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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77204-5641

Synthesis of Oxometals from Carbonylmetal Complexes by Oxidative Decarbonylation with Dioxirane

S. Wolowiec and J. K. Kochi*

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The oxidative decarbonylation of the tricarbonylrhenium(I) and -molybdenum(0) complexes $Cp^*Re(CO)_3$ (I, Cp* = pentamethylcyclopentadienide) and $TpMo(CO)_3^-$ (II, Tp = hydridotris(1-pyrazolyl)borate) occurs quantitatively to the corresponding trioxo complexes Cp^*ReO_3 and $TpMoO_3^-$, respectively, simply upon the addition of dimethyldioxirane [$(CH_3)_2CO_2$, DMDO] in anhydrous acetone solutions. In each case, the loss of all three carbonyl ligands can be effected rapidly at <0 °C with the stoichiometric amounts (4 equiv) of DMDO to yield a mixture of CO_2 and CO, concomitant with the formal 6-electron change at the metal centers. The spectral titration of I with DMDO is consistent with the initial separation of CO_2 from $Cp^*Re(CO)_3$, followed by rapid oxygen-atom transfer and dissociation of CO, presumably via transient oxo(carbonyl)rhenium intermediates that are too labile to detect. Although the oxidative decarbonylation of II to $TpMoO_3^-$ [III, (X-ray crystallography: space group, $P2_1/c$ (monoclinic); $a = 9.232$ (2) Å; $b = 12.489$ (2) Å; $c = 20.677$ (5) Å; $\beta = 99.77$ (2)°; $V = 2349$ Å^3; $Z = 4$)] also occurs with equal facility, a pair of noncarbonyl-containing molybdenum(V) intermediates, $(TpMoO_2)_2$ (V) and $(TpMoO_2)_4$ (IV), were successfully isolated. The yellow solid V is the same as the bis(μ-oxo)-bridged binuclear complex $Tp_2Mo_2(O)_2(\mu\text{-}O)_2$, previously characterized by Lincoln and Koch (*Inorg. Chem.* **1986**, *25*, 1594). The black crystal IV is structurally characterized by X-ray crystallography [space group, *Pccn* (orthorhombic); $a = 15.540$ (5) Å; $b = 16.734$ (7) Å; $c = 24.469$ (7) Å; $V = 6363$ Å^3; $Z = 4$] as a unique monocyclic oxomolybdenum(V) tetramer, $Tp_4Mo_4(O)_4(\mu\text{-}O)_4$. The ready isolation of such oxometals underscores the potential utility of dioxiranes as selective yet highly active oxygen-atom donors for the oxidative decarbonylation of metal carbonyls to various types of other oxometallic complexes, particularly in nonaqueous solvents such as acetone.

Introduction

The decarbonylation of various metal carbonyls via the oxidative elimination of carbon dioxide is a useful synthetic strategy that can be effected with oxygen-atom donors [O] such as amine oxides, sulfoxides, iodoxides, etc.[1-8] The rapid subsequent ligation of the resulting metal fragment by a variety of added nucleophiles (L) is tantamount to an overall ligand substitution of the metal carbonyl in eq 2, where L = phosphines, nitriles, amines, sulfides, etc.[9-12]

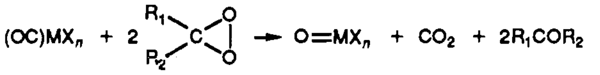
$$(OC)MX_n \xrightarrow{[O]} MX_n + CO_2 \qquad (1)$$

$$MX_n + L \xrightarrow{\text{fast}} LMX_n \qquad (2)$$

More interesting would be the effective interception of the coordinatively unsaturated intermediate by the oxygen-atom donor itself to afford the corresponding oxometal derivative, i.e.[13,14]

$$MX_n \xrightarrow{[O]} O{=}MX_n \qquad (3)$$

which is particularly relevant to a growing interest in a variety of metal-centered oxygen-transfer reactions.[15,16] Such an oxidative conversion of a metal carbonyl to its oxometal derivative corresponds to a formal 4-electron change. As such, it requires an oxygen-atom donor [O] with sufficient activity to selectively effect both of the steps outlined in eqs 1 and 3. Thus, the recent availability of the highly active dioxiranes as terminal oxidants[17-20] is particularly relevant, owing to the potentially clean stoichiometric transfer of an oxygen atom to form the rather innocuous ketone as the byproduct; i.e.



(4)

In particular, the volatile dimethyl analogue ($R_1 = R_2 = CH_3$) allows the excellent solvent properties of acetone to be exploited for oxygen-atom transfer to the metal carbonyl in eq 1 (with [O] = $(CH_3)_2CO_2$) as well as in eq 3 under homogeneous, nonaqueous conditions. As a test case, we have focused in this study on the effect of dimethyldioxirane (DMDO) toward a pair of structurally similar metal tricarbonyls I and II, which presented the possibility of the oxidative decarbonylation of 1, 2, or 3 CO ligands. Thus the efficacy of DMDO as a reagent was initially examined with the rhenium analogue $Cp^*Re(CO)_3$ (I,[21] Cp* = pentamethylcyclopentadienide) which was earlier converted to the full trioxide with hydrogen peroxide in aqueous sulfuric acid and with *tert*-butyl hydroperoxide.[13,22,23] Selectivity in the oxidative decarbonylation of a single ligand in a metal polycarbonyl by DMDO was also examined with the tricarbonylmolybdate $TpMo(CO)_3^-$ (II,[24] Tp = hydridotris(1-pyrazolyl)borate), particularly in an attempt to generate the expectedly metastable oxocarbonylmetal species.

Results

Oxidative Decarbonylation of the Rhenium Carbonyl I. The addition of an anhydrous acetone solution of DMDO (0.05 M) to a pale yellow solution of $Cp^*Re(CO)_3$ (I) (0.01 M in acetone) at 0 °C was accompanied by the copious evolution of gas. Spectral inspection of the reaction mixture indicated the presence of Cp^*ReO_3 in 94% yield, as judged by the presence of the intense absorption band at $\lambda_{max} = 299$ nm ($\epsilon = 5300$ M^{-1} cm^{-1}) together with a weaker, partially resolved band with a shoulder at $\lambda = 400$ nm ($\epsilon = 1000$ M^{-1} cm^{-1}).[13] Removal of the solvent in vacuo followed by crystallization from hexane at 0 °C afforded yellow needles of Cp^*MoO_3 in 74% yield.

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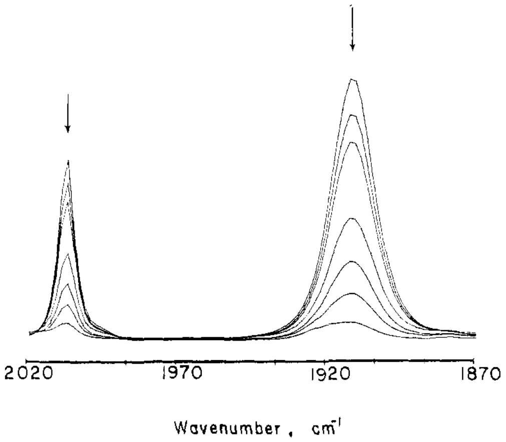

Figure 1. Changes in the IR spectrum of 12 mM Cp*Re(CO)$_3$ in anhydrous acetone (4.1 mL), showing the absorbance decreases of the A$_1$ and E carbonyl bands that follow the (top-to-bottom) addition of 0, 12.6, 25, 52, 63, 84, and 105 μmol 0.042 M DMDO.

