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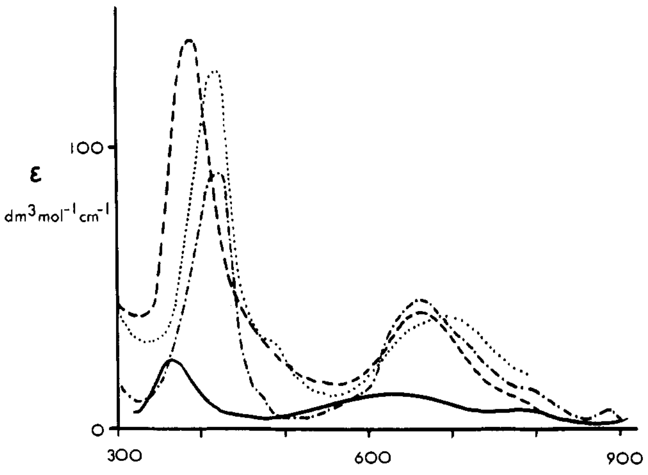

Figure 3. Electronic spectra of complexes of Ni(II) in aqueous solution: spectra of the Ni(II) complex with THEC at (—) pH 7.48, where the complex is blue, and (-•-•) pH 9.99, where it is an intense green. The other two spectra are those generated for the pure high-spin form of TMC at low pH (···) with use of the reported equilibrium constant for the high-spin/low-spin equilibrium (Herron, N.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 89) and that for the Ni(II) complex with TMC at high pH (- - -), where it is present as the monohydroxy complex. It should be noted that the THEC complex of Ni(II) does not produce a spin-paired form at high ionic strength.

The most interesting property of THEC is its ability to complex rapidly with metal ions. In a recent study of the formation constants of TMC complexes,[12] it was found necessary to allow several hours between each addition of acid in the potentiometric titrations with metal ions such as Co^{II} and up to 1 week for equilibration with the Ni^{II} complex.[18] Equilibration with the complexes of THEC appeared instantaneous on the time scale of the potentiometric titration, except for Ni(II), where equilibrium was established within 2 min after each addition of acid. This is in contrast to tetrakis(2-cyanoethyl)cyclam, which, in spite of having lower pK_a values than THEC (Table I), equilibrates only very slowly even with Cu^{II}. We must conclude, therefore, that a lowering of the pK_a values of the macrocycle is by itself insufficient to produce rapid metalation of macrocycles and that the hydroxyethyl groups of THEC are aiding the metalation reaction by providing points of attachment outside the macrocyclic ring for the incoming metal ion. What is important about these points of initial attachment is that they should not provide a structure of such stability that, as with CTA, the metal ion prefers to remain outside of the macrocyclic ring. The reason for nonentry of the metal ions into the macrocyclic ring of CTA becomes clear in examining Table II, where we see that the stability of the TMC and THEC complexes which appear to be bound in the macrocyclic ring is very much lower than that of the analogous CTA complexes.

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Contribution from the Department of Chemistry
and the Scarborough Campus, University of Toronto,
Toronto, Ontario M5S 1A1, Canada

Reversible Binding of Dinitrogen and Dihydrogen by $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$: Use of $[9\text{-}BBN]_2$ as a Phosphine Sponge Reagent

Rudy Luck and Robert H. Morris*

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There are only a few complexes known that react with dinitrogen by dissociation of a tertiary phosphine ligand, PR_3 (eq 1). These include $Ni(PEt_3)_4$,[1] $Mo(N_2)(PMe_3)_5$,[2]

$$L_nM\text{-}PR_3 + N_2 \xrightleftharpoons{K_1} L_nM{-}N{\equiv}N + PR_3 \tag{1}$$

$RuH_2(PPh_3)_4$,[3] $FeH_2(PEt_2Ph)_4$,[4] $Mo(PMe_3)_6$,[5] and $Ta(C_2H_4)(PMe_3)_4Cl$[6] written qualitatively in the order of increasing values of K_1. The sizes of these equilibrium constants are determined by the strength of the metal–nitrogen and metal–phosphorus interactions, the latter being weakened usually because of steric congestion around the binding site. These compounds are powerful reductants, and all[2-5] but two[1,6] have been reported to give dihydride complexes upon reaction with dihydrogen (eq 2).[7]

$$L_nM{-}PR_3 + H_2 \xrightleftharpoons{K_2} L_nM{<}^{H}_{H} + PR_3 \tag{2}$$

Difficulties sometime arise in the separation of the product complexes from these equilibrium mixtures containing free phosphine ligand and starting material.[1,3,4] Ideally a "phosphine sponge" reagent[8] is needed to drive these equilibria to the right, but metal complexes[8a] or methyl iodide[8b] added to such mixtures in order to remove free phosphine is expected to oxidize or modify the desired complexes. In one case, the method of reverse osmosis was successfully applied to the purification of $RuH_2(N_2)(PPh_3)_3$.[3a]

