the bond angles at the four-ring oxygen atoms vary from 130.0 (2)° up to 150.9 (2)°. The formation of the eight-membered ring also constrains the triphosphate chain to be in a much more highly folded configuration than in the β,γ complex or in other crystal structures of the triphosphate ion. The α,γ complex exhibits a PPP angle of 86.0° and a P1–P3 distance of 3.987 Å as compared to 116.1° and 4.905 Å for the β,γ complex.

Acknowledgment. We are grateful to Professors Delbert Mueller at Kansas State University and P. A. Hart at the University of Wisconsin—Madison for recording the NMR spectra. This research was supported by Research Corporation, by the National Science Foundation (Grant CHE-7809301), and by the National Institutes of Health (Grant GM-17378).

Supplementary Material Available: Fractional coordinates and thermal parameters (Table II) of α,γ-$Co(NH_3)_4H_2P_3O_{10}\cdot H_2O$ (1 page). Ordering information is given on any current masthead page.

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Received April 21, 1980

Reactions of Coordinated Dinitrogen. 8.[1] Formation of Ammonia by Protonation of a Molybdenum–Dinitrogen Complex and Isolation and Characterization of the Molybdenum-Containing Product

Sir:

The conversion of metal-bound dinitrogen, N_2, into ammonia by protonolysis in high stoichiometric yield was first reported in 1975,[2,3] and an example is shown in eq 1, where L = PMe_2Ph or

$$W(N_2)_2L_4 \xrightarrow[\text{MeOH, 20 °C}]{H_2SO_4} 2[NH_4^+] + N_2 + 4[HL][HSO_4] + [\text{W(VI) oxide?}] \quad (1)$$

$PMePh_2$. A similar reaction occurred with the molybdenum analogues although the yield of ammonia was lower than for the corresponding tungsten complexes. By variation of the protic acid and the solvent, it is possible to produce hydrazine as well as ammonia.[5]

In this communication, we present our recent results concerning the conversion of coordinated N_2 into ammonia, which differ in a number of significant ways from work previously reported.[2-5] We have successfully accomplished the first reported conversion of metal-coordinated dinitrogen into ammonia in which the fate of the metal has been determined. This reaction is shown in eq 2, where triphos = $PhP(CH_2CH_2PPh_2)_2$ and L = PPh_3. Complex

$$\underset{\mathbf{1}}{2Mo(N_2)_2(\text{triphos})(L)} + 8HBr \rightarrow 2NH_4Br + 2MoBr_3(\text{triphos}) + 3N_2 + 2L \quad (2)$$

1,[1] a new subclass of bis(dinitrogen) complexes of molybdenum, reacted in tetrahydrofuran (THF) solution with anhydrous hydrogen bromide to produce ammonium bromide. No hydrazine or hydrazinium bromide was detected among the reaction products.[6] Ammonium bromide was detected by infrared spectroscopy among the reaction products after solvent and excess HBr had been removed in vacuo. The yield of ammonia was determined quantitatively by the indophenol method after either aqueous, nonaqueous (ethanol), or two-phase (dichloromethane–water) extraction of ammonium bromide from the residue.

There are a number of significant features of this reaction that deserve mention. (i) The six electrons that are required for the conversion of N_2 into $2NH_3$ came from 2Mo(0) → 2Mo(III) + $6e^-$. In previous work, it has been proposed that the six electrons necessary for the reduction of N_2 to ammonia came from M(0) → M(VI) + $6e^-$.[2] (ii) This was the first time that the metal-containing (molybdenum in this case) product has been characterized after ammonia formation; $MoBr_3$(triphos) was isolated in >90% yield.[7] (iii) Base distillation *was not required* in order to liberate (or produce) ammonia from the reaction products. This is to be contrasted with other work where base distillation was required either to separate ammonia from the reaction products or to assist in the final step(s) of the conversion of metal-bound N_2 into ammonia.[2,5] (iv) The isolated molybdenum-containing product was the precursor for the preparation of the bis(dinitrogen) complex **1**.[8]

In a typical reaction carried out on a vacuum line, THF (10 mL) and anhydrous HBr (3.6 mmol) were condensed into a round-bottomed flask (25 mL) cooled to −196 °C, containing complex **1** (0.2 mmol) and a small magnetic stirring bar. When the mixture was warmed, the solvent melted to give a bright orange suspension. Just above 0 °C, a gas was observed to bubble from the suspension, which eventually became a yellow homogeneous solution when gas evolution had ceased. At this time, between 0.9 and 1.0 mol of N_2 per molybdenum atom had been evolved as determined by Toepler pump measurements.[9] A further 0.4–0.5 mol of N_2 per molybdenum atom was evolved when the solution was allowed to stir for 24–36 h at room temperature. By this time, both NH_4Br and $MoBr_3$(triphos) had precipitated from solution. The total amount of N_2 evolved ranged between 1.3 and 1.5 mol. Solvent was removed and the residue extracted with a mixture of dichloromethane and water. The dichloromethane layer was separated and extracted with more water. The combined aqueous fractions were made up to a known volume and analyzed for ammonia by the indophenol method. Generally, yields of ammonia approached or slightly exceeded 0.7 mol per atom of molybdenum. The molybdenum-containing product slowly decomposed during the dichloromethane–water extraction step. Isolation of pure $MoBr_3$(triphos) was carried out in a separate experiment in which only N_2 evolution was measured. All volatiles were removed from the reaction vessel, and the resulting yellow solid was washed with ethanol and dried. Its identity was confirmed by elemental analysis.[7]

