Reactions of Coordinated Dinitrogen. 12.[1] Identification of Intermediates in the Conversion of Molybdenum-Bound Dinitrogen into Ammonia and Hydrazine. Factors Affecting the Ammonia-Forming Reaction

Sir:

When bis(dinitrogen) complexes of molybdenum and tungsten are treated with an excess of strong acid, with few exceptions, a complex containing the hydrazido(2–) ligand has been identified either as a product in the reaction or as an intermediate on the way to the formation of ammonia and hydrazine.[2–4] In the case of those molybdenum complexes that produce ammonia, the stoichiometry of the reaction can be represented by eq 1 and 2, with a molybdenum(III) complex

$$\{Mo^0(N_2)_2\} \xrightarrow{H^+} \{Mo(NNH_2)\} + N_2 \qquad (1)$$

$$\{Mo(NNH_2)\} \xrightarrow{H^+} {}^1/_2N_2 + NH_4^+ + \{Mo(III)\} \qquad (2)$$

as the final molybdenum-containing product.[3,5] We wish to report the identification of *two isomeric hydrazido(2–) complexes*, **2A** and **2B** (Scheme I), that are formed as a mixture in the reaction of excess HBr in tetrahydrofuran (THF) solution with *trans*-[Mo(N_2)$_2$(triphos)(PPh$_3$)] (**1**),[6] where triphos = PhP(CH$_2$CH$_2$PPh$_2$)$_2$.[7] From this mixture of hydrazido(2–) complexes ammonia and a trace of hydrazine are produced in THF solution, but in benzene or toluene solution more hydrazine than ammonia is produced.[9] On the basis of data presented below, reversible phosphine dissociation is the next recognizable step toward ammonia formation.

The reaction of **1** with anhydrous HBr (ca. 18 mol) in THF occurred with rapid evolution of dinitrogen (ca. 1.0 mol) to give a golden brown solution.[10] The $^{31}P\{^1H\}$ NMR spectrum[11] revealed two [(triphos)(PPh$_3$)]-containing hydrazido(2–) complexes, **2A** and **2B** (see Figure 1).[12] The solution was monitored at different time intervals (see Figure 1). Resonances due to **2B** began to decrease and soon a resonance due to uncoordinated PPh$_3$ was observed, increasing at a rate commensurate with the rate of decrease of **2B**. After about 1 h only **2A** and PPh$_3$ were observed in the spectrum. The intensities of resonances due to **2A** slowly decreased until little remained after 24 h. Thus, once PPh$_3$ dissociates, to form **2C** for example, subsequent chemistry occurs rapidly, leading to eventual ammonia formation. Any diamagnetic intermediates beyond **2A** and **2B** must have very small steady-state concentrations.

