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Higher Oxidation State Molybdenum η^3-Allyl Complexes. Synthesis, Characterization, and Reactivity

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Halogen oxidation of $CpMo(CO)_2(\eta^3$-2-R-allyl) complexes (R = chloro, bromo, and methyl) provides an approach to generating molybdenum(IV) compounds containing η^3-allyl ligands. Bromine oxidation of $CpMo(CO)_2(\eta^3$-2-R-allyl) yields surprisingly stable $CpMo(CO)(Br)_2(\eta^3$-allyl) complexes. Organometallic complexes which have the combination of such soft ligands as a η^5-C_5H_5 group, an η^3-allyl group, and carbon monoxide bound to a metal center of oxidation state IV are rarely encountered. The crystal and molecular structures of $CpMo(CO)Br_2(\eta^3$-2-bromoallyl) were determined by X-ray crystallographic analysis. The compound crystallizes with a half molecule of methylene chloride per molybdenum complex in the monoclinic space group $P2_1/n$ with $a = 6.903$ (2) Å, $b = 8.307$ (2) Å, $c = 24.307$ (4) Å, $\beta = 95.82$ (2)°, and $V = 1386.7$ (9) Å^3. Anisotropic refinement of the molybdenum, bromine, and chlorine atoms without the inclusion of hydrogen atoms converged to the residuals $R_1 = 0.064$ and $R_2 = 0.074$. Reduction of $CpMo(CO)Br_2(\eta^3$-2-methallyl) provides a route to the unsaturated $CpMo(CO)(\eta^3$-2-methallyl) intermediate and a nonphotochemical synthesis of phosphine-substituted derivatives, such as $CpMo(CO)(PPh_3)(\eta^3$-2-methallyl).

Introduction

The chemistry of halogen oxidation of organometallic molybdenum complexes has been actively studied in the last two decades, but most of the reactions carried out previously were involved with the oxidation of molybdenum(0) complexes to molybdenum(II) complexes.[1-4] The oxidation of Mo(II) complexes with halogen has neither been studied extensively nor intensively.[5] We have examined the reactions of $CpMo(CO)_2(\eta^3$-2-R-allyl) (R = Cl, Br, Me, and H) with chlorine, bromine, and iodine. Formally eight-coordinate complexes $CpMo(CO)Br_2(\eta^3$-2-R-allyl) with R = Cl, Br, and Me have been isolated in reasonable yields from reactions of $CpMo(CO)_2L$ with bromine. They are believed to be the first examples of the [Mo(terdentate)(bidentate)(monodentate)$_3$] stereochemistry.[6]

Additions of nucleophiles to $[CpMo(CO)_2(\eta^4\text{-diene})]^+$ systems to yield substituted $CpMo(CO)_2(\eta^3$-allyl) complexes have proven to be of value in stereo-controlled organic syntheses.[7,8] Indeed, Pearson et al.[8] have already demonstrated that iodine could serve as a general decomplexation reagent for $CpMo(CO)_2(\eta^3$-allyl) complexes. The details of the mechanism for the iodolactonization which occurs upon the decomplexation of some complexes are not fully understood, and the studies described here may, by inference, shed light on that potentially important synthetic reaction. For example, the reaction with bromine indicates that the path of the reaction is not only dependent on the oxidation potential of the reagent but on the steric character of the allyl substituents. Molybdenum(IV) organometallic chemistry has only been studied on a few occasions owing to the limited number of complexes.[1,5,9-11] Whereas a fairly large number of η^5-cyclopentadienyl complexes with metals in relatively high oxidation state are known, compounds which have an η^3-allyl group and carbon monoxide coordinated to a high oxidation state metal are especially rare.

Experimental Section

All operations involving the handling of organometallic complexes in solution were carried out under an atmosphere of nitrogen by using standard inert-atmosphere techniques. Dichloromethane and acetonitrile were distilled from CaH_2 under nitrogen before use. However, undistilled solvents have also provided acceptable results.