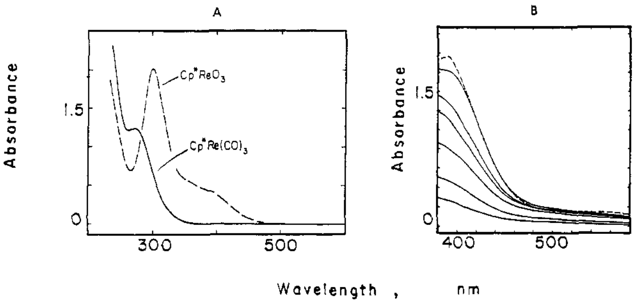

Figure 2. (A) Comparative UV–vis absorption spectra of 4.4 × 10^{-4} M Cp*Re(CO)$_3$ (—) and 3.8 × 10^{-4} M Cp*ReO$_3$ (- -) in dichloromethane from ref 13. (B) Absorbance increase of Cp*ReO$_3$ following the addition to 2.5 × 10^{-3} M Cp*Re(CO)$_3$ of 0.040 DMDO in acetone in increments that correspond to those shown in Figure 3. The dashed spectrum resulted from the addition of more than 4 equiv of DMDO.

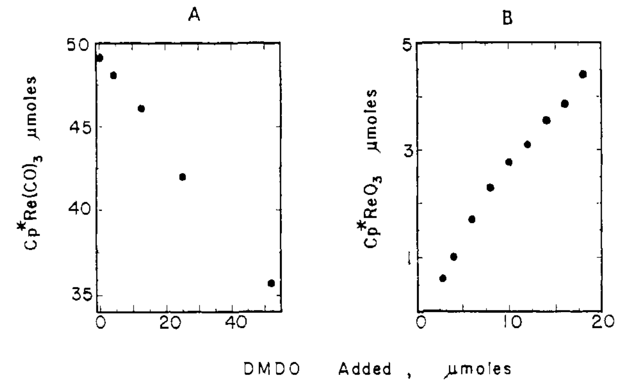

Figure 3. Spectral titration of Cp*Re(CO)$_3$ with DMDO, showing quantitatively (A) the disappearance of the rhenium carbonyl and (B) the appearance of the trioxide by IR and UV–vis spectrophotometry, respectively.

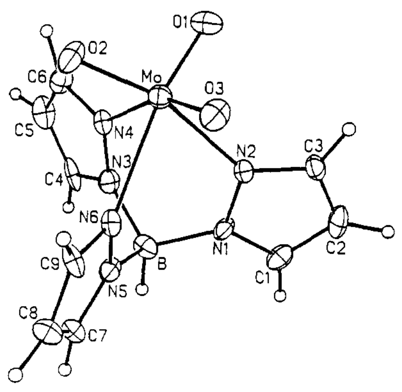

Figure 4. ORTEP diagram of the 6-coordinate TpMoO$_3^-$ (III), showing the *fac*-trioxo ligands staggered relative to the hydridotris(1-pyrazolyl)borate. The thermal ellipsoids are 30% equiprobability envelopes, with hydrogens as arbitrary spheres.

The stoichiometry for the oxidative conversion of I to Cp*ReO$_3$ was established by spectral titration. Thus the disappearance of Cp*Re(CO)$_3$ following the incremental addition of DMDO was monitored by FTIR spectrophotometry of the characteristic carbonyl stretching bands at ν = 1910 and 2005 cm^{-1}.[25] During the spectral titration of Cp*Re(CO)$_3$, no other extraneous bands were observed in the carbonyl stretching region between 1800 and 2000 cm^{-1} (Figure 1). The appearance of Cp*ReO$_3$ following the incremental addition of DMDO to an acetone solution of Cp*Re(CO)$_3$ was monitored by UV-vis spectrophotometry of the diagnostic absorbance at 400 nm (Figure 2).[26] [Note the oxo–rhenium stretching bands at 917 and 877 cm^{-1} could not be employed in the analysis of Cp*ReO$_3$ owing to spectral interference from acetone.]

The monotonic decrease of Cp*Re(CO)$_3$ during the spectral titration with DMDO occurred with a 1:4 stoichiometry, as indicated by the slope in Figure 3A. The same conclusion is derived from the accompanying increase in Cp*ReO$_3$ that is shown in Figure 3B. Accordingly, the stoichiometry for the oxidative decarbonylation is represented as

$$\underset{\text{I}}{\text{Cp*Re(CO)}_3} + 4(\text{CH}_3)_2\text{CO}_2 \rightarrow \text{Cp*ReO}_3 + 4(\text{CH}_3)_2\text{CO} + \text{CO}_2 + 2\text{CO} \quad (5)$$

The liberated gas upon infrared and gas chromatographic analysis indicated a mixture of carbon monoxide and carbon dioxide, the relative amounts of which were highly dependent on the concentration of Cp*Re(CO)$_3$, the rate of DMDO addition, and the temperature (see Experimental Section). The limiting amounts of 1 mol of CO$_2$ and 2 mol CO, as given in eq 5, were obtained upon the very slow addition of 1 equiv of 40 mM DMDO to 2.5 mM Cp*Re(CO)$_3$ at 25 °C. Control experiments established the ready oxidation of carbon monoxide by DMDO quantitatively to CO$_2$ under these reaction conditions.

Oxidative Decarbonylation of the Carbonylmolybdate II. The oxidative decarbonylation of TpMo(CO)$_3^-$ (II) was initially carried out with DMDO (~50% excess, according to the stoichiometry in eq 5) in order to effect the full conversion of all the carbonyl ligands. Thus, the yellow solution of Et$_4$N$^+$TpMo(CO)$_3^-$ in

$$\underset{\text{II}}{\text{TpMo(CO)}_3^-} + 6(\text{CH}_3)_2\text{CO}_2 \rightarrow \underset{\text{III}}{\text{TpMoO}_3^-} + 6(\text{CH}_3)_2\text{CO} + \text{CO/CO}_2 \quad (6)$$

acetone was treated with ~6 equiv of DMDO under an argon atmosphere at 25 °C. Following the rapid evolution of gas, the solution darkened slightly but remained homogeneous. Inspection of the ^{1}H NMR spectrum indicated that TpMo(CO)$_3^-$ was cleanly converted to a single product by the complete replacement of the characteristic triplet resonance at δ 6.06 for H$_4$ of the pyrazolyl moiety by a new triplet resonance shifted upfield to δ 6.12. Concentration of the deep yellow reaction mixture in vacuo, followed by the vapor diffusion of *n*-pentane into the concentrate at 0 °C afforded the pale pink crystals with the molecular formula Et$_4$N$^+$TpMoO$_3^-$ as the dihydrate in 59% yield (see Experimental Section). X-ray crystallography (vide infra) revealed the 6-coordinate molybdate(VI) TpMoO$_3^-$ (III). The ORTEP diagram of TpMoO$_3^-$ in Figure 4 shows the *fac*-trioxo ligands with the IR bands at 897 and 845 cm^{-1} assigned to the trioxo–molybdenum stretching frequencies in a structure with C_{3v} symmetry. The 3,5-dimethyl analogue Tp*MoO$_3^-$ under similar conditions with dimethyldioxirane afforded the trioxo complex Tp*MoO$_3^-$ with

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(25) Herrmann, W. A.; Serrano, R.; Schäfer, A.; Floel, M. *J. Organomet. Chem.* **1985**, *297*, C5. ν(CO): in KBr, 1996 and 1898 cm^{-1}; in acetone solution, 2005 and 1910 cm^{-1}.

(26) See Wallis, J. in ref 13.

