Preparation and Molecular Structure of the First Structurally Characterized M_{ABCDEF} Octahedral Dimer, [Cl(CO)(PPh$_3$)(η^2-MeC$_2$Me)Mo(μ-SCN)(μ-NCS)MoCl(CO)(PPh$_3$)(η^2-MeC$_2$Me)]

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The synthesis of transition-metal complexes containing six-different monodentate ligands has been one of the aims of the transition-metal chemist. An early report of such a complex is [PtCl(Br)I(NO$_2$)(NH$_3$)(py)];[1] however, hitherto no structurally characterized complexes have been published. In this communication we describe the synthesis of the anionic six-different ligand complexes [NBu$^n_4$][MoCl(GeCl$_3$)X(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (X = Br, I, I$_3$, SCN) (**1**–**4**) and the rearrangement of the thiocyanate complex **4** to the structurally characterized six-different coordination dimeric complex [Cl(CO)(PPh$_3$)(η^2-MeC$_2$Me)Mo(μ-SCN)(μ-NCS)MoCl(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (**5**).

Equimolar quantities of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)][2] and [NBu$^n_4$]X (X = Br, I, I$_3$, SCN) react in CH$_2$Cl$_2$ at room temperature to give the acetonitrile-displaced products [NBu$^n_4$][MoCl(GeCl$_3$)X(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (**1**–**4**) in good yield.[3] Complexes **1**–**4** were characterized by elemental analysis (C, H, N) and IR and ^{1}H NMR spectroscopy.[4] The complexes are reasonably stable in the solid state when stored under nitrogen; however, in solution they are much less stable. There are very few anionic alkyne complexes known; an early example is [Mo$_2$(μ-Cl)$_3$(η^7-C$_7$H$_7$)$_2$][MoCl(η^2-CF$_3$C$_2$CF$_3$)$_3$][5] and a very recent example is [NEt$_4$][W(SnMe$_3$)(η^2-PhC$_2$Ph)$_3$].[6]

Dissolving the thiocyanate complex **4** in acetone for 3 h allowed the complex to rearrange to the new complex **5** with a single carbonyl band at 2065 cm^{-1} in its infrared (in CHCl$_3$) spectrum. The carbonyl band is at considerably higher wavenumber compared to its anionic counterpart **4**. Suitable single crystals of **5** were grown for X-ray analysis, and the structural determination showed the complex to be the highly novel thiocyanate-bridged dimer [Cl(CO)(PPh$_3$)(η^2-MeC$_2$Me)Mo(μ-SCN)(μ-NCS)MoCl(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (**5**).

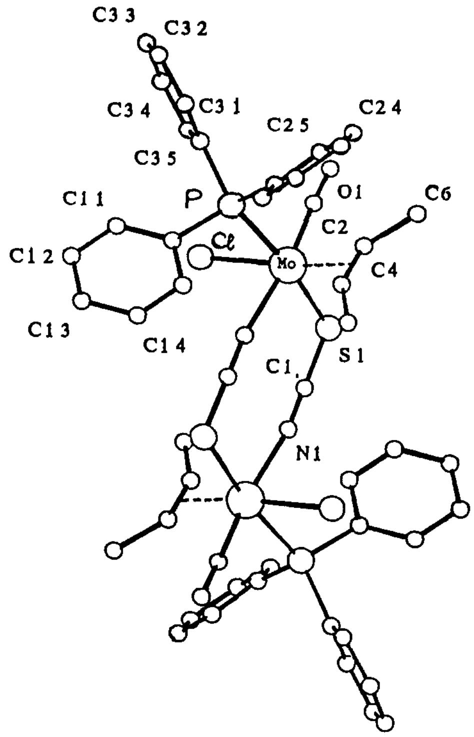

Figure 1. Molecular structure of [Cl(CO)(PPh$_3$)(η^2-MeC$_2$Me)Mo(μ-SCN)(μ-NCS)MoCl(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (**5**).