We report here the discovery of such equilibria in the reactions of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (**1**)[9] with dinitrogen and dihydrogen to give dinitrogen and dihydride derivatives (**2** and **4**, respectively) and the use of the dimeric borane 9,9′-bi-borabicyclo[3.3.1]nonane, $[9\text{-}BBN]_2$,[10] as a Lewis acid or "phosphine sponge" reagent to drive eq 1 to the right. We have described elsewhere some properties of other derivatives of **1** containing strongly coordinating ligands[9] including the crystal structure of $Mo(\eta^6\text{-}PhPMePh)(CN\text{-}t\text{-}Bu)(PMePh_2)_2$.[9c] Other complexes of the type $Mo(\eta^6\text{-arene})(PR_3)_3$ are

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* To whom correspondence should be addressed at the Department of Chemistry.

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known,[9b,11] but complex **1** appears to be unique in containing very labile σ-bonded ligands. Some derivatives of these η^6-arene complexes, $Mo(\eta^6\text{-arene})(N_2)(PR_3)_2$ and $Mo(\eta^6\text{-arene})(H)_2(PR_3)_2$, have been prepared indirectly from molybdenum(II) precursors.[11b,12]

Experimental Section

Oxygen and water were excluded during all operations as described previously.[13] The preparation of complex **1** has been reported.[9a,c] Crystalline $[9\text{-BBN}]_2$ was used as supplied by Aldrich; the borane must be free of hydrolysis products (verification by mass spectroscopy) for the successful preparation of complex **3**. Samples for gas-uptake measurements were weighed into glass buckets, suspended above the gas-saturated solvent in a thermostated, constant-pressure gas–buret apparatus,[14] and dropped to initiate uptake. The ^{31}P NMR spectra (referenced to 85% H_3PO_4) were recorded at 81 MHz and the ^1H spectra at 200 MHz on a Varian XL-200 spectrometer. Samples, handled under nitrogen, were analyzed by the Canadian Microanalytical Laboratory.

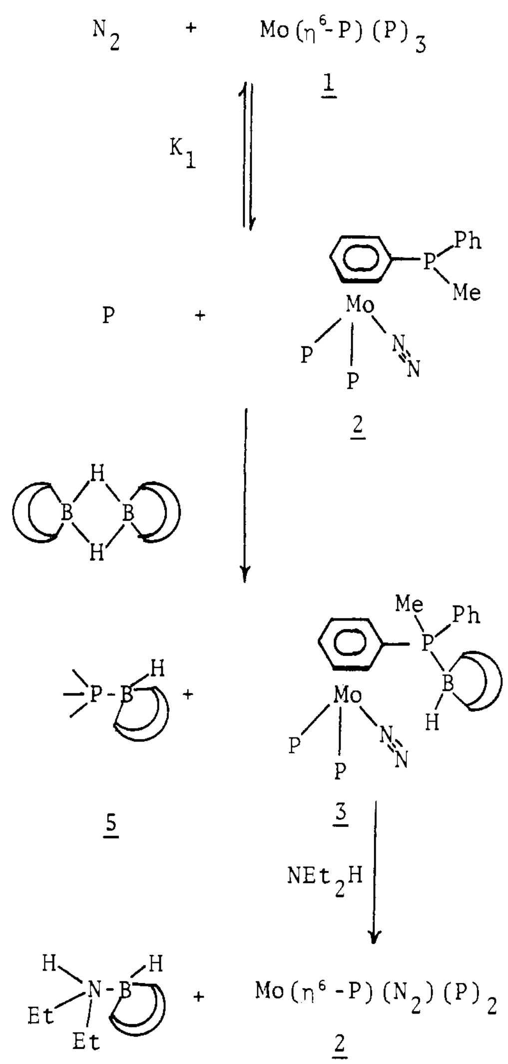
Formation of $Mo(\eta^6\text{-PhPMePh})(N_2)(PMePh_2)_2$ (2). Complex **1** (0.141 g, 0.157 mmol) when dropped into 10 mL of toluene at 35 °C saturated with nitrogen at 610 torr took up 0.0552 mmol of nitrogen in 600 s to give a red-brown solution at equilibrium: [**1**] = 0.0102 M; [**2**] = $[PMePh_2] = 5.5 \times 10^{-3}$ M. The solubility of nitrogen in toluene was determined separately: $[N_2] = 3.8 \times 10^{-3}$ M. These values could be reproduced. A ^{31}P NMR spectrum of a similar reaction solution in benzene gave peaks of correct intensity: for **1**, δ −31.0, 34.1;[9a] for free $PMePh_2$, δ −27.7; for **2**, δ −24.8 (s, 1, P-η^6-Ph), 34.4 A, 35.1 B (AB spin system, J_{AB} = 28 Hz, 2, PMo). ^1H NMR (C_6D_6, only the peaks of **2** are listed): δ 1.47 (d, J_{PH} = 5 Hz, 3, H_3CP-η^6-Ph), 1.61 (d, J_{PH} = 4 Hz, 3, H_3CPMo), 1.63 (d, J_{PH} = 4Hz, 3, H_3CPMo), 3.3–3.9 (m, 5, η^6-C_6H_5), 7.0–8.0 (m, 25, C_6H_5P). IR (C_6H_6): 1980 cm^{-1} (s, NN).

