tube at 20 °C for 1 h. For conversion to the perchlorate salt, a 1.0-g sample of the dried crude product was dissolved in 2 mL of 0.1 N HCl, 2 mL of methanol was added, 60% $HClO_4$ was added dropwise to the point of incipient precipitation, and the solution was cooled to 0 °C. The yellow product (with a slight orange tint due to $[Cr(en)_2(NH_3)_3H_2O](ClO_4)_3)$ was filtered off, washed with methanol and then with ether, and air-dried (yield 1.0 g, ca. 90%). The crude perchlorate salt was purified by fractional recrystallization. Spectral data are given in Table I. Anal. Calcd for $[Cr(en)(NH_3)_4](ClO_4)_3 \cdot H_2O$: Cr, 10.47; C, 4.84; H, 4.66; N, 16.92. Found: Cr, 10.8; C, 5.0; H, 4.5; N, 17.0.

***cis*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$.** *cis*-$[Cr(en)_2Cl_2]ClO_4$, prepared as described by Rollinson and Bailar,[8] was reacted with ammonia (ca. 2 mL/g of starting material) at 20 °C for 2 h. The crude $[Cr(en)_2(NH_3)_2]Cl_2ClO_4$ product was >97% cis as based on the UV–visible spectrum. For replacement of the chloride counterion and for recrystallization, a 3-g sample was dissolved in 0.01 N HCl (12 mL) at 30 °C and the solution was filtered. Then 4 mL of 60% $HClO_4$ was added to the filtrate followed by methanol added dropwise until a small amount of precipitate was formed. The solution was again filtered to remove any trans product and then cooled to 0 °C to give fraction 1. This was filtered off, washed with a small amount of methanol followed by ether, and dried in vacuo. Fraction 2 was obtained in the same manner subsequent to the further addition of two volumes of methanol to the filtrate. Chromium determinations on fractions 1 and 2 indicated counterion purity had not been achieved (expected value 10.3% for the triperchlorate salt; found 12.6 and 12.0%, respectively) by the single recrystallization. About three or four similar recrystallizations were necessary to give analytically pure triperchlorate. Spectral data are given in Table I.

Anal. Calcd for $[Cr(en)_2(NH_3)_2](ClO_4)_3$: Cr, 10.30; C, 9.54; H, 4.39; N, 16.65. Found: Cr, 10.4; C, 9.7; H, 4.3; N, 16.5.

***trans*-$[Cr(en)_2(NH_3)_2](ClO_4)_3 \cdot H_2O$.** *trans*-$[Cr(en)_2(NH_3)Cl](ClO_4)_3$, prepared as described earlier,[5] except that the thermal anation was accomplished by heating at 70 °C for 24 h, was reacted with liquid ammonia (ca. 1 g to 1 mL) at 20 °C for 1 h in a sealed Carius tube. The crude material was a mixture of *cis-/trans-*$[Cr(en)_2(NH_3)_2]Cl(ClO_4)_2$, approximately 2:1 based on the UV–visible spectrum.

The trans isomer was isolated by fractional recrystallization. The crude mixture (1 g) was dissolved in 2 mL of 0.1 N HCl, and 0.5 mL of 60% $HClO_4$ was added. The solution was cooled to −5 °C to initiate crystallization and the pale yellow precipitate filtered off, washed with 2 mL of methanol followed by ether, and air-dried. The yield of crude *trans*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$ was 0.11 g. The filtrate could be treated with methanol (20 mL) to recover most (ca. 0.70 g) of the remaining complex(es).

In a subsequent fractional recrystallization, crystals of the crude trans material were used to seed the solution. The crude trans product was recrystallized by dissolving in warm (30 °C) 0.1 N HCl (ca. 6 mL/g), adding 60% $HClO_4$ (ca. 1 mL/g), and cooling to 0 °C. The yellow platelets were filtered, washed with 5 mL of ice-cold 2 M $HClO_4$, 50/50 methanol/ether, and ether, and air-dried. The yield was about 0.75 g/g of the crude product. Spectral data are given in Table I.

