Oxidation of Molybdenum(0) and Tungsten(0) Carbonyl Complexes with Silver Triflate

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Benzyltriethylammonium chloropentacarbonylmolybdate (**1**) and chloropentacarbonyltungstate (**2**) complexes react with CF_3SO_3Ag in DME via a combination of chloride exchange and a redox process, as revealed by cyclic voltammetry and ESR spectrometry. The resulting intermediate M(I) species disproportionate to M(0) and M(II) so that 3 equiv of TfOAg are required for the quantitative conversion into the M(II) complex. Analogous PPN complexes **3** and **4** only undergo the redox process (in DME); in this instance, the chloride exchange is precluded, presumably due to strong pairing of the complex anion with the counterion.

Introduction

The late transition metals owe their success in catalytic chemistry to the readiness with which they change their coordination number and exist as 18−, 16−, and 14−electron species.[1] Analogous changes in the coordination sphere of the group 6 metals are usually more difficult to achieve. As a result, relatively few catalytic processes employing the latter metals (in lower oxidation states) have been developed to date.[1,2] One successful example is the Mo(0)- and W(0)-catalyzed allylic substitution.[3,4] However, its variant employing Pd(0) as the catalyst[5,6] proceeds much more readily, often at room temperature, in contrast to refluxing in higher boiling solvents for several hours typically required by Mo−carbonyl and W−carbonyl complexes.[3,4] This striking difference can be attributed, in part, to the ease of ligand dissociation in the case of palladium catalysts,[1] i.e., $(Ph_3P)_4Pd \rightleftarrows (Ph_3P)_3Pd + Ph_3P$, as opposed to the relative stability of $Mo(CO)_6$, $W(CO)_6$, and related complexes.

We reasoned that the inherent coordination rigidity of the group 6 metal complexes could be offset by implementing one or two weakly coordinating ligands (in place of the CO group(s)) that could be more readily replaced by the reactants.[7−9] In combination with the ability of Mo and W to form heptacoordinated complexes,[1,10] this ligand effect can be expected to result in an enhanced or even novel catalytic activity.

Herein, we report on the attempted replacement of the strongly coordinating chloride in the benzyltriethylammonium and bis(triphenylphosphine)ammonium (PPN) complexes of molybdenum and tungsten of the type $[M(CO)_6Cl]^-$ (M = W or Mo) by a weakly coordinating trifluoromethanesulfonate anion (TfO−) and on the associated redox processes. Also reported is the effect of the counterion and the solvent polarity on the formation and properties of these new complexes.

Results and Discussion

In the search for new group 6 metal catalysts, we endeavored to prepare Lewis−acidic, carbonyl complexes of Mo and W with a weakly coordinating anion, such as triflate (TfO−), in their coordination sphere.[7−9] We envisaged a viable route to such complexes from the halopentacarbonylmetalate(0) salts $[M(CO)_5X]^-$ whose halogen atom (X) could be replaced by the desired anion on reaction with the corresponding silver(I) salt.[7,8]

The required chloropentacarbonylmolybdate and chloropentacarbonyltungstate complexes **1** and **2** were prepared using a known procedure,[11] via heating the corresponding metal carbonyls with benzyltriethylammonium chloride in diglyme at 120 °C (Scheme 1). The reaction can also be carried out in refluxing DME (at 80 °C),[11] but we have now found that both the ammonium salt and the solvent have to be rigorously dry.

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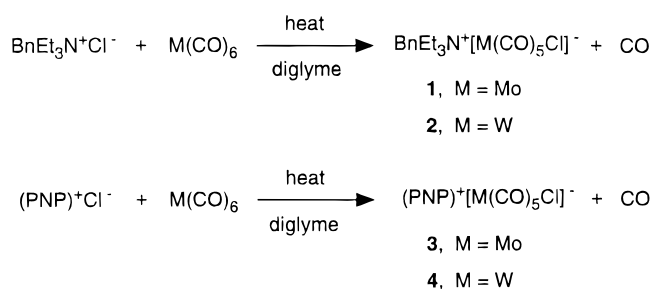(2) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446.
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Scheme 1[a]

$$BnEt_3N^+Cl^- + M(CO)_6 \xrightarrow[\text{diglyme}]{\text{heat}} BnEt_3N^+[M(CO)_5Cl]^- + CO$$

1, M = Mo

2, M = W

$$(PNP)^+Cl^- + M(CO)_6 \xrightarrow[\text{diglyme}]{\text{heat}} (PNP)^+[M(CO)_5Cl]^- + CO$$

3, M = Mo

4, M = W

[a] Bn = $PhCH_2$; PNP^+ = $[Ph_3P=N=PPh_3]^+$; M = Mo or W.

