perature. After filtration and washing, pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ is obtained as a solvent-free, free-flowing solid in 75–80% yield. No evidence for the presence of other, more highly reduced species was found.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + 2K[(C_6H_5)_2CO] \xrightarrow{THF} 2K[(\eta^5\text{-}C_5H_5)Fe(CO)_2] + 2(C_6H_5)_2CO$$

This work represents the first reported isolation of a simple alkali metal salt of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ ion, although two salts with complex counterions, $[(C_4H_9)_4N][(\eta^5\text{-}C_5H_5)Fe(CO)_2]$[3] and $[(\eta^5\text{-}C_5H_5)Fe(CO)dmpe][(\eta^5\text{-}C_5H_5)Fe(CO)_2]$[7] (dmpe = 1,2-bis(dimethylphosphino)ethane), have previously been isolated.

Pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ is a yellow-orange, powdery solid which can be stored under nitrogen for a period of at least several months with no apparent loss of purity. Exposure of solid $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ to air results in the formation of purple $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ within several minutes. The solution infrared spectrum (THF) of the $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ isolated in this report is in good agreement with literature values.[3] As a Nujol mull, $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ exhibits two broad carbonyl bands at 1880 and 1735 cm^{-1}.

Previous uses of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ have involved generation of the anion in situ and subsequent addition of appropriate reagents to effect a desired reaction.[1,2] We anticipate that prior preparation and storage of pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ would save time and permit very precise control of reaction stoichiometries. Furthermore, choice of reaction solvents and temperatures[8] would no longer need to be limited by conditions required for the initial cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Experimental Section

All operations were performed on a standard high-vacuum system[9] or under an atmosphere of prepurified nitrogen. Benzophenone (J. T. Baker Chemical Co.) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (Strem Chemical Co.) were used as received. Elemental potassium (Mallinckrodt Chemical Co.) was washed free of mineral oil with pentane and stored under nitrogen in a sealed vessel in a nitrogen filled drybox. *Caution! Potassium metal can form peroxides and superoxides even when stored under mineral oil if there is an atmosphere of air above the liquid.*[10] Therefore, we opened and sealed the bottle containing potassium under mineral oil only in the drybox. Tetrahydrofuran (THF) was initially distilled from $LiAlH_4$ and stored over sodium benzophenone ketyl. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using matched 0.1-mm KBr cells. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Potassium benzophenone ketyl was prepared by magnetically stirring 3.64 g (20 mmol) of benzophenone and 0.78 g (20 mmol) of small, freshly cut pieces of potassium metal in 20 mL of dry THF. Typically, this mixture was stirred overnight to ensure complete solubilization of the potassium metal. Addition of 3.89 g (11 mmol, 10% excess) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to the rapidly stirred ketyl solution resulted in disappearance of the characteristic deep blue color of the potassium benzophenone within minutes and formation of a red solution and an orange precipitate.[11] The orange precipitate was isolated by vacuum-line filtration.[12] While still on the vacuum-line filter, the precipitate was washed repeatedly with benzene to free it of benzophenone and unreacted $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to yield 3.22 g (74.5% yield) of analytically pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$. Anal. Calcd for $C_7H_5FeO_2K$: C, 38.89; H, 2.34; Fe, 25.86; K, 18.10. Found: C, 39.09; H, 2.61; Fe, 25.83; K, 17.95.

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Registry No. $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, 60039-75-0; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; potassium benzophenone ketyl, 19333-28-9; benzophenone, 119-61-9.

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Contribution from the Department of Chemistry,
University of Nebraska—Lincoln, Lincoln, Nebraska 68588

Reactions of Coordinated Dinitrogen. 7.[1] Preparation and Characterization of Molybdenum Bis(dinitrogen) Complexes Containing Mixed Tertiary Phosphine Ligands[2]

T. Adrian George* and Roger A. Kovar[3]

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The notable contrast between the chemistry of the bis(dinitrogen) complexes of molybdenum and tungsten containing two bidentate tertiary phosphine ligands and those containing four monodentate tertiary phosphines is exemplified by two series of reactions.[4] First, reaction with strong protic acids leads to the formation of hydrazido(2−) complexes in the former series of bis(dinitrogen) complexes[5,6] (e.g., eq 1, where

$$trans\text{-}Mo(N_2)_2(dppe)_2 + 2HX \rightarrow MoX(NNH_2)(dppe)_2X + N_2 \quad (1)$$

dppe = $Ph_2PCH_2CH_2PPh_2$ and X = Br, I, or HSO_4) whereas in the latter series ammonia (and occasionally hydrazine) is produced (e.g., eq 2)[5c,7] The extent of this latter reaction (eq

$$cis\text{-}Mo(N_2)_2(PMe_2Ph)_4 \xrightarrow{HX} N_2 + NH_4X + HPMe_2PhX + Mo^{VI}? \quad (2)$$

