COMMUNICATION

THE SYNTHESIS, SPECTROSCOPIC PROPERTIES AND REACTIONS WITH NEUTRAL DONOR LIGANDS OF THE NOVEL SIX DIFFERENT LIGAND MOLYBDENUM(II) COMPLEX [MoCl(GeCl₃)(CO)(NCMe)(PPh₃)(η²-MeC₂Me)]

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Abstract—The seven-coordinate complex [MoCl(GeCl₃)(CO)₂(NCMe)₂(PPh₃)] reacts with an excess of but-2-yne in CH₂Cl₂ at room temperature to give the six different ligand compound [MoCl(GeCl₃)(CO)(NCMe)(PPh₃)(η^2 -MeC₂Me)] (1) in good yield. Solid-state ¹³C NMR spectroscopy suggests that the but-2-yne ligand is donating four electrons to the molybdenum in 1. Preliminary studies of the reaction chemistry of 1 with neutral donor ligands are also described.

Many attempts to prepare octahedral complexes with six different monodentate ligands attached have been made with little success. Hitherto, no examples of molybdenum(II) or tungsten(II) complexes of this type have been made. We have been studying the chemistry of the seven-coordinate complexes $[MI_2(CO)_3(NCMe)_2]$ $(M = Mo \text{ or } W)^1$ with donor ligands² and alkynes.³ In our attempt to potentially increase the number of different ligands attached to the metal, more recently we have been investigating the reactions with donor ligands⁴ of the seven-coordinate compound [MoCl(GeCl₃) (CO)₃(NCMe)₂]. This is prepared in high yield by reacting the zero-valent trisacetonitrile compound $[Mo(CO)_3(NCMe)_3]^5$ in situ with GeCl₄. In this communication we report the preparation of the first example of a six different monodentate ligand molybdenum(II) complex [MoCl(GeCl₃) (CO)(NCMe)(PPh₃)(η^2 -MeC₂Me)] (1), and describe preliminary reports of its reaction chemistry.

Reaction of [MoCl(GeCl₃)(CO)₂(NCMe)₂(PPh₃)] and a four-fold excess of but-2-yne in CH₂Cl₂ at room temperature affords the dark green complex [MoCl(GeCl₃)(CO)(NCMe)(PPh₃)(η^2 -MeC₂Me)] (1) in greater than 70% yield. Complex 1 is particularly sensitive to water, and is also air-sensitive and can only be stored for a few days under nitrogen. It is soluble in polar solvents such as CH₂Cl₂, CHCl₃ and acetonitrile, but insoluble in hydrocarbon solvents and diethyl ether. Compound 1 has been fully characterized by elemental analysis (C, H and N), IR, ¹H and solid-state ¹³C NMR spectroscopy.† Many attempts were made to grow suitable single crystals of 1 for X-ray analysis without success.

The IR spectrum of 1 shows, as expected, a broad single carbonyl band at 1975 cm⁻¹, and a weak asymmetric doublet due to coordinated acetonitrile at $v(N \equiv C) = 2313$ and 2286 cm⁻¹. A very weak band at 1684 cm⁻¹ due to coordinated but-2-yne is observed, which is at a considerably lower wavenumber compared to uncoordinated but-2-yne suggesting there is considerable back-donation of elec-

^{*}Author to whom correspondence should be addressed. † Selected data for compound (1): Found: C, 43.2; H, 3.5; N, 1.4. $C_{25}H_{24}NOCl_4PGeMo$ requires: C, 43.2; H, 3.5; N, 2.0%. IR (CHCl₃) ν (CN) = 2313 (w) and 2286 (w) cm⁻¹; ν (CO) = 1975 (s) cm⁻¹; ν (C=C) = 1684 (w) cm⁻¹. ¹H NMR (25°C) (CD₂Cl₂) 7.4 (m, 15H, Ph-H), 3.0 (vbrs, 6H, =CMe), 2.35 (s, 3H, NCMe) ppm. ¹³C NMR (25°C, solid) 228.98 (bs, C=C), 200.86 (bs, C=O), 131.18 (bm, CH₃C=N), 23.18 (vbrs, CH₃C=C), 4.53 (bs. CH₃C=N).

tron density from filled metal d orbitals to empty π^* orbitals on the but-2-yne. The solid-state ¹³C NMR spectrum shows a broad alkyne carbon (C≡=C) resonance at 228.98 ppm which suggests⁶ that the but-2-yne ligand is utilizing both of its filled $p\pi$ orbitals and donating four-electrons to the molybdenum. It is difficult to postulate a structure for 1 from the spectroscopic data, and there are at least 30 (15 diastereomers, each one with an enantiomer) possible isomers for this compound. The ³¹P NMR spectrum (CDCl₃, $+25^{\circ}$ C) of 1 shows a number of resonances, and hence confirms the existence of several different isomers in solution. The ¹H NMR spectrum of 1 from 243–308 K shows a very broad resonance at $\delta = 3.0$ ppm due to the but-2-yne methyl resonances which may again suggest several isomers for this complex.

