Elimination Reactions of Alkyl-, Nitro-, and Sulphato-molybdenum(II) Complexes

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Summary Reaction of *cis*-[$Mo(CO)_2(dmpe)_2$] (dmpe = $Me_2PCH_2CH_2PMe_2$) with RX (CCl_4 or $PhCH_2Br$), Me_3CI, $AgNO_2$, and Ag_2SO_4 gives the molybdenum(II) products [$MoX(CO)_2(dmpe)_2$]X (X = Cl, Br), [$MoH(CO)_2(dmpe)_2$]I, [$Mo(CO)(NO)(NO_2)(dmpe)_2$] and [$Mo(CO)(SO_4)(dmpe)_2$], respectively as a result of the elimination of neutral species.

Complexes of the general type [$M(R_2PCH_2CH_2PR_2)_2L^1L^2$] [M = Mo, W; R = Ph (dppe); $L^1 = L^2 = N_2$,[1] C_2H_4,[2] CNQ,[3] CO;[4] L^1 = CO, L^2 = CS;[4] R = Me (dmpe), $L^1 = L^2$ = CO[5]] react with formal oxidising (electrophilic) agents such as X_2, HX and RX (X = halogen) in a variety of different ways. The photochemical reaction[1] of [$M(N_2)_2(dppe)_2$] with alkyl halides to give alkyldiazenido complexes, *trans*-[$MX(N_2R)(dppe)_2$] may be compared with the alkylation[3] of *trans*-[$M(CNMe)_2(dppe)_2$], which affords cationic carbyne complexes [$M(CNMe_2)(CNMe)(dppe)_2$]$^+$.

The addition of $PhCH_2Br$ to *cis*-[$Mo(CO)_2(dmpe)_2$], (**1**), at room temperature gives [$MoX(CO)_2(dmpe)_2$]X, (**2**), [X = Br, ν(CO) 1952 and 1890 cm^{-1}] and 1,2-diphenylethane quantitatively. With CCl_4 at 195K, (**1**) gives (**2**) (X = Cl) and C_2Cl_4, together with minor ($<10\%$) amounts of C_2Cl_6 in a reaction which may be homolytic.[6] With Me_3CI, the products of reaction with (**1**) are the hydride [$MoH(CO)_2(dmpe)_2$]I (δ 6·80, tt) and 2-methylpropene. Alkylation of (**1**) with Et_3OBF_4 gives yellow [$MoEt(CO)_2(dmpe)_2$] BF_4 [ν(CO) 1874 cm^{-1}, δ 3·55 quartet, 1·30 t] which decomposes readily (*cf.* ref. 4) to [$MoH(CO)_2(dmpe)_2$]BF_4 and ethylene. With $MeSO_3F$ (distilled from Me_2SO_4), (**1**) gave orange [$MoMe(CO)_2(dmpe)_2$]SO_3F [δ 1·77 (3H, quintet, *J* 10 Hz)] which also decomposes to form [$MoH(CO)_2(dmpe)_2$]SO_3F.

Complex (**1**) reacts with $AgNO_2$ (2 moles) in CH_2Cl_2 solution, but not with Et_4NNO_2 in the same solvent, at room temperature to give [$Mo(CO)(NO)(NO_2)(dmpe)_2$] [ν(CO) 1938, ν(NO) 1606 cm^{-1}; Λ (CH_2Cl_2–acetone) 8 S cm^3 mol^{-1}] together with CO_2, N_2O, and CO, in a process which is formally similar to the reduction of NO by CO, catalysed by di-nitrosyl complexes of rhodium and iridium.[7] The addition of Et_4NNO_2 to pure *trans*-[$Mo(CO)_2(dmpe)_2$]BF_4 gave [$Mo(CO)(NO)(dmpe)_2$]BF_4 [ν(CO) 1945, ν(NO) 1650 cm^{-1}; Λ(CH_2Cl_2–acetone) 105 S cm^3 mol^{-1}] and (**1**), together with CO_2 and CO only;[8] N_2O was not found. These are the first observations of the conversion of nitrite to N_2O and of CO to CO_2 on a metal outside group VIII. The need for elimination of CO_2 in this reaction is emphasized by the observation that (**1**) reacts with $NOPF_6$ in liquid SO_2 to form *cis*-[$Mo(CO)_2(SO_2)(dmpe)_2$]$(PF_6)_2$, [ν(CO) 1952, 1889; ν(SO_2) 1313, 1298, 1160, 558 cm^{-1}] only; in all hydrogen-containing solvents investigated, the product of this reaction is [$MoH(CO)_2(dmpe)_2$]PF_6. Oxidation of (**1**) with $AgNO_3$ (2 moles) gives[9] [$Mo(NO_3)(CO)_2(dmpe)_2$]NO_3.

When Ag_2SO_4 (1 mole) is added to (**1**) in CH_2Cl_2 solution in the dark, a diamagnetic yellow complex $[Mo(CO)_2(dmpe)_2(SO_4)]$ [$\nu(CO)$ 1932, 1872, $\nu(SO_4)$ 1167, 1030, 977 665 cm^{-1}; m/e 548 (8%, M^+); Λ $(MeNO_2)$ 11 S cm^3 mol^{-1}] is formed. This is the first example of a neutral metal complex containing a monodentate sulphate ligand which must therefore be zwitterionic in the sense $[M^+–O–SO_3^-]$. In normal laboratory light, this compound is converted to a diamagnetic reddish-violet compound $[Mo(CO)(dmpe)_2(SO_4)]$ [$\nu(CO)$ 1802, ν (SO_4) 1220, 1150, 1025, 960, 665 cm^{-1}; λ_{max} 490 nm; M(cryoscopic in CH_2Cl_2) 636; m/e 520 (M^+), 424; $\Lambda(MeNO_2)$ 18 S cm^3 mol^{-1}] containing bidentate sulphate,[10] with elimination of CO. These eliminations appear to be driven by the need for the metal atom to avoid the eight co-ordinate structures {$[MoR(CO)_2(dmpe)_2X]$, $[Mo(CO)_2(NO_2)_2(dmpe)_2]$, and $[Mo(CO)_2$(bidentate-SO_4)$(dmpe)_2]$} which are possible alternatives in each instance. An eight co-ordinate intermediate, *e.g.*, $[MoH(CH_2)(CO)_2(dmpe)_2]$ SO_3F, may perhaps be implicated[11] in the decomposition of the alkyl-molybdenum(II) complexes.

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