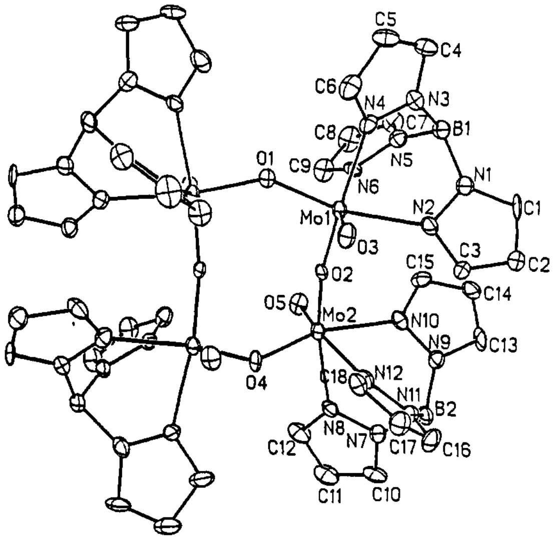

Figure 5. Molecular structure of the black $(\mathrm{TpMoO_2})_4$ (IV), showing the tetrameric (μ-oxo)molybdenum(V) monocyclic framework. The thermal ellipsoids are 20% equiprobability envelopes.

$\nu(\mathrm{O{=}Mo})$ = 924 and 898 cm^{-1} (see Experimental Section).

The oxidative decarbonylation of II was repeated with the stoichiometric 4 equiv of DMDO just required for the transformation to the trioxo complex, by comparison with the rhenium analogue in eq 5. Indeed, the IR spectrum of the reaction mixture following the rapid evolution of gas showed that the characteristic carbonyl stretching bands of $\mathrm{TpMo(CO)_3^-}$ at $\nu(\mathrm{CO})$ = 1890, 1760, and 1743 cm^{-1} were completely gone, but no other carbonyl bands were apparent in the spectral region between 1800 and 2000 cm^{-1}. Inspection of the ^{1}H NMR spectrum revealed the presence of three triplet resonances for $\mathrm{H_4}$ of the pyrazolyl moiety at δ 6.12, 6.20, and 5.83 (all with $J \cong 2.1$ Hz) in a relative intensity ratio of approximately 1:8:1 that was indicative of a mixture of at least three components. The trioxo product III (δ 6.12) was clearly formed as a minor component under these stoichiometric conditions. [When the mixture was treated with additional amounts (2 equiv) of DMDO, it was cleanly converted to a solution containing only $\mathrm{TpMoO_3^-}$, as judged by the presence of a single triplet at δ 6.12 in the characteristic region of the ^{1}H NMR spectrum.] Moreover the concentration of the original reaction mixture in vacuo, followed by the vapor diffusion of pentane into the concentrate at 0 °C, yielded a small amount (~5%) of the colorless crystals of III as the tetraethylammonium salt spectrally identical with that formed in eq 6. Additionally, a highly insoluble black crystal of IV with an elemental analysis consistent with $(\mathrm{TpMoO_2})_n$ was obtained in low yield (see Experimental Section). The subsequent X-ray crystallography established the highly unusual tetrameric molybdenum(V) structure for $(\mathrm{TpMoO_2})_4$ (IV), as illustrated in Figure 5 (vide infra). The residual molybdenum was accounted for as an amorphous yellow solid V, which resisted all further attempts at crystallization. Nonetheless, as the major product (>50% by weight), V was subjected to elemental and spectral analysis (see Experimental Section), and it was shown to be the dimeric analogue of IV, viz., $(\mathrm{TpMoO_2})_2$, by the direct comparison with an authentic sample previously prepared by Lincoln and Koch from molybdenum(V) pentachloride and potassium hydridotris(1-pyrazolyl)borate in aqueous hydrochloric acid.[27] [Thus, the IR spectrum of the yellow solid obtained by Lincoln and Koch (and designated by them as **3** with $\nu(\mathrm{O{=}Mo})$ = 960, 750, and 733 cm^{-1}) compares with $\nu(\mathrm{O{=}Mo})$ = 957, 749, and 733 cm^{-1} for V. This binuclear compound is similar to the yellow (syn) isomer of the structurally related bis(μ-oxo) dication $[(\text{triazacyclononanone})\mathrm{MoO_2}]_2^{2+}$ as well as the red (anti) isomer $\nu(\mathrm{O{=}Mo})$ = 940 cm^{-1}.[28]] Barring the structural transformation of the molybdenum products in the course of the simple isolation procedure described above,[29] we conclude that the oxidative decarbonylation of $\mathrm{TpMo(CO)_3^-}$ with stoichiometric (4 equiv) amounts of DMDO proceeded to a mixture of three products, with none of them retaining a carbonyl ligand; i.e.

$$\underset{\text{II}}{\mathrm{TpMo(CO)_3^-}} + 4(\mathrm{CH_3})_2\mathrm{CO_2} \rightarrow \underset{\text{III}}{\mathrm{TpMoO_3^-}} + \underset{\text{V}}{(\mathrm{TpMoO_2})_2} + \underset{\text{IV}}{(\mathrm{TpMoO_2})_4} \quad (7)$$

Treatment of the 3,5-dimethyl analogue $\mathrm{Tp^*Mo(CO)_3^-}$ under the same conditions afforded a similar mixture of at least four components.

Discussion

The clean transformation of the rhenium carbonyl I in Figure 1 to $\mathrm{Cp^*ReO_3}$ in Figure 2 produced no spectral intermediate of any detectable lifetime. Accordingly, the most economical explanation for the highly efficient production of the trioxide according to eq 5 involves the prior loss of a single carbonyl ligand by oxidative elimination; i.e.

$$\mathrm{Cp^*Re(CO)_3} + (\mathrm{CH_3})_2\mathrm{CO_2} \rightarrow \mathrm{Cp^*Re(CO)_2} + \mathrm{CO_2} + (\mathrm{CH_3})_2\mathrm{CO} \quad (8)$$

The resulting coordinatively unsaturated dicarbonylrhenium intermediate must then be rapidly converted to the trioxide; i.e.

$$\mathrm{Cp^*Re(CO)_2} + 3(\mathrm{CH_3})_2\mathrm{CO_2} \xrightarrow{\text{fast}} \mathrm{Cp^*ReO_3} + 2\mathrm{CO} + 3(\mathrm{CH_3})_2\mathrm{CO} \quad (9)$$

The multiple stoichiometric relationship of the reactants in eq 9 suggests that such a transformation occurs via the labile intermediate(s) capable of dissociative CO loss. [Since dimethyldioxirane is a weak donor, it is unlikely to be a ligand and to be involved in any reaction other than a bimolecular one.] Whether a *transient* oxocarbonylrhenium species is included among these intermediates is not indicated by the results on hand. Furthermore no information is available as to how the three oxo ligands are ultimately incorporated into the rhenium center of I, owing to the rapidity with which several dimethyldioxiranes are apparently able to effect multiple oxygen-atom transfers.

In the oxidative transformation of the molybdenum carbonyl II, the partially oxidized binuclear and tetranuclear molybdenum(V) dioxides V and IV were intermediates in the formation of the molybdate(VI), since the treatment of the reaction mixture with additional DMDO led to a single product III (vide supra). Thus the decarbonylation of $\mathrm{TpMo(CO)_3^-}$ by the active oxygen-atom donor DMDO apparently proceeded much like that observed with the tricarbonylrhenium analogue I, described in eqs 8 and 9. Likewise, if the transformation to the trioxo product proceeded in a stepwise manner, any oxocarbonylmetal intermediate was too unstable to isolate—even under the mild reaction conditions allowed by the highly reactive oxygen-atom donor examined in this study. Nonetheless, the simple experimental procedure for the use of dimethyldioxirane encourages its further use in the oxidative decarbonylation of various metal carbonyls[30] to generate other unusual oxometal complexes, such as III and IV, that are described below.