2) is dependent on HX and the solvent used. Intermediates in the reaction have been isolated.[7,8]

Second, reaction of the $(dppe)_2Mo$ and -W complexes with alkyl bromides and iodides afford 2-alkyldiazenido-*N* derivatives[9,10] (e.g., eq 3, where R = Me, Et, etc. and X = Br or

$$Mo(N_2)_2(dppe)_2 + RX \rightarrow MoX(NNR)(dppe)_2 + N_2 \quad (3)$$

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I). However, similar reactions with the tetrakis(monodentate phosphine) complexes lead only to mixed halo–phosphine–metal complexes, e.g., $MoBr_4(PMe_2Ph)_2$, and total loss of dinitrogen.

These differences in reactivity are probably due to the relative ease with which the monodentate phosphine ligands can be displaced from the metal center compared with the more tightly held bidentate ligands.[4,5c] In order to investigate the reactivity of coordinated dinitrogen as a function of the coordinating ability of the tertiary phosphine coligands, we undertook to prepare two new series of bis(dinitrogen) complexes of molybdenum, one containing a bidentate ligand and two monodentate ligands and the other a tridentate ligand and a monodentate ligand. Here we report the preparation and characterization of examples of both these new series.

Experimental Section

General Manipulations. Air-sensitive compounds of molybdenum were handled in a water- and oxygen-free environment which was provided by use of Schlenk equipment, drybags, a Vacuum Atmosphere Corp. drybox, and/or syringe technique.[11]

All solvents and selected liquid reagents were rigorously dried by heating at reflux over an appropriate drying agent[12] followed by distillation in a dinitrogen atmosphere. The liquids, tetrahydrofuran, benzene, methanol, dichloromethane, acetonitrile, and heptane were saturated with dinitrogen immediately prior to use by bubbling the gas through the liquid for a minimum of 0.5 h.

General Chemicals. Chemicals were purchased from commercial sources and used without further purification.

The following compounds were prepared by published procedures or modifications of them. The modified procedures are given for the following compounds in the references indicated: $MoCl_3(THF)_3$,[13] $Mo(N_2)_2(PPh_2Me)_4$,[12] $Mo(N_2)_2(PPhMe_2)_4$,[12] and $Mo(N_2)_2(dppe)_2$.[12]

Physical Measurements. Infrared spectra were obtained on either a Perkin-Elmer Model 621 or 727B infrared spectrometer. Solid samples were run as pellets in KBr. The progress of reactions in solution was monitored by allowing from 5 to 10 drops of the appropriate reaction solution to evaporate to dryness from the surface of a KBr salt plate in a dinitrogen atmosphere. The resulting thin film was pressed against another, similar salt plate and the infrared spectrum of the resulting film recorded. For example, the infrared spectra of authentic $Mo(N_2)_2(PPh_2Me)_4$ as a solid in KBr and as a thin film from THF were found to be essentially identical.

Proton-decoupled phosphorus-31 NMR spectra were run on a Varian XL-100 spectrometer with benzene-d_6 as the solvent. The chemical shifts were measured relative to external 85% H_3PO_4. The spectrum of $Mo(N_2)_2(dppe)(PPh_2Me)_2$, vide infra, was accumulated by using a CAT program and Varian 620-1 computer.

The solvent of crystallization in $Mo(N_2)_2(triphos)(PPh_3)\cdot{}^1/_2THF$, vide infra, was confirmed by using a Varian EM-600 mass spectrometer with direct inlet accessory.

Combustion analyses were performed by Schwarzkopf Analytical Laboratories, Woodside, N.Y. Alternatively, coordinated dinitrogen in a weighted sample of molybdenum complex was liberated by reaction with a measured excess of Br_2 in CH_2Cl_2 solution in an all-glass ampule connected to a multipurpose vacuum system. The evolved gas was fractionated through two traps cooled with liquid nitrogen and collected in a calibrated gas buret with use of a Toepler pump.

