I. Compound **1** (0.400 g, 0.345 mmol) and PPh_3 (0.181 g, 0.690 mmol) were dissolved in 15 mL of CH_2Cl_2, and $FcBF_4$ (0.188 g, 0.689 mmol) was added to the solution. After 30 min of stirring, 25 mL of benzene was added and CH_2Cl_2 was slowly removed on a rotary evaporator to precipitate $[CpMo(CO)_2(PPh_3)_2][BF_4]$. The resulting benzene solution of $[CpMo(CO)_2(PPh_3)HgPPh_3][BF_4]$ was chromatographed on an 18 × 250 mm column of Florisil. Ferrocene and other neutral impurities were eluted with methanol, after which compound **6** was eluted with 0.1 M $[Et_4N][BF_4]$ in methanol. The methanol was removed on a rotary evaporator, the residue was treated with 100 mL of benzene to dissolve **6**, and the mixture was filtered to isolate the insoluble $[Et_4N][BF_4]$. Benzene was removed from the filtrate, and the residue was redissolved in ethanol. Addition of diethyl ether precipitated the product as a yellow powder (99 mg, 14%). ^1H NMR ($CDCl_3$): δ 5.20 (d, J_{PH} = 1.1 Hz, trans, 4.3 H), 5.41 (s, cis, 0.7 H), 7.2–7.6 (m, 30 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.4 (s, J_{HgP} = 385 Hz), 94.2 (s, br). IR (CH_2Cl_2): ν_{CO} 1854 vs, 1925 m cm^{-1}. Anal. Calcd for $C_{43}H_{35}BF_4HgMoO_2P_2$: C, 50.19; H, 3.43; F, 7.38; P, 6.02. Found: C, 50.85; H, 3.59; F, 7.28; P, 5.74 (for acceptable analysis, see method II).

$[CpMo(CO)_2(PPh_3)HgPPh_3][BF_4]$ (6): Method II. Compound **1** (0.200 g, 0.173 mmol) and PPh_3 (0.091 g, 0.346 mmol) were dissolved in 10 mL of CH_2Cl_2. HgO (0.075 g, 0.346 mmol) was dissolved in 48% aqueous HBF_4 (0.127 g, 0.692 mmol). The resulting $Hg(BF_4)_2$ solution was diluted to 5 mL with deionized water and transferred to the flask containing the solution of **1** and PPh_3. The mixture was stirred vigorously for 1 h, the layers were separated, and the CH_2Cl_2 layer was dried with $MgSO_4$. After filtration, CH_2Cl_2 was removed on a rotary evaporator. The residue was dissolved in 5 mL of hot ethanol, and the solution was slowly cooled to −10 °C. The resulting mat of needlelike crystals was filtered off, washed with cold ethanol and ether, and then vacuum-dried to afford **6** (0.355 g, 86%). ^1H NMR ($CDCl_3$): δ 5.22 (d, J_{PH} = 1.1 Hz, trans, 4.3 H), 5.42 (s, cis, 0.7 H), 7.2–7.6 (m, 30 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.9 (s, J_{HgP} = 377 Hz), 95.4 (s, br). IR (CH_2Cl_2): ν_{CO} 1854 vs, 1925 m cm^{-1}. Anal. Calcd for $C_{43}H_{35}BF_4HgMoO_2P_2$: C, 50.19; H, 3.43; F, 7.38; P, 6.02. Found: C, 50.35; H, 3.64; F, 7.47; P, 6.29.

Oxidation of 1 in CCl_4/CH_3CN. Compound **1** (0.200 g, 0.173 mmol) was dissolved in 20 mL of 1:1 CH_3CN/CCl_4. Three portions of $FcBF_4$, each weighing 0.0235 g (0.258 mmol total), were added at 10-min intervals. After the complete addition of $FcBF_4$ and 10 min of stirring, the solvent was removed on a rotary evaporator. The residue was dissolved in dichloroethane, and the solution was transferred to a 10-mL volumetric flask and diluted with dichloroethane. IR: 1857, 1925, 1993 cm^{-1}. The yields of $CpMo(CO)_2(PPh)_3HgCl$ (0.189 mmol) and $[CpMo(CO)_2(PPh_3)(CH_3CN)][BF_4]$ (0.126 mmol) were calculated by comparison of the absorbances at 1857 and 1993 cm^{-1}, respectively, with those of standard solutions. The mixture was subsequently separated on an 18 × 120 mm silica gel column using CH_2Cl_2 as the eluent.