Molecular Structure of the Trioxomolybdate $\mathrm{TpMoO_3^-}$ (III). The molybdenum complex $\mathrm{TpMoO_3^-}$ (III) (as well as $\mathrm{Cp^*ReO_3}$) is a unique representative of a limited number of known trioxometal complexes (Table I),[31-35] in which the ancillary ligand (Tp

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(27) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594.

(28) Hahn, M.; Wieghardt, K. *Inorg. Chem.* **1984**, *23*, 3977.

(29) For example, it is possible that the $\mathrm{TpMoO_2}$ units undergo polymeric (cyclization) rearrangements in nonpolar solvents. See: Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

(30) (a) $\mathrm{TpRe(CO)_3}$ and $\mathrm{TpMn(CO)_3}$ did not react with excess DMDO at 25 °C or under photolytic (350 < λ < 400 nm) conditions. (b) For a similar difference in the reactivity of $\mathrm{Tp^*Re(CO)_3}$ and $\mathrm{TpMo(CO)_3^-}$, see part c. (c) McCleverty, J. A.; Wolochowicz, I. *J. Organomet. Chem.* **1979**, *169*, 289. (d) Curtis, M. D.; Shiu, K. B. *Inorg. Chem.* **1985**, *24*, 1213.

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(32) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659.

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Table I. Structural Parameters (Average) of *fac*-Trioxometal Complexes

O_3ML	M=O, Å	M—N, Å	∠OMO, deg	ref
O_3ReCp'[a]	1.71		105.0	34
$O_3Re(tan)^+$[b]	1.756 (5)	2.197 (5)	102.7 (4)	35
$O_3Mo(tan)$[b]	c			36
$O_3MoTp^-\cdot 2H_2O$	1.731 (7)	2.335 (8)	105.1	this work
$O_3Mo(dien)$[d]	1.736 (8)	2.324 (9)	106.0 (8)	37
$(O_3Mo)_2EDTA\cdot 8H_2O$[e]	1.740		105.6	38

[a] Cp′ = $EtMe_4C_5$. [b] tan = 1,4,7-triazacyclononanone. [c] Not structurally characterized. [d] dien = diethylenetriamine. [e] EDTA = ethylenediaminetetraacetate.

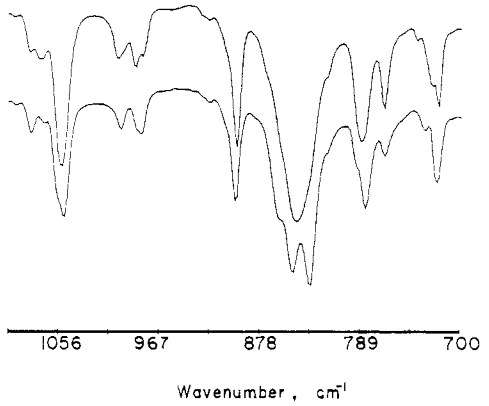

Figure 6. IR spectra of the anhydrous form (upper) and the dihydrate (lower) of $TpMoO_3^-$ (III), showing the splitting of the degenerate E band at ν(O=Mo) = 845 cm^{-1} by the presence of water.

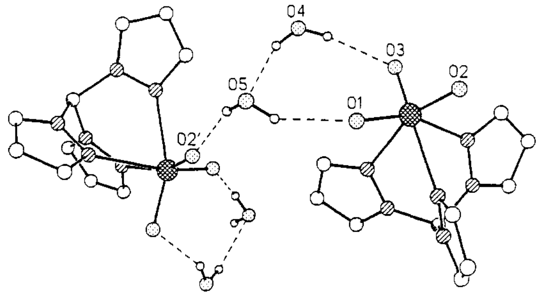

Figure 7. Unsymmetrical hydrogen bonding of water molecules to the oxo ligands of $TpMoO_3^-\cdot 2H_2O$ established by X-ray crystallography.

or Cp*) enforces the *cis*(*fac*)-trioxo configuration. Indeed the IR spectrum of $TpMoO_3^-$ in Figure 6 (upper) shows the pair of oxo-metal stretching bands at 898 and 845 cm^{-1} for the A_1 and E representations, respectively, predicted for ideal C_{3v} symmetry.[36] Such an assignment is confirmed in the IR spectrum shown in Figure 6 (lower) of the dihydrate $TpMoO_3^-\cdot 2H_2O$ by the splitting of the degenerate E band in the slightly asymmetric (from C_{3v} symmetry) MoO_3 unit arising from the hydrogen bonding of two water molecules to the oxo ligands, as established by X-ray crystallography (see Figure 7). The bond distances and bond angles in the MoO_3 moiety of III (Table II) are otherwise the same as those extant in the only other known trioxomolybdenum(VI) complex (dien)MoO_3[34] with a tripod ligand (see Table I).

Molecular Structure of the Tetranuclear $[TpMoO_2]_4$ (IV). X-ray crystallography and elemental analysis of the black crystals IV (isolated as one of the products from the partial oxidation of $TpMo(CO)_3^-$ with 4 equiv of DMDO) have established its tetranuclear structure, as presented as the ORTEP diagram in Figure 5 (Table III). The monocyclic structure consisting of four $TpMoO_2$ units with alternating (μ-oxo)molybdenum bridges has only one other analogy in the tetranuclear (μ-oxo)tungsten cluster

Table II. Selected Bond Distances and Bond Angles for $TpMoO_3^-$ (III)

Bond Lengths, Å			
Mo–O(1)	1.737 (6)	Mo–O(2)	1.725 (6)
Mo–O(3)	1.731 (7)	Mo–N(2)	2.347 (8)
Mo–N(4)	2.306 (8)	Mo–N(6)	2.351 (7)
N(1)–N(2)	1.373 (11)	N(1)–B	1.535 (15)
N(1)–C(1)	1.328 (15)	N(2)–C(3)	1.331 (13)
N(3)–N(4)	1.362 (11)	N(3)–B	1.551 (15)
N(3)–C(4)	1.330 (14)	N(4)–C(6)	1.333 (14)
Bond Angles, deg			
O(1)–Mo–O(2)	105.8 (3)	O(1)–Mo–O(3)	104.8 (3)
O(2)–Mo–O(3)	104.6 (3)	O(1)–Mo–N(2)	84.3 (3)
O(2)–Mo–N(2)	160.5 (3)	O(3)–Mo–N(2)	88.5 (3)
O(1)–Mo–N(4)	89.8 (3)	O(2)–Mo–N(4)	86.9 (3)
O(3)–Mo–N(4)	157.9 (3)	N(2)–Mo–N(4)	76.3 (3)
O(1)–Mo–N(6)	156.8 (3)	O(2)–Mo–N(6)	90.6 (3)
O(3)–Mo–N(6)	86.3 (3)	N(2)–Mo–N(6)	75.5 (3)
N(4)–Mo–N(6)	74.5 (3)	N(2)–N(1)–B	120.1 (8)
N(2)–N(1)–C(1)	109.0 (8)	B–N(1)–C(1)	130.9 (9)
Mo–N(2)–N(1)	124.7 (6)	Mo–N(2)–C(3)	128.5 (7)

Table III. Selected Bond Distances and Bond Angles for $(TpMoO_2)_4$ (IV)