Anal. Calcd for $[Cr(en)_2(NH_3)_2](ClO_4)_3 \cdot H_2O$: Cr, 9.95; C, 9.19; H, 4.63; N, 15.92. Found: Cr, 10.1; C, 9.4; H, 4.6; N, 15.9.

The water of crystallization could be removed by heating the sample at 50 °C for 1 h.

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Registry No. $[Cr(en)(NH_3)_4](ClO_4)_3$, 65982-67-4; *cis*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$, 66008-06-8; *trans*-$[Cr(en)_2(NH_3)_2](ClO_4)_3$, 65982-65-2; $[Cr(en)(NH_3)_3(H_2O)]Br_3$, 65982-73-2; $[Cr(en)(NH_3)(H_2O)Cl_2]Cl$, 16702-52-6; $[Cr(en)(NH_3)_3Br]Br_2$, 65982-72-1; *cis*-$[Cr(en)_2Cl_2]ClO_4$, 15654-71-4; *trans*-$[Cr(en)_2(NH_3)Cl](ClO_4)_2$, 58437-87-9.

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Contribution from the Department of Chemistry,
Princeton University, Princeton, New Jersey 08540

In Search of Metal–Metal Metathesis in the Chemistry of Compounds Containing Metal-to-Metal Triple Bonds between Molybdenum and Tungsten Atoms

M. H. Chisholm,* M. W. Extine, R. L. Kelly, W. C. Mills, C. A. Murillo, L. A. Rankel, and W. W. Reichert

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The occurrence of transition-metal complexes containing metal-to-metal multiple bonds is now well documented.[1] Scores of such compounds have been structurally characterized and several have been subjected to detailed spectroscopic examination. Recently X_α–SW calculations have been carried out on compounds containing M–M bonds of order 3[2] and 4[3-5] and the results have been correlated with the observed spectroscopic data. Despite the emergence of a basic understanding of the electronic structure of these compounds little is known about (i) the mechanisms of their formation and (ii) the relationships that exist between the formation/existence of dinuclear compounds with M–M multiple bonds and cluster or polynuclear compounds of the same empirical formula.

We have sought to gain insight into some of these mystiques by looking for the formation of heterodinuclear compounds containing M–M′ multiple bonds. We report here some findings relating to compounds containing triple bonds between molybdenum and tungsten atoms.

Results and Discussion

M_2L_6 Compounds (M = Mo, W; L = R (alkyl), NR_2). Recent work has established a structurally related series of compounds of general formula M_2L_6, where M = Mo and W and L = R (β-elimination-stabilized alkyl),[6,7] NR_2[8,9] and OR.[10,11] The alkyls and dialkylamides are formed in metathetic reactions represented by eq 1–4; the alkoxides are formed by alcoholysis reactions involving the dialkylamides.

The nature of these reactions (eq 1–4) is clearly complex. It has been suggested[15] that the dinuclear compounds might arise from the coupling of two reactive mononuclear species, eq 5.

$$\mathrm{WCl_6 + 6Me_3SiCH_2MgBr \rightarrow W_2(CH_2SiMe_3)_6} \qquad \text{(1a)}^{6,7}$$

$$\mathrm{WCl_4 + 4Me_3SiCH_2Li \rightarrow W_2(CSiMe_3)_2(CH_2SiMe_3)_4} \qquad \text{(1b)}^{7,12}$$

$$\mathrm{MoCl_5 + 5Me_3SiCH_2Li \rightarrow Mo_2(CH_2SiMe_3)_6 + Mo(CHSiMe_3)(CH_2SiMe_3)_3 + Mo(CSiMe_3)(CH_2SiMe_3)_3} \qquad \text{(2)}^{7,13}$$

$$\mathrm{WCl_6 + 6LiNMe_2 \rightarrow W_2(NMe_2)_6 + W(NMe_2)_6} \qquad \text{(3a)}^{9}$$