Results

Oxidation of $[CpMo(CO)_2(PPh_3)]_2Hg$ (1) in CH_2Cl_2. Ferrocenium tetrafluoroborate, $FcBF_4$, oxidized **1** in CH_2Cl_2, requiring 2 equiv to produce a solution initially displaying carbonyl stretching bands at 1988, 1906, and 1848 cm^{-1}. Over the course of a few hours, the band at 1848 cm^{-1} decreased in intensity while the higher frequency bands grew. The carbonyl bands at 1988 and 1906 cm^{-1} have frequencies close to the values reported[21] for $CpMo(CO)_2(PPh_3)FBF_3$ (**2**) in CH_2Cl_2 (1991 and 1903 cm^{-1}).

As would be expected if **2** were a product of the oxidation, the addition of ligands such as acetonitrile, triphenylphosphine, or iodide produced the corresponding substituted complexes, as identified by their IR and NMR spectra.[16] Maximum yields of substituted products were obtained by waiting 15–20 min between treatment with $FcBF_4$ and addition of the ligand. Some wait was necessary to allow the product displaying the band at 1848 cm^{-1} to decay to **2**, but long waits led to decreased yields, probably because of thermal instability of **2**.[21]

The other product observed in these reactions was a dark gray powder which microscopy revealed to be droplets of liquid mercury.

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Sometimes a shiny film of metallic mercury could also be observed on the walls of the reaction flask. The mercury formed as the product responsible for the band at 1848 cm^{-1} disappeared.

Oxidation of 1 in CH_2Cl_2/CH_3CN. The chemical oxidation of **1** in a 3:1 mixture of CH_2Cl_2 and CH_3CN consumed 2 equiv of $FcBF_4$ and immediately produced 2 mol of the CH_3CN complex *cis*-$[CpMo(CO)_2(PPh_3)(CH_3CN)][BF_4]$ (**3**). The structure of this complex has been previously determined by X-ray crystallography.[22] Mercury was also produced in this reaction. Quantitative analysis of the powdery residue accounted for 0.8 mol of mercury/mol of **1** oxidized.

Oxidation of 1 in CCl_4/CH_3CN. The chemical oxidation of **1** in a 1:1 mixture of CCl_4 and CH_3CN consumed only 1 equiv of $FcBF_4$. IR spectra after the addition of ≥1 equiv of $FcBF_4$ showed carbonyl stretching bands at 1992, 1914, and 1858 cm^{-1}. The two higher frequency bands correspond to those of compound **3**, while the lower frequency band matches exactly the most intense carbonyl stretching frequency of $CpMo(CO)_2(PPh_3)HgCl$ (**4**) in the same solvent mixture. Compound **4** also displays a weaker carbonyl stretch at 1930 cm^{-1}, which apparently overlaps with the band due to **3** at 1914 cm^{-1}. The yields of **3** (0.83 equiv) and **4** (1.03 equiv) were determined spectrophotometrically by removing the original solvent, dissolving the products in dichloroethane, and comparing the absorbances at 1993 and 1858 cm^{-1}, respectively, with those of authentic samples of known concentrations. The compounds **3** and **4** were also separated by chromatography on silica gel and their identities confirmed by IR and TLC co-spot experiments with authentic samples. No mercury was produced in this reaction.

Oxidation of 1 in CH_2Cl_2 Containing Triphenylphosphine. The chemical oxidation of **1** in CH_2Cl_2 containing 2 equiv of triphenylphosphine consumed 2 equiv of $FcBF_4$ and produced a solution showing carbonyl stretching bands at 1976, 1923, 1899, and 1854 cm^{-1}. Mercury was not produced. The bands at 1976 and 1899 cm^{-1} correspond exactly to those of $[CpMo(CO)_2(PPh_3)_2][BF_4]$ (**5**) prepared by other methods.

The second product, **6**, had solubilities in most solvents very similar to those of **5**, which made their separation very difficult. However, compound **6** was significantly more soluble in benzene than **5**, so extraction of the crude product with benzene, followed by chromatography on Florisil and elution with 0.1 M $[Et_4N][BF_4]$ in methanol, allowed separation of the two products. Another extraction with benzene removed $[Et_4N][BF_4]$, and crystallization from ethanol gave almost analytically pure **6**.