Bond Lengths, Å			
Mo(1)–O(1)	1.909 (3)	Mo(1)–O(2)	1.870 (7)
Mo(1)–O(3)	1.674 (7)	Mo(1)–N(2)	2.237 (9)
Mo(1)–N(4)	2.223 (9)	Mo(1)–N(6)	2.327 (9)
Mo(2)–O(2)	1.862 (7)	Mo(2)–O(4)	1.905 (3)
Mo(2)–O(5)	1.665 (7)	Mo(2)–N(8)	2.226 (9)
Mo(2)–N(10)	2.207 (8)	Mo(2)–N(12)	2.318 (9)
N(1)–N(2)	1.368 (12)	N(1)–B(1)	1.560 (17)
N(1)–C(1)	1.345 (14)	N(2)–C(3)	1.350 (14)
N(3)–N(4)	1.364 (13)	N(3)–B(1)	1.540 (17)
N(3)–C(4)	1.353 (15)	N(4)–C(6)	1.317 (15)
Bond Angles, deg			
O(1)–Mo(1)–O(2)	94.2 (3)	O(1)–Mo(1)–O(3)	107.5 (2)
O(2)–Mo(1)–O(3)	103.6 (4)	O(1)–Mo(1)–N(2)	161.5 (3)
O(2)–Mo(1)–N(2)	91.1 (3)	O(3)–Mo(1)–N(2)	88.5 (3)
O(1)–Mo(1)–N(4)	86.5 (3)	O(2)–Mo(1)–N(4)	162.5 (3)
O(3)–Mo(1)–N(4)	92.8 (4)	N(2)–Mo(1)–N(4)	83.3 (3)
O(1)–Mo(1)–N(6)	84.0 (3)	O(2)–Mo(1)–N(6)	85.8 (3)
O(3)–Mo(1)–N(6)	164.2 (3)	N(2)–Mo(1)–N(6)	78.6 (3)
N(4)–Mo(1)–N(6)	76.8 (3)	O(2)–Mo(2)–O(4)	94.7 (3)
O(2)–Mo(2)–O(5)	102.3 (3)	O(4)–Mo(2)–O(5)	107.0 (2)
O(2)–Mo(2)–N(8)	162.9 (3)	O(4)–Mo(2)–N(8)	86.1 (4)
O(5)–Mo(2)–N(8)	93.8 (3)	O(2)–Mo(2)–N(10)	91.1 (3)
O(4)–Mo(2)–N(10)	160.6 (3)	O(5)–Mo(2)–N(10)	89.8 (3)
N(8)–Mo(2)–N(10)	83.0 (3)	O(2)–Mo(2)–N(12)	86.1 (3)
O(4)–Mo(2)–N(12)	84.9 (2)	O(5)–Mo(2)–N(12)	164.6 (3)
N(8)–Mo(2)–N(12)	76.9 (3)	N(10)–Mo(2)–N(12)	77.0 (3)
Mo(1)–O(1)–Mo(1′)	144.3 (5)	Mo(1)–O(2)–Mo(2)	169.8 (4)
Mo(2)–O(4)–Mo(2′)	144.1 (6)	N(2)–N(1)–B(1)	119.4 (9)
N(2)–N(1)–C(1)	107.3 (9)	B(1)–N(1)–C(1)	133.2 (10)
Mo(1)–N(2)–N(1)	123.4 (7)	Mo(1)–N(2)–C(3)	130.0 (7)

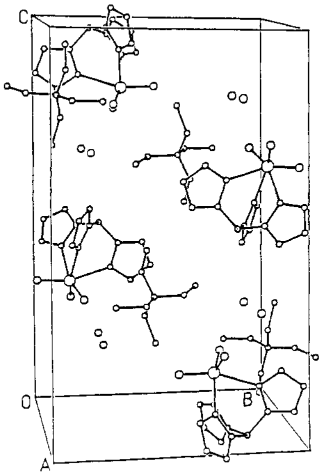

Figure 8. Packing diagram of the unit cell of $TpMoO_3^-$ (III), showing the oxygen-atom location of the waters of hydration.

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(35) Park, J. J.; Glick, M. D.; Hoard, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 301.

(36) See, e.g.: Braterman, P. S. *Metal Carbonyl Spectra*; Academic: New York, 1975; p 44 ff.

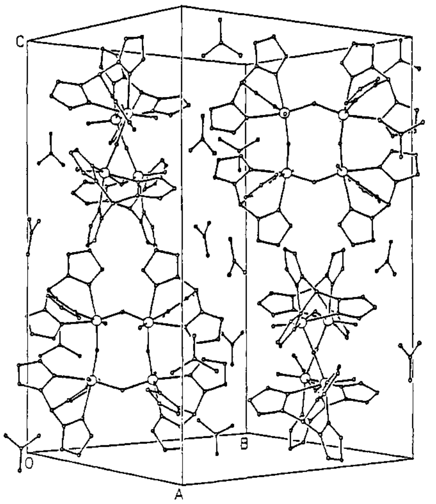

Figure 9. Packing diagram of the unit cell of the tetranuclear cluster $(TpMoO_2)_4$ (IV), each associated with three acetone solvates.

$[(H_2O)Cl_2WO_2]_4^{2-}$, previously obtained from the addition of tungstate to an aqueous 10 M HCl solution of tungsten(V).[37] Structurally, this dianion, like IV, consisted of an eight-membered (μ-oxo)metallacycle with alternating syn/anti terminal oxo ligands. Unlike the mixed-valence W^V/W^{VI} cluster, however, each of the constituent MoO_2 moieties in IV contains identical dioxomolybdenum(V) units. Since the electronic coupling among the individual (paramagnetic) molybdenum(V) centers is likely to be attenuated somewhat by the μ-oxo bridges, the ground state of IV should be readily accessible from several closely spaced energy levels. Indeed, the highly unusual black color of IV may be a manifestation of the multiple low-energy electronic transitions associated with this near degeneracy. [The spectral characterization of IV is as yet incomplete owing to its extreme insolubility in various solvents (see Experimental Section). The synthesis of more tractable derivatives is in progress.] Be that as it may, the tetranuclear oxomolybdenum(V) monocycle IV is alone[38] among the various oxomolybdenum(V) clusters[39] that have been heretofore characterized crystallographically in connections with their possible relevance to molybdenum catalysis of organic oxidation.[15,16] Thus Lincoln and Koch[27] have suggested that the tetranuclear molybdenum(V,VI) mixed-valence cluster $Mo_4Cl_4(\mu\text{-}O)_2(\mu_3\text{-}O)_2(O)_4(OEt)_4^{2-}$ that has been crystallographically characterized[40] is actually the tetranuclear molybdenum(V) cluster consisting of two parts of ethoxide and ethanol ligands. We hope that the synthesis of more soluble analogues of IV will provide an opportunity to examine the redox properties of these unique tetranuclear oxomolybdenum clusters.

Experimental Section

Materials. Cp*Re(CO)$_3$ was prepared from the treatment of rhenium pentacarbonyl bromide (Pressure Chemical Co.) with lithium permethylcyclopentadienide[21] and oxidized to CP*ReO$_3$ according to the procedure described by Hermann and co-workers.[22] TpRe(CO)$_3$ and TpMn(CO)$_3$ were obtained from the substitution of rhenium and manganese pentacarbonyl bromides with potassium hydridotris(1-pyrazolyl)borate (K^+Tp^-; Alfa).[24,30c] $Et_4N^+TpMo(CO)_3^-$ was prepared from molybdenum hexacarbonyl and K^+Tp^-, according to the general method described by Trofimenko.[24] The 3,5-dimethyl derivative $Tp^*Mo(CO)_3^-$ was synthesized from the same procedure with $Mo(CO)_6$ and potassium hydridotris[(3,5-dimethyl-1-pyrazolyl)borate] or (K^+Tp^{*-}).[24] Dimethyldioxirane (DMDO) was prepared as a ~0.05 M acetone solution by the method of Murray and Jeyaraman,[41] dried with anhydrous $MgSO_4$, and transferred from flask to flask in vacuo prior to use. The concentration of DMDO was determined iodometrically[42] and checked (±2%) by gas chromatographic analysis of triphenylphosphine oxide formed from the quantitative oxidation of triphenylphosphine.[41] On the basis of these analyses, the extinction coefficient at λ = 335 nm was calculated to be ϵ = 13.9 M^{-1} cm^{-1}.

