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REACTIONS OF MONODINITROGEN COMPLEXES OF MOLYBDENUM. ISOLATION AND CHARACTERIZATION OF HYDRAZIDO(2−) AND MONO- AND DIHYDRIDE COMPLEXES

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Abstract—The mono-N_2 complex *fac*-$Mo(N_2)(triphos)(L_2)$ (**1**), where triphos = $PhP(CH_2CH_2PPh_2)_2$ and L = PMe_2Ph, reacts with HX (X = Br, Cl) to give the hydrazido(2−) complex, $[Mo(NNH_2)(\eta^2\text{-triphos})(PMe_2Ph)_2]X$ (**2**), in which triphos is bidentate. Complex **1** reacts with HBr (1 mol) to give an almost quantitative yield of MoHBr(triphos)(PMe_2Ph) (**3**). With HBr (1 mol), **3** produces MoH_2Br(triphos)(PMe_2Ph).

The bis-N_2 complexes of molybdenum and tungsten occupy a unique position among the N_2 complexes of the transition metal elements, because of their reactivity with (i) acids to afford high yields of ammonia and (ii) alkyl halides to produce organonitrogen ligands.[1-3] Some of these reactions have shown encouraging catalytic behaviour.[4,5] It has been stated that one reason for the unique reactivity behaviour of these complexes is the fact that they contain two rather than the single N_2 ligand found in other metal complexes. Recently we synthesized a series of mono-N_2 complexes of molybdenum and demonstrated that they generate ammonia and hydrazine in an analogous fashion to the bis-N_2 complexes.[6] We now report the isolation and characterization of species formed in the early part of the reactions of acids with *fac*-$Mo(N_2)(triphos)(L_2)$ (**1**).

The reaction of **1** with either 2 mol of HX (X = Br, Cl) in toluene or excess (*ca* 20 mol) of HX in the absence of solvent, afforded a pinkish-yellow hydrazido(2−) complex in moderate yield (eq. 1; X = Br, Cl). Addition of THF to the solid (X = Cl) produced a solution from which **2** (X = Cl) was isolated by the addition of pentane.

$$Mo(N_2)(triphos)(PMe_2Ph)_2 \xrightarrow{HX} \underset{(\mathbf{2})}{[MoX(NNH_2)(\eta^2\text{-triphos})(PMe_2Ph)_2]X}. \quad (1)$$

Evidence for the formation of a hydrazido(2−) ligand comes from (i) the IR spectrum: ν(NH) 2800–2500 cm^{-1}; 3350 (w) and 3250 (m) cm^{-1} in the BPh_4 salt; (ii) the ^{15}N NMR data: δ −63.34 (m, 1, N_α), −212.30 (m, 1, N_β) which agrees with published data;[7] and (iii) the ^1H NMR spectrum; $\delta(NNH_2)$ 10.6 ppm broad; 5.2 and 5.4 ppm in the BPh_4 and PF_6 salts, respectively.

The ^{31}P NMR spectrum shows the presence of four coordinated phosphorus atoms and with a fifth appearing as a doublet at δ −17.19 ppm, very near to the position for the terminal phosphorus atoms of free triphos. The data suggest that triphos is behaving as a bidentate ligand with P_a and P_b coordinated, and P_c pendant. Therefore, the reaction of **1** is formally analogous to that of the bis-N_2 complexes; a hydrazido(2−) ligand is formed *trans* to the conjugate base of the acid used.[3a,8]

Complex **2** (X = Br) was similarly obtained in greater than 90% yield by thorough extraction of the solid prepared by the reaction of **1** with HBr.

Heating either **6** or **7** in toluene solution resulted in the loss of one PMe_2Ph per mol of complex and the re-coordination of P_c to form *mer*-$[MoX(NNH_2)(triphos)(PMe_2Ph)]X$.

The reaction of **1** with 1 mol of HBr in benzene at room temperature, rapidly (0.25 h) produced an equimolar mixture of **1** and **2** (X = Br). When the orange solution was allowed to stir for 15 h, a dark green hydride *mer*-Mo(H)Br(triphos)(PMe_2Ph) (**3**) was isolated in quantitative yield. The corresponding chloride, **4**, was obtained in lower yield. Each 16-electron complex exhibited ν(MoH) in the IR spec-

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trum at 1876 (**3**) and 1874 (**4**) cm^{-1}. The hydride resonance appeared as a split doublet of triplets in the ^1H NMR spectrum at δ −3.60 (**3**) and −3.82 (**4**) ppm, respectively. The ^{31}P NMR spectrum of each complex was interpreted as arising from a coplanar arrangement of *mer*-triphos and PMe_2Ph. Free PMe_2Ph was identified in the ^{31}P NMR spectrum of the reaction mixture and 0.9 mol of N_2 were evolved. The reaction of **3** with HBr (1 mol) resulted in the very rapid formation of the orange eight-coordinate dihydride MoH_2Br_2(triphos)(PMe_2Ph) (**5**). In the IR spectrum ν(MoH) appears at 1878 cm^{-1} and in the ^1H NMR spectrum the hydride resonance occurs as a multiplet at δ −5.90 ppm.

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