The ^1H NMR spectrum of **6** was consistent with a stoichiometry containing two PPh_3 ligands. The ^{31}P NMR spectrum showed one broad singlet at 94.2 ppm and a second sharp singlet at 66.4 ppm with Hg satellite peaks ($J_{HgP} = 385$ Hz). The ^{31}P NMR resonance at 66.4 ppm is assigned to a phosphorus coordinated to Mo by comparison with ^{31}P NMR spectra of $CpMo(CO)_2(PPh_3)HgX$ compounds ($\delta \approx 67$ ppm, $J_{HgP} \approx 400$ Hz).[23] The ^{31}P NMR resonance at 94.2 ppm is assigned to a phosphorus coordinated to Hg and is likely broadened by dissociation. The elemental analysis for compound **6** prepared by oxidation of **1** was close to that required for a stoichiometry containing an atom of mercury. Thus, the proposed structure of **6** is $[CpMo(CO)_2(PPh_3)HgPPh_3][BF_4]$. From the ratio of the integrals of the doublet and singlet Cp resonances in the ^1H NMR spectrum of **6**, it appears to exist in solution as a 5.8:1 mixture of trans and cis isomers. The dominance of the trans isomer would be expected, considering the steric demands of the triphenylphosphine ligands.

The identity of compound **6** was confirmed by its preparation in analytically pure form by an alternate route. Treatment of **1** and PPh_3 in CH_2Cl_2 with $Hg(BF_4)_2$ in water produced **6** in high yield. This process is analogous to the reaction of **1** with mercuric halides used to prepare compounds such as **4**. The initial product would be $CpMo(CO)_2(PPh_3)HgBF_4$, in which the BF_4^- anion is only weakly bound to the mercury. Unlike the halides, the BF_4^- anion is readily displaced by triphenylphosphine. The compound produced by this route had IR and NMR spectra essentially identical to those of **6** produced by oxidation of **1** and, in addition, gave an acceptable elemental analysis.

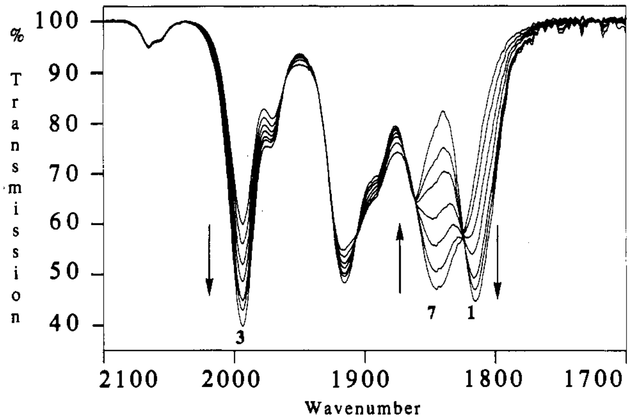

Figure 1. IR spectral changes accompanying the decomposition of the pentametallic intermediate **7** formed by one-electron oxidation of **1** in 3:1 CH_2Cl_2/CH_3CN. Spectra were acquired after 0, 10, 30, 60, 120, 180, and 420 min inside the spectrometer at 26 °C. The band appearing at 2065 cm^{-1} arises from CH_2Cl_2.

Partial Oxidation of 1. IR spectra of solutions of **1** oxidized by less than 2 equiv of $FcBF_4$ revealed the presence of an intermediate complex (**7**) with an intense carbonyl stretching band at 1845 cm^{-1}. Compound **7** was present in the largest amounts after approximately 1 equiv of $FcBF_4$ had been added. Attempts to isolate **7** proved unsuccessful because of its thermal and chromatographic instability.

When a solution of **1** in 3:1 CH_2Cl_2/CH_3CN was treated with 1 equiv of $FcBF_4$, the resulting solution initially displayed carbonyl stretching bands at 1993, 1971, 1916, and 1845 cm^{-1}, as shown in Figure 1. The bands at 1993 and 1916 cm^{-1} arose from the expected product **3**. This solution was kept in the IR spectrometer, and spectra were collected over a period of 7 h. During this period, the absorbance of the band at 1993 cm^{-1}, arising solely from **3**, almost doubled. During the same period, the band at 1845 cm^{-1} smoothly decreased in intensity and bands at 1890, 1861, and 1815 cm^{-1} appeared. The original band at 1971 cm^{-1} was replaced by a very similar band at 1972 cm^{-1}. The bands at 1815, 1861, 1890, and 1972 cm^{-1} correspond exactly to those of **1** in the same solvent. TLC co-spot experiments confirmed the production of **1**.