Instrumentation. IR spectra were recorded on a Nicolet 10DX FT spectrometer in KBr pellets for solid complexes and NaCl cells for solutions. The ^1H NMR spectra were obtained on a JEOL FX 90Q FT spectrometer, and the chemical shifts are reported relative to TMS. Gas chromatographic analysis of the gaseous mixture was carried out on a GOW-MAC model 550 gas chromatograph equipped with thermal conductivity detectors and standardized with known mixtures of CO and CO_2. The 2-ft column was packed with 5-Å molecular sieves (60–80 mesh) and operated isothermally at 250 °C. The UV–vis spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer.

Oxidation of Cp*Re(CO)$_3$ with Dimethyldioxirane. To a chilled solution of CP*Re(CO)$_3$ (80 mg, 0.20 mmol) in 20 mL of anhydrous acetone at 0 °C was added dropwise 25 mL of a 0.05 M DMDO solution (1.25 mmol). The immediate gas evolution was accompanied by a slight darkening of the pale yellow solution. The reaction mixture was concentrated to ~3 mL by solvent removal in vacuo, and 15 mL of hexane was added. Yellow needles (54 mg, 74%) of Cp*ReO$_3$ were obtained upon cooling to 0 °C for 3 h. IR (KBr): ν(O=Re) = 913 and 878 cm^{-1}.

The spectral titration of a 2.47 mM solution of Cp*Re(CO)$_3$ in acetone (2 mL) was carried out at 25 °C by the incremental addition of 0.040 M DMDO in anhydrous acetone. The formation of Cp*ReO$_3$ was measured by the absorbance change at λ = 400 nm (ϵ = 1000 M^{-1} cm^{-1}). The 1:4 stoichiometry was applicable up to 18 μmol of added DMDO, but further addition of the oxidant caused a broad new absorption band centered at λ = 560 nm to appear. Similarly, a solution of Cp*Re(CO)$_3$ (19.9 mg, 49 μmol) in 4 mL of anhydrous acetone (containing dichloromethane as an internal standard) was incrementally treated with 0.042 M DMDO. The simultaneous diminution of the pair of carbonyl stretching bands Cp*Re(CO)$_3$ is shown in Figure 1. For the quantitative analysis of the gaseous mixture, the oxidation of Cp*Re(CO)$_3$ was carried out under an atmosphere of helium for the gas chromatography of CO and CO_2 on a molecular sieve column (thermal conductivity detection) with retention times of 1 and 6 min, respectively. In a typical set of reactions, a 0.040 M solution of DMDO was added to Cp*Re(CO)$_3$ dissolved in 1.0 mL of acetone at 25 and 0 °C yielded CO/CO_2 ratios as follows for the respective micromolar amounts of DMDO and Cp*Re(CO)$_3$: 148, 25, 1:4, 1:10; 196, 49, ..., 1:10; 98, 49, 1:1, ...; 49, 49, 2:1, 1:1.

Oxidation of TpMo(CO)$_3^-$ with Dimethyldioxirane. A yellow solution of $Et_4N^+TpMo(CO)_3^-$ (100 mg, 0.19 mmol) in 15 mL of degassed acetone was treated at 25 °C with 25 mL of 0.05 M DMDO (1.25 mmol) by a slow transfer with the aid of a Teflon cannula under an argon atmosphere. The immediate gas evolution was accompanied by the color change of the solution to golden yellow (15 min). Solvent removal from the homogeneous solution in vacuo left a residual solid showing no IR bands at ν(CO) = 1890, 1760, and 1743 cm^{-1} (KBr) of II. Recrystallization from a mixture of pentane/dichloromethane afforded colorless crystals of $Et_4N^+TpMoO_3^-$ in 59% yield. Alternatively, the recrystallization of II from acetone by vapor diffusion of pentane afforded pale pink crystals of the dihydrate of quality suitable for X-ray crystallography (vide infra). Anal. Calcd for $C_{17}H_{34}N_7O_5BMo$: C, 39.02; H, 6.55; N, 18.73. Found:[43] C, 39.03; H, 6.57; N, 18.73. ^1H NMR ($CHCl_3$): δ 8.15 (3 H, d, J = 1.6 Hz), 7.51 (3 H, d, J = 2.2 Hz), 6.12 (3 H, dd, J = ~2 Hz), 3.08 (8 H, q, J = 7.2 Hz), 1.07 (12 H, t, J = 7.2 Hz). IR (KBr): 898 (m), 847 (s), and 832 (s) cm^{-1}. [For anhydrous II, IR(KBr): 897 (m, sh), 845 (s, br) cm^{-1}.]

The oxidation of $Et_4N^+Tp(CO)_3^-$ (102 mg, 0.25 mmol) at 25 °C with 20 mL of 0.05 M DMDO (1.0 mmol) yielded a clear yellow-brown solution. The partial removal of the solvent in vacuo to a volume of 5 mL was followed by the vapor diffusion of *n*-pentane at 0 °C for 12 h to yield colorless crystals of III (~10 mg) and black crystals of IV (~15 mg) on the walls of the flask, together with the yellow solid V (~40 mg) as the major product. ^1H NMR ($CDCl_3$) of V: δ 7.92 (1 H, br s), 7.75 (1 H, d), 6.20 (1 H, br s) with no Et_4N^+ resonances. Anal. Calcd for $C_9H_{10}N_6BMoO_2$: C, 31.70; H, 2.96; N, 24.65. Found:[43] C, 31.47; H, 3.29; N, 24.32. IR (KBr): 957, 749, and 733 cm^{-1} (unique to V). Anal. Calcd for $(TpMoO_2)_4$ (the black crystals IV) as the trisacetonate,

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(37) Jeannin, Y.; Launay, J.-P.; Livage, J.; Nel, A. *Inorg. Chem.* **1978**, *17*, 374.

(38) For various types of other molybdenum(V) oligomers and clusters, see ref 27 and: Darensbourg, D. J.; Gray, R. L.; Delord, T. *Inorg. Chim. Acta* **1985**, *98*, L39.

(39) Including the mixed-valence Mo^V/Mo^{VI} clusters such as those reported by: Beaver, J. A.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1973**, 1376. Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C.; Leonelli, J.; Folting, K. *J. Am. Chem. Soc.* **1981**, *103*, 6093.

(40) Belicchi, M. F.; Fava, G. G.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* **1983**, 65.

(41) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

(42) Adam, W.; Chan, Y. Y.; Cremer, D.; Gauss, J.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800.

(43) Atlantic Microlab, Inc., Atlanta, GA.