Synthesis. *trans*-$Mo(N_2)_2(PPh_2Me)_4$. To 4.0 g (9.5 mmol) of $MoCl_3(THF)_3$ dissolved in 200 mL of THF in a 250-mL flask were added 7.6 g (38 mmol) of PPh_2Me and 262 g (57 mmol of Na) of 0.5% sodium amalgam. This mixture was attached to a source of dinitrogen and stirred vigorously with a magnetic stirrer. Dinitrogen uptake was monitored qualitatively by observing the bubbling rate through an oil-filled bubbler incorporated into the system to provide a vent for unreacted dinitrogen. Dinitrogen uptake was first detected at about 0.25-h reaction time and was rapid by 0.5 h. No uptake was detected after 1 h. The mixture was stirred for a total of 4 h, and then the THF solution was decanted and filtered through Celite on a coarse glass frit. Tetrahydrofuran was removed from the filtrate by using a rotary evaporator with a water aspirator to give an orange solid. This solid was dissolved in 100 mL of benzene and the solution filtered through Celite on a medium frit to give a clear, red-orange solution from which the complex was precipitated by the addition of 150 mL of methanol and chilling at 0 °C. The complex was isolated as a bright, red-orange solid by filtration, washed with methanol, and dried in vacuo. The yield was 6.7 g (74%). Anal. Calcd for $Mo(N_2)_2(PPh_2Me)_4\cdot C_6H_6$, $C_{58}H_{58}MoN_4P_4$: C, 67.6; H, 5.68; N, 5.44. Found: C, 67.4; H, 5.77; N, 5.43.

***cis*-$Mo(N_2)_2(PPhMe_2)_4$.** With use of the procedure described above, 4.0 g (9.5 mmol) of $MoCl_3(THF)_3$, 200 mL of THF, 5.2 g (38 mmol) of $PPhMe_2$, and 250 g (56 mmol of Na) of 0.5% sodium amalgam were stirred under dinitrogen for 4 h. The product solution was then decanted and filtered through Celite on a medium frit. An equal volume of heptane was added and the volume of this solution reduced to about 50 mL in vacuo. Another volume of heptane (200 mL) was added, and the volume was again reduced to 50 mL in vacuo. The yellow-brown needles produced during this procedure were isolated by filtration, heptane washed, and dried in vacuo. The yield was 3.7 g (55%). Anal. Calcd for $Mo(N_2)_2(PPhMe_2)_4$, $C_{32}H_{44}MoN_4P_4$: C, 54.6; H, 6.29; N, 7.95. Found: C, 54.4; H, 6.25; N, 7.58.

***trans*-$Mo(N_2)_2(dppe)(PPh_2Me)_2$.** Into a 250-mL round-bottom flask containing a magnetic stirring bar were placed 5.33 g (5.59 mmol) of $Mo(N_2)_2(PPh_2Me)_4$ and 100 mL of benzene. This mixture was stirred until the solution was clear, and then 2.33 g (5.6 mmol) of dppe was added. The mixture was stirred for 2 h to form a deep yellow solution. The thin-film infrared spectrum revealed $\nu(NN)$ at 1955 cm^{-1} (very strong) and approximately 1938 cm^{-1} (shoulder). Chilled methanol at 0 °C was added until a precipitate formed, and then the mixture was allowed to stand in a 5 °C refrigerator for 16 h. The resulting yellow-orange solid was isolated by filtration, washed with methanol, and dried in vacuo. The yield was 4.33 g (81%). The infrared spectrum showed $\nu(NN)$ at 1950 cm^{-1} (very strong). Anal. Calcd for $Mo(N_2)_2(dppe)(PPh_2Me)_2$, $C_{52}H_{50}MoN_4P_4$: C, 65.7; H, 5.30; N, 5.89. Found: C, 65.2; H, 5.15; N, 5.47.

$MoCl_3(triphos)$. In a 250-mL round-bottom flask containing a magnetic stirring bar were placed 5.35 g (12.8 mmol) of $MoCl_3(THF)_3$, 50 mL of CH_2Cl_2, and 50 mL of THF. When $MoCl_3(THF)_3$ dissolved, 6.14 g (11.5 mmol) of triphos dissolved in a mixture of 25 mL of CH_2Cl_2 and 25 mL of THF was added. The yellow solid which formed when the above mixture was stirred for 24 h was isolated by filtration, washed with THF, and dried in vacuo at 60 °C for 12 h. The yield was 7.1 g (76%). Anal. Calcd for $MoCl_3(triphos)$, $C_{34}H_{33}Cl_3MoP_3$: C, 55.4; H, 4.5; Cl, 14.5. Found: C, 55.6; H, 4.5; Cl, 14.3.