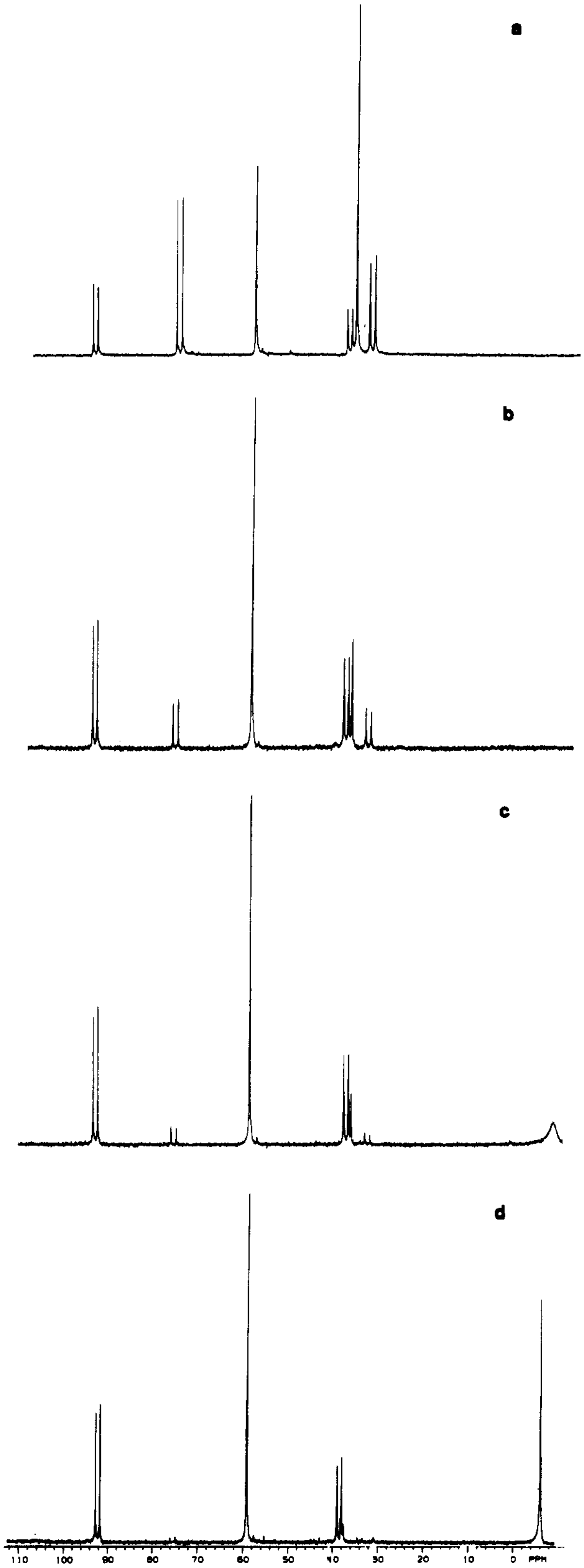

Figure 1. Successive $^{31}P\{^1H\}$ NMR spectra (146 MHz, –60 °C) of a mixture of two isomers of [MoBr(NNH$_2$)(triphos)(PPh$_3$)]Br, **2A** and **2B**, showing **2B** disappearing and PPh$_3$ appearing in THF solution with excess anhydrous HBr added: (a) initial spectrum (0 min); (b) spectrum after 16 min at room temperature; (c) spectrum after 26 min at room temperature; (d) spectrum after 36 min at room temperature. The broadness of the resonance due to PPh$_3$ may be explained by the presence of acid in solution (spectrum c). Due to the reaction of HBr with THF, little acid remains after 36 min. An adjustment in the intensities of the resonances is made between spectra a and b. For phosphorus atom assignments see ref 12.

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(5) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153–6154.

(6) George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285–287.

(7) Resonances in the ^{15}N NMR spectrum assigned to two hydrazido(2–) complexes have been reported in the reaction of *cis*-[Mo($^{15}N_2$)$_2$(PMe$_2$Ph)$_4$] with H$_2$SO$_4$ in THF solution.[8]

(8) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980.

(9) For analytical procedures employed, see ref 5.

(10) Typically, between 0.1 and 0.3 g of **1** was employed in a reaction. Dinitrogen measurements were made by using a Toepler pump. For experimental details, see ref 5.

(11) The $^{31}P\{^1H\}$ NMR spectra were obtained with a Nicolet 360-MHz spectrometer operating at 146 MHz. Solvent contained 10% of the corresponding perdeuterio solvent for locking purposes. Chemical shifts (ppm) are referenced to 85% H$_3$PO$_4$.

(12) ^{31}P NMR [THF, PhP$_a$(CH$_2$CH$_2$P$_b$Ph$_2$)$_2$, Ph$_3$P$_x$, $^2J_{P_aP_b}$ = 0.0 Hz]: **2A**, 92.6 (d, $^2J_{P_aP_x}$ = 145.2 Hz, P$_a$), 58.6 (d, $^2J_{P_bP_x}$ = 16.3 Hz, P$_b$), 38.0 (dt, P$_x$); **2B**, 75.4 (d, $^2J_{P_aP_x}$ = 163.7 Hz, P$_a$), 37.3 (d, $^2J_{P_bP_x}$ = 17.5 Hz, P$_b$), 33.7 ppm (dt, P$_x$).