IR spectra were obtained with a Nicolet 5SX FTIR instrument. NMR spectra were recorded with Bruker spectrometers operating at 250 and 500 MHz, as well as a JEOL FX-90Q 90-MHz spectrometer. The chemical shifts were reported as parts per million downfield from Me_4Si by using solvent peaks as references.

The $[CpMo(CO)Br_2(\eta^3$-2-R-allyl)] and $[CpMo(CO)Br(CH_3CN)(\eta^3$-2-R-allyl)]$^+$ complexes are stable under nitrogen for several days at room temperature and a month or more at −10 °C. Consistent analyses of neutral dibromides were obtained only when samples were shipped to a local laboratory in dry ice and the analyses performed within several days after the synthesis. The acetonitrile substituted cations are considerably more stable thermally. The analyses were performed by Baron Consulting in Milford, Connecticut and Atlantic Microlabs in Atlanta, GA.

Preparation of $[CpMo(CO)Br_2(\eta^3$-2-chloroallyl)] (1). The $[CpMo(CO)_2(\eta^3$-2-chloroallyl)] complex (500 mg, 1.7 mmol) was dissolved in 5 mL of freshly distilled dichloromethane, and 1.7 mL of 1 M solution of bromine in dichloromethane was added dropwise to the resulting solution over a period of 5 min. A gas was evolved, and a small amount of orange precipitate appeared. After an additional 5 min of stirring, the supernatant was poured into 30 mL of pentane. The precipitate that formed was washed with 30 mL of anhydrous diethyl ether. After removal of ether, the orange-red powder was dried in vacuo overnight at room temperature to yield 396 mg (55%) of $[CpMo(CO)Br_2(\eta^3$-2-chloroallyl)] (1). The NMR spectrum indicates that this precipitate does not contain appreciable amounts of CH_2Cl_2. Recrystallization from a mixture of diethyl ether and dichloromethane gave dark red crystals, 1′, which crystallized with a half molecule of methylene chloride per molecule of 1 and were used for an X-ray crystal structure determination. When this com-

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[9] Daniello M. J., Jr.; and Barefield, E. K. *J. Organomet. Chem.* **1976**, *76*, C50 [Cp_2MH_2].

[10] Ephritikhine, M.; Green, M. L. H.; MacKenzie R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619 [$Cp_2M(\eta^1$-allyl)$_2$].

[11] Copper, N. J.; Green, M. L. H.; and MacKenzie, S. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1557 [$Cp_2WH(Me)$].

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pound crystallizes slowly, it has a half molecule of methylene chloride per molybdenum in the monoclinic space group $P2_1/n$ with a = 6.888 (1) Å, b = 8.273 (2) Å, c = 24.276 (4) Å, β = 95.78 (2)°, and V = 1376.3 (9) Å^3. This structure was refined without making an absorption correction to R = 10.2 with anisotropic Mo and Br atoms. As it was clear that it had essentially the same structure as **2′**, the refinement was not carried further.

Compound **1** was characterized as follows: ^{1}H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 5.80 (s, HCp, 5 H), 4.86 (dd, 1 H, J = 0.7, 2.9 Hz), 4.61 (dd, 1 H, J = 4.0, 6.2 Hz), 4.42 (d, 1 H, J = 6.2 Hz), 3.64 (dd, 1 H, J = 2.8, 4.0 Hz); IR (CH_2Cl_2, ν_{CO}) 2044 cm^{-1}. Anal. Calcd for $C_9H_9MoOBr_2Cl$: C, 25.47; H, 2.14. Found: C, 25.79; H, 2.14.

A low intensity CH_2Cl_2 signal at δ 5.28 was observed, indicating the presence of a very small quantity of **1′**. The presence of a minor conformer (11%) was indicated by a Cp resonance at δ 5.78 and analogous multiplets ranging from 3.7 to 4.6 ppm [δ 4.69 (dd, 1 H obscured), 4.57 (d, 1 H, J = 2.9 Hz), 3.72 (d, 1 H, J = 6.2 Hz), 3.73 (dd, 1 H, J = 2.9, 4.0 Hz)]. In addition, a very small singlet at δ 6.65 indicated that there was still slight contamination by $CpMo(CO)_2Br_3$ in the sample. The orange material which had precipitated in the reaction mixture was identified as $CpMo(CO)_2Br_3$ by its IR (ν_{CO}, CH_2Cl_2) of 2095 and 2061 cm^{-1} and NMR spectra (δ 6.65). The ^{1}H NMR spectrum of the recrystallized material **1′** showed the expected 5:1 intensity ratio of the Cp to CH_2Cl_2 resonances.