$$\mathrm{WCl_4 + 4LiNMe_2 \rightarrow W_2(NMe_2)_6} \qquad \text{(3b)}^{9}$$

$$\mathrm{WCl_6 + 6LiNEt_2 \rightarrow W_2(NEt_2)_6 + W(NEt_2)_2(NEt)_2} \qquad \text{(3c)}^{9,14}$$

$$\mathrm{MoCl_5 + 5LiNMe_2 \rightarrow Mo_2(NMe_2)_6 + Mo(NMe_2)_4} \qquad \text{(4a)}^{8}$$

$$\mathrm{MoCl_3 + 3LiNMe_2 \rightarrow Mo_2(NMe_2)_6} \qquad \text{(4b)}^{8}$$

$$\mathrm{2ML_3 \rightarrow L_3M{\equiv}ML_3} \qquad (5)$$

In an attempt to ascertain whether (5) might be operative we reacted a finely divided mixture of WCl_6 and $MoCl_5$ with $LiNMe_2$ and analyzed the crystalline dimethylamides obtained from this reaction by mass spectroscopy. No heterodinuclear ion $MoW(NMe_2)_6^+$ was observed nor were any other MoW dinuclear ions detected.[16] (The mass spectrum was a superimposition of those obtained for the pure compounds $Mo_2(NMe_2)_6$, $W_2(NMe_2)_6$, and $W(NMe_2)_6$.) This observation by no means rules out a coupling reaction, reaction 5, but it does indicate that neither the microscopic reverse of (5) (involving M≡M bond rupture) nor a reversible association reaction, eq 6, is operative.

$$\begin{aligned} &\mathrm{Mo_2(NMe_2)_6 + W_2(NMe_2)_6 \rightleftarrows Mo_2W_2(NMe_2)_{12}} \\ &\mathrm{Mo_2W_2(NMe_2)_{12} \rightleftarrows 2MoW(NMe_2)_6} \end{aligned} \qquad (6)$$

Further support of this conclusion is seen in the following. In two separate experiments equimolar amounts of $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$ were dissolved in toluene and placed in sealed tubes. One tube was heated to 80 °C for 24 h; the other was exposed to UV irradiation at 25 °C for 24 h. The tubes were then opened, the solvent was stripped off, and the solids were analyzed by mass spectroscopy. No MoW-containing ions were observed. (The mass spectrum was merely a superimposition of those obtained for the pure compounds $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$.)

It could be argued that formation of $MoW(NMe_2)_6$, either by the microscopic reverse of (5) or by an associative process such as (6), was not favored due to thermodynamic factors. Consequently, we set out to make $MoW(NMe_2)_6$. We reacted $Mo(CO)_6$ (1 equiv) with WCl_6 (2 equiv) and obtained a halide of empirical composition MoW_2Cl_{12} (the analogous reaction $W(CO)_6$ (1 equiv) + WCl_6 (2 equiv) yields WCl_4[17]). The mixed-metal halide was then reacted with $LiNMe_2$ and the crystalline dimethylamides obtained were analyzed by mass spectroscopy. Ions corresponding to $Mo_2(NMe_2)_6^+$, $MoW(NMe_2)_6^+$, and $W_2(NMe_2)_6^+$ were detected in the approximate intensity ratio 1:2:2, respectively. Although this ratio of intensities need have no correlation with the thermodynamic equilibrium of the species present, it does show that M–M′ metathesis reactions involving either the microscopic reverse of eq 5 or associative reactions of the type 6 are not kinetically facile.

This conclusion is further supported by our observation that when $W_2(NMe_2)_6$ and the perdeuterio compound $W_2(NMe_2)_6$-d_{36} were allowed to react both thermally and photochemically, only $W_2(NMe_2)_6^+$ and $W_2(NMe_2)_6$-d_{36}^+ ions were detected. No ions corresponding to ligand exchange, i.e., $W_2(NMe_2)_x(N(CD_3)_2)_{6-x}$, were detected.

