Oxidation of Tertiary Phosphine Ligands by a Sulphonyl Azide: Formation of a Phosphine Imine Derivative of Molybdenum(v)

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Summary A molybdenum(v) derivative of n-propyldiphenylphosphine imine, $[MoCl_4(NPPr^nPh_2)(OPPr^nPh_2)]$, is formed by oxidation of the tertiary phosphine ligands of $[MoCl_4(PPr^nPh_2)_2]$ by *p*-tolylsulphonyl azide.

The reaction of organo-azides with certain co-ordinatively unsaturated tertiary phosphine complexes of molybdenum(iv) was investigated with an aim to produce organo-imido (organonitrene) compounds by reaction (1).

$$[MoCl_4(PR^1_3)_2] + RN_3 \rightarrow [MoCl_4(NR)(PR^1_3)_2] + N_2 \qquad (1)$$

However, the reaction involving *p*-tolylsulphonyl azide and n-propyldiphenylphosphine at room temperature in CH_2Cl_2 at a background pressure (excluding solvent vapour pressure) of 5×10^{-4} mm Hg appears to follow the stoicheiometric reaction(2).

$$\begin{aligned}&2[MoCl_4(PPr^nPh_2)_2] + 2p\text{-}MeC_6H_4{\cdot}SO_2{\cdot}N_3 \rightarrow\\ &2MoCl_4(PPr^nPh_2)_2NO +\\ &\qquad 2N_2 + p\text{-}MeC_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_6H_4Me\text{-}p \qquad (2)\\ &\qquad (I)\end{aligned}$$

1 mol of dinitrogen is evolved for each mol of azide consumed and the thiosulphonate ester[1] has been isolated (70% yield) The product (I) is a yellow, crystalline solid whose solutions are extremely air- and moisture-sensitive. Careful micro-analysis† was necessary to verify N and O as constituents of (I). Thermal gravimetric analysis indicated that the weight loss upon decomposition at 260 °C, corresponded, within an error of 2%, to two molecules of PPr^nPh_2 per molar mass of compound and the residue corresponded to the formula Cl_4MoNO (confirmed by micro-analysis). Thus, formula (I) appears to differ from the true one by, at most, a few hydrogen atoms. The source of N and O is certainly the azide as the reaction was carried out under strict vacuum conditions and careful attention was paid to the purity of the starting materials.

Compound (I) is non-conducting and monomeric‡ in CH_2Cl_2. It exhibits a solid state magnetic moment of $1{\cdot}78 \pm 0{\cdot}03$ B.M. which is consistent with a Mo^V complex. This is supported by the e.s.r. spectrum of a CH_2Cl_2 solution at 20 °C which shows a single central absorption (g 1·94) and weaker satellites due to molybdenum isotopes with spin $I = 5/2$ (hyperfine constant 50 G). Two intense i.r. absorptions occur at 1128 and 1093 cm^{-1} in CH_2Cl_2 solutions of concentration 5×10^{-2} mol/dm³. After partial ^{15}N labelling (using *p*-tolylsulphonyl [$^{15}N_1$]azide), about one third of the N atoms in the molybdenum product were labelled. This led to a lowering of the peak height of the absorption at 1128 cm^{-1} relative to that at 1093 cm^{-1} and the appearance of a pronounced shoulder at 1120 cm^{-1}. This is taken as evidence that the nitrogen atom in (I) is involved in the vibrational mode associated with the absorption at 1128 cm^{-1}. A careful search of the 4000—3000 cm^{-1} region failed to locate any absorptions consistent with the presence of N—H or O–H bonds.

We formulate (I) as an Mo^V derivative of n-propyldiphenylphosphine imine, $[MoCl_4(NPPr^nPh_2)(OPPr^nPh_2)]$ formed by oxidation of the tertiary phosphine ligands by nitrogen and oxygen originating from the azide, and assign the i.r. absorptions at 1128 and 1093 cm^{-1} to vibrations involving coordinated 'P=N' and 'P=O' functional groups,[2] respectively.

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† Satisfactory data were obtained (to ± 0·2%) for the formula $C_{30}H_{34}Cl_4MoNOP_2$.

‡ The molecular weight determined isopiestically (using $Ph_2PC_2H_4PPh_2$ as a standard) was 743 compared with a theoretical 724·31 for a monomer (error: 3%).

The following observations support the formulation:—

(1) A mass spectrum taken at 220 °C exhibits the characteristic patterns expected for $[MoCl_n(NPPr^nPh_2)]^+$ (n = 4,3) in the mass intervals 474—486 and 439—449 respectively. These ions are predicted§ if the parent ion loses a $OPPr^nPh_2$ unit followed by a chlorine atom.

(2) The fact that no splitting of the e.s.r. signal by the phosphorus nuclei is observed is evidence that direct molybdenum–phosphorus bonds are not present in (I). The nitrido-complex $[MoCl_2N(PPh_3)_2]$ exhibits[3] a 1:2:1 triplet (hyperfine constant 24·5 G) due to splitting by the two phosphorus nuclei bound directly to molybdenum(v).

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§ It is interesting to note that the pathways are different for thermal decomposition and decomposition in the mass spectrometer probe. The former produces $MoNOCl_4$ and 2 mol of PPr^nPh_2 while the latter apparently produces $MoCl_4(NPPr^nPh_2)^+$ and $OPPr^nPh_2$.

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[2] H. Bock and H. Dieck, *Z. Naturforsch.*, 1966, **21B**, 739; W. P. Griffith and D. Pawson, *J.C.S. Chem. Comm.*, 1973, 418; F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 1960, 2199.

[3] J. Chatt and J. R. Dilworth, personal communication.