Preparation of [CpMo(CO)Br$_2$(η^3-2-bromoallyl)] (2). The procedure followed that employed for its chloro analogue. Using 500 mg (1.5 mmol) of [CpMo(CO)$_2$(η^3-2-bromoallyl)] and 1.5 mL of 1 M solution of bromine in CH_2Cl_2 gave 408 mg (59%) of [CpMo(CO)Br$_2$(η^3-2-bromoallyl)] (**2**), characterized by the following: ^{1}H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 6.65 (s, CpH, $CpMo(CO)_2Br_3$), 5.80 (s, CpH, 5 H), 5.05 (dd, 1 H, J = 1.1, 3.0 Hz), 4.55 (dd, 1 H, J = 3.9, 6.5 Hz), 4.39 (ddd, 1 H, J = 6.5, 0.6, 1.1 Hz), 3.69 (ddd, 1 H, J = 0.6, 3.0, 3.9 Hz); IR (ν_{CO}, CH_2Cl_2) 2044 cm^{-1}. Anal. Calcd for $C_9H_9MoOBr_3$: C, 23.05; H, 1.93. Found: C, 23.35; H, 1.91. Recrystallization of **2** from methylene chloride and diethyl ether gave [CpMo(CO)Br$_2$(η^3-2-bromoallyl)]·$^1/_2$CH$_2$Cl$_2$ (**2′**) which was subjected to X-ray crystallographic analysis (vide infra). The ^{1}H NMR of **2′** showed the same resonance positions as in **2** with the addition of a resonance at δ 5.28 for the methylene chloride in a ratio of 1:5 to the Cp resonance at δ 5.80.

Preparation of [CpMo(CO)Br$_2$(η^3-2-methallyl)] (3). The synthesis of this compound followed that for the chloro analogue. But the yield of this reaction was 85%, which was much better than its halogen-containing counterparts, and $CpMo(CO)_2Br_3$ did not precipitate and could only be detected as a minor impurity in the NMR spectrum. Compound **3** is characterized by the following: ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) δ 5.08 (s, CpH, 5 H), 4.49 (s, 1 H), 4.18 (d, 1 H, J = 3.9 Hz), 4.15 (dd, 1 H, J = 3.0, 3.9 Hz), 3.06 (d, 1 H, J = 3.0 Hz), 2.31 (s, 3 H); IR (ν_{CO}, CH_2Cl_2) 2023 cm^{-1}. Anal. Calcd for $C_{10}H_{12}MoOBr_2$: C, 29.73; H, 2.99. Found C, 29.68; H, 3.10.

Preparation of [CpMo(CO)(CH$_3$CN)Br(η^3-2-chloroallyl)]PF$_6$ (4). Complex **1**, CpMo(CO)Br$_2$(η^3-2-chloroallyl) (276 mg, 0.65 mmol), was dissolved in 5 mL of acetonitrile, and 165 mg (0.65 mmol) of $AgPF_6$ was added to the resulting solution. An immediate reaction resulted in an orange supernatant and an off-white precipitate. After centrifugation, the supernatant was poured into 35 mL of anhydrous diethyl ether. An orange crystalline solid precipitated immediately. After being cooled to −20 °C for 5 h, the supernatant was decanted and the solid was washed with 15 mL of dichloromethane in three portions. The product was dried in vacuo at ambient temperature for 2 h to yield 267 mg (77%) of **4**, characterized by the following: ^{1}H NMR (CD_3CN, 25 °C, 250 MHz) δ 6.10 (s, CpH, 5 H), 4.59 (dd, 1 H, J = 7.0, 4.4 Hz), 3.86 (ddd, 1 H, J = 4.4, 3.8, 0.5 Hz), 3.77 (dd, 1 H, J = 3.8, 0.9 Hz), 3.40 (ddd, 1 H, J = 7.0, 0.9, 0.5 Hz); IR (CH_3CN, ν_{CO}) 2064 cm^{-1}. Anal. Calcd for $C_{11}H_{12}MoONBrClF_6P$: C, 24.91; H, 2.28; N, 2.64. Found: C, 25.14; H, 2.35; N, 2.49.