Preparation of $Mo(\eta^6\text{-PhP}(BH(C_8H_{14}))MePh)(N_2)(PMePh_2)_2$ (3). Complex **1** (0.50 g, 0.56 mmol) was stirred under N_2 as a suspension in a solution of $[9\text{-BBN}]_2$ (0.34 g, 1.39 mmol) in rigorously dry hexanes (30 mL) for 20 h. The yellow-orange, oxygen-sensitive solid was filtered off and washed with cold hexanes (0.45 g, 95%). This sample contains small amounts of $MePh_2P{\cdot}BH(C_8H_{14})$. An analytically pure sample was obtained by dissolving this sample in benzene saturated with $[9\text{-BBN}]_2$, filtering, concentrating, and then adding hexanes carefully and by cooling the resultant mixture to precipitate the product as clumps of orange powder (0.1 g, 21%). Anal. Calcd for $C_{47}H_{54}N_2MoP_3B$: C, 66.67; H, 6.43; N, 3.31. Found: C, 66.18; H, 6.96; N, 2.91. ^{31}P NMR (C_6H_6, excess $[9\text{-BBN}]_2$): δ 32.2 A, 33.8 B (AB spin system, J_{AB} = 29 Hz, 2, PMo), 6.4 (br s, 1, η^6-PhP-$BH(C_8H_{14})$). ^1H NMR (C_6D_6): δ 1.5–4.0 (m, 29, 3 H_3CP + H_{14}-C_8BH + η^6-C_6H_5), 7.0–8.0 (m, 25, C_6H_5P). IR (Nujol): 1995 (s, NN), 2260 (m, $H^{11}B$), 2300, 2230 cm^{-1} (w, HB).

Formation of $Mo(\eta^6\text{-PhPMePh})(H)_2(PMePh_2)_2$ (4). Complex **1** (72 mg, 0.080 mmol) when dropped into 10 mL of toluene at 30.5 °C saturated with hydrogen at 712 torr took up 0.040 mmol of H_2 in 50 min. Equilibrium concentrations: [**1**] = [**4**] = $[PMePh_2]$ = 2.0×10^{-3} M; $[H_2] = 2.8 \times 10^{-3}$ M (independent solubility measurement). The ^{31}P NMR spectrum in C_6H_6 gave only peaks of correct intensities for **1**, free $PMePh_2$, and **4**: δ −25.2 (s, 1, P–η^6-Ph), 50.9 (s, 2, PMo). ^1H NMR (C_6D_6, **4** only): δ −4.34 (t, J_{PH} = 49 Hz, 2, MoH), 1.41 (d, J_{PH} = 4 Hz, 3, H_3CP-η^6-Ph), 1.86 (d, J_{PH} = 6 Hz, 6, H_3CPMo), 3.9–4.5 (m, 5, η^6-H_5C_6-P), 7.0–8.0 (m, 25, H_5C_6P). IR (C_6H_6): Mo–H (or Mo–D using D_2) were not observed by FT IR in the 1900–1700-cm^{-1} region[11b] or elsewhere.