The analogous $[Ph_3P=N=PPh_3]^+$ salts (PPN)[12] **3** and **4** were prepared in a similar manner. The structure of these complexes was corroborated by comparison of their data with those published by other authors for analogous complexes. Thus, for instance, in accordance with the literature,[11] the Mo complex **1** showed four carbonyl vibrations in the IR spectrum (at 1853 (s), 1926 (vs), 1982 (w), and 2061 (w) cm^{-1}; in CH_2Cl_2). The complexes **2**–**4**, prepared in an analogous way, exhibited similar characteristics.[13]

Reaction of Complexes 1–4 with Silver(I). Treatment of the halopentacarbonylmetalate halides $R_4N^+[M(CO)_5X]^-$ with silver(I) or thallium(I) carboxylates has been reported to yield the expected carboxylate complexes $R_4N^+[M(CO)_5(O_2CR)]^-$ and precipitated AgCl (M = Mo, W);[12] silver tosylate is known to react in the same way.[12] In contrast to these reports, we have now found that silver trifluoromethanesulfonate (TfOAg) behaves differently: while the addition of 1 equiv still gives mainly AgCl (in DME), the addition of an excess of TfOAg results in the formation of a grey precipitate of Ag(0) upon reaction with **1**. Apparently, TfOAg is a somewhat stronger oxidant than the corresponding carboxylates.[17]

The cyclic voltammograms for the starting Mo and W halopentacarbonyl complexes **1–4** gave similar re-
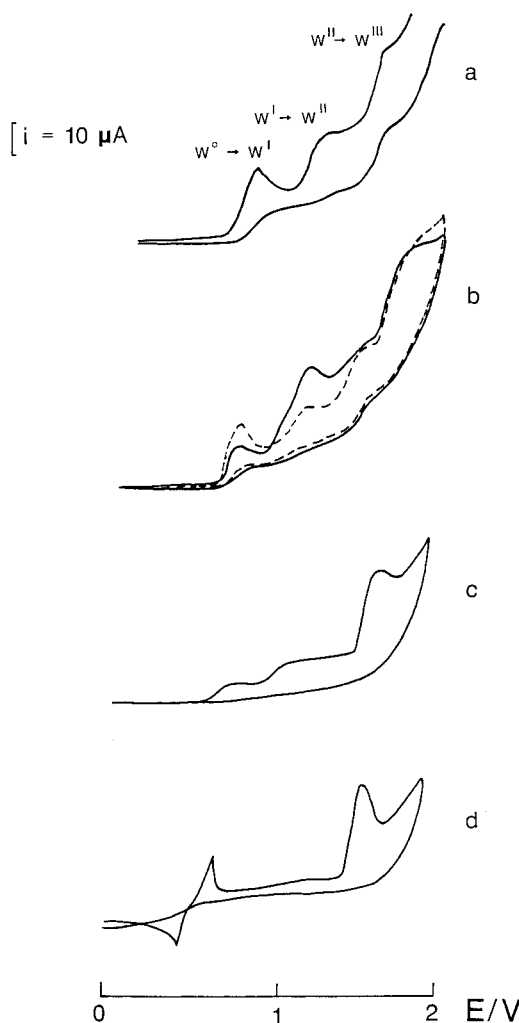

Figure 1. Elucidation of the reaction of complex **2** with TfOAg in DME by cyclic voltammetry. (a) Voltammogram of the parent complex **2**. (b) Voltammogram of **2** after addition of the first equivalent of TfOAg (—) and 80 s later (- - -). (c) Voltammogram after addition of the second equivalent of TfOAg. (d) Voltammogram after addition of the third equivalent of TfOAg.

sults to those reported by Bond[18] who used Bu_4N^+-$[M(CO)_5X]^-$: all samples showed an irreversible, one-electron transfer process at about +0.7 V.[19] Elucidation of the reaction between TfOAg and each of the complexes **1–4** by cyclic voltammetry is described below. The reactions have been found to be remarkably dependent on the type of the quaternary ammonium counterion and on the polarity of the solvent in which the reaction was carried out.

Reaction of $[W(CO)_5Cl]^-$ with TfOAg in Dimethoxyethane. The starting benzyltriethylammonium complex $BnEt_3N^+[W(CO)_5Cl]^-$ (**2**) shows three oxidation processes on a sweep from 0 to +2 V (Figure 1a), which can be assumed to correspond to the oxidation of **2** to the W^I, W^{II}, and W^{III} states, respectively. The first two processes are irreversible and can be attributed to the

(12) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398. (b) Doyle, G. *J. Organomet. Chem.* **1975**, *84*, 323. (c) Connor, J. A.; Jones, E. M.; McEwen, G. K. *J. Organomet. Chem.* **1972**, *43*, 357.

(13) By contrast, the reaction of $Mo(CO)_6$ with *wet* $BnEt_3N^+Cl^-$ took a different course when carried out in DME (but not in diglyme!): instead of the formation of the soluble complex **1**, we have obtained a sparingly soluble, presumably polymeric material, which exhibited distinct carbonyl vibrations at 1723 (s), 1741 (s), 1782 (w), and 1887 (w) cm^{-1} in the IR spectrum (in KBr), the first three bands being suggestive of the presence of bridged carbonyl group(s). The ^{1}H NMR spectrum (in DMSO-d_6) showed a signal for water (singlet at 3.49 ppm exchangeable with D_2O), which was in ca. 1:1 ratio to the PhCH_2 signal. The presence of water is further evidenced by a broad band at 3260–3500 cm^{-1} in the IR spectrum (in KBr or Nujol), in accord with the behavior of related aqua complexes.[14] Elemental analysis (C, H, N, Mo) was compatible with the formula $\{(BnEt_3N)_4[Mo_3(CO)_9Cl_4]\cdot3H_2O\}_n$. The tungsten complex, synthesized in the same way (from wet $BnEt_3N^+Cl^-$ in DME), exhibited analogous spectral characteristics.[15,16]

(14) (a) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, S. L.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390. (b) Cotton, F. A.; Kühn, F. E. *J. Am. Chem. Soc.* **1996**, *118*, 5826.