The molecular structure for **5** can be considered as two octahedrons which are unsymmetrically bridged by two thiocyanate ligands. The molecular structure of the dimer is shown in Figure 1 together with the atomic numbering scheme.[7] The equatorial sites are occupied by two thiocyanate ligands, one bonded to each metal through the nitrogen atom and the other through the sulfur atom. The remaining two equatorial sites are occupied by the PPh$_3$ and carbonyl ligands, with the chloride and but-2-yne ligands mutually *trans* in the axial positions. The carbonyl ligand is *trans* to the nitrogen atom of the SCN moiety with the PPh$_3$ ligand *trans* to the sulfur atom. The structure is highly unusual in two respects, which are that each molybdenum atom in the structure is surrounded by six-different ligands and also the ring formed upon dimerization contains eight atoms. There is no precedence for a six-different monodentate ligand complex in structural transition-metal chemistry. The metal–

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(3) Preparation of [NBu$^n_4$][MoCl(GeCl$_3$)Br(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (**1**): To [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] (0.500 g, 0.719 mmol) dissolved in CH$_2$Cl$_2$ (15 cm^3) with continuous stirring under a stream of dry nitrogen was added [NBu$^n_4$]Br (0.232 g, 0.719 mmol). The mixture was stirred for 30 min, after which the product was filtered and the solvent was removed *in vacuo* to give the green compound [NBu$^n_4$][MoCl(GeCl$_3$)Br(CO)(PPh$_3$)(η^2-MeC$_2$Me)] (**1**) (yield = 0.39 g, 56%), which was recrystallized from CH$_2$Cl$_2$. Similar reactions of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] with [NBu$^n_4$]X (X = I, I$_3$, SCN) gave the complexes [NBu$^n_4$][MoCl(GeCl$_3$)X(CO)(PPh$_3$)(η^2-MeC$_2$Me)] [X = I (**2**), I$_3$ (**3**), SCN (**4**)].

(4) Selected data for complexes **1**–**4**: (**1**) Anal. Calcd for C$_{39}$H$_{57}$NOCl$_4$BrGePMo: C, 47.9; H, 5.9; N, 1.4. Found: C, 48.6; H, 5.8; N, 1.3. IR (CHCl$_3$): ν(CO) = 1955 cm^{-1}. ^{1}H NMR (25 °C, CD$_3$COCD$_3$) (ppm): 7.45 (m, 15H, Ph), 3.3 (m, 8H, NC*H*$_2$), 2.2 (br s, 6H, ≡C*Me*), 1.85 (m, 8H, NCH$_2$C*H*$_2$), 1.5 (m, 8H, C*H*$_2$CH$_3$), 1.0 (m, 12H, *Me*). (**2**) Anal. Calcd for C$_{39}$H$_{57}$NOCl$_4$IGePMo: C, 45.7; H, 5.6; N, 1.4. Found: C, 45.0; H, 5.5; N, 1.1. IR (CHCl$_3$): ν(CO) = 1962 cm^{-1}. ^{1}H NMR (25 °C, CD$_3$COCD$_3$) (ppm): 7.4 (m, 15H, Ph), 3.45 (m, 8H, NC*H*$_2$), 2.45 (brs, 6H, ≡C*Me*), 1.85 (m, 8H, NCH$_2$C*H*$_2$), 1.45 (m, 8H, C*H*$_2$CH$_3$), 1.0 (t, 12H, *Me*). (**3**) Anal. Calcd for C$_{39}$H$_{57}$NOCl$_4$I$_3$GePMo: C, 36.7; H, 4.5; N, 1.1. Found: C, 35.6; H, 5.2; N, 1.2. IR (CHCl$_3$): ν(CO) = 1963 cm^{-1}. ^{1}H NMR (25 °C, CD$_3$COCD$_3$) (ppm): 7.6 (m, 15H, Ph), 3.45 (m, 8H, NCH$_2$), 2.2 (br s, 6H, ≡C*Me*), 1.85 (m, 8H, NCH$_2$C*H*$_2$), 1.45 (m, 8H, C*H*$_2$CH$_3$), 1.0 (t, 12H, *Me*). (**4**) Anal. Calcd for C$_{40}$H$_{57}$N$_2$OSCl$_4$GePMo: C, 50.3; H, 6.0; N, 2.9. Found: C, 50.6; H, 6.2; N, 2.9. IR (CHCl$_3$): ν(CO) = 1964 cm^{-1}. ^{1}H NMR (25 °C, CD$_3$COCD$_3$) (ppm): 7.45 (m, 15H, Ph), 3.5 (m, 8H, NC*H*$_2$), 2.45 (br s, 6H, ≡C*Me*), 1.85 (m, 8H, NCH$_2$C*H*$_2$), 1.5 (m, 8H, C*H*$_2$CH$_3$), 1.0 (m, 12H, *Me*).