In similar experiments $Mo_2(CH_2SiMe_3)_6$ and $W_2(CH_2SiMe_3)_6$ were mixed together in toluene. Neither heating to 80 °C nor exposure to UV irradiation for 24 h led to formation of $MoW(CH_2SiMe_3)_6$, or, at least, no ion corresponding to $MoW(CH_2SiMe_3)_6^+$ was found in the mass spectrum of the resulting solids. However, a considerable degree of decomposition occurred in these reactions since the tungsten compound is thermally and photochemically sensitive. The decomposition products were not characterized.

$Cp_2M_2(CO)_4$ Compounds (M = Mo and W). On the basis of short M–M distances and attainment by the metal atoms of an 18-valence shell of electrons, the compounds $Cp_2M_2(CO)_4$, where M = Mo or W, may be considered to have M–M triple bonds.[18] These compounds have been shown to add acetylenes,[18,19] allenes,[20,21] and other unsaturated[22] molecules, un, to form adducts $Cp_2M_2(CO)_4$(un), in which the unsaturated group adds across the M–M bond. Evidence has been presented to support the view that this addition involves the direct interaction of the dinuclear compound and the unsaturated organic substrate; mononuclear species are not involved in adduct formation.[21] It seemed plausible that these compounds ($Cp_2M_2(CO)_4$) might be capable of showing M–M metathesis reactions by a reversible associative reaction sequence akin to that shown in eq 6.

In separate experiments $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ were allowed to react in toluene for 24 h (i) at room temperature, (ii) at 80 °C, and (iii) at 20 °C in the presence of UV irradiation. Subsequently, the solvent was stripped and the resulting solids were analyzed by mass spectroscopy. The room temperature reaction gave rise to ions derived from the respective homodinuclear species. However, in both the thermal reaction at 80 °C and photochemical reaction heterodinuclear ions derived from $Cp_2MoW(CO)_4$ were observed in the mass spectra.

In these reactions M–M metathesis could occur as a result of either an associative or dissociative process. However, a CO-catalyzed mechanism could also be operative. See eq 7.

$$\mathrm{Cp_2M_2(CO)_6 \rightleftarrows 2CpM(CO)_3} \qquad \text{(7a)}$$

$$\mathrm{Cp_2M_2(CO)_6 \rightleftarrows Cp_2M_2(CO)_4 + 2CO} \qquad \text{(7b)}$$

It is difficult to remove all traces of $Cp_2M_2(CO)_6$ compounds from solutions of the dinuclear tetracarbonyls because (i) equilibrium 7b lies well to the left and (ii) thermal or photochemical decomposition of $Cp_2M_2(CO)_4$ compounds liberates CO.

Conclusions

M–M metathesis reactions may be used as mechanistic probes in the chemistry of compounds containing M–M multiple bonds. (1) $M_2(NMe_2)_6$ compounds (M = Mo, W) are not formed by the coupling of two reactive mononuclear species, $M(NMe_2)_3$. (2) $M_2(NMe_2)_6$ compounds (M = Mo, W) are not labile toward M–M bond cleavage or associative reactions which lead to M–M metathesis. (3) $Cp_2M_2(CO)_4$ compounds (M = Mo, W) readily undergo M–M′ metathesis in solution at 80 °C or at 25 °C in the presence of UV irradiation. The mechanism leading to metathesis remains to be established.

Experimental Section

General procedures have been described previously.[8]

$Mo_2(NMe_2)_6$,[8] $W_2(NMe_2)_6$,[9] $W_2(NMe_2)_6$-d_{36},[9] $Mo_2(CH_2SiMe_3)_6$,[6] $W_2(CH_2SiMe_3)_6$,[7] $Cp_2Mo_2(CO)_4$,[18] and $Cp_2W_2(CO)_4$[23] were prepared according to methods described in the literature.