$Mo(N_2)_2(triphos)(PPh_2Me)$. Small, equal molar quantities of $Mo(N_2)_2(PPh_2Me)_4$ and triphos were allowed to react in THF at −78 °C. Thin-film infrared spectra of the solution at time intervals revealed that a new $Mo–N_2$ species having $\nu(NN)$ at 1950 cm^{-1} was very slowly produced. The mixture was warmed and allowed to react at 0 °C. Infrared spectroscopy revealed that conversion to this new species was complete after 16 h. Analysis of an aliquot of this solution for coordinated dinitrogen revealed that 80% of the original dinitrogen introduced as $(Mo(N_2)_2(PPh_2Me)_4$ was still present. A bright, yellow-orange solid was isolated by a combination of adding heptane and volume reduction in vacuo. The infrared spectrum had a single absorption for $\nu(NN)$ at 1950 cm^{-1}. The sample appeared to be stable when stored at 0 °C but decomposed slowly when stored at room temperature. Anal. Calcd for $Mo(N_2)_2(triphos)(PPh_2Me)_2$, $C_{47}H_{46}MoN_4P_4$: C, 63.7; H, 5.2; N, 6.3. Found: C, 63.8; H, 5.6; N, 4.3.

***trans*-$Mo(N_2)_2(triphos)(PPh_3)$.** In a 250-mL flask connected to a source of dinitrogen and containing a magnetic stirring bar were placed 3.92 g (5.32 mmol) of $MoCl_3(triphos)$, 1.4 g (5.3 mmol) of PPh_3, and 200 mL of THF. After the solution became clear, 108 g (33 mmol of Na) of a 0.7% sodium amalgam was added rapidly. The

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mixture was stirred rapidly for 2 h to give a rich, orange-gold solution. The solution was decanted and filtered through Celite on a coarse frit. Tetrahydrofuran was removed from the filtrate by using a rotary evaporator to give a red-orange solid which dissolved readily in 50 mL of benzene. Filtration and slow addition of approximately 100 mL of methanol caused precipitation of a dull orange solid (4.1 g) which was isolated by filtration, washed with methanol, and dried in vacuo. The infrared spectrum of this material revealed $\nu(NN)$ absorptions at 1955 and 1970 cm^{-1}. Recrystallization was accomplished by dissolving 1.0 g of this material in 20 mL of THF followed by slow addition of 40 mL of methanol. Filtration, washing with methanol, and drying in vacuo gave 0.5 g of bright orange solid. The infrared spectrum revealed that the band at 1970 cm^{-1} was present as a very weak shoulder on the very intense band at 1955 cm^{-1}. Recrystallization of this material using the above procedure gave 0.4 g of bright orange solid whose infrared spectrum revealed a symmetrical $\nu(NN)$ band at 1955 cm^{-1}. A portion of this product was heated to 200 °C by the direct inlet assembly of an EM-600 mass spectrometer. The mass spectrum revealed that THF was present. Anal. Calcd for $Mo(N_2)_2(triphos)(PPh_3)\cdot{}^1/_2THF$, $C_{54}H_{52}MoN_4O_{1/2}P_4$: C, 65.9; H, 5.28; N, 5.69. Found: C, 64.8; H, 5.3; N, 5.7.

Results and Discussion

Two approaches were taken toward the synthesis of bis(dinitrogen) complexes of molybdenum containing mixed ancillary phosphine ligands. The first method involved phosphine ligand displacement in a preformed bis(dinitrogen) complex (e.g., eq 4). The second method was to coordinate

$$trans\text{-}Mo(N_2)_2(PPh_2Me)_4 + dppe \rightarrow Mo(N_2)_2(dppe)(PPh_2Me)_2 + 2PPh_2Me \tag{4}$$

the phosphine ligand(s) prior to or during the reduction step in which dinitrogen became coordinated. Examples of these procedures are shown in eq 5 and 6.

$$MoCl_3(triphos) + PPh_3 \xrightarrow[N_2]{Na/Hg} Mo(N_2)_2(triphos)(PPh_3) \tag{5}$$

$$MoCl_3(THF)_3 + triphos + PPh_3 \xrightarrow[N_2]{Na/Hg} Mo(N_2)_2(triphos)(PPh_3) \tag{6}$$

Synthesis of *trans*-$Mo(N_2)_2(dppe)(PPh_2Me)_2$. The ligand displacement reaction (eq 4) proved to be the most satisfactory method for preparing this compound in high yield. Attempts to prepare this same compound by reduction of $MoCl_3(THF)_3$ with sodium amalgam in the presence of stoichiometric quantities of dppe and PPh_2Me produced a mixture of $Mo(N_2)_2(dppe)_2$, $Mo(N_2)_2(PPh_2Me)_4$, and $Mo(N_2)_2(dppe)(PPh_2Me)_2$. The infrared spectrum of the title compound exhibited a very strong absorption at 1955 cm^{-1} due to $\nu(NN)$. In the proton-decoupled phosphorus-31 NMR spectrum the four phosphorus atoms displayed an AA′XX′ spectrum centered at −42.9 ppm.[14] While this work was in progress, this compound was reported in the literature.[15]