During the decomposition of compound **7**, isosbestic behavior was observed at 1823, 1862, and 1908 cm^{-1}. Absorbances measured at 1993, 1845, and 1815 cm^{-1}, after baseline correction, were treated according to standard first-order-kinetics analysis and yielded linear behavior.[24] This linearity, combined with the isosbestic behavior, indicated that compounds **1** and **3** were produced from **7** in equimolar amounts in a first-order reaction. This reaction had a rate constant of approximately 1.7×10^{-4} s^{-1} and a half-life of about 1 h at 26 °C. On the basis of comparisons with absorbances of authentic compounds at known concentrations, the oxidation produced approximately 0.5 mol of **3** initially and another 0.5 mol during the decomposition of **7**. Approximately 0.5 mol of **1** was formed during the decomposition. Spectral subtraction indicated that **7** had a very intense carbonyl stretching band at 1845 cm^{-1} and relatively weak bands at 1968, 1920, and 1892 br cm^{-1}.

Attempts were made to observe compound **7** by ^1H NMR spectroscopy during the oxidation of **1** in 3:1 CD_2Cl_2/CD_3CN. However, at room temperature, only a single cyclopentadienyl resonance, other than those for compound **3** and ferrocene, was observed. This resonance shifted continuously toward higher fields (approaching the chemical shift observed for pure **1**) and

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Scheme I

$$\mathrm{M_2Hg - e^- \longrightarrow MHg\cdot + M^+}$$

$$\mathrm{MHg\cdot \longrightarrow \tfrac{1}{2}MHgHgM}$$

$$\mathrm{\tfrac{1}{2}M^+ + \tfrac{1}{2}CH_3CN \longrightarrow \tfrac{1}{2}[M(CH_3CN)]^+ \quad (3)}$$

$$\mathrm{\tfrac{1}{2}M^+ + \tfrac{1}{2}MHgHgM \longrightarrow \tfrac{1}{2}[M_3Hg_2]^+ \quad (7)}$$

$$\mathrm{\tfrac{1}{2}[M_3Hg_2]^+ \longrightarrow \tfrac{1}{2}[MHg]^+ + \tfrac{1}{2}M_2Hg \quad (1)}$$

$$\mathrm{\tfrac{1}{2}[MHg]^+ + \tfrac{1}{2}CH_3CN \longrightarrow \tfrac{1}{2}[M(CH_3CN)]^+ + \tfrac{1}{2}Hg}$$

$$\mathrm{M = CpMo(CO)_2(PPh_3)}$$

broadened during the time when IR spectroscopy indicated **7** should be decomposing to compounds **1** and **3**. Also during this time, the integral of the signal for compound **3** increased, in agreement with the observed increases in absorbance of the carbonyl stretching bands of **3** observed in separate IR experiments. Variable-temperature NMR spectroscopy of solutions which should have contained similar amounts of compounds **1** and **7** revealed substantial broadening of the unidentified resonance as the temperature was decreased. However, separation of this broad peak into individual resonances could not be clearly observed before freezing of the solvent caused loss of resolution. Therefore, it was concluded that compound **7** was undergoing an intermolecular exchange reaction with compound **1** and possibly also an intramolecular exchange reaction. These exchange processes prevented the observation of discrete cyclopentadienyl resonances for **7**.

Electrochemistry of 1. The electrochemistry of **1** was complex. Cyclic voltammetry in CH_2Cl_2 at a glassy-carbon electrode gave the most well-shaped voltammograms. Two chemically and electrochemically irreversible oxidations were seen at +0.13 and +0.37 V vs Fc^+/Fc. The irreversibility of the oxidations makes assigning "*n*" values difficult. However, the two oxidations had similar peak currents which were somewhat lower than those of the reversible one-electron oxidation of $CpMo(CO)_2(PPh_3)I$ under the same conditions, suggesting that they are one electron oxidations. Only at scan rates of 10 V/s or above did the first oxidation of **1** display any degree of chemical reversibility. Thus, the Mo–Hg bond cleavage following the first electron transfer must be very rapid. In 3:1 CH_2Cl_2/CH_3CN, **1** displayed very broad oxidations at both platinum and glassy-carbon electrodes at +0.19 and +0.13 V, respectively. The peak currents in the mixed solvent were almost double those in CH_2Cl_2 alone. In both solvents at both electrodes, **1** displayed large multielectron waves at potentials above +0.50 V.