Table IV. X-ray Crystallographic Data for $TpMoO_3^-$ (III) and $(TpMoO_2)_4$ (IV)

space group	$P2_1/c$ (monoclinic)	*Pccn* (orthorhombic)
cell constants		
a, Å	9.232 (2)	15.540 (5)
b, Å	12.489 (2)	16.734 (7)
c, Å	20.677 (5)	24.469 (7)
β, deg	99.77 (2)	
V, Å^3	2349	6363
molec formula	$C_8H_{20}N^+C_9H_{10}N_6O_3BMo^-\cdot 2H_2O$	$[C_9H_{10}N_6O_2BMo]_4\cdot 3C_3H_6O$
fw	523.33	1538.27
Z	4	4
density, g cm^{-3}	1.48	1.61
abs coeff, cm^{-1}	5.83	8.21
coll range, deg	$4 \leq 2\theta \leq 42$	$4 \leq 2\theta \leq 45$
independent data, $I > 3\sigma(I)$	1831	2343
R	0.054	0.049
R_w	0.052	0.042

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $TpMoO_3^-$ (III)

	x	*y*	*z*	*U* (eq)[a]
Mo	8590 (1)	8611 (1)	6749 (1)	31 (1)
O(1)	10130 (7)	8431 (6)	7350 (3)	44 (3)
O(2)	8307 (8)	9975 (5)	6694 (4)	46 (3)
O(3)	7140 (8)	8129 (5)	7097 (3)	44 (3)
O(4)	8025 (9)	7266 (8)	8380 (4)	66 (4)
O(5)	11231 (13)	7151 (7)	8485 (4)	71 (4)
N(1)	9072 (9)	6509 (7)	5820 (3)	34 (3)
N(2)	9060 (9)	6847 (7)	6451 (4)	30 (3)
N(3)	10136 (9)	8186 (6)	5440 (4)	32 (3)
N(4)	10093 (9)	8817 (7)	5974 (4)	31 (3)
N(5)	7445 (10)	7867 (6)	5201 (4)	34 (3)
N(6)	7059 (9)	8362 (6)	5730 (4)	31 (3)
N(7)	4479 (9)	5571 (7)	6744 (4)	40 (3)
B	8922 (14)	7326 (10)	5259 (6)	33 (5)
C(1)	9240 (11)	5453 (9)	5820 (6)	41 (5)
C(2)	9321 (12)	5093 (9)	6443 (6)	48 (5)
C(3)	9206 (11)	5973 (9)	6825 (5)	33 (4)
C(4)	11121 (11)	8561 (11)	5097 (5)	44 (4)
C(5)	11762 (13)	9444 (10)	5422 (6)	49 (5)
C(6)	11098 (11)	9577 (9)	5954 (5)	37 (4)
C(7)	6386 (13)	7953 (8)	4690 (5)	39 (4)
C(8)	5230 (12)	8494 (10)	4880 (5)	45 (4)
C(9)	5713 (12)	8729 (9)	5534 (5)	43 (4)
C(10)	5070 (12)	6003 (9)	6167 (5)	49 (5)
C(11)	4073 (15)	5907 (11)	5521 (5)	75 (6)
C(12)	3002 (13)	6060 (10)	6799 (6)	61 (6)
C(13)	3027 (13)	7269 (12)	6818 (6)	79 (7)
C(14)	5609 (11)	5810 (9)	7345 (5)	43 (4)
C(15)	5202 (12)	5435 (10)	7994 (5)	52 (5)
C(16)	4268 (16)	4363 (10)	6690 (6)	65 (6)
C(17)	5519 (17)	3716 (11)	6596 (6)	90 (7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(TpMoO_2)_4$ (IV)

	x	*y*	*z*	*U*(eq)[a]
Mo(1)	2038 (1)	1502 (1)	1778 (1)	36 (1)
Mo(2)	1425 (1)	2080 (1)	3192 (1)	37 (1)
O(1)	2500	2500	1539 (4)	45 (2)
O(2)	1802 (4)	1866 (4)	2485 (3)	38 (2)
O(3)	2866 (4)	875 (4)	1867 (3)	58 (2)
O(4)	2500	2500	3432 (4)	50 (2)
O(5)	770 (4)	2855 (4)	3098 (3)	58 (2)
N(1)	532 (6)	256 (6)	1515 (4)	50 (2)
N(2)	1147 (5)	465 (5)	1888 (4)	48 (2)
N(3)	1193 (6)	856 (5)	676 (4)	55 (2)
N(4)	1911 (6)	1196 (5)	898 (4)	47 (2)
N(5)	133 (6)	1646 (5)	1211 (4)	48 (2)
N(6)	724 (5)	2069 (6)	1539 (3)	47 (2)
N(7)	747 (6)	1282 (6)	4293 (4)	53 (2)
N(8)	1101 (5)	1961 (6)	4075 (3)	46 (2)
N(9)	135 (6)	651 (6)	3448 (4)	53 (2)
N(10)	327 (5)	1258 (5)	3091 (4)	48 (2)
N(11)	1601 (6)	285 (6)	3752 (4)	48 (2)
N(12)	2007 (6)	849 (5)	3422 (3)	43 (2)
B(1)	359 (9)	812 (10)	1015 (6)	56 (3)
B(2)	698 (9)	491 (9)	3957 (6)	54 (3)
C(1)	194 (7)	−444 (7)	1678 (5)	63 (2)
C(2)	592 (8)	−700 (8)	2145 (5)	65 (3)
C(3)	1171 (7)	−137 (7)	2255 (5)	54 (2)
C(4)	1361 (10)	666 (8)	149 (5)	72 (3)
C(5)	2188 (9)	873 (8)	45 (5)	76 (3)
C(6)	2506 (8)	1200 (7)	515 (5)	66 (3)
C(7)	−550 (7)	2131 (8)	1134 (5)	64 (3)
C(8)	−408 (8)	2826 (8)	1384 (6)	75 (3)
C(9)	400 (7)	2781 (7)	1657 (5)	61 (2)
C(10)	509 (8)	1435 (9)	4820 (5)	68 (3)
C(11)	715 (9)	2214 (9)	4934 (5)	82 (3)
C(12)	1095 (8)	2516 (9)	4452 (5)	71 (3)
C(13)	−634 (7)	310 (7)	3276 (6)	65 (2)
C(14)	−910 (8)	676 (8)	2825 (5)	67 (3)
C(15)	−295 (7)	1255 (8)	2720 (5)	58 (2)
C(16)	2120 (8)	−330 (7)	3833 (5)	68 (3)
C(17)	2859 (8)	−191 (7)	3560 (5)	67 (3)
C(18)	2779 (7)	550 (7)	3305 (5)	59 (2)
C(19)	2878 (9)	6396 (8)	321 (6)	112 (4)
C(20)	2153	6095	647	112 (4)
C(21)	3711	6574	578	112 (4)
O(9)	2786	6503	−181	112 (4)
C(22)	7329 (39)	2315 (34)	2471 (21)	130 (1)
C(23)	7628	3032	2181	130 (1)
C(24)	7032	1609	2168	130 (1)
O(10)	7328	2306	2982	130 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$C_{45}H_{58}N_{24}O_{11}B_4Mo_4$: C, 35.14; H, 3.80; N, 21.85. Found:[43] C, 34.81; H, 4.03; N, 21.71. IR (Kbr): 951, 768, and 745 cm^{-1}. The powder of IV was EPR silent at room temperature, and it was insoluble in acetone, dichloromethane, chloroform, toluene, THF, ether, DMSO, acetonitrile, nitromethane, and water. In addition, a small amount (<5 mg) of bright blue crystals VI was found among the products III, IV, and V. The IR spectrum of VI [ν(O=Mo) = 965, 783 (sh), 773 (sh), and 764 (s) cm^{-1}] suggested an oligomeric oxo(μ-oxo)molybdenum structure related to IV and V, but further attempts to obtain single crystals suitable for X-ray crystallography were unsuccessful.