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(7) Crystal data for C$_{48}$H$_{42}$N$_2$O$_2$P$_2$S$_2$Cl$_2$Mo$_2$·solv (a molecule of solvent, probably acetone, was disordered and was represented by a cluster of four carbon atoms with suitably reduced occupancies of 0.25) (**5**): orange crystals; monoclinic; $P2_1/A$, a = 11.633(3), b = 15.892(2), c = 14.079(2) Å; β = 91.51(1)°; V = 2612.4 Å^3; Z = 2. The structure was refined to R = 0.062 (R_G = 0.081) for 3463 reflections with $F_o > 3\sigma F_o$. The structure was solved by the heavy-atom method and refined by full-matrix least squares. Only the Mo, S, P, N, and O atoms were refined anisotropically, the remaining non-hydrogens isotropically; hydrogens were not located or included. Phenyl rings were treated as ideal hexagons with C–C = 1.395 Å.

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alkyne distance of 2.06 Å for **5** compares with those previously reported[8] for alkyne complexes of molybdenum and tungsten where the alkyne is donating four electrons to the metal center. The C≡C—Mo angle is 144.5° (±0.2°) for **5**, which again lies in the expected range for four-electron alkyne complexes. In order for **5** to obey the effective atomic number rule each but-2-yne ligand must donate four electrons to the molybdenum atoms.

The elimination, followed by dimerization of $[NBu^n_4][MoCl(GeCl_3)(SCN)(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)]$ (**4**) to $[Cl(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)Mo(\mu\text{-}SCN)(\mu\text{-}NCS)MoCl(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)]$ (**5**) (fully characterized[9]) in acetone solution, may occur from the presence of trace amounts of water in the acetone solution. This could result in the protonation of $GeCl_3^-$ to give $GeCl_3H$ and $[NBu^n_4]OH$, which would allow creation of a vacant coordination site for the thiocyanate to bridge the two metal centers. Further work is currently in progress in order to study the mechanism of this rearrangement and prepare and characterize the related dimers $[\{Mo(\mu\text{-}X_3)Cl(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)\}_2]$ (X = I, Br, *etc.*).

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Supplementary Material Available: Tables of crystallographic details, atomic coordinates and anisotropic temperature factors, bond lengths and angles, and selected nonbonded distances for **5** (6 pages). Ordering information is given on any current masthead page.

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(9) Selected data for complex **5** are as follows. Anal. Calcd for $C_{48}H_{42}N_2O_2P_2S_2Cl_2Mo_2$: C, 53.9; H, 4.0; N, 2.6. Found: C, 52.6; H, 3.5; N, 2.2. IR ($CHCl_3$): $\nu(CO) = 2065\ cm^{-1}$. ^1H NMR (25 °C, CD_3COCD_3) (ppm): 7.4, 7.2 (m, 30H, Ph), 2.3 (br s, 12H, ≡C*Me*).