The reaction appeared to proceed in two steps. The first step was the relatively rapid loss of 1 mol of N_2. This is very similar to the reported reactions of excess HBr with $M(N_2)_2(dppe)_2$ and $M(N_2)_2(PMe_2Ph)_4$ (where M = Mo or W and dppe = $Ph_2PCH_2CH_2PPh_2$) to form the corresponding hydrazido(2−) complexes $[MBr(NNH_2)(dppe)_2]Br$ and $MBr_2(NNH_2)(PMe_2Ph)_3$, respectively, with the rapid loss of 1 mol of N_2.[10]

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(1) Part 7: George, T. A.; Kovar, R. A. *Inorg. Chem.*, submitted for publication.

(2) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature (London)* **1975**, *253*, 39–40. *J Chem. Soc., Dalton Trans.* **1977**, 1852–1860.

(3) Many other reports of the formation of ammonia from dinitrogen in the presence of metal ions and reducing agents have appeared. Most of the work has been critically analyzed and published in a recent review article.[4]

(4) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.

(5) Takahasti, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405–3407.

(6) Analysis for hydrazine was carried out by the *p*-(dimethylamino)benzaldehyde method: Watt, G.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006–2008.

(7) Anal. Calcd for $MoBr_3$(triphos), $C_{34}H_{33}Br_3MoP_3$: C, 46.93; H, 3.82; Br, 27.55. Found: C, 47.0; H, 3.78; Br, 27.76.

(8) Complex **1** was prepared by the reduction of MoX_3(triphos) (X = Cl or Br) with sodium amalgam in THF under an atmosphere of dinitrogen with PPh_3 (1.1 mol) present. ^{1}Anal. Calcd for $Mo(N_2)_2(\text{triphos})(PPh_3)\cdot{}^1/_2THF$, $C_{54}H_{52}MoN_4O_{1/2}P_4$: C, 65.9; H, 5.28; N, 5.69. Found: C, 64.8; H, 5.30; N, 5.70. IR (ν_{NN}) (KBr) 1955 cm^{-1}.

(9) Gases were analyzed by mass spectroscopy and results compared with N_2–H_2 mixtures of known different ratios. The maximum amount of dihydrogen found in the dinitrogen gas never exceeded 0.1% of the total amount of gas evolved.

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Therefore, we propose that in this first step a hydrazido(2–) complex is formed as an intermediate. The reaction is shown in eq 3. The hydrazido(2–) complex may alternatively form as

$$2Mo(N_2)_2(triphos)(L) + 4HBr \rightarrow 2MoBr_2(NNH_2)(triphos) + 2N_2 + 2L \quad (3)$$

$[MoBr(NNH_2)(triphos)(L)]Br$. So far we have not been able to isolate and characterize this intermediate.

The second, slower step involves further loss of $^1/_2$ of a mol of N_2 and formation of ammonia. This latter step appears to be best described as a valence disproportionation involving two $[Mo(N\text{-}NH_2)]$ units (eq 4). The reaction appears to be at least bimolecular since reducing the volume of solvent at ambient temperature after loss of 1 mol of N_2 causes an increase in the rate of evolution of the remaining $^1/_2$ of a mol of N_2. The intimate details of this second step remain a mystery at present. However, we do know that there is no scrambling of nitrogen atoms between NN units. This was shown by reacting HBr with **1** that had been partially labeled with dinitrogen-30. Analysis of the total amount of N_2 evolved showed *no* increase in the amount of $^{14}N\equiv^{15}N$ present over that occurring in the original N_2 gas used to prepare labeled complex **1**. This result together with the absence of hydrazine among the products rule out a linear tetrazane-type intermediate.

$$2MoBr_2(NNH_2)(triphos) + 4HBr \rightarrow 2MoBr_3(triphos) + 2NH_4Br + N_2 \quad (4)$$