Mass spectra were obtained from an AEI MS9 mass spectrometer by the method of direct insertion (90–120 °C).

$Cp_2Mo_2(CO)_4$ + $Cp_2W_2(CO)_4$. (a) At Room Temperature. $Cp_2Mo_2(CO)_4$ (0.3 g) and $Cp_2W_2(CO)_4$ (0.4 g) were dissolved in toluene (2 mL) in a round-bottomed flask (100 mL) under an atmosphere of dry and oxygen-free nitrogen. This solution was stirred magnetically for 12 h. The solvent was then stripped off and the solids were analyzed by mass spectroscopy. No MoW-containing ions were observed. The spectrum was merely a superimposition of those obtained for $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$.

(b) At 25 °C, 12 h. $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ were dissolved in toluene as in (a) above. The solution was then kept at ca. room temperature (25 °C) by rapid air cooling while UV irradiation from a GE 275-W sunlamp was directed at the flask for 12 h. The solids obtained after stripping the solvent were analyzed by mass spectroscopy. MoW-containing ions were present, in particular $Cp_2MoW(CO)_4^+$ and Cp_2MoW^+. The relative intensities of Mo_2^+-, MoW^+-, and W_2^+-containing ions were ca. 1:2:1.

(c) At 120 °C, 12 h. $Cp_2Mo_2(CO)_4$ and $Cp_2W_2(CO)_4$ were dissolved in *m*-xylene (20 mL) as in (a) above. The solution was heated in an oil bath and maintained at ca. 120 °C (reflux) for 24 h. The solid obtained after stripping the solvent was analyzed by mass spectroscopy. The mass spectrum was virtually identical with that obtained in (b) above.

$Mo_2(NMe_2)_6$ + $W_2(NMe_2)_6$; $W_2(NMe_2)_6$ + $W_2(NMe_2)_6$-d_{36}. Equimolar quantities of the appropriate dimethylamides were dissolved in toluene as above and either heated to 80 °C in an oil bath or maintained at ca. room temperature and exposed to UV irradiation for 12 h. The solids obtained after stripping the solvent were analyzed by mass spectroscopy. The spectra corresponded to a superimposition of the spectra obtained for $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$. No MoW-containing ions were observed.

$Mo_2(CH_2SiMe_3)_6$ + $W_2(CH_2SiMe_3)_6$. Equimolar quantities of $Mo_2(CH_2SiMe_3)_6$ and $W_2(CH_2SiMe_3)_6$ were dissolved in toluene and reacted thermally and photochemically as above. No MoW-containing ions were detected in the mass spectrum of the resulting solids.

Preparation of the Tungsten–Molybdenum Chloride of Empirical Formula "MoW_2Cl_{12}". WCl_6 (28.03 g, 70.68 mmol) was added to $Mo(CO)_6$ (9.33 g, 35.34 mmol) in a 500-mL flask. A reaction appeared to take place between the two solids and on addition of chlorobenzene (50 mL) a vigorous, but smooth, reaction occurred with gas evolution. After 12 h, a brown solid had formed and the reaction mixture was then refluxed for a further 3 h. Removal of solvent gave 29.15 g of a black solid (92.8% yield based on "MoW_2Cl_{12}"), which did not show any evidence of residual CO ligands in the infrared spectrum. The product was used without further purification and is assigned the empirical formula "MoW_2Cl_{12}" based on the following analytical data. Anal. Calcd: Mo, 10.79; W, 41.36; Cl, 47.85. Found: Mo, 10.91; W, 41.09; Cl, 46.58.

Reaction of "MoW_2Cl_{12}" with $LiNMe_2$. $LiNMe_2$ was generated by the addition of $HNMe_2$(142.1 mmol) to BuLi (142.1 mmol) in hexane (62 mL) at −80 °C. The reaction mixture was allowed to warm to room temperature and then diethyl ether (100 mL) was added to give a slurry of white $LiNMe_2$. The slurry was then cooled to 0 °C and "MoW_2Cl_{12}" (10.53 g, 11.84 mmol) added over a period of 30 min, after which time the reaction was allowed to warm to room temperature. After stirring for 24 h, the yellow-brown solution was filtered from the gray precipitate of lithium chloride and the solvent removed under vacuum. The residue was then dissolved in boiling hexane (100 mL) and filtered and the solvent removed from the filtrate to give a dark brown solid.