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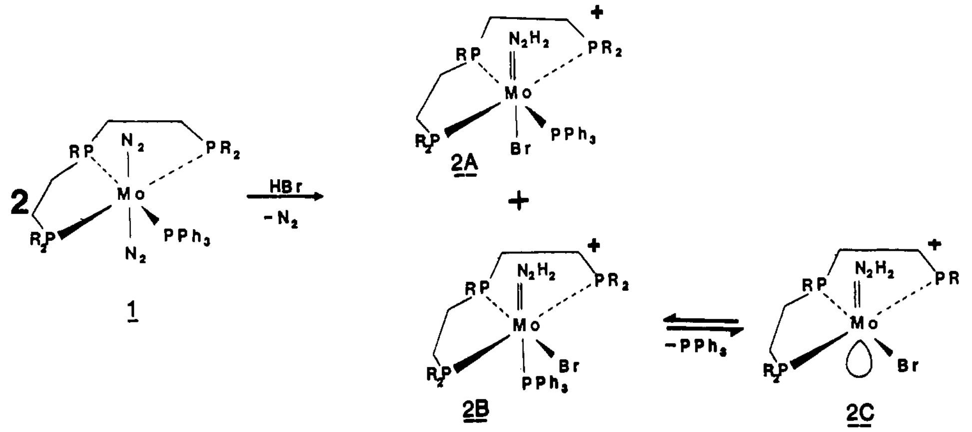
Scheme I



Addition of excess PMe_2Ph to a mixture of **2A** and **2B** in THF solution resulted in the appearance in the $^{31}P\{^1H\}$ NMR spectrum of resonances due to a new species, $[MoBr(NNH_2)(triphos)(PPhMe_2)]Br$ (**3**),[13] commensurate with the disappearance of **2B**. Slowly, resonances due to **2A** decreased in intensity until only **3**, PPh_3, and PMe_2Ph were observed. Significantly, no ammonia was formed in this reaction. We believe **3** is the PMe_2Ph analogue of **2B** from which the more basic PMe_2Ph does not dissociate. Although PPh_3 is not labile in **2A** (no PMe_2Ph incorporation), there is a pathway by which **2A** is converted into **3** (via **2B** or **2C**).

The reaction of **1** with sulfuric acid in either THF or methanol solution at room temperature produced 1.0 mol of dinitrogen but no ammonia.[14] Coordination of sulfate as a bidentate ligand (PPh_3 loss) would prevent development of the five-coordinate intermediate **2C**. Interestingly, *trans*-$[Mo(N_2)_2(dppe)(PMe_2Ph)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which contains two monodentate phosphines, did react with sulfuric acid to produce ammonia.[15]

Solid **1** reacted with liquid HBr (or HCl) in the absence of solvent to produce a green-brown solid. At this point excess acid can be removed (to give an acid-free solid[16]) or left. Addition of solvent (THF, benzene, toluene, or CH_2Cl_2) gave a solution, the $^{31}P\{^1H\}$ NMR spectrum of which showed a mixture of **2A** and **2B** identical with that obtained from the reaction carried out in solution. On the basis of the relative rates of disappearance of **2A** and **2B**, we can say that **2A** and **2B** are not formed sequentially from **1**.

The $^{31}P\{^1H\}$ NMR spectrum of an *acid-free* mixture of **2A** and **2B** in THF showed rapid decrease in resonances due to **2B** and appearance of PPh_3. This reaction produced ammonia.[17] However, a similar mixture in toluene showed no change over an 18-h period, although PMe_2Ph incorporation occurred. Thus, it appears that reactions occurring after phosphine dissociation require a solvent of higher dielectric constant and/or solvating ability than toluene to facilitate reactions involving polar (ionic) intermediates.

Attempts to isolate **2A** and **2B** have been unsuccessful. However, in reactions using anhydrous HCl two hydrazido(2−) complexes have been isolated. Thus, addition of HCl to **1** in the absence of solvent produced a mixture of **4A** and **4B**.[18] Addition of excess PMe_2Ph to a toluene solution of the acid-free mixture produced brown crystals that were filtered off after 18 h. Reduction of the filtrate volume by half caused a lime green solid to form over 18 h. The brown crystals were identified as **4A**, $[MoCl(NNH_2)(triphos)(PPh_3)]Cl\cdot C_7H_8$,[19] and the lime green solid was identified as the PMe_2Ph analogue of **4B**, $[MoCl(NNH_2)(triphos)(PPhMe_2)]Cl\cdot{}^1/_2C_7H_8$ (**5**).[20]

In order to account for the greater lability of PPh_3 in **2B** than in **2A**, it is proposed that in **2B** PPh_3 is trans to the multiply bonding hydrazido(2−) ligand. Since $[MoF(NNH_2)(triphos)(PPh_3)]BF_4$ (**6**) did not produce ammonia (HBr/THF) or incorporate PMe_2Ph (THF, 17 h, 25 °C) we assume a structure analogous to **2A** for **6**. Whereas **2A** did eventually give ammonia, presumably by isomerizing to **2B** or by direct conversion to **2C**, **6** remained inert. This suggests that halide ion dissociation is important in the reactivity of those complexes with the same structure as **2A**.