Controlled-potential electrolyses of **1** in 3:1 CH_2Cl_2/CH_3CN at a platinum electrode at +0.20 V vs Fc^+/Fc consumed approximately 2 faradays/mol of charge. However, a precise electron count could not be obtained because the current did not decrease to the background level. The persistent anodic current probably resulted from oxidation of either **3** or the mercury coproduct. The consumption of 2 faradays/mol in the electrolyses of **1** agrees with the observation that chemical oxidation requires 2 equiv of $FcBF_4$. IR spectra of electrolysis product solutions showed carbonyl stretching bands at 1995 and 1915 cm^{-1}, corresponding to complex **3**. Extraction with THF, followed by precipitation with diethyl ether, allowed separation of the supporting electrolyte and isolation of **3** in about 50% yield.

Discussion

The net reaction for the oxidation of **1** in CH_2Cl_2 is a two-electron process yielding 2 mol of $[CpMo(CO)_2(PPh_3)]^+$ and 1 mol of mercury (eq 1). The 16-electron cation will coordinate BF_4^- when the chemical oxidation is performed with $FcBF_4$ or

$$\mathrm{[CpMo(CO)_2(PPh_3)]_2Hg - 2e^- \rightarrow 2[CpMo(CO)_2(PPh_3)]^+ + Hg \quad (1)}$$

the electrochemical oxidation is carried out in the presence of $[Et_4N][BF_4]$ supporting electrolyte. The tetrafluoroborate anion is easily displaced by other ligands such as CH_3CN, triphenylphosphine, or iodide. Oxidation in a mixed solvent containing both CH_2Cl_2 and CH_3CN produces the CH_3CN complex, **3**, directly.

Details of the pathway for of the oxidation of **1** have been uncovered by conducting the reaction in the presence of species capable of intercepting reactive intermediates. For example, one-electron oxidation of **1** in 1:1 CCl_4/CH_3CN produces an equimolar mixture of **3** and $CpMo(CO)_2(PPh_3)HgCl$ (**4**). This result is explained by the reactions shown in eqs 2–5. Following

$$\mathrm{[CpMo(CO)_2(PPh_3)]_2Hg - e^- \rightarrow [CpMo(CO)_2(PPh_3)]_2Hg^+ \quad (2)}$$

$$\mathrm{[CpMo(CO)_2(PPh_3)]_2Hg^+ \rightarrow [CpMo(CO)_2(PPh_3)]^+ + CpMo(CO)_2(PPh_3)Hg^\bullet \quad (3)}$$

$$\mathrm{[CpMo(CO)_2(PPh_3)]^+ + CH_3CN \rightarrow [CpMo(CO)_2(PPh_3)(CH_3CN)]^+ \quad (4)}$$

$$\mathrm{CpMo(CO)_2(PPh_3)Hg^\bullet + CCl_4 \rightarrow CpMo(CO)_2(PPh_3)HgCl + {}^\bullet CCl_3 \quad (5)}$$

the one-electron oxidation of **1** (eq 2), cleavage of a Mo–Hg bond would generate a cation and a radical (eq 3). The cation would coordinate CH_3CN to form **3** (eq 4), while compound **4** probably arises from reaction of the radical with CCl_4 (eq 5). It is known that chlorine atoms can be abstracted easily from CCl_4. In fact, alkylmercury radicals have been reported[25] to abstract chlorine from CCl_4 as part of a chain-reaction chlorination.

The absence of the chloro complex $CpMo(CO)_2(PPh_3)Cl$ as a product of the oxidation of **1** in the presence of CCl_4 argues against the alternative cleavage to produce the neutral 17-electron species, $CpMo(CO)_2(PPh_3)$, and the mercury-containing cation $[CpMo(CO)_2(PPh_3)Hg]^+$. We have observed that thermal or photochemical cleavage of **1** in the presence of CCl_4 produces both $CpMo(CO)_2(PPh_3)Cl$ and $CpMo(CO)_2(PPh_3)HgCl$, demonstrating that if $CpMo(CO)_2(PPh_3)$ had been formed in the oxidation reaction, the chloro complex would have been observed as a product.