(15) The striking difference between the reaction course in diglyme and DME is difficult to understand. Presumably, diglyme, being a tridentate ligand, can better coordinate water molecules, preventing their reaction with the metal complex.

(16) For the effect of water contained in tetraalkylammonium salts on the Heck-type reactions, see: (a) Jeffery, T. *Tetrahedron Lett.* **1994**, *35*, 3051. For other, recent examples of the effect of small amounts of water on reativity, see: (b) Almeida, M. L. S.; Kočovský, P.; Bäckvall, J.-E. *J. Org. Chem.* **1996**, *61*, 6587. (c) Almeida, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *2*, 1533. (d) Posner, G. H.; Dai, H. Y.; Bull, P. S.; Lee, J. K.; Eydoux, F.; Ishihara, Y.; Welsh, W.; Pryor, N.; Peter, S. *J. Org. Chem.* **1996**, *61*, 671. (e) Terada, M.; Matsumoto, Y.; Nakamura, Y.; Mikami, K. *J. Chem. Soc., Chem. Commun.* **1997**, 281.
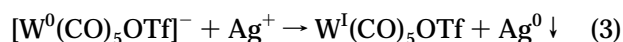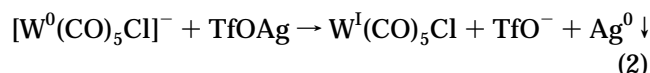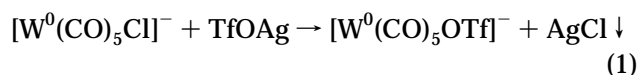
(17) Cyclic voltammetry of CF_3CO_2Ag and TfOAg showed a 0.10 V difference in the redox potential of the Ag^+ ion, which corresponds to a difference of approximately 10 kJ·mol^{-1} in the Gibbs energy of the two processes.

(18) Bond, G.; Bowden, J. A.; Colton, R. *Inorg. Chem.* **1974**, *13*, 605.

(19) The slight differences between the potentials reported in this work and those in ref 18 result from the different reference electrodes used.

electrochemical reactions described by Bond;[18] the third process is quasi reversible.

Addition of 1 equiv of TfOAg to a solution of **2** in DME resulted in an instantaneous formation of a predominantly white precipitate and changed the voltammogram of the solution, as shown in Figure 1b. It should be noted that no signal was observed for Ag^+ ions, showing that they were removed from the solution in the reaction with **2**. Moreover, the signal corresponding to the oxidation of W^0 to W^I did not remain constant, indicating that some of the complex had been oxidized. This observation can be rationalized by assuming that two reactions occur simultaneously (eqs 1 and 2).

$$[W^0(CO)_5Cl]^- + TfOAg \rightarrow [W^0(CO)_5OTf]^- + AgCl \downarrow \quad (1)$$

$$[W^0(CO)_5Cl]^- + TfOAg \rightarrow W^I(CO)_5Cl + TfO^- + Ag^0 \downarrow \quad (2)$$

$$[W^0(CO)_5OTf]^- + Ag^+ \rightarrow W^I(CO)_5OTf + Ag^0 \downarrow \quad (3)$$

Reaction 1 (apparently the dominant process) can also be followed by the corresponding oxidation of the triflate complex (eq 3),[20] provided the latter process occurs with a comparable or higher rate.

The current for $W^I \rightarrow W^{II}$ has been found to decrease with time while that for $W^0 \rightarrow W^I$ gradually increased (Figure 1b). This behavior is clearly indicative of a disproportionation[18] process that can be proposed to occur as shown in eq 4. The kinetics of this dispropor-

$$2[W^I(CO)_5(OTf)] \rightarrow$$
$$[W^{II}(CO)_5(OTf)]^+ + [W^0(CO)_5(OTf)]^- \quad (4)$$

tionation correspond to an expected second-order process with the rate constant 1.87 mol^{-1} dm^3 s^{-1} at 20 °C. Hence, the disproportionation is relatively slow ($^\tau/_2 \approx 3$ min), which means that at least 5% of this species should still be present after 30 min at room temperature so that it could easily be investigated by ESR (*vide infra*).