Preparation of [CpMo(CO)(CH$_3$CN)Br(η^3-2-bromoallyl)]PF$_6$ (5). This procedure followed that for its chloro analogue. Using 110 mg of CpMo(CO)Br$_2$(η^3-2-bromoallyl) (**2**) and 56 mg of $AgPF_6$ gave 96 mg (70%) of **5** characterized by the following: ^{1}H NMR (CD_3CN, 25 °C, 250 MHz) δ 6.09 (s, CpH, 5 H), 4.53 (dd, 1 H, J = 7.2, 4.0 Hz), 3.91 (dd, 1 H, J = 4.0, 3.8, 1.1 Hz), 3.89 (ddd, 1 H, J = 4.0, 4.0, 0.5 Hz), 3.40 (ddd, 1 H, J = 7.2, 1.1, 0.5 H); IR (CH_3CN, ν_{CO}) 2065 cm^{-1}. Anal. Calcd for $C_{11}H_{12}MoONBr_2F_6P$: C, 22.98; H, 2.10; N, 2.44. Found: C, 23.12; H, 2.14; N, 2.51.

Preparation of [CpMo(CO)(CH$_3$CN)Br(η^3-2-methallyl)]PF$_6$ (6). This procedure followed that for its chloro analogue. Using 251 mg (0.62 mmol) of CpMo(CO)Br$_2$(η^3-2-methallyl) (**3**) and 157 mg of $AgPF_6$ gave 251 mg (80%) of **6** characterized by the following: ^{1}H NMR (CD_3CN, 25 °C, 250 MHz) δ 5.96 (s, CpH, 5 H), 4.09 (dd, 1 H, J = 4.5, 3.7 Hz), 3.29 (s, 1 H), 3.28 (d, 1 H, J = 3.7 Hz), 2.95 (d, 1 H, J = 4.5 Hz), 2.30 (s, 3 H); IR (CH_3CN, ν_{CO}) 2048 cm^{-1}. Anal. Calcd for $C_{11}H_{12}MoONBr_2F_6P$: C, 28.26; H, 2.96; N, 2.75. Found: C, 28.24; H, 3.16; N, 2.49.

Preparation of [CpMo(CO)(PPh$_3$)(η^3-2-methallyl)] (7). Complex **3**, [CpMo(CO)Br$_2$(η^3-2-methallyl)] (0.877 g, 2.17 mmol), was dissolved in a solution containing 75 mL of THF. After being stirred continuously with excess sodium amalgam for 30 min, the solution was treated with triphenylphosphine (0.850 g, 3.24 mmol) and was stirred for 2 h under N_2. The solvent was removed from the resulting solution on a rotary evaporator. The residue was chromatographed on a silica gel column with a 1:3 mixture of methylene chloride and petroleum ether to remove a small band of yellow unidentified byproduct. Then, a large yellow band was eluted with a 1:1 ratio of solvents to yield 0.536 g of CpMo(CO)(PPh$_3$)(η^3-2-methallyl) (49%). Anal. Calcd for $C_{28}H_{27}OPMo$: C, 66.42; H, 5.37. Found: C, 66.31; H, 5.41.