It is interesting to contrast the ligand arrangement of the three groups of bis(dinitrogen) complexes: $Mo(N_2)_2(dppe)_2$, $Mo(N_2)_2L_4$ (where L = PMe_2Ph or $PMePh_2$), and **1**. The former complex contains two bidentate tertiary phosphine ligands, and protonolysis stops at the stage where diprotonation has been achieved and the hydrazido(2–) complex formed, e.g., $[MoBr(NNH_2)(dppe)_2]Br$. In contrast, the bis(dinitrogen) complexes of molybdenum containing four monodentate phosphine ligands are protonated to varying extents, depending upon the acid and the solvent, with the ultimate product being ammonia (with hydrazine often as a coproduct). Apparent intermediates in the ammonia-forming reaction that have been isolated and characterized for the molybdenum complexes are, e.g., $MoBr(NNH)(dppe)_2$[12] and $MoBr_2(NNH_2)(PMe_2Ph)_3$.[11] It has been proposed that the difference in behavior between these two groups of bis(dinitrogen) complexes rests with the ease with which coordination sites become available during the course of protonolysis together with the nature of the conjugate base of the acid.[2] Complex **1** is a hybrid of these two types. On the one hand, it contains the tridentate ligand which remains coordinated to molybdenum in the molybdenum-containing product while on the other hand it contains a monodentate phosphine which is displaced at some stage during protonolysis.

Further work is in progress to (i) isolate and characterize the proposed intermediate, (ii) elucidate the mechanism of the reaction, (iii) study the tungsten analogue, and (iv) carry out the protonolysis reaction in the presence of a reducing agent in order to regenerate the N_2-binding species in situ and hence produce a catalytic cycle.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(12) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1520–1524.

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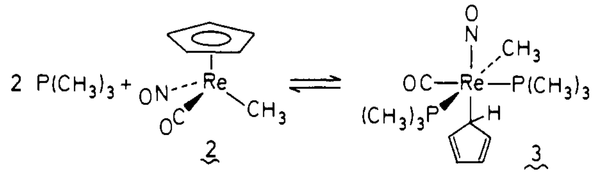
Received May 12, 1980

Conversion of an η^5-Cyclopentadienyl–Metal Complex to an η^1-Cyclopentadienyl–Metal Complex upon Addition of Trimethylphosphine

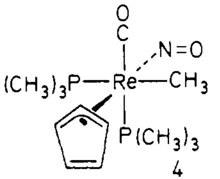
Sir:

We recently reported several synthetic routes to a hydroxymethyl metal compound, $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_2OH)$ (**1**). Hydroxymethyl metal compounds have been suggested as important intermediates in the metal-catalyzed reduction of carbon monoxide[2] but have previously been unavailable for study.[3,4] Pruett has suggested that CO insertion into a $Rh\text{–}CH_2OH$ species is a likely step in the rhodium cluster catalyzed synthesis of ethylene glycol from CO and H_2. In an attempt to find a model for such a CO-insertion process, we have studied the reactions of $P(CH_3)_3$ with $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_2OH)$ (**1**) and with $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$ (**2**). We were surprised to find that reaction of $P(CH_3)_3$ with **2** does not produce an acetylrhenium complex but instead produces an η^1-cyclopentadienyl bis(phosphine) derivative (**3**).



An equimolar solution of **2** and $P(CH_3)_3$ (0.24 M) in acetone-d_6 undergoes a rapid reaction at room temperature. Proton NMR (270 MHz) spectra indicate that 50% of methylrhenium compound **2** (δ 5.80; 0.88) and 95% of the free $P(CH_3)_3$ [δ 0.96 (d, J = 2.2 Hz)] are consumed while a new product **3** appears with resonances at δ 5.57 (t, J = 1.5 Hz, 5 H), 1.70 (d, J = 8 Hz, 9 H), 1.49 (d, J = 8.3 Hz, 9 H), and 0.60 (dd, J = 8.3, 2.0 Hz, 3 H). The NMR spectrum thus requires that adduct **3** contain a methyl group which is cis to one $P(CH_3)_3$ ligand and trans to another $P(CH_3)_3$ ligand. When 2.5 equiv of $P(CH_3)_3$ were employed, complete conversion of the red methyl compound **2** to the yellow bis(phosphine) adduct **3** was observed. The reaction of $(PCH_3)_3$ with **2** is rapid in THF, acetone, benzene, and hexane. For synthetic purposes, hexane is the solvent of choice since **3** crystallizes from solution as it is formed and drives the equilibrium (vide infra) toward **3**. Reaction of **2** (0.111 g, 0.341 mmol) with $P(CH_3)_3$ (1.10 mmol) followed by rapid removal of hexane (0 °C, 10^{-3} mmHg) gave **3** as a yellow solid (0.163 g; 100%). The infrared spectrum (cyclohexane) of **3** has bands at 1994 and 1690 cm^{-1} compared with 1970 and 1715 cm^{-1} for starting material **2**.

The spectroscopic properties of **3** are consistent with either of two different 18-electron formulations: a fluxional $\eta^1\text{-}C_5H_5Re^I$ derivative with a linear nitrosyl unit (**3**) or a fluxional $\eta^3\text{-}C_5H_5Re^{III}$ derivative[6] with a bent nitrosyl ligand (**4**). Structure **4** seemed



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