The addition of 2 equiv of TfOAg led to the deposition of a grey precipitate; suppression of the peaks corresponding to $W^0 \rightarrow W^I$ and $W^I \rightarrow W^{II}$ transitions was observed in the cyclic voltammogram (Figure 1c). These results suggest that reaction 1 dominates when the first equivalent is added, and reaction 3 occurs on addition of the second equivalent. The second equivalent of TfOAg would also replace Cl$^-$ in W^I(CO)$_5$Cl (formed in the reaction 2) by TfO$^-$. If we assume that each step proceeds quantitatively and no other undetected side reactions occur, 1 equiv of **2** would generate 0.5 equiv of [W^{II}(CO)$_5$(OTf)]$^+$ and 0.5 equiv of [W^0(CO)$_5$(OTf)]$^-$, consuming 2 equiv of TfOAg. For the oxidation of the latter species, another equivalent of TfOAg would have to be used. Hence, a total of 3 equiv of TfOAg will be required for the quantitiative conversion of W^0 to W^{II}. However, if the individual steps did not proceed quantitatively, 3 equiv would actually represent a slight

Figure 2. ESR spectra obtained in frozen DME solutions at 77 K for (**a**) W^I(CO)$_5$(OTf) and (**b**) W^I(CO)$_5$Cl.

excess. In consonance with this analysis, addition of a third equivalent of TfOAg has been found to result in the characteristic deposition and stripping peaks in the voltammogram (Figure 1d). The latter features are associated with the electrochemical reduction of Ag^I to Ag^0 (eq 5), showing that there is an excess of Ag$^+$ in

$$Ag^+ + e^- \rightleftharpoons Ag^0 \quad (5)$$
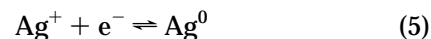
the solution and that the reaction has gone to completion.

The ESR spectrum obtained at 77 K for the DME solution of the complex generated from **2** and 1 equiv of TfOAg showed a broad, weak feature with $g_\parallel = 1.801$ and $g_\perp = 1.764$ (species A). With 2 equiv of TfOAg, the spectrum (Figure 2a) became much stronger and better resolved but with the central feature shifted to $g_\parallel = 1.963$ and $g_\perp = 1.932$ (species B). Weak satellite lines, arising from the ^{183}W isotope that has a nuclear spin of $^1/_2$ and natural abundance of 14.28%, were observed. These hyperfine couplings were $A_\parallel = 188$ G and $A_\perp = 125$ G.[21] A trace of the signal from species A was still present. Species B can be assigned the structure W^I(CO)$_5$OTf (eq 3), whereas species A may arise via a minor reaction of the original complex with the first equivalent of Ag$^+$. The ESR spectrum obtained after

(20) Both TfOAg and the precipitated AgCl may, *a priori*, serve as oxidants. For an analogous oxidation of Cu(I) to Cu(II) by means of AgCl, see: Smrčina, M.; Poláková, J.; Vyskočil, Š.; Kočovský, P. *J. Org. Chem.* **1993**, *58*, 4534. However, AgCl should react more slowly in view of its low solubility.
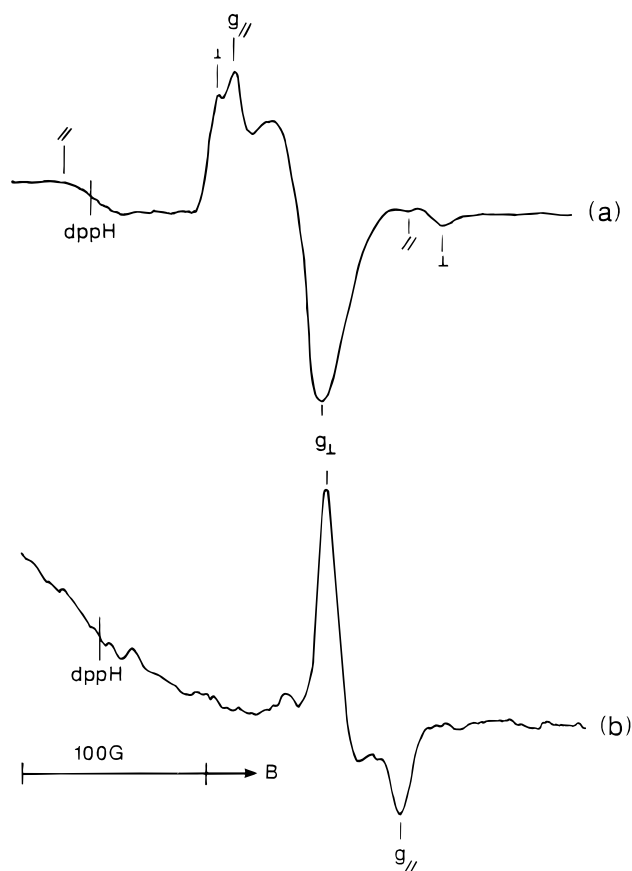
(21) Few other related systems have been investigated by ESR spectroscopy. Electrochemical oxidation of [W(CO)$_2$(CNR)$_2$(PR$_3$)$_2$] has yielded ESR spectra with similar parameters: $g_\parallel = 1.903$ and $g_\perp = 2.212$. The Mo analogues had $g_\parallel = 1.97-1.99$, $g_\perp = 2.00-2.02$, and $A_\parallel = 50$ G.[22]

