

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

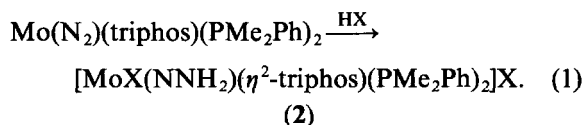
T. ADRIAN GEORGE* and ROBERT C. TISDALE

Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304, U.S.A.

Abstract—The mono-N₂ complex *fac*-Mo(N₂)(triphos)(L₂) (**1**), where triphos = PhP(CH₂CH₂PPh₂)₂ and L = PMe₂Ph, reacts with HX (X = Br, Cl) to give the hydrazido(2-) complex, [Mo(NNH₂)(η²-triphos)(PMe₂Ph)₂]X (**2**), in which triphos is bidentate. Complex **1** reacts with HBr (1 mol) to give an almost quantitative yield of MoHBr(triphos)(PMe₂Ph) (**3**). With HBr (1 mol), **3** produces MoH₂Br(triphos)(PMe₂Ph).

The bis-N₂ complexes of molybdenum and tungsten occupy a unique position among the N₂ 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 N₂ ligand found in other metal complexes. Recently we synthesized a series of mono-N₂ complexes of molybdenum and demonstrated that they generate ammonia and hydrazine in an analogous fashion to the bis-N₂ complexes.⁶ We now report the isolation and characterization of species formed in the early part of the reactions of acids with *fac*-Mo(N₂)(triphos)(L₂) (**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.



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 BPh₄ salt; (ii) the ¹⁵N 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; δ(NNH₂) 10.6 ppm broad; 5.2 and 5.4 ppm in the BPh₄ and PF₆ salts, respectively.

The ³¹P 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-N₂ 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 PMe₂Ph per mol of complex and the re-coordination of P_c to form *mer*-[MoX(NNH₂)(triphos)(PMe₂Ph)]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)(PMe₂Ph) (**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-

* Author to whom correspondence should be addressed.

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 $\text{MoH}_2\text{Br}_2(\text{triphos})(\text{PMe}_2\text{Ph})$ (5). In the IR spectrum $\nu(\text{MoH})$ 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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