Oxomolybdenum(IV) Complexes with Tertiary and Ditertiary Phosphines

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Summary Diamagnetic complexes of the types $MoOCl_2L_3$, $MoOCl_2L(LL)$, and $[MoOCl(LL)_2]X$ (L = alkylaryl phosphine; LL = ditertiary phosphine; $X = BF_4^-$, BPh_4^-) have been prepared.

THE rarity of oxomolybdenum(IV) complexes contrasts with the abundance of oxo-species in the +5 and +6 oxidation states. A few poorly characterized oxalate complexes have been reported,[1] and the species obtained on irradiation of solutions of $[Mo(CN)_8]^{4-}$ has been identified as *trans*-$[MoO_2(CN)_4]^{4-}$.[2] Recently, five-co-ordinate, square-pyramidal complexes of the type $MoO(BB)_2$ [BB = dialkyl- or diaryl-dithiophosphate,[3] diethyldithiocarbamate,[4] or ½(phthalocyanine)[5]] and a six-co-ordinate complex, $MoO(EtOCS_2)_2(C_5H_5N)$[6] have been reported. All these complexes have low, or zero, magnetic moments.

We report new series of diamagnetic, six-co-ordinate complexes of oxomolybdenum(IV) with tertiary and ditertiary phosphines. These are of the types $MoOCl_2L_3$, $MoOCl_2L(LL)$, and $[MoOCl(LL)_2]X$ (L = $MePPh_2$, Me_2PPh, $EtPPh_2$, Et_2PPh; LL = $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, *cis*-$Ph_2P{\cdot}CH{:}CH{\cdot}PPh_2$, $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$; $X = BF_4^-$, BPh_4^-).

The blue to green complexes $MoOCl_2L_3$ were prepared by the reaction of sodium molybdate with alkylarylphosphines in ethanol containing a small amount of hydrochloric acid. Triphenylphosphine, under the same conditions, has been reported to yield $[PPh_3H]_2[MoOCl_5]$,[7] and in the presence of larger amounts of hydrochloric acid analogous phosphonium salts are obtained from alkylarylphosphines. The latter are, however, reduced to $MoOCl_2L_3$ by zinc dust in the presence of an excess of the ligand. Alternatively, the phosphines react with $MoOCl_3(C_4H_8O)_2$[8] in tetrahydrofuran to yield, initially, unstable red solutions, probably of $MoOCl_3L_2$, which are readily reduced by zinc amalgam to $MoOCl_2L_3$. The complexes $MoOCl_2L_3$ decompose in air, at rates increasing in the order $MePPh_2$ (stable), Me_2PPh, $EtPPh_2$, Et_2PPh (very unstable). *X*-Ray diffraction studies of a single crystal of $MoOCl_2(Me_2PPh)_3$ gave a molecular weight of $n \times 580$ (required: 597). The presence of a terminal Mo=O group in the complexes is indicated by a strong, sharp i.r. absorption in the range 940—956 cm^{-1} (Nujol).

On heating under reflux in ethanol with an excess of diphosphine, the monophosphine ligands of the complexes $MoOCl_2L_3$ are rapidly displaced, with the formation of stable, violet to purple complexes $[MoOCl(LL)_2]Cl$, which may be precipitated as the fluoroborate or tetraphenylboron salts. Of the diphosphines investigated, only $Ph_2P{\cdot}CH_2{\cdot}PPh_2$ failed readily to displace the monophosphines. The complexes are 1 : 1 electrolytes in nitrobenzene and have i.r. absorptions due to ν(Mo=O) in the range 950—959 cm^{-1}. The complex $[MoOCl(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ $[ZnCl_3(Me_2CO)]$, prepared by a different route, has been shown by a full *X*-ray structural analysis to have a *trans*-configuration,[9] and from the close similarity of the i.r. spectra the present complexes are assumed also to be *trans*.

The intermediate complexes $MoOCl_2L(LL)$ (L = $MePPh_2$, Me_2PPh; LL = *cis*-$Ph_2P{\cdot}CH{:}CH{\cdot}PPh_2$) were prepared by stoicheiometric reaction of $MoOCl_2L_3$ with LL in ethanol. They are air-stable and are readily recoverable from solution. They are non-electrolytes in nitrobenzene.

These oxomolybdenum(IV) complexes are analogous to the isoelectronic diamagnetic oxorhenium(V) complexes of the types $ReOCl_3L_2$ and $ReOCl_3(LL)$ prepared by Chatt and Rowe.[10]

The lability of the $MoOCl_2L_3$ complexes makes them potential precursors for the preparation, by exchange reactions, of a further wide range of oxomolybdenum(IV) complexes.

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