(22) (a) Conner, K. A.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 4422. See also: (b) Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, H. D.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 7917.
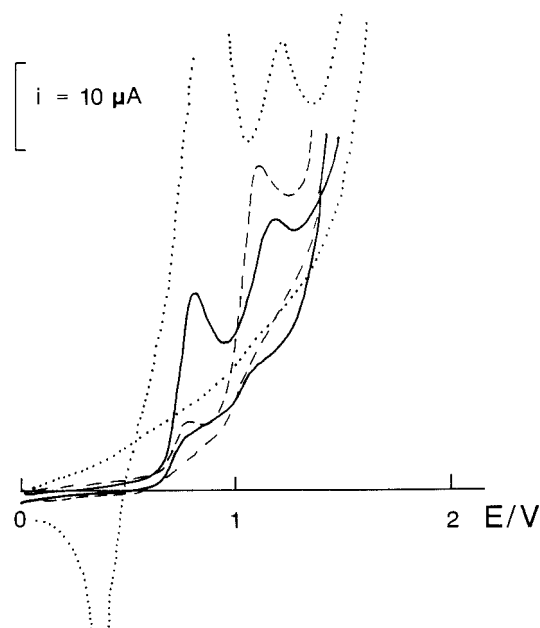
Figure 3. Elucidation of the reaction of complex **4** with TfOAg in DME by cyclic voltammetry: (—) voltammogram of the parent complex **4**; (- - -) voltammogram of **4** after addition of the first equivalent of TfOAg; (•••) voltammogram after addition of the second equivalent of TfOAg.

addition of 3 equiv of TfOAg showed a very broad, weak, and featureless signal arising from a third species of low abundance, with $g = 2.08$. No satellite lines arising from the ^{183}W isotope could be resolved. Presumably, this signal originates from an impurity, which implies that most of the metal has been oxidized to W(II), which should give no signal. Furthermore, the absence of the species B after the addition of the first equivalent of Ag$^+$ rules out reaction 3 as a process competing with reactions 1 and 2.

In the IR spectrum of the final species [i.e., (CO)$_5$W-(OTf)$_2$] measured in CH$_2$Cl$_2$, peaks at 1975 (vs), 2010 (sh), and 2095 (w) cm^{-1} were identified, which is in agreement with the pattern published for the analogous isonitrile complex (t-BuNC)$_5$Mo(OAc)$_2$.[23,24]

The stoichiometry of the whole cascade would, theoretically, require exactly 3 equiv of Ag$^+$. However, the above experiments show that, in fact, slightly less than 3 equiv is sufficient to drive the process to completion, which can be attributed to a nonquantitative conversion in some of the transformation(s), presumably due to undetected side reaction(s).

Replacement of BnEt$_3$N$^+$ by (PPN)$^+$ as the counterion had a significant effect on the reaction of the complex with TfOAg. The cyclic voltammogram for a solution containing **4** prior to the addition of TfOAg was similar to that obtained for the BnEt$_3$N$^+$ complex **2**, although no signal was observed for the oxidation of W^{II} to W^{III} (Figure 3). The addition of 1 equiv of TfOAg led to the formation of a grey precipitate and to a dramatic decrease of the current corresponding to oxidation of W^0 to W^I (Figure 3); little or no disproportionation was subsequently observed. After the addition of a second equivalent of TfOAg to this solution, a large voltam-

metric signal for Ag$^+$ reduction was detected (Figure 3), showing that the reaction had gone to completion. These observations suggest that reaction 2 dominates and reaction 1 is precluded.

Elucidating the latter reaction by ESR spectroscopy further supported these conclusions: when 1 equiv of TfOAg was added to 1 equiv of **4**, the solution showed an ESR spectrum having clear axial symmetry with $g_\parallel = 1.909$ and $g_\perp = 1.930$ (Figure 2b). Satellite lines arising from the ^{183}W isotope were insufficiently resolved to allow reliable measurement. The observation of an ESR spectrum indicates immediate oxidation of the tungsten without the initial substitution of the Cl$^-$ by TfO$^-$. This constrasts with the case of the BnEt$_3$N$^+$ salt **2** where adding 1 equiv of TfOAg resulted mainly in substitution of Cl$^-$ by TfO$^-$ without oxidation. It is pertinent to note that $g_\parallel$ is sensitive to the axial ligand field, and since Cl$^-$ has a weaker ligand field than TfO$^-$, the energy separation upon which $g_\parallel$ depends, i.e., $\Delta E(d_{x^2-y^2} - d_{xy})$, will be smaller, thus making $g_\parallel$ deviate from that of W^{I}C(O)$_5$(OTf), as found.

It can be speculated that the difference in the reactivity of these two complexes toward TfOAg is due to the association of ions in DME (a medium of relatively low polarity[23]). It has been recently shown[26] that small anions can penetrate into the interstices of bulky quaternary ammonium anions forming a "penetrating ion pair". The (PPN)$^+$ ion has a cavity between the phenyl groups into which the [W(CO)$_5$Cl]$^-$ ion could fit. The strong interaction between these two ions would prevent the exchange of Cl$^-$ by TfO$^-$ ligands. Hence, the role of TfOAg is only to oxidize the [W(CO)$_5$Cl]$^-$ anion, as in reaction 2. The latter oxidation strengthens the W$-$Cl bond, thereby further preventing the ligand exchange. By contrast, the BnEt$_3$N$^+$ cations, which does not have such a cavity, allows the ligand exchange to occur readily. Further oxidation of the latter W(I) complex leads to the expected W(II) species, as evidenced by the IR spectrum, which is almost identical to that of the triflate.