Vacuum sublimation (10^{-2} mmHg) of the brown residue gave a trace of the purple compound $Mo(NMe_2)_4$ at 50 °C, and at 100–120 °C an orange solid sublimed (1.18 g). The mass spectrum of the orange solid showed in addition to ions derived from $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$, several ions attributable to MoW-containing species, most notably $MoW(NMe_2)_6^+$.

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Registry No. $Cp_2Mo_2(CO)_4$, 56200-27-2; $Cp_2W_2(CO)_4$, 62853-03-6; $Mo_2(NMe_2)_6$, 51956-20-8; $W_2(NMe_2)_6$, 54935-70-5; $W_2(NMe_2)_6$-d_{36}, 60475-04-9; $Mo_2(CH_2SiMe_3)_6$, 34439-17-3; $W_2(CH_2SiMe_3)_6$, 36643-37-5; WCl_6, 13283-01-7; $Mo(CO)_6$, 13939-06-5; $LiNMe_2$, 3585-33-9; $Cp_2MoW(CO)_4$, 65995-85-9; MoW_2Cl_{12}, 66102-07-6; $MoW(NMe_2)_6$, 65995-84-8.

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Contribution from the Department of Chemistry and Geology,
Clemson University, Clemson, South Carolina 29631

Bidentate Chelate Compounds. 2. Peroxobis(2,2′-bipyridylamine)cobalt(III) Perchlorate: a Novel Monomeric Cobalt(III) Peroxide Complex[1]

W. Leo Johnson III and John F. Geldard*

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The ability of 2,2′-bipyridylamine (HL) to coordinate to transition-metal ions has been extensively investigated.[2-4] A diversity of metal ions has been used (nickel(II),[5] cobalt(II),[3] iron(II),[6] copper(II),[7] palladium(II),[8] rhodium(III), iridium(III)[9]) and studied by various techniques (x-ray structures,[10-12] ESR and single-crystal polarized spectra,[13] Mössbauer spectra,[14] far-IR spectra[15]). To date, however, no cobalt(III) complexes of this ligand have been reported.

In conjunction with our interest in the circular dichroism of chiral molecules of various symmetries, we undertook the preparation and resolution of the tris(2,2′-bipyridylamine)cobalt(III) ion, $Co(HL)_3^{3+}$. It has been reported[3] that the obvious precursor, $Co(HL)_3^{2+}$ ion, is degraded by good competing ligands, such as halide ions, and that its attempted oxidation with any of H_2O_2, Cl_2, Br_2, $Pb(OAc)_4$, or $KMnO_4$ does not yield $Co(HL)_3^{3+}$ ion.[16]

We now report that the oxidation of $Co(HL)_3^{2+}$ ion with H_2O_2 does indeed degrade the ion, but with the formation of the title compound, apparently a unique monomeric peroxocobalt(III) complex.

Experimental Section

All analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Diffuse-reflectance spectra were measured with a Cary 14 recording spectrophotometer, modified with a Varian Model 1411 diffuse-reflectance accessory. Infrared spectra were measured with Perkin-Elmer 137 Infracord and 621 spectrophotometers. A Faraday balance was used to determine the magnetic moments of the complexes. The reagents $Co(ClO_4)_2 \cdot 6H_2O$ and $NaClO_4 \cdot H_2O$ were obtained from the G. Frederick Smith Co.; reagent grade H_2O_2 (30%) was obtained from Fisher Scientific Co. The ligand 2,2′-bipyridylamine (Aldrich Chemical Co.) was recrystallized from ethanol before use.