Properties of $MePh_2P{\cdot}BH(C_8H_{14})$ (5). This complex was formed as a colorless, hexane-soluble oil. ^{31}P NMR (C_6H_6): δ −1.9 (br, s, 1). ^1H NMR (C_6D_6): δ 1.47 (d, J_{PH} = 9 Hz, 3, H_3CP), 1.6–2.4 (m, 15, HBC_8H_{14}), 6.8–7.7 (m, 10, PC_6H_5). IR (neat): 2250 (m, $H^{11}B$), 2290, 2210 cm^{-1} (w, HB).

Scheme I. Formation of the Dinitrogen Complexes (P = Methyldiphenylphosphine)



Results and Discussion

A toluene solution of complex **1** (0.01 M) at 35 °C rapidly takes up 0.34 ± 0.02 mol of N_2/mol of Mo to give an equilibrium mixture of **1**, free $PMePh_2$, and the dinitrogen complex $Mo(\eta^6\text{-PhPMePh})(N_2)(PMePh_2)_2$ (**2**) as evidenced by the ^{31}P NMR and IR spectra (Scheme I). The equilibrium constant, K_1, at 35 °C is 0.76 ± 0.04 as determined by gas-uptake measurements. The reaction can be reversed by adding excess phosphine to the mixture. Purging the mixture with argon does not give back compound **1** quantitatively; instead, other molybdenum species that possibly contain bridging η^6-PhPMePh ligands[9b,15] are formed as well since several new small doublets in the ^1H NMR spectra in the region δ 1.5–2.3 assignable to methyl resonances of coordinated $PMePh_2$ appear during this reaction. Thus, the solution behavior of complex **1** under nitrogen is complicated; however, the ^1H NMR peaks assigned previously to "oligomeric" species[9a] are now known to be due mainly to the presence of compound **2** in solutions of **1** under nitrogen.

The IR absorption of **2** at 1980 cm^{-1} suggests a terminally bonded dinitrogen ligand as observed also for $Mo(\eta^6\text{-}C_6H_5Me)(N_2)(PMePh_2)_2$ ($\nu(N_2)$ = 1970 cm^{-1}).[11b] The ^{31}P

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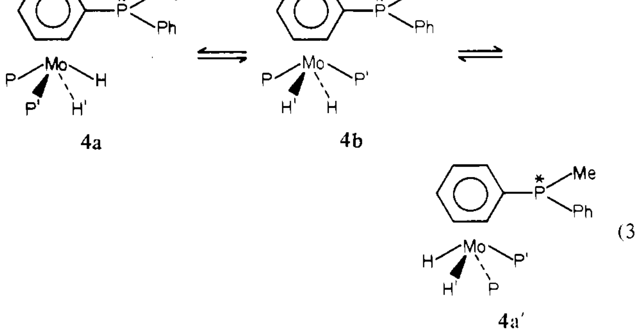
NMR resonance of the reaction solution at −24.8 ppm is characteristic of a "dangling" phosphorus moiety,[9] and it falls downfield of the corresponding resonance for complex **1** (at −31.0 ppm) in keeping with the greater π acidity of the dinitrogen ligand relative to the phosphine ligand.[9b,c] The nuclei (^{1}H, ^{31}P) in the σ-bonded ligands are diastereotopic because of the chiral, dangling phosphorus center; the ^{31}P NMR spectrum shows an AB pattern characteristic of such monosubstituted complexes.[9b,c] Inequivalent σ-bonded-phosphine methyl and η^6-arene protons are observed in the ^{1}H NMR spectrum.

Small amounts of 90% pure complex **2** can be obtained by triturating complex **1** with large volumes of hexanes under nitrogen to wash away dissociating phosphine. A more effective preparation involves the use of $[9\text{-BBN}]_2$ as a phosphine sponge reagent (Scheme I). The dinitrogen complex **3** containing the borane attached to the "dangling" phosphorus is isolated in 90% yield simply by stirring a suspension of complex **1** in a solution of excess $[9\text{-BBN}]_2$ in dry hexanes for 20 h under nitrogen and then filtering off the oxygen-sensitive yellow solid. The adduct $MePh_2P{\cdot}BH(C_8H_{14})$ (**5**) is hexane soluble and can be washed away from the product. Complex **3** ($\nu(N_2)$ = 1995 cm^{-1}) is stable in benzene solution in the presence of excess $[9\text{-BBN}]_2$ and can be recrystallized to analytical purity in this solution. Its ^{31}P NMR spectrum shows a broad singlet due to the "dangling" phosphorus bonded and coupled to boron isotopes and the expected AB system for the σ-bonded ligands. The IR spectra of compounds **3** and **5** have terminal boron–hydride absorptions at ca. 2250 cm^{-1} that signal the presence of boron adducts; these compounds do not contain free $[9\text{-BBN}]_2$, which gives an absorption at 1560 cm^{-1} due to bridging hydrides. There is no evidence for an interaction between the hydride and the dinitrogen ligand. The borane can be quantitatively removed from complex **3** in benzene solution (^{31}P NMR experiment) by adding 1 equiv of diethylamine that has been dried over $LiAlH_4$, but the extremely air-sensitive dinitrogen complex produced has not been isolated in a pure form. All the borane adducts react readily with traces of water to generate hydrogen. Thus, if anhydrous conditions are not maintained, the dihydride complex **4** forms at the expense of complex **2**. The use of other nonoxidizing Lewis acids such as $BF_3{\cdot}THF$, $AlCl_3$, and BEt_3 to abstract a ligand from complex **1** gave products other than a dinitrogen complex.