Reaction of [Mo(CO)$_5$Cl]$^-$ with TfOAg in Dimethoxyethane. The response of the Mo(0) complexes **1** and **3** was similar to that for their W(0) analogues **2** and **4**, respectively,[27] which demonstrates that the behavior of these species is independent of the metal center. One slight exception was that the BnEt$_3$N$^+$[Mo(CO)$_5$Cl]$^-$ complex exhibited only two signals, one for the oxidation Mo$^0 \rightarrow$ M^I (at +1.45 V) and one combined for Mo$^I \rightarrow$ Mo^{II} $\rightarrow$ Mo^{III} (at +1.40 V). These two signals are again resolved following the addition of 1 equiv of TfOAg.

In analogy with the tungsten complex, the ESR spectrum of the solution prepared by adding 1 equiv of TfOAg to **1** exhibited a broad weak feature with $g_\parallel = 1.911$ and $g_\perp = 1.881$ flanked by very weak satellite lines. With 2 equiv of TfOAg, the spectrum (Figure 4) was much stronger and better resolved with the same central feature and satellite lines arising from ^{95,97}Mo

(23) The IR spectrum of (t-BuNC)Mo(OAc)$_2$ exhibits the following features: 2115 (s), 2170 (sh) cm^{-1}.[24]

(24) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2040.

(25) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; J. Wiley and Sons: New York, 1986.

(26) Abbott, A. P.; Schiffrin, D. J. *J. Chem. Soc., Faraday Trans.* **1989**, *86*, 1453. (b) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 731.

(27) Oxidation of other molybdenum complexes by means of Ag(I) has previously been reported to afford Mo(II) species.[28] Thus, for instance, treatment of [Mo(CO)$_2$(bipy)$_2$]$^+$BF$_4^-$ with AgBF$_4$ in MeCN gives [Mo(CO)$_2$(bipy)$_2$(MeCN)]$^{2+}$(BF$_4^-$)$_2$. The same product has also been obtained from Mo(CO)$_2$(bipy)$_2$ on reaction with 2 equiv of AgBF$_4$.[28]

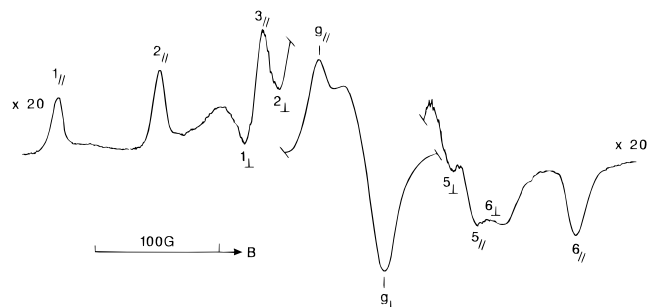(28) Connor, J. A.; James, E. J.; Overton, C.; El Murr, N. *J. Chem. Soc., Dalton Trans.* **1984**, 255.

Figure 4. ESR spectrum of Mo^I(CO)$_5$(OTf) in DME.

isotopes (having a nuclear spin of $^5/_2$ and total natural abundance of 25.35%). The hyperfine couplings to ^{95,97}Mo were $A_{||} = 84$ G and $A_\perp = 40$ G. This spectrum can be attributed to the Mo^I(CO)$_5$OTf species. The ESR spectrum obtained after addition of 3 equiv of TfOAg showed a weak, poorly resolved signal arising from two species, one with $g_{||} = 2.063$ and $g_\perp = 2.095$ and the other with $g_1 = 1.954$, $g_2 = 1.931$, and $g_3 = 1.911$. No satellite lines arising from the Mo isotopes could be resolved. Due to the low intensity of the signals, it was not possible to characterize these species; the signals are apparently associated with very minor byproducts. The IR spectrum of the final species exhibited a similar pattern to that of the tungsten analogue (*vide supra*),[23,24] namely peaks at 1985 (vs), 2005 (sh), and 2080 (w) cm^{-1}.

Reaction of [W(CO)$_5$Cl]$^-$ and [Mo(CO)$_5$Cl]$^-$ with TfOAg in Acetonitrile. We reasoned that increasing the polarity of the solvent would decrease the degree of association between the complex anion and (PPN)$^+$ (*vide supra*). Therefore, acetonitrile, which has a higher relative permittivity ($\epsilon = 35.9$) than DME ($\epsilon = 7.2$),[25] was selected to test this hypothesis.