A significant difference between reactions carried out in THF and benzene is the concentration of HBr at any given time since HBr is rapidly consumed by reaction with THF.[21] In THF (HBr, 7 days), **4A** and **4B** yielded 0.17 and 0.03 mol of ammonia/mol of Mo, respectively, whereas in benzene (HBr, 3 days), **4A** yielded hydrazine (0.13 mol) and ammonia (0.29 mol) and **4B** yielded hydrazine (0.37 mol) and ammonia (0.24 mol).[22]

We are presently attempting to isolate and characterize further intermediates in the ammonia-forming reaction and

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(13) ^{31}P NMR [THF, −40 °C, $PhP_a(CH_2CH_2P_bPh_2)_2$, $PhMe_2P_x$, $^2J_{P_aP_b} = 0.0$ Hz]: **3**, 72.4 (d, $^2J_{P_aP_x} = 162.2$ Hz, P_a), 42.0 (d, $^2J_{P_bP_x} = 19.3$ Hz, P_b), −2.8 ppm (dt, P_x).

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(16) We cannot eliminate the possibility of HBr of solvation due to strong hydrogen bonding with **2A** and **2B**. Cycles of dissolution and evaporation using CH_2Cl_2 and pentane have been used to ensure minimum HBr concentrations.

(17) Nitrogen-15 labeling experiments[5] have ruled out the formation of any new N–N bonds and hence the net reaction following hydrazido(2−) complex formation is more accurately represented by $2\{Mo(NNH_2)\} \rightarrow N_2 + 2NH_4^+ + 2\{Mo(III)\}$, rather than by eq 2. In the absence of acid, the reaction cannot go to completion but there are theoretically sufficient protons for up to 50% NH_4^+ formation.

(18) ^{31}P NMR [THF, −40 °C, $PhP_a(CH_2CH_2P_bPh_2)_2$, Ph_3P_x, $^2J_{P_aP_b} = 0.0$ Hz]: **4B**, 76.7 (d, $^2J_{P_aP_x} = 169.3$ Hz, P_a), 40.3 (d, $^2J_{P_bP_x} = 17.4$ Hz, P_b), 35.3 ppm (dt, P_x).

(19) Anal. Calcd for $C_{59}H_{58}Cl_2MoN_2P_4$: C, 64.76; H, 5.34; N, 2.56. Found: C, 64.86; H, 5.59; N, 2.67. ^{31}P NMR[6] [CH_2Cl_2, 23 °C, $PhP_a(CH_2CH_2P_bPh_2)_2$, Ph_3P_x, $^2J_{P_aP_b} = 0.0$ Hz]: 92.0 (d, $^2J_{P_aP_x} = 152.2$ Hz, P_a), 57.5 (d, $^2J_{P_bP_x} = 16.6$ Hz, P_b), 36.1 ppm (dt, P_x). ^1H NMR [CD_2Cl_2, 90 MHz, 23 °C)]: 2.4 (s, CH_3), 2.6 (br, CH_2) 6.8–7.8 (m, C_6H_5), 8.5 ppm (br, NH_2 disappears upon addition of D_2O). IR (KBr): 3307 w, 2872 m, br, 2575 cm^{-1} m, vbr.

(20) Anal. Calcd for $C_{45.5}H_{50}Cl_2MoN_2P_4$: C, 59.38; H, 5.48; N, 3.04. Found: C, 58.82; H, 5.52; N, 3.02. ^{31}P NMR[6] (CH_2Cl_2, 23 °C, $PhP_a(CH_2CH_2P_bPh_2)_2$, $PhMe_2P_x$, $^2J_{P_aP_b} = 0.0$ Hz): 70.6 (d, $^2J_{P_aP_x} = 171.0$ Hz, P_a), 39.8 (d, $^2J_{P_bP_x} = 19.3$ Hz, P_b), 0.6 ppm (dt, P_x). IR (KBr): 3210 w, 2895 m, sh, 2730 cm^{-1} s, br.

