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Pentagonal Bipyramidal $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_2]$; A Geometry not Previously Observed for Group VI Metal Allyls

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Because η^3-allyl–phosphite complexes of transition elements from Groups VII and VIII have been shown to be very effective homogeneous catalysts or exhibit unusual structural features [1, 4], we recently synthesised the Group VI complexes $[MoX(CO)_2(\eta^3\text{-}C_3H_5)\{P(OR)_3\}_2]$, (X = Cl, Br, or I, R = Me and X = Cl or I, R = Et), as part of our investigations into complexes containing the $M(CO)_2(\eta^3\text{-}C_3H_5)$ moiety [5]. Some of the spectral properties of these complexes were inconsistent with the pseudooctahedral structure, which can alternatively be described as a capped trigonal prism (CTP) if the allyl group is regarded as occupying two coordination sites, found for all other $[Mo(CO)_2(\eta^3\text{-}C_3H_5)L_3]^{n\pm}$ complexes of known structure [6, 7]. This preliminary communication reports the results of a single crystal structure determination on the title compound, which is shown to be of a structural type not previously found for this class of d^4 M(II) compounds.

Experimental

The title compound was prepared in high yield by the reaction of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ [8] with freshly distilled and dried trimethylphosphite.

A solution of 0.31 g (1.0 mmol $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)MeCN)_2]$ dissolved in 8 ml of dried, deoxygenated methanol was stirred with 0.42 ml (2.0 mmol) $P(OMe)_3$ under a N_2 atmosphere for 1 h, and the product then filtered off, washed with methanol and vacuum dried. *Anal.* Calcd. for $C_{11}H_{23}ClP_2MoO_8$: C, 27.2; H, 4.9. Found: C, 27.5; H, 4.8%. Yield 75%.

Crystal Data

$C_{11}H_{23}ClP_2MoO_8$, M = 476.5, triclinic, Space group $P\bar{1}$, a = 13.309(11), b = 10.093(10), c = 8.148(7) Å, α = 114.9(8)°, β = 93.1(8)°, γ = 100.6(7)°, U = 965.1 Å^3, Z = 2. 1534 above background reflections, measured on a G.E.XRD5 diffractometer have been refined to R 0.072, all atoms with anisotropic thermal parameters.

Results and Discussion

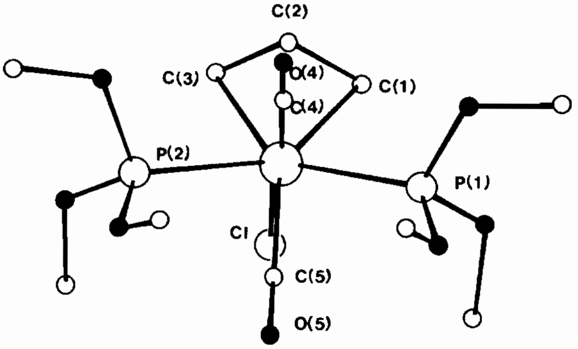

Fig. 1. Molecular structure of $[MoCl(CO)_2(\eta^3\text{-}C_3H_5)\{(P(OMe)_3\}_2]$. Mo–P(1) 2.431(7); Mo–P(2) 2.425(5); Mo–Cl 2.606(8); Mo–C(1) 2.40(2); Mo–C(2) 2.35(3); Mo–C(3) 2.41(3); Mo–C(4) 1.92(3); Mo–C(5) 2.04(3) Å.

The structure (Fig. 1) has C_s symmetry within experimental error, with the mirror plane containing the metal atom, both carbonyl groups, the chlorine atom and the central carbon of the allyl group. The geometry is best described as pentagonal bipyramidal (PB) with Cl and C(4) in axial positions [Cl–Mo–C(4) 178.3(6)°], and the allyl ligand occupying two adjacent sites in the equatorial girdle. However, this girdle is very distorted, the Mo–Cl bond subtending angles of 78.0, 80.0, 80.5° with Mo–C(5), Mo–C(1) and Mo–C(3), and 100.8, 98.7° with Mo–P(1) and Mo–P(2). The angle between the allyl plane and the girdle plane [formed by atoms Mo, P(1), P(2), C(1), C(3), C(5) which are –0.05, –0.42, –0.39, 0.18, 0.12, 0.57 Å from the least squares plane respectively] is 67.8°. Thus the allyl group can be regarded as a bidentate ligand with a small normalised bite [9] of 1.02. In seven-coordinate complexes of the type $[M(bidentate)(monodentate)_5]^{n\pm}$ when the normalised bite of the bidentate is small (0.7 to 1.1) the molecular geometry is found to be a PB [9] or a CTP [10], a result consistent with the shape characteristics of the ideal polyhedra. In all previous $[Mo(CO)_2(\eta^3\text{-}C_3H_5)L_3]^{n\pm}$ structures, the allyl and carbonyl groups have occupied the unique edge and two adjacent sites in the equatorial plane of a CTP. Although this arrangement is almost obligatory when L_3 is a tridentate ligand, this is not so for complexes containing bidentates, or for $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_3]^+$ [11]. It seems likely therefore that this particular arrangement of the two carbonyl groups and the allyl ligand in d^4 CTP complexes is electronically favoured. In the phosphite complex such an arrangement would result in the bulky phosphorus ligands occupying *cis* positions, so giving rise to a sterically crowded molecule, and in addition, at least one phosphite ligand would be *trans* to a carbonyl group and hence competing as a π-acceptor. Consequently the distorted PB geometry may be adopted as the only alternative low energy solid-state structure*.

As frequently observed for seven-coordinate complexes, the molecule is stereochemically non-rigid in solution at room temperature. ^1H and ^{13}C NMR data show equivalence of the ends of the allyl group and equivalence of the carbonyl groups under these conditions. Below ~230 K the NMR data is in accord with the solid-state structure.

NMR ($CDCl_3$): ^{13}C (δ, downfield from Me_4Si), 232.98{t, C(4), J(P–C) 35.9 Hz}, 225.04{t, C(5), J(P–C) 27.2 Hz}, 114.43{s, C(2)}, 76.02{s, C(1, 3)}, 53.63{d, (OMe), J(P–C) 4.6 Hz}, and ^1H, τ, 6.78 (d, 2H, allyl, J, 13.5 Hz), 6.13{d, 6H, J(P–H) 11.5 Hz}, 5.38{dd, 2H, allyl, J(H–H) and J(P–H) both 7 Hz}, 4.81 (m, 1H, allyl).

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*The distribution of ligands between the equatorial and axial sites of the PB is inconsistent with molecular orbital predictions for ML_7 complexes, and the distortions from ideal PB geometry do not appear to be obviously related to steric interactions.

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