In MeCN, all of our complexes (**1**–**4**) gave the same electrochemical response, irrespective of the metal center or the quaternary ammonium counterion. In each case, a white precipitate of AgCl was formed on the addition of 1 equiv of TfOAg; a grey precipitate was then produced on addition of the second equivalent. This behavior shows that reaction 1 occurs in preference to 2. The lack of any disporportionation signal suggests that the chemical reaction, which M^I(CO)$_5$OTf undergoes to form the new complex, is much faster in MeCN than in DME.

Catalytic Activity of the M(II) Complexes. In a preliminary communication, we have recently demonstrated that the M(II) species generated on TfOAg oxidation of the tetraalkylammonium complexes are capable of catalyzing allylic substitution.[9] The full scope of this reactivity as well as the catalysis in other reactions, such as carbonyl−ene and Prins reaction and Diels−Alder addition will be reported in due course.[29] By contrast, the M(II) species generated from the PPN complexes (in DME) proved catalytically inert, which shows that the exchange of the Cl$^-$ ligand by TfO$^-$ is essential for catalytic activity.

Conclusion

Electrochemical elucidation of the reaction of chloropentacarbonylmolybdate and chloropentacarbonyltung-

state complexes **1**–**4** with TfOAg revealed that complex redox processes occur, as well as halogen replacement. The M(0) complex is first oxidized to M(I), which then disproportionates to give the more stable M(II) species. In the case of the tetraalkylammonium complexes **1** and **2**, concomitant replacement of Cl$^-$ by TfO$^-$ has been observed. By contrast, the latter reaction is precluded for the PPN complexes **3** and **4**, presumably due to strong association to the counterion. However, this association can be suppressed by using MeCN instead of DME as the solvent, which enables the Cl$^-$ replacement to occur. Some of the M(II) complexes exhibit catalytic activity in allylic substitution[9] and have the promise of becoming a novel, wide-ranging class of Lewis-acidic catalysts in organic chemistry.

Experimental Section

Methods. The reactions between the metal complexes and TfOAg were monitored using cyclic voltammetry on a 1 mm diameter Pt disc electrode. An EG & G model 173 potentiostat and a model 175 wave form generator were used in these studies. Potentials are given with respect to a saturated calomel electrode (SCE). Tetrabutylammonium tetrafluoroborate (Fluka, electrochemistry grade) [TBABF$_4$] (0.1 mol dm^{-3}) was used as an electrolyte in all electrochemical experiments. Acetonitrile (BDH, HPLC grade) and 1,2-dimethoxyethane (Lancaster, 99+%) were used as received. The ESR spectra of frozen solutions of the complexes in DME were recorded at 77 K; g-values were calculated using Mn^{2+} in MgO as an internal standard. The IR spectra were recorded in CH$_2$Cl$_2$. The NMR spectra were recorded for CDCl$_3$ solutions at 25 °C on 250 or 300 MHz instruments. The coupling constants were obtained by first-order analysis. The mass spectra were measured using direct inlet and the lowest temperature enabling evaporation or in a thermospray mode; chemical ionization was used in certain cases (with NH$_4$). GC analysis was carried out using capillary columns (BP10 25 m × 2.65 μm). All reactions were carried out under nitrogen.

Benzyltriethylammonium Chloropentacarbonylmolybdate (1). A mixture of molybdenum hexacarbonyl (1.32 g, 5 mmol) and benzyltriethylammonium chloride (1.14 g, 5 mmol) in dry diglyme (50 mL)[30] was heated at 120 °C for 2 h. After the reaction mixture was cooled, the solution was filtered, and to the filtrate was added petroleum ether (50 mL). The precipitate was isolated by filtration, washed with petroleum ether, and dried in vacuum to give **1** (1.68 g, 72%) as a yellow solid: IR (KBr) ν(C≡O) 1821 (s), 1916 (vs), 2067 (w) cm^{-1}; IR (CH$_2$Cl$_2$) ν(C≡O) 1853 (s), 1926 (vs), 1982 (w), 2061 (w) cm^{-1}; MS (negative FAB) m/z 273 [Mo(CO)$_5$Cl$^-$], 242 [Mo(CO)$_4$Cl$^-$], 217 [Mo(CO)$_3$Cl$^-$]. Anal. Calcd for C$_{18}$H$_{22}$ClMoNO$_5$: C, 46.62; H, 4.78; N, 3.02; Cl, 7.64. Found: C, 46.14; H, 5.08; N, 3.23; Cl, 7.66.

Benzyltriethylammonium Chloropentacarbonyltungstate (2). A mixture of tungsten hexacarbonyl (1.76 g, 5 mmol) and benzyltriethylammonium chloride (1.14 g, 5 mmol) in dry diglyme (50 mL) was heated at 120 °C for 2 h. After the reaction mixture was cooled, the solution was filtered, and to the filtrate was added petroleum ether (50 mL). The precipitate was isolated by filtration, washed with petroleum ether, and dried in vacuum to give **2** (2.06 g, 74%) as a yellow solid: IR (KBr) ν(C≡O) 1820 (s), 1906 (vs), 2066 (w) cm^{-1}; IR (CH$_2$Cl$_2$) ν(C≡O) 1848 (s), 1918 (vs), 1959 (sh), 2060 (w) cm^{-1}. Anal. Calcd for C$_{18}$H$_{22}$ClNO$_5$W: C, 39.19; H, 4.02; N, 2.54; Cl, 6.43. Found: C, 39.08; H, 4.10; N, 2.65; Cl, 6.40.