(21) Fried, S.; Kleene, R. D. *J. Am. Chem. Soc.* **1941**, *63*, 2691.

(22) Hidai[4] has proposed that the formation of hydrazine in the reaction of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ with HCl in 1,2-dimethoxyethane arose via a pathway involving protonation of a hydrazido(2−) complex at the metal to form a hydride–hydrazido(2−) complex. We have not detected a metal hydride spectroscopically but cannot eliminate the possibility of such a complex in these reactions.

delineate the mechanisms of ammonia and hydrazine formation from the same bis(dinitrogen) complex.

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Articles

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Mixed-Valence Ions of Ruthenium Containing Fumaronitrile and Tetracyanoethylene as Bridging Groups

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Complexes of the type $[(H_3N)_5Ru]_nL^{2n+}$ (L = Fum, $n = 2$; L = TCNE; $n = 4$) were synthesized and characterized. Cyclic voltammetry of the $[(H_3N)_5Ru]_2Fum^{4+}$ ion in CH_3CN shows two reversible one-electron waves for the stepwise oxidation of the two Ru(II) centers. The potential difference, $\Delta E_{1/2}$, and the appearance of an intervalence transfer (IT) band at 975 nm ($\epsilon = 150\ M^{-1}\ cm^{-1}$) for the mixed-valence ion $[(H_3N)_5Ru]_2Fum^{5+}$ indicate that the [2,3] ion is stable in solution with respect to disproportionation to the 4+ and 6+ ions. The IT half-bandwidth, $\Delta\bar{\nu}_{1/2}$, was found to be broader than calculated. The extent of electron delocalization, α^2, estimated for the [2,3] ion, was found to be 3×10^{-4}, implying that the ion belongs to class II, weakly coupled systems. The IT band showed the expected solvent dependence. The tetraruthenium TCNE ion displayed five reversible one-electron waves; the negative one corresponds to the $TCNE^{0/-}$ couple. The presence of MLCT and LMCT bands at low energy (800-nm region) indicates strong interaction between Ru(II) and Ru(III) centers, suggesting a strongly coupled ion. The potential differences between the ruthenium couples also support a strongly coupled system. The failure to detect IT bands is believed due to the fact that they appear in the same region as the MLCT and LMCT bands. The doubly oxidized ion $[(NH_3)_5Ru]_4TCNE^{10+}$ was found to be more stable than the 9+ and 11+ ions.

Introduction

The first mixed-valence ion, containing two rutheniums and a pyrazine bridging group, was reported by Creutz and Taube more than a decade ago.[2] Since then, a number of such ions have been studied. These studies have involved systematic variations of the bridging ligand[3–8] as well as the auxiliary ligand.[5–7] Most of the ions reported are homonuclear with two metal centers that are usually ruthenium or ferrocene iron, although ions containing pentacyanoiron[5,7,9] and platinum and palladium[10] have been reported. There are also a few examples of heteronuclear mixed-valence ions.[8–12] Mixed-valence ions have been classified by Robin and Day[13] according to the extent of electronic interaction between the metal centers. Most ions are of class II or weakly interacting systems. Class II ions have been treated by theories advanced by Hush[14] and Marcus.[15] In particular, class II ions display an intervalence-transfer transition (IT) that corresponds to a light-induced electron transfer between the metal centers. This transition provides evidence for the extent of electron delocalization in the ground state.[13,14]

Our interest in mixed-valence ions focuses on new briding groups, heteronuclear ions,[12] and polynuclear ions, especially those with metal ions attached to a common bridging group. To our knowledge, there are only two reports[16,17] of polynuclear mixed-valence ions containing ruthenium centers both of which were weakly interacting.

In this paper we describe the preparation and characterization of mixed-valence ions containing fumaronitrile (Fum) and tetracyanoethylene (TCNE) bridging ligands. The bimetallic fumaronitrile might be expected to serve as a model for the TCNE complex. However, there might well be differences since TCNE is a better acceptor than fumaronitrile.[18]

Experimental Section

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by a literature procedure,[19] recrystallized twice from

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