This compound was characterized by the analysis and the IR (ν_{CO}, C_6H_{12}) at 1840 and 1830 cm^{-1}. The ^{1}H NMR ($CDCl_3$, 30 °C, 500 MHz) shows the overlap of slightly broadened spectra of two conformational isomers. At −10 °C the limiting spectrum is observed having resonances from each conformer in a ratio of 3:2 and a complex resonance at ~δ 7.5 from the Ph_3P: major, δ 4.73 (s, CpH, 5 H), 2.34 (d, 1 H, J = 3.3 Hz), 2.31 (s, 1 H), 1.93 (dd, 1 H, J = 3.3 Hz, J_{PH} = 13.2 Hz), 1.74 (s, 1 H), 0.83 (s, Me, 3 H); minor, δ 4.69 (d, CpH, 5 H, J_{PH} ≈ 0.5 Hz), 2.58 (d, 1 H, J ≈ 3.0 Hz), 2.09 (dd, 1 H, J ≈ 3.0 Hz, J_{PH} = 5.9 Hz), 2.01 (s, Me, 3 H), 1.23 (s, 1 H), 0.28 (d, 1 H, J_{PH} = 13.2 Hz).

A future publication will discuss the conformers, assignments, and interconversion rates.

Crystallographic Analyses. Crystals of CpMo(CO)Br$_2$(η^3-2-bromoallyl)·$^1/_2$CH$_2$Cl$_2$ (**2**) suitable for diffraction analysis were obtained from dichloromethane–ether solutions by cooling to −10 °C. A crystal of dimensions 0.092 × 0.098 × 0.446 mm^3 bounded by faces 02$\bar{1}$, 011, 001, 0$\bar{1}\bar{1}$, 100, and $\bar{1}$00 was mounted in a thin-walled glass capillary. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Data processing was performed on a Digital 11/23 computer using the Enraf-Nonius SDP program library (Version 18.5). An absorption correction using a 14 × 6 × 8 grid was performed owing to the linear absorption coefficient of 96.60 cm^{-1}. This led to maximum and minimum per cent transmission of 55.5 and 12.3 with an average of 46.6. Neutral atom scattering factors were calculated by standard procedures, and anomalous dispersion corrections were applied to all atoms. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (PF_o^2)^2]^{1/2}/Lp$.

The space group $P2_1/n$ was established by the systematic absences. This compound crystallizes with a half molecule of methylene chloride per molybdenum complex with cell dimensions of a = 6.903 (2) Å, b = 8.307 (2) Å, c = 24.307 (4) Å, β = 95.82 (2)°, and V = 1386.7 (9) Å^3. Loss of solvent from the crystal and disorder of the solvent prevented a high quality structure. Refinement of two other data sets on larger crystals with more nearly equal dimensions showed essentially the same features in the structure, and all showed disordered solvent near a special position requiring a center of symmetry. Anisotropic refinement of the molybdenum, bromine, and chlorine atoms without the inclusion of hydrogen atoms converged to the residuals R_1 = 0.064 and R_2 = 0.074. Complete data collection parameters, the values of the fractional coordinates, bond lengths and angles, and the estimated standard deviations obtained from the inverse matrix obtained on the final cycle of refinement are given in tables in the supplementary material. Tables of anisotropic thermal parameters

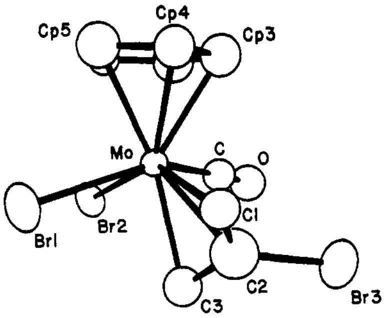


Figure 1. An ORTEP diagram of 2 with 50% probability ellipsoids.

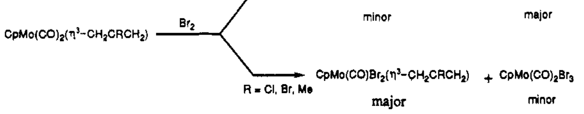
and structure factor amplitudes are also available there.