Synthesis of *trans*-$Mo(N_2)_2(triphos)(PR_3)$. The reaction of $Mo(N_2)_2(PPh_2Me)_4$ with triphos produced a complex formulated as *trans*-$Mo(N_2)_2(triphos)(PPh_2Me)$ based upon the elemental analysis and infrared spectrum, $\nu(NN)$ 1950 cm^{-1}. However, it slowly decomposed at room temperature in the dark both in the solid state and in solution.

An infrared study of the reduction of $MoCl_3(triphos)$ (readily prepared from $MoCl_3(THF)_3$ and triphos; see Experimental Section) in the presence of PR_3 (R = Ph, *m*-tolyl, or *p*-tolyl) under dinitrogen with 100% excess of sodium amalgam was carried out. The reactions were monitored with respect to time in an effort to measure the relative rates of formation and the solution stabilities of the dinitrogen complexes. These spectra revealed that the dinitrogen complexes were formed rapidly in all three cases but that, in the case of PPh_3, the complex had superior solution stability. The crude product solution of this complex did not show appreciable decomposition on standing for a period of 7 days at room temperature under dinitrogen. However, isolated yields of pure, recrystallized product were very low. The presence of only one strong NN stretch (1955 cm^{-1}) in the infrared spectrum showed that the two dinitrogen ligands occupy mutually trans positions on the coordination polyhedron.

The corresponding $(p\text{-}MeOC_6H_4)_3P$ complex has also been prepared in low yield and shows a very strong NN stretch at 1962 cm^{-1}.

Protonation of $Mo(N_2)_2(triphos)(PPh_3)$ with anhydrous hydrogen bromide produced ammonia under mild conditions.[16] The reactions of this interesting bis(dinitrogen) complex are under investigation.

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Registry No. *trans*-$Mo(N_2)_2(PPh_2Me)_4$, 33248-03-2; *cis*-$Mo(N_2)_2(PPhMe_2)_4$, 32457-67-3; *trans*-$Mo(N_2)_2(dppe)(PPh_2Me)_2$, 65498-66-0; $MoCl_3(triphos)$, 75365-55-8; *trans*-$Mo(N_2)_2(triphos)(PPh_2Me)$, 75365-56-9; *trans*-$Mo(N_2)_2(triphos)(PPh_3)$, 75420-24-5; $MoCl_3(THF)_3$, 39210-30-5; *trans*-$Mo(N_2)_2(triphos)((p\text{-}MeOC_6H_4)_3P)$, 75365-57-0; $Mo(N_2)_2(dppe)_2$, 25145-64-6.

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[14] The AA′ part of the spectrum is centered at −64.0 ppm and is associated with the phosphorus atoms of the dppe ligands: in $Mo(N_2)_2(dppe)_2$, $\delta(P) = -65.1$ (singlet). The XX′ part of the spectrum is centered at −21.8 ppm and is associated with the phosphorus atoms of the PPh_2Me ligands: in $Mo(N_2)_2(dppe)_2$, $\delta(P) = -18.8$.

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Contribution from the Chemistry Department,
Faculty of Science, Tohoku University, Sendai, 980 Japan

Rotation of Olefins in *trans*(N,olefin)-Bromochloro(η^2-ethylene)platinum(II) Containing Pyridine Derivatives

Sin'ya Miya and Kazuo Saito*

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The kinetic trans effect for the ligand-substitution reactions of Pt(II) has been studied for various ligands but not for the exchange of olefins, despite its importance as an elementary process in transition-metal complex catalysis.[1] We have studied the kinetics of substitution of an olefin for a coordinated olefin molecule with the aid of optical activity and measured the second-order rate constant k_{py} for reaction 1,

$$trans(N,olefin)\text{-}[PtCl_2(4\text{-}X\text{-}py)(S\text{-}mbn)] + dce \text{ or } dmb \rightarrow trans(N,olefin)\text{-}[PtCl_2(4\text{-}X\text{-}py)(dce \text{ or } dmb)] + mbn \tag{1}$$

where mbn, dce, and dmb stand for 2-methyl-2-butene (prochiral), 1,2-dichloroethylene (nonprochiral), and 1,2-dimethyl-2-butene (nonprochiral), respectively, and 4-X-py denotes 4-substituted pyridines.[2] The plot of log k_{py} vs. pK_a of the pyridine bases gave parallel straight lines. We have thus

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