The rather insoluble 3,5-dimethyl analogue $Et_4N^+Tp^*Mo(CO)_3^-$ (116 mg, 0.19 mmol) was suspended in 10 mL of acetone and treated with 25 mL of 0.054 M DMDO as described above. ^{1}H NMR analysis of the reaction mixture indicated the presence of a single product by the singlet resonance of H_4 at δ 5.66 and the pair of methyl groups at δ 2.83 and 2.26. Isolation of the pale yellow residue following the removal of acetone in vacuo indicated the complete conversion to the trioxo complex $Tp^*MoO_3^-$ with ν(O=Mo) = 924 and 898 cm^{-1} similar to that of $TpMoO_3^-$. Furthermore the oxidation of $Tp^*Mo(CO)_3^-$ (as either the Et_4N^+ or more soluble Bu_4N^+ salt) with 4 equiv of DMDO at 25 °C afforded a complex mixture (similar to that obtained with $TpMo(CO)_3^-$), as indicated by the four singlet H_4 resonances at δ 5.83, 5.40, 4.62, and 4.26 in relative intensity ratios of ~50, 5, 15, and 30%, respectively.

The treatment of $TpRe(CO)_3$ with excess DMDO under various conditions (including actinic radiation with a blue filter for 350 < λ < 400 nm) led to no gas evolution, and it was recovered intact, as shown by the inspection of the IR spectrum with ν(CO) = 2016 and 1885 cm^{-1}. The manganese analogue $TpMn(CO)_3$ with ν(CO) = 2024 and 1912 cm^{-1} was similarly unreactive at 25 °C.

X-ray Crystallography of $TpMoO_3^-$ (III) and $(TpMoO_2)_4$ (IV). The crystallographic measurements were carried out on a Nicolet R3m/V automatic diffractometer, with the Mo Kα radiation monochromatized by a highly ordered graphite crystal. The space groups in Table IV were determined unambiguously from the systematic absences noted. Intensities were measured by using the ω-scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Only the unique data were collected ($^1/_4$ sphere for III and $^1/_8$ sphere for IV), at ambient temperature (17 °C). Two standard reflections were monitored after every 2 h or every 100 data collected. These showed no significant variation in III, but a 15% decay over the course of the experiment were found in IV that necessitated the application of a normalizing factor as a function of X-ray exposure time. During the data reduction, Lorentz and polarization corrections were applied; however, no corrections for absorption were made due to the small absorption coefficients. Convergence of the refinement was reached at a maximum shift/esd ratio of 0.1 for III and 0.3 for IV. No unusually high correlations were noted between any of the variables in the last cycles of full-matrix least-squares fitting. All calculations were made by using Nicolet's SHELXTL (1987) series of crystallographic programs. The pertinent crystallographic data for III and IV are summarized in Table IV, and the final atomic coordinates are listed in Tables V and VI, respectively.

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Supplementary Material Available: For $[Et_4N][TpMoO_3]\cdot 3H_2O$ (III) and $(TpMoO_2)_4\cdot 2H_2O$ (IV), tables of anisotropic displacement parameters, bond lengths and angles, H atom coordinates, and isotropic displacement parameters (7 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

Synthesis and Structure of Seven-Coordinate Rhenium(III) Mixed Halo–Phosphine Isocyanide Complexes

Steve Warner,[1a] Linda K. Cheatham,[1b] Thomas H. Tulip,[1b] Ian D. Williams,[1a] and Stephen J. Lippard*,[1a]

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The synthesis of mixed halo–phosphine isocyanide complexes of general formula $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ is described. The crystal structure of a representative member of this class, $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2](SbF_6)$ (**1**), has been determined. This complex adopts the C_{2v} capped trigonal prismatic geometry with close nonbonded contacts of 2.341 (8) and 2.330 (9) Å between coordinated isocyanide carbon atoms. Such distances in seven-coordinate compounds reveal that they are good candidates for reductive coupling of the isocyanide ligands, a reaction previously studied for **1**. The syntheses of $[ReCl_3(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2]$ and $[ReCl_3(CN\text{-}2,6\text{-}Me_2Ph)_3(PMePh_2)]$ are also reported. Red crystals of $[Re(O)(OEt)Cl_2(PMePh_2)_2]$ (**2**) were isolated in 25% yield as a side product during the preparation of $[ReCl_3(PMePh_2)_3]$ starting material from $AgReO_4$. The identity of **2** was established by IR spectroscopy, elemental analysis, and X-ray crystallography. The Re–O bond distance of 1.699 (5) Å is characteristic of a metal–oxygen triple bond. Crystal data: for **1**, a = 10.486 (2) Å, b = 13.201 (2) Å, c = 17.559 (2) Å, α = 76.21 (1)°, β = 89.73 (1)°, γ = 87.05 (1)°, triclinic, $P\bar{1}$ (C_i^1; Z = 2); for **2**, a = 11.015 (1) Å, b = 12.745 (1) Å, c = 21.035 (3) Å, β = 105.19 (1)°, monoclinic, $P2_1/n$ (C_{2h}^5; Z = 4).

Introduction

Our interest in seven-coordinate early-transition-metal isocyanide complexes stems from their propensity to undergo reductive coupling to form coordinated bis(alkylamino)acetylenes (eq 1).[2,3] Mechanistic studies, currently in progress, indicate that

$$[M(CNR)_6X]^+ \xrightarrow[H^+]{Zn(s)} [M(RHNC{\equiv}CNHR)(CNR)_4X]^+ \quad (1)$$

$$M = Mo, W$$

this reaction proceeds by a sequence of steps involving reduction to $[M(CNR)_6]$ followed by protonation to form an aminocarbyne species and, ultimately, the coupled product (eq 2).[4] A parallel

$$[M(CNR)_6X]^+ \xrightarrow[-X^-]{Zn(s)} [M(CNR)_6] \xrightarrow{H^+} [M{\equiv}CNHR(CNR)_5]^+ \xrightarrow{HX} [M(RHNC{\equiv}CNHR)(CNR)_4X]^+ \quad (2)$$

series of reactions occurs in the reductive coupling of CO ligands in $[M(CO)_2(dmpe)_2X]$ (M = Nb, Ta; dmpe = 1,2-bis(dimethylphosphino)ethane; X = halide)[3,5] to afford disiloxyacetylene complexes and, in the case of mixed CO/CNR coupling, to form $[M(R_3SiOC{\equiv}CN(SiR_3)R')(dmpe)_2Cl]$ (M = Nb, Ta; R, R′ = alkyl groups).[6]

The present study was undertaken as part of a systematic investigation to extend the scope of the reductive coupling chemistry to group VII metals. Previously we showed that, with $[M(CNR)_6X]^{2+}$ cations (M = Tc, Re, R = *t*-Bu, Me, and X = Br; M = Tc, R = *t*-Bu, and X = Cl), these conditions afford only $[M(CNR)_6]^+$ by reductive elimination, analogous to the first step in eq 2.[7] Since mechanistic studies revealed that increasing the electron density at the metal center favors the reductive coupling reaction,[8] the more electron-rich complexes $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ were examined.[9] Here we report a general synthetic route to cations in this class, the crystal structure of one member, $[ReCl_2(CN\text{-}t\text{-}Bu)_3(PMePh_2)_2]SbF_6$, and the preparation and structure of $[ReCl_2(O)(OEt)(PMePh_2)_2]$, a side product formed during the synthesis of the $[ReCl_3(PMePh_2)_3]$ starting material.

Experimental Section

Materials and Methods. $AgReO_4$ (Alfa), diphenylmethylphosphine (Strem), $KSbF_6$ (Strem), and 37% hydrochloric acid (Mallinckrodt) were obtained from commercial sources and used as received. $[ReCl_3(PMePh_2)_3]$[10] and $[ReCl_2I(PMePh_2)_3]$[11] were prepared by literature procedures. Dichloromethane was predried over calcium chloride and then distilled from calcium hydride under nitrogen, or it was purified by

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(1) (a) Massachusetts Institute of Technology. (b) E. I. Du Pont de Nemours & Co.

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