The structure is shown in Figure 1 and is based on a distorted 3:4:1 structure with the Cp occupying three positions and the CO, two cis Br's, and one terminus of the allyl roughly at the corners of a square. The 2-bromo substituent of the allyl is oriented toward the CO. The bond lengths (Å) are unexceptional with the following: Mo–Br(1) = 2.694 (2); Mo–Br(2) = 2.626 (2); Mo–CO = 1.95 (2); Mo–C(1) = 2.40 (2); Mo–C(2) = 2.30 (2); Mo–C(3) = 2.35 (2); C(1)–C(2) = 1.40 (2); C(2)–C(3) = 1.43 (2). Some angles (deg) of interest are as follows: Br(1)–Mo–Br(2) = 82.90 (5); Br(1)–Mo–C = 153.5 (5); Br(1)–Mo–C(1) = 79.7 (4); Br(1)–Mo–C(2) = 94.5 (5); Br(1)–Mo–C(3) = 83.8 (4); Br(2)–Mo–C(1) = 143.6 (4); Br(2)–Mo–C(3) = 81.5 (4).

Results and Discussion

The reactions of $CpMo(CO)_2(\eta^3\text{-2-R-allyl})$ complexes with different halogens show no common pattern. The products vary with the halogen used and with the allyl substituent. Some of the examples of reaction with halogen in CH_2Cl_2 are shown in reactions 1–3.

$$\underset{R\,=\,Me,\ Cl,\ Br}{CpMo(CO)_2(\eta^3\text{-}CH_2CRCH_2)} \xrightarrow{Cl_2} \underset{minor}{CpMo(CO)Cl_2(\eta^3\text{-}CH_2CRCH_2)} + \underset{major}{CpMo(CO)_2Cl_3} \qquad (1)$$



(2)

$$CpMo(CO)_2(\eta^3\text{-}CH_2CRCH_2) \xrightarrow{I_2} CpMo(CO)_2I_3 \qquad (3)$$

Some quantity of the $CpMo(CO)_2X_3$ complexes, which were originally prepared by Nyholm,[5] were produced in each case and were identified by their characteristic IR and NMR spectra. In some cases, we obtained high yields of $CpMo(CO)Br_2(\eta^3\text{-2-R-allyl})$ complexes characterized by having a high carbonyl frequency near 2044 cm^{-1} consistent with a Mo(IV) formalism. Reaction with iodine gave no η^3-allyl product, and reaction with chlorine gave low yields of η^3-allyl product. The method would require substantial improvement to constitute a practical preparation of the dichloride. The origin of these variations in product distributions is not obvious.

The bromination studies are the most informative and show clearly that two competitive paths are present. This is evidenced by the formation of both $CpMo(CO)_2Br_3$ and $CpMo(CO)Br_2(\eta^3\text{-2-R-allyl})$ in the bromination of $CpMo(CO)_2(\eta^3\text{-2-R-allyl})$. The fractional yield of $CpMo(CO)_2Br_3$, however, varied substantially depending upon allyl substitution. The reactions of $[CpMo(CO)_2(\eta^3\text{-2-methallyl})]$ and $[CpMo(CO)_2(\eta^3\text{-allyl})]$ reveal two extreme cases. The former gave such a small amount of $CpMo(CO)_2Br_3$ (<5%) that it did not precipitate from the reaction mixture, whereas the latter produced predominantly the $CpMo(CO)_2Br_3$ precipitate under the reaction conditions. A minute quantity of $[CpMo(CO)Br_2(\eta^3\text{-}C_3H_5)]$ is formed in the supernatant, as indicated by a diagnostic 2031 cm^{-1} band in the IR spectrum. Unfortunately, we were unable to isolate it owing to the low yield and instability of this complex in solution.

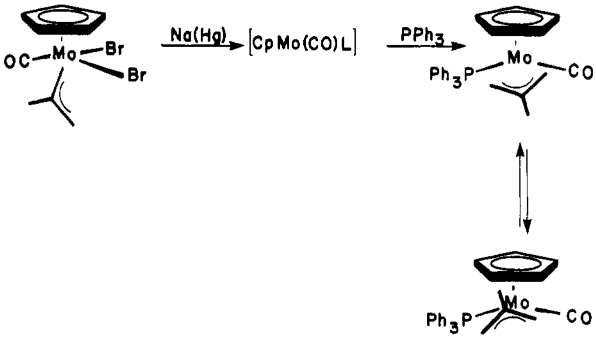
The mechanistic factors affecting the selection of the two competing paths are not clear at this stage. Nevertheless, it appears that a major consideration in correlating the directions of the bromination reactions must be related to effects of the substituents on the allylic groups. According to our observations, allylic groups with a substituent on the central carbon tend to yield a predominance of dibromide. The yield of dibromide increases in the order of 2-substituent of $H < Cl \lesssim Br < CH_3$.