Bis(triphenylphosphoranylidene)ammonium Chloropentacarbonylmolybdate (3). A mixture of molybdenum

(29) Malkov, A. V.; Ahmed, G.; Steele, J.; Kočovský, P. To be published.

(30) In diglyme, the commercially available (i.e., wet) BnEt$_3$N$^+$Cl$^-$ is suitable. However, if DME is used as the solvent, BnEt$_3$N$^+$Cl$^-$ has to be rigorously dried (in vacuo over P$_2$O$_5$ at room temperature for 2 weeks).

hexacarbonyl (1.32 g, 5 mmol) and bis(triphenylphosphoranylidene)ammonium chloride (2.87 g, 5 mmol) in dry DME (50 mL) was refluxed for 4 h. After the reaction mixture was cooled, the solution was filtered, and to the filtrate was added hexane (50 mL) to give rise to a brown-yellow oil. The solvent was decanted, and a new portion of hexane was added. This procedure was repeated several times until the oil began to crystallize. The yellow solid was then isolated by filtration, washed with hexane, and dried in vacuum to give **3** (2.83 g, 70%): IR (KBr) ν(C≡O) 1850 (s), 1919 (vs), 1977 (w), 2061 (w) cm^{-1}; IR (CH$_2$Cl$_2$) ν(C≡O) 1850 (s), 1925 (vs), 1975 (w), 2062 (w) cm^{-1}, in accordance with the literature.[12]

Bis(triphenylphosphoranylidene)ammonium Chloropentacarbonyltungstate (4). A mixture of tungsten hexacarbonyl (1.76 g, 5 mmol) and bis(triphenylphosphoranylidene)ammonium chloride (2.87 g, 5 mmol) in dry DME (50 mL) was refluxed for 4 h. After the reaction mixture was cooled, the solution was filtered, and to the filtrate was added hexane (50 mL) to give rise to a brown-yellow oil. The solvent was decanted, and a new portion of hexane was added. This procedure was repeated several times until the oil began to crystallize. The yellow solid was then isolated by filtration, washed with hexane, and dried in vacuum to give **4** (3.19 g, 71%): IR (KBr) ν(C≡O) 1855 (s), 1903 (vs), 2050 (w) cm^{-1}; IR (CH$_2$Cl$_2$) ν(C≡O) 1840 (s), 1909 (vs), 1968 (w), 2060 (w) cm^{-1}, in accordance with the literature.[12]

Oxidation of Benzyltriethylammonium Chloropentacarbonyltungstate (2) with Silver(I) Trifluoromethanesulfonate. To a solution of benzyltriethylammonium chloropentacarbonyltungstate (50 mg, 0.09 mmol) in DME or CH$_2$Cl$_2$ (1 mL)[31] was added at room temperature silver(I) triflate (70 mg, 0.27 mmol) in one portion. The reaction mixture turned

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(31) The solvent (i.e., DME or CH$_2$Cl$_2$) does not seem to have an effect on the result. Thus, the same ESR spectra were obtained, regardless of whether the species was generated in DME or CH$_2$Cl$_2$. For the measurement of the IR spectra, only the complex prepared in CH$_2$Cl$_2$ was used.

black, and a precipate formed. After 30 min of stirring, the mixture was filtered through a pad of Celite. The filtrate was subjected to IR measurements: IR ν(C≡O) 1975 (vs), 2010 (sh), 2095 (w) cm^{-1}. ESR spectra are described in the Results and Discussion. Attempted removal of the solvent and redissolving (e.g., in CH$_2$Cl$_2$) led to a considerable decomposition and reduction of the intensity of the IR signals.

Oxidation of PNP Chloropentacarbonyltungstate (4) with Silver(I) Trifluoromethanesulfonate. The oxidation of TfOAg (2 equiv only) was carried out in the same way as that of **2**. The product showed IR ν(C≡O) 1975 (vs), 2010 (sh), 2100 (w) cm^{-1}.

Oxidation of Benzyltriethylammonium Chloropentacarbonylmolybdate (1) with Silver(I) Trifluoromethanesulfonate. This oxidation was carried out as described above for the tungsten analogue. IR ν(C≡O) 1985 (vs), 2005 (sh), 2080 (w) cm^{-1}. ESR spectra are described in the Results and Discussion. Attempted isolation of a solid material was unsuccessful.

Oxidation of PNP Chloropentacarbonylmolybdate (3) with Silver(I) Trifluoromethanesulfonate. The oxidation with TfOAg (2 equiv only) was carried out in the same way as that of **1**. The product showed IR ν(C≡O) 1985 (vs), 2010 (sh) cm^{-1}.

Supporting Information Available: Text giving the experimental details for the reaction of Mo(CO)$_6$ with wet PhCH$_2$(Et)$_3$N$^+$Cl$^-$ (1 page). Ordering information is given on any current masthead page.

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