In the absence of easily abstractable atoms, one might expect the mercury-centered radical to dimerize to a tetrametallic complex, $[CpMo(CO)_2(PPh_3)Hg]_2$. Such a dimerization has been suggested in the reduction of organomercury halides.[26–28] Although dimerization probably does occur during the oxidation of compound **1**, the tetrametallic species is not observed. Instead, partial oxidation of **1** produces a species **7** having an intense carbonyl stretching band at 1845 cm^{-1} and weaker bands at 1968, 1920, and 1892 cm^{-1}. This compound is not stable enough to allow isolation and characterization. In the presence of CH_3CN, complex **7** decomposes in a first-order manner with a half-life of about 1 h to produce equimolar amounts of compounds **1** and **3**.

The production of both **1** and **3** from **7** eliminates the tetrametallic dimer as a candidate for **7**. Because the reaction of **1** with 1 equiv of $FcBF_4$ immediately produces 0.5 mol of **3**, with the remaining expected 0.5 mol produced by decomposition of **7**, 0.5 mol of $[CpMo(CO)_2(PPh_3)]^+$ must be incorporated in **7**. Since the other products of the decomposition are 0.5 mol of **1** and metallic mercury, the stoichiometry of **7** must be $\{[CpMo(CO)_2(PPh_3)]_3Hg_2\}^+$. Because of the presence of inter- and/or intramolecular exchange reactions, ^1H NMR spectroscopy could

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not be used to verify this stoichiometry.

The overall stoichiometry of the one-electron oxidation of **1** in the presence of CH_3CN can be accounted for by the reactions shown in Scheme I. The one-electron oxidation initially produces the mercury-centered radical and 16-electron cation as described above. The radical most likely dimerizes to an unobserved tetrametallic species. Half of the available 16-electron cation coordinates CH_3CN to produce complex **3**. The other 0.5 mol of the 16-electron cation is incorporated into the species **7**, most likely generated by reaction with the proposed tetrametallic dimer. Decomposition of **7** would produce **1** and the mercury-containing cation, $[CpMo(CO)_2(PPh_3)Hg]^+$, in a 1:1 ratio. It is proposed that the mercury-containing cation reacts rapidly with CH_3CN to produce complex **3** and metallic mercury, as in the two-electron oxidation of **1** in CH_2Cl_2/CH_3CN (see below).

Since the pentametallic intermediate **7** is not stable enough for isolation, we cannot structurally characterize it. However, on the basis of the apparent stoichiometry of three $CpMo(CO)_2(PPh_3)$ fragments and two atoms of mercury, we propose a structure in which a $CpMo(CO)_2(PPh_3)Hg$ unit is bonded through the Hg atom to the Hg atom of a unit resembling **1**. The five metal atoms would form a distorted T-shape, with the **1** unit probably being bent back by steric interactions. This structure would readily result from attack of $CpMo(CO)_2(PPh_3)^+$ on the dimer, $[CpMo(CO)_2(PPh_3)Hg]_2$, and could simply cleave at the Hg–Hg bond to yield the observed products.

The next step in the two-electron oxidation of **1** we suggest involves formation of the cationic mercury-containing species mentioned above through a further one-electron oxidation, presumably of the pentametallic intermediate (eq 6). The 0.5 mol

$$0.5\{[CpMo(CO)_2(PPh_3)]_3Hg_2\}^+ - e^- \rightarrow [CpMo(CO)_2(PPh_3)Hg]^+ + 0.5[CpMo(CO)_2(PPh_3)]^+ \quad (6)$$