The selectivity of the bromination suggests that it may provide a valuable separation technique by allowing selective demetalation of certain isomeric allylic and olefinic complexes.

Reactivity. Halo ligands can be removed by treatment with Ag$^+$. Reaction of **1**, **2**, or **3** with equimolar $AgPF_6$ removes one bromide ligand (see reaction 4) and gives stable products, whereas 2:1 ratios lead to decomposition. When the reaction is carried out in acetonitrile, single isomers of $[CpMo(CO)Br(MeCN)(\eta^3\text{-2-R-allyl})]PF_6$ appear to crystallize. But upon preparation of solutions in various solvents, other isomers and solvent-substituted isomers appear. Owing to the large number of isomeric possibilities in this system, we will report structural studies of these complexes separately. We are still exploring this area in an attempt to prepare $[CpMo(CO)Br(\eta^4\text{-2-R-allyl})]PF_6$ complexes.

$$CpMo(CO)Br_2(\eta^3\text{-2-}RC_3H_4) + AgPF_6 = [CpMo(CO)Br(MeCN)(\eta^3\text{-2-}RC_3H_4)]PF_6 + AgBr \quad (4)$$

Reduction of the dibromides provides an alternate route to the photochemical production of the 16-electron intermediate $CpMo(CO)(\eta^3\text{-allyl})$. For example, this provides a convenient nonphotochemical route to the compound $[CpMo(CO)(PPh_3)(\eta^3\text{-2-methallyl})]$, which was recently synthesized for the first time.[12] Relatively few chiral complexes of this type containing the CpMo(CO)(phosphine) moiety have been prepared.[13] As shown in eq 5,



(5)

the methallyl complex can be conveniently prepared by reducing $[CpMo(CO)Br_2(\eta^3\text{-2-methallyl})]$ with sodium amalgam followed by addition of an equal molar amount of PPh_3. This offers a route to $CpMo(CO)(PPh_3)L$ which was not easily accessible previously by other means. Unfortunately, this method does not give satisfactory yields for 2-haloallyl complexes. We speculate that the halogen atoms on the allyl groups of those compounds may provide

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(12) $CpMo(CO)(PPh_3)(\eta^3\text{-allyl})$ complexes can be prepared by irradiation of the dicarbonyl complexes in hydrocarbons containing PPh_3. (Berryhill, S., to be submitted for publication).

(13) (a) Collin, J.; Charrier, C.; Pouet, M. J.; Cadiot, P.; Roustan, J. L. *J. Organomet. Chem.* **1979**, *168*, 321–336. (b) Collin, J.; Roustan, J. L.; Cadiot, P. *J. Organomet. Chem.* **1979**, *169*, 53–62.

an unstable CpMo(CO)(η^4-2-haloallyl) intermediate and are continuing our investigation of these processes.

As found with CpMo$(CO)_2$(2-methallyl),[14] two conformers of CpMo(CO)(PPh_3)L are in rapid equilibrium at room temperature. In the dicarbonyl case, a strong steric interaction of the methyl with the Cp ring produces a substantial preference of endo to exo conformer. The expected tilting of the allyl[15] so that it aligns with the Mo–P bond relieves this interaction and produces more nearly equal concentrations of conformers.

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Registry No. **1**, 103751-81-1; **1′**, 103751-88-8; **2**, 103751-82-2; **2′**, 103751-89-9; **3**, 103751-83-3; **4**, 103751-85-5; **5**, 103776-04-1; **6**, 103751-87-7; **7**, 103776-05-2; CpMo$(CO)_2$(η^3-2-chloroallyl), 35208-92-5; CpMo$(CO)_2$(η^3-2-bromoallyl), 35208-93-6; CpMo$(CO)_2$(η^3-2-methylallyl), 12307-49-2.