Complex **1** also reversibly reacts with hydrogen at 31 °C to give a dihydride complex, **4**, in equilibrium with **1** and free $PMePh_2$, $K_2 = 0.71 \pm 0.03$ (eq 2). Addition of excess phosphine or purging with argon at 35 °C for 20 min regenerates **1**. The dihydride has not been isolated in a pure form but can be characterized in solution. It must undergo a dynamic process that is fast on the NMR time scale that renders the σ-bonded phosphine ligands equivalent since these nuclei give a singlet in the $^{31}P\{^1H\}$ spectrum instead of the AB pattern expected for a static *cis*-dihydride (**4a**, **4a′**) or *trans*-dihydride (**4b**) structure. Consistent with a low-energy fluxional process, the hydride resonance remains a triplet and the methyls of the σ-bonded phosphines remain equivalent when toluene-d_8 solutions of the equilibrium mixture are cooled to −80 °C or heated to +50 °C. A trans structure was found for $Mo(\eta^6\text{-}C_6H_6)(Me)_2(PMe_3)_2$ in the solid state[16] and was proposed as a possible explanation for the magnetic equivalence of ligands in the other known complexes of this type, $Mo(\eta^6\text{-arene})(H)_2(PPh_3)_2$, which are also likely to be fluxional.[11b] A site-exchange mechanism involving structure **4b** as an intermediate is likely (eq 3) although species involving coordinated molecular hydrogen as observed for $W(P(i\text{-}Pr)_3)_2(CO)_3(H_2)$[17] cannot be ruled out.



4a 4b 4a′ (3)

The rates of reaction of **1** with nitrogen and hydrogen are approximately five times slower than that with carbon monoxide under similar conditions. The reaction with carbon monoxide is known to proceed via the rate-determining dissociation of phosphine from **1**.[9c] The former reactions likely also involve dissociation of phosphine from **1** prior to a rate-determining addition of the gas molecules. Ligand lability in **1** likely results from steric crowding of the three bulky *fac* ligands (cone angle 136°).

The reactions of Scheme I represent the first example of the preparation of a dinitrogen complex by phosphine abstraction using a Lewis acid. The 9-BBN dimer is a convenient Lewis acid to use because it is an easily handled, crystalline solid and it forms highly soluble phosphine adducts. On the other hand, it is a strong reducing agent that reacts readily with water. We have found that although it aids in converting $FeH_2(PMePh_2)_4$[4] into $FeH_2(N_2)(PMePh_2)_3$ ($\nu(N_2)$ = 2039 cm^{-1}), it also causes decomposition of the complexes to iron metal. This borane may play an additional role in the formation of complex **3** by providing a nitrogen binding site that is more sterically protected than that of **2** toward attack of larger Lewis bases in solution. Other applications of this "phosphine sponge" reagent are being investigated.

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Registry No. **1**, 84430-77-3; **2**, 87902-59-8; **3**, 89486-69-1; **4**, 89486-70-4; **5**, 89486-71-5; $[9\text{-BBN}]_2$, 21205-91-4.

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Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York 14214

Determination of Equilibrium Constants for the Tetrachloroaluminate Ion Dissociation in Ambient-Temperature Ionic Liquids

Zenon J. Karpinski[†] and Robert A. Osteryoung*

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The major equilibrium describing acid–base properties of tetrachloroaluminate ionic liquids is the dissociation of the tetrachloroaluminate anion.[1-7]

[†] Present address: Department of Chemistry, University of Warsaw, 02093 Warsaw, Poland.