The reaction chemistry of 1 is diverse, and some reactions with neutral donor ligands are given in Scheme 1. For example, 1 reacts with an equimolar amount of PPh₃ in CH₂Cl₂ at room temperature to afford the dark green acetonitrile displaced product [MoCl(GeCl₃)(CO)(PPh₃)₂(η^2 -MeC₂Me)] in good yield. All the new complexes described in Scheme 1 have been characterized by elemental analysis (C, H and N), IR, ¹H, and in selected cases ¹³C NMR spectroscopy.*

Variable-temperature ¹H NMR studies were carried out on the complex [MoCl(GeCl₃)(CO)(PPh₃)₂ (η^2 -MeC₂Me)]. These studies suggested that the but-2-yne ligand was undergoing rapid propellerlike rotation at room temperature (298 K) (single resonance for the but-2-yne methyl groups at δ = 2.45 ppm), whereas at 228 K two different but-2yne methyl resonances were observed at δ = 2.32 and 2.40 ppm. Using the equation⁷ ΔG^{\ddagger} =



 $[Mo(GeCl_3)(CO)(PPh_3)(bipy)(\eta^2-MeC_2Me)][BPh_4]$

Scheme 1. Reagents: (i) PPh₃ in CH₂Cl₂ at room temperature for 24 h; (ii) bipy in CH₂Cl₂ at room temperature for 1 h; (iii) Na[BPh₄] in NCMe at room temperature for 24 h.

 $\pi\Delta\nu h/\sqrt{2} K_{\rm B}T_{\rm C}$ ($\Delta\nu = 24.22$ Hz, $T_{\rm C} = 239$ K), the barrier to but-2-yne rotation of [MoCl(GeCl₃) (CO)(PPh₃)₂(η^2 -MeC₂Me)] was calculated to be 50.4 kJ mol⁻¹. This value is typical of other calculated values for dihaloalkyne complexes of molybdenum(II) or tungsten(II) of the type [MX₂(CO)L₂ (η^2 -MeC₂Me)].^{3o-d,8} After many attempts, no suitable single crystals for X-ray crystallography have been grown of the products shown in Scheme 1.

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^{*} Selected data for $[MoCl(GeCl_3)(CO)(PPh_3)_2(\eta^2 -$ MeC₂Me)]. Found : C, 54.2 ; H, 3.8. C₄₁H₃₆OCl₄GePMo requires: C, 53.7; H, 4.0%. IR (CHCl₃) v(CO) = 1973 (s), v(C = C) = 1682 (w) cm⁻¹. ¹H NMR [25°C, $(CD_3)_2CO$, 7.4 (s, 30H, Ph—H); 2.45 (s, 6H, $\equiv CMe$). Selected data for $[Mo(GeCl_3)(CO)(PPh_3)(bipy)(\eta^2-MeC_2)]$ Me)]Cl. Found: C, 49.2; H, 4.0; N, 3.2. C₃₃H₂₉N₂O Cl₄GePMo requires: C, 48.8; H, 3.9; N, 3.4%. IR $(CHCl_3) v(CO) = 1948 (s), v(C = C) = 1687 (w) cm^{-1}.$ ¹H NMR [25°C, (CD₃)₂CO] 9.55 (d, 2H, bipy), 8.5 (m, 4H, bipy), 7.8 (d, 2H, bipy), 7.35 (m, 15H, Ph-H), 3.0 (d, 6H, $\equiv CMe$). Selected data for [Mo(GeCl₃)(CO) $(PPh_{3})(bipy)(n^{2}-MeC_{2}Me)[BPh_{4}]$. Found: C, 62.2; H, 4.8; N, 2.6. C₅₇H₄₉N₂OCl₄GeBPMo requires: C, 62.5; H, 4.5; N, 2.6%. IR (CO) = 1956 (s) cm⁻¹. ¹H NMR [25°C, (CD₃)₂CO]: 9.7 (d, 2H, bipy), 8.4 (m, 4H, bipy), 7.9 (d, 2H, bipy), 7.5 (m, 35H, Ph), 3.05 (d, 6H, $\equiv CMe).$

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