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Reactions of Coordinated Dinitrogen.
9.[‡] A Comparison between the Reactions of Molybdenum and Tungsten Bis(dinitrogen) complexes with Hydrogen Bromide in Tetrahydrofuran Solution

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Recently [1], we reported the reaction of a new sub-class of bis(dinitrogen) complex, **1**, [2] where triphos = $PhP(CH_2CH_2PPh_2)_2$ and L = PPh_3, with anhydrous hydrogen bromide in tetrahydrofuran (THF) solution to give ammonium bromide, $MoBr_3$(triphos) and dinitrogen (according to eqn. 1). One of the significant features of this reaction was the isolation of a molybdenum(III) complex. Previously reported reactions of bis(dinitrogen)tetrakis(monotertiaryphosphine)molybdenum and tungsten complexes to form ammonia had implied formation of a metal(VI) product when oxyacids (or methanol) were used [3, 4]. We therefore set about to see whether or not the tridentate phosphine, triphos, was having an untoward influence on the course of the reaction.

$$\underset{\mathbf{1}}{\textit{trans}\text{-}Mo(N_2)_2(\text{triphos})(L)} + 5\ HBr \rightarrow NH_4Br + MoBr_3(\text{triphos}) + 3/2\ N_2 + [LH]Br \qquad (1)$$

The mixed phosphine complex *trans*-$Mo(N_2)_2(dppe)(PPh_2Me)_2$, **2**, [2] where dppe = $Ph_2PCH_2CH_2PPh_2$, was reacted with anhydrous hydrogen bromide in THF solution. The reaction was conducted using identical experimental conditions as those used for the first reaction (eqn. 1). The amount of dinitrogen evolved (1.49 mol per molybdenum atom) was measured using a Toepler pump. Ammonia (0.68 mol per molybdenum atom) was analyzed by the indophenol method. No hydrazine was detected. The molybdenum-containing product, $MoBr_3(dppe)(PPh_2Me)$, was isolated in 86% yield. The overall reaction is summarized in eqn. 2 and is totally analogous to that reported in eqn. 1. Analogous results have recently been reported for *cis*-$Mo(N_2)_2(Me_2PPh)_4$ [4] and *trans*-$Mo(N_2)_2(Ph_2PMe)_4$ [5]. Clearly, triphos is not dictating the pathway of the reaction. This is a general reaction for this particular acid/solvent system with bis(dinitrogen) complexes of molybdenum that contain at least one monodentate phosphine ligand.

$$\mathbf{2} + 5\ HBr \rightarrow NH_4Br + MoBr_3(dppe)(PPh_2Me) + 3/2\ N_2 + [Ph_2MePH]Br \qquad (2)$$

Another question to be answered was how would the analogous tungsten–triphos complex behave under similar conditions? We do not know since we have not been able to synthesize *trans*-$W(N_2)_2(\text{triphos})(PPh_3)$ in significant yields. However, *trans*-$W(N_2)_2(dppe)(PPh_2Me)_2$, **3**, is a known compound [6] so we switched our attention to it in light of the above results (eqn. 2). Complex **3** reacted with an excess of hydrogen bromide in THF solution but only 1.0 mol of dinitrogen per tungsten atom was evolved. No ammonia or hydrazine was produced. Protonation stopped at the hydrazido comples, $[W\ Br(NNH_2)(dppe)(PPh_2Me)_2]Br$. When the mixture was heated to 60 °C following the evolution of one mol of dinitrogen, ammonia was formed[†] *but no further dinitrogen was liberated.* This clearly demonstrates a major difference between analogous molybdenum and tungsten bis(dinitrogen) complexes; a point already noted in the literature [7]. It is worth remembering that nitrogen-fixing bacteria grown on tungstate rather than molybdate ion are incapable of producing ammonia [8].

The reactions (eqns. 1 and 2) appear to occur in two distinct steps. There is the rapid loss of one mol of dinitrogen per molybdenum atom, followed by the slow formation of ammonium bromide, $MoBr_3$(triphos) and a further half mol of dinitrogen. We have tried to identify and isolate an intermediate (or intermediates) after the rapid loss of one mol of dinitrogen. We have not been successful when the acid is hydrogen bromide. On the other hand, use of fluoroboric acid (aqueous or anhydrous) or triphenylphosphonium tetrafluoroborate enabled the stable hydrazido complex $[MoF(NNH_2)(\text{triphos})(PPh_3)]BF_4$, **4**, to be isolated and characterized. The ^{31}P NMR spectrum[§] showed that all four phosphorus atoms still occupy the equatorial positions in the coordination sphere. Reaction of **4** with hydrogen bromide in THF solution for 110 hr produced no ammonia or hydrazine at room temperature. Similarly, when **1** was treated with 48% aqueous hydrofluoric acid one mol of dinitrogen was evolved but no ammonia or hydrazine were produced. However, ammonia was

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[‡] See ref. 1.

[†] Under these reaction conditions, the yield of ammonia is limited due to consumption of HBr in the competing HBr/THF reaction to give 4-bromobutanol and 1,4-dibromobutane.

[§] ^{31}P NMR (40.5 MHz), δ (ppm): 82.50 (dd, 1P, P^a, $J_{P^a-P^b}$ = 0.0, $J_{P^a-P^c}$ = 170.9, J_{P^a-F} = 34.0 Hz); 51.59 (dd, 2P, P^b, $J_{P^b-P^c}$ = 16.8, J_{P^b-F} = 46.6 Hz); 30.36 (ddt, 1P, P^c, J_{P^c-F} = 23.3 Hz). P^c is due to Ph_3P and P^b the terminal phosphorus atoms of triphos; d = doublet, t = triplet.

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produced when **1** was treated with triphenylphosphonium bromide in THF solution.

The effect of changing acid and solvent upon the reactions of both **1** and **2** have been investigated. In THF solution, anhydrous HCl and HI behaved similarly to HBr in terms of N_2 evolved, and ammonia and molybdenum(III) halide formation, although the yield of ammonia in the HI reaction was diminished due to rapid consumption of HI by THF. Complex **2** also behaved similarly with anhydrous HCl and HI in THF solution. However, a 6% yield of hydrazine was obtained in the HCl reaction. This was the first example in which we have seen a hydrazine yield greater than *ca.* 0.1%. In methanol solution, **2** reacted totally analogously with anhydrous HBr (see eqn. 2). In contrast, **1** gave only a small amount of ammonia (8%) with anhydrous HBr with the nitrogen balance appearing as dinitrogen. No ammonia or hydrazine was produced with concentrated sulfuric acid in methanol. With HBr, $MoBr_3$(triphos) was the molybdenum-containing product. The extremely low solubility of **1** in methanol may account for these differences from THF solution; **2** is noticeably more soluble in methanol.

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