Supplementary Material Available: Tables of complete data collection parameters, the values of the fractional coordinates, bond lengths and angles, and anisotropic thermal parameters (5 pages); a listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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[14] Faller, J. W.; Chen, C. C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

[15] Olefins and allyls tend to align with the bond of the weaker π-acceptor. See, for example: (a) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. *J. Am. Chem. Soc.* **1979**, *101*, 2570. (b) Shilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (c) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227-231.

Reactions of Bimetallic Group VI (6[†]) Complexes. 3.[1] Synthesis, Characterization, and Reactivity of Dimeric Molybdenum(III) and Tungsten(III) Compounds with Bridging Thiolate Ligands. A Molybdenum-95 NMR Study on Dinuclear Molybdenum Complexes. Crystal Structure of $[\text{Mo}^{\text{III}}{}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{SMe})_3(\text{CO})_2]\text{Br}\cdot\text{H}_2\text{O}$

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Cationic tris(thiolato)-bridged dimolybdenum(III) and ditungsten(III) complexes $[\text{M}_2(\text{CO})_2(\mu\text{-SMe})_3(\eta^5\text{-C}_5\text{H}_5)_2]\text{X}$ (**1**, M = Mo, **2**, M = W; X = Cl, Br) are formed by treating $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\mu\text{-SMe})_2\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ with dimethyl disulfide in the presence of allyl halides. The corresponding BF_4^- and PF_6^- salts have been prepared by metathetical reactions. The bromide salt of **1**, $[\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3(\eta^5\text{-C}_5\text{H}_5)_2]\text{Br}\cdot\text{H}_2\text{O}$, has been characterized by an X-ray diffraction study. Crystals are triclinic of space group $P\bar{1}$ with two molecules in a unit cell of dimensions a = 9.209 (2) Å, b = 10.203 (2) Å, c = 11.706 (2) Å, α = 106.73 (2)°, β = 101.31 (2)°, and γ = 93.58 (2)°. The structure has been solved by direct methods and refined by least squares to R = 0.070 for 1472 independent diffractometer-measured reflection intensities. The structure shows that **1** contains three μ-SMe ligands. The Mo–Mo bond length is 2.785 (2) Å, and two unusually short nonbonded contacts (3.00 (1) and 2.80 (1) Å) between the bridging sulfur atoms are observed. An ^{95}Mo NMR study suggests that the positive charge is located on one sulfur atom in **1**. The reactivity of the new dimers toward nucleophiles has been studied, yielding dimeric compounds $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\overline{\underline{\text{M}(\mu\text{-SMe})_2\text{M}}}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$ (M = Mo). Thermal treatment of **1** gives neutral products $[(\eta^5\text{-C}_5\text{H}_5)\overline{\text{M}(\mu\text{-SMe})_3(\mu\text{-X})\text{M}}(\eta^5\text{-C}_5\text{H}_5)]$ (M = Mo; X = Cl, Br). On photolysis in CH_2X_2 (X = Cl, Br) complexes **1** or **2** are transformed into dimeric species $[(\eta^5\text{-C}_5\text{H}_5)\text{X}(\text{CO})\overline{\text{M}(\mu\text{-SMe})_2\text{M}}\text{X}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)]$ (M = Mo, W; X = Cl, Br). The reactivity of the sulfur donor ligands in dimolybdenum compounds resulting from **1** has also been examined. Molybdenum-95 spectra have been recorded for a series of dinuclear molybdenum complexes, and a new chemical shift range for molybdenum(III) and molybdenum(IV) is given.

Introduction

Thiolate–molybdenum or –tungsten complexes are of current interest, both because of their biological[3] and catalytic[4] implications and also because thiols and thiolate anions undergo a variety of rections with metal species. As a result, a wide range of binuclear molybdenum or

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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