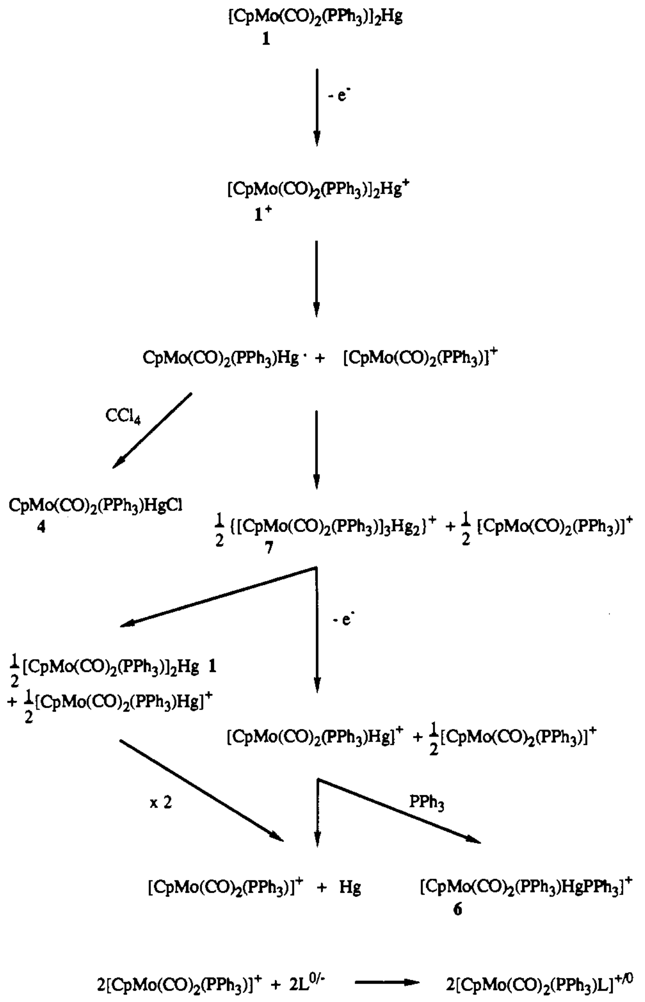
of the 16-electron cation that was initially incorporated into **7** is returned to the reaction system at this stage.

The first piece of evidence supporting the formation of the mercury-containing cation is a carbonyl stretching band at approximately 1848 cm^{-1} observed initially after the two-electron oxidation of **1** in CH_2Cl_2. Complexes of the type $CpMo(CO)_2(PPh_3)HgX$ absorb in this region.[19] Additionally, the isolation of $[CpMo(CO)_2(PPh_3)HgPPh_3][BF_4]$ (**6**) after oxidation of **1** by two electrons in the presence of triphenylphosphine strongly supports the intermediacy of the mercury-containing cation.

Compound **6** proved difficult to isolate in pure form, since it was produced along with an equal amount of $[CpMo(CO)_2(PPh_3)_2][BF_4]$ (**5**), which has very similar solubilities. The elemental analysis of **6** produced by oxidation of **1** was not acceptable, so this compound was also synthesized by reaction of **1** with $Hg(BF_4)_2$ and triphenylphosphine. This route gave analytically pure **6** with IR and NMR spectra identical to those of **6** produced by oxidation of **1** in the presence of triphenylphosphine. The observation of both a doublet and a singlet in the Cp region of the ^1H NMR spectrum of **6** suggests that both cis and trans isomers are formed.[22] The doublet, corresponding to the trans isomer, is about 6 times larger than the singlet taken to be the cis isomer. The preference for the trans conformation is consistent with the steric demands of the PPh_3 ligands.

Compound **6** represents an unusual type of mercury complex. Many organometallic compounds are known containing HgX, where X is an anion, bound to a transition metal.[29] However, as far as we are aware, there are no such complexes containing a neutral ligand bound to the mercury. Organomercury compounds of the type $[RHgPR_3]^+$ have been prepared by reaction of phosphines with organomercury halides.[30] In addition, neutral gold complexes, such as $CpMo(CO)_3AuPPh_3$, which are isoelectronic with **6** are known.[31]

Scheme II



It is suggested that the final step in the oxidation of **1** (eq 7) is extrusion of mercury from the cation. In CH_2Cl_2 this reaction

$$[CpMo(CO)_2(PPh_3)Hg]^+ \rightarrow [CpMo(CO)_2(PPh_3)]^+ + Hg \quad (7)$$

proceeds much more slowly than the first Mo–Hg bond cleavage. The carbonyl stretch at 1848 cm^{-1} assigned to the mercury-containing cation decreases in intensity slowly over a period of several hours, during which time mercury precipitates from solution as a gray powder and/or a shiny film. The demercuration reaction is much faster in CH_2Cl_2/CH_3CN solvent mixtures, occurring essentially immediately upon oxidation of **1**.

Extrusion of mercury from numerous cationic alkylmercury species has been reported.[32] Our observations are in agreement with studies of the demercuration of cyclohexylmercuric salts. Demercuration in acetic acid was reported to be much more rapid for the more highly ionized salts containing ClO_4^- or BF_4^- anions than for acetate or bromide compounds.[33] In addition, demercuration occurred more rapidly in more ionizing solvents. In solvents of similar ionizing ability, the demercuration was slower in more nucleophilic solvents which coordinate to the mercury. We have observed slow demercuration in CH_2Cl_2, which would suppress ionization of the BF_4^- salt, rapid demercuration in CH_2Cl_2/CH_3CN, which would enhance ionization, and no demercuration in the presence of the good ligand triphenylphosphine.

Conclusions

Scheme II shows our proposed mechanism for the oxidative cleavage of the Mo–Hg bonds in **1**. An initial one-electron transfer

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is followed by a rapid cleavage of one of the Mo–Hg bonds, producing a mercury-centered radical and a 16-electron molybdenum-containing cation. This cation coordinates solvent, the anion of the oxidant, or any other available ligand. The radical will abstract a chlorine atom from CCl_4 if it is present. If no easily abstractable atoms are available, the radical is proposed to dimerize to a tetrametallic species, which reacts with half of the available 16-electron cation to produce an observable pentametallic intermediate **7**. Compound **7** may decompose to **1** and a 16-electron cation, or it may undergo further oxidation, leading to a mercury-containing cation. This cation will coordinate triphenylphosphine to form a stable product **6**. Other ligands, such as CH_3CN or BF_4^-, form unstable adducts which extrude mercury to yield a second mole of the 16-electron Mo-containing cation.

In the absence of species which intercept reactive intermediates, the overall oxidation is a two-electron process, as confirmed by electrochemical measurements. The resulting tetrafluoroborate complex is a useful intermediate in the synthesis of substituted complexes. This work has demonstrated an alternate route to complexes of the type $CpMo(CO)_2(PR_3)L$, including the synthesis of the previously unreported CH_3CN complex (**3**). The unique mercury–phosphine complex $[CpMo(CO)_2(PPh_3)HgPPh_3]^+$ (**6**) has been discovered. And finally, the mechanism for this oxidative metal–metal bond cleavage reaction has been elucidated in detail.

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Intramolecular Energy Transfer in Ruthenium(II)–Chromium(III) Chromophore–Luminophore Complexes. $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$

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A new trinuclear Ru(II)–Cr(III) chromophore–luminophore complex, $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$, has been synthesized and characterized. Visible light absorption by the $Ru(bpy)_2^{2+}$ chromophore leads to emission from the $Cr(cyclam)(CN)_2^+$ luminophore, as a consequence of very efficient (≥99%) and fast (subnanosecond time scale) chromophore–luminophore exchange energy-transfer process. The emission is intense ($\Phi = 5.3 \times 10^{-3}$ in H_2O) and long-lived ($\tau = 260$ μs in H_2O). The photophysical properties of the luminophore are slightly perturbed by interaction with the chromophore, resulting in a sharper emission band shape and shorter radiative and radiationless lifetimes. The presence of a Ru(II) → Cr(III) intervalence transfer state, hardly detectable in the ground-state spectrum, is clearly revealed by the excited-state absorption spectrum of the chromophore–luminophore complex.

Introduction

In the recent development of supramolecular photochemistry,[1] a relevant role has been played by studies on covalently linked multicomponent systems.[2,3] The field has seen a progressive evolution from the study of simple donor–acceptor systems ("dyads") toward that of more and more complex supramolecular species ("triads", "tetrads", and "pentads").[2-16] The main purpose of such studies has been the understanding of fundamental aspects of light-induced intercomponent electron and energy-transfer processes[4-11] and its application to the design of artificial biomimetic systems for light energy conversion[12-14,17] and photochemical molecular devices.[18-21] In this context, an interesting class of covalently linked systems is that of *chromophore–luminophore* complexes, i.e., systems in which the light energy is efficiently absorbed by appropriate molecular components (chromophores) and is then conveyed, by means of intercomponent energy-transfer processes, to a specific molecular component, which gives back the energy in the form of light emission (luminophore).[15,22,23] An interesting aspect of the behavior of such chromophore–luminophore complexes is the mimicry of the "antenna effect" of natural systems.[21,24,25] From a more practical standpoint, their peculiarity lies in the possibility to achieve separate optimization of the absorption and emission properties. From this viewpoint, chromophore–luminophore complexes are likely to be useful wherever

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