= 2.27 (2) Å; Cu(1)–O = 1.990 (2) Å; Cu–Cl$_{ax}$ = 2.832 (1) and 3.206 Å), and Cu(2) exhibits a 4 + 1 coordination geometry ((Cu–Cl$_{eq}$)$_{av}$ = 2.28 (6) Å; Cu–Cl$_{ax}$ = 2.898 (1) Å). The difference between terminal and bridging Cu–Cl distances ((Cu–Cl$_{term}$)$_{av}$ = 2.24 (4) Å; (Cu–Cl$_{br}$)$_{av}$ = 2.30 (3) Å) and the divergence in lengths of the semicoordinate bonds as one distance shortens are generally observed.[6,7]

The cations and anions do not form segregated stacks;[8] instead, the cation is approximately coplanar with the anion and located over the region containing Cu(2). The presence of the cation prevents Cu(2) from forming a semicoordinate bond with one neighbor, forcing the ($-^3/_2$, $-^1/_2$) displacement, while it is still free to form a semicoordinate bond with the other neighbor, resulting in the ($^1/_2$, $^1/_2$) displacement. A weak interaction between N and Cl(5), as pictured in Figure 2, is responsible for the partial insertion of the cation in the stack. Similar interactions have been observed by Prout and Murray-Rust in a series of paraquat halometalate salts in which N···Cl interaction distances and interaction vector angles range from 3.44 Å and 90° (for the $Cu_2Cl_6^{2-}$ salt) to 3.83 Å and 61° (for the $CoCl_4^{2-}$ salt) (interaction vector angle taken with respect to the cation plane).[9] The interaction distances and vector angles for the title compound (3.70 Å, 75°) compare favorably to these.

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Registry No. $(C_7H_{10}N)Cu_2Cl_5(H_2O)$, 120881-60-9; Cu, 7440-50-8.

Supplementary Material Available: A table of data collection conditions and parameters, a complete description of the experimental conditions, tables of non-hydrogen atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom coordinates, bond lengths, and bond angles, a stereographic view of the contents of a unit cell, and a comprehensive table and diagram of known pseudoplanar, bibridged $Cu_nX_{2n+2}^{2-}$, $Cu_nX_{2n+1}L^-$, and $Cu_nX_{2n}L_2$ oligomer stacking patterns (16 pages); a table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Cis and Trans Isomers of $Mo(N_2)_2(PMe_2Ph)_4$[1]

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There are many six-coordinate, bis(dinitrogen) complexes of chromium, molybdenum, and tungsten known of the type $[M(N_2)_2L_4]$, where the ligands L are usually[4] some combination of mono-, bi-, and tridentate organophosphines.[6] In the majority of examples the N_2 ligands adopt a trans configuration. However, there are a few examples of complexes with the cis configuration specifically when L ligands are small, e.g., *cis*-$[M(N_2)_2(PMe_3)_4]$ (M = Cr,[7] Mo,[8] W[8]) and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo,[9] W[10]). Recently, a relatively stable mixture of *cis*- and *trans*-$[Mo(N_2)_2(Me_2PCH_2CH_2PMe_2)_2]$ was isolated.[11] We wish to report the first example of the effective separation of the cis and trans isomers of a bis(dinitrogen) complex, $[Mo(N_2)_2(PMe_2Ph)_4]$.

Experimental Section

All manipulations were carried out under an inert atmosphere with standard Schlenk techniques,[12] in the dark (wrapping with aluminum foil) wherever possible. Solvents were dried by standard procedures and distilled under dry dinitrogen prior to use. Infrared spectra were recorded with a Perkin-Elmer 283 instrument. ^{31}P NMR spectra were recorded in C_6D_6 on a Varian VXR-200 spectrometer operating at 80.894 MHz. $MoCl_3(THF)_3$ was prepared according to published procedures.[13]

Preparation of *cis*- and *trans*-$[Mo(N_2)_2(PMe_2Ph)_4]$. Into a 250-mL Fischer–Porter bottle was placed THF (70 mL), 2.282 g (16.5 mmol) of PMe_2Ph, 2.040 g (4.88 mmol) of $MoCl_3(THF)_3$, and a magnetic stirbar. After the mixture was stirred briefly, 100 g of 1% sodium amalgam was added. The bottle was closed and pressurized with N_2 (75 psi) and the mixture stirred (17 h). The light red color changed to green within 1 h and eventually turned dark yellow-brown. After the bottle was depressurized, the solution was decanted and filtered through diatomaceous earth (acid washed) and washed with Et_2O (5 × 5 mL). A brown solid remained. The combined filtrate was evaporated to dryness in vacuo to yield a black oily residue. The residue was dissolved in Et_2O (40 mL) and filtered through diatomaceous earth. Solvent was removed from the filtrate by bubbling N_2 through the solution to produce a red-brown residue. Pentane (50 mL) was added to the flask and the suspension stirred (1 h). The yellow-brown solid was filtered off, washed with pentane (2 × 10 mL), and dried in vacuo. The yield of product was 1.672 g (2.4 mmol, 58%). IR (KBr): $\nu(N_2)$ 2010 (s), 1940 (s) cm^{-1}. ^{31}P NMR: cis, δ 4.5 (m, 27); trans, δ 3.3 (s, 1).

The red-brown pentane filtrate was evaporated to dryness by blowing N_2 across the surface of the solution. Methanol (30 mL) was added and the suspension stirred (1.5 h). The orange-brown solid was collected by filtration, washed with methanol (2 × 5 mL), and dried in vacuo. The product (yield 0.40 g, 0.57 mmol, 14%), was a 1:1 mixture of isomers.

Pentane (20 mL) was added to 0.372 g of the 1:1 mixture and the suspension stirred (1 h). The yellow cis isomer was filtered off, washed with pentane (2 × 10 mL), and dried in vacuo to yield 0.149 g (0.21 mmol). IR (KBr): $\nu(N_2)$ 2010 (vs), 1935 (vs) cm^{-1}. The filtrate was stripped to dryness in vacuo. Deoxygenated reagent methanol (10 mL) was added to the residue. After 1 h the orange trans isomer was isolated by filtration and washed with methanol (10 mL) to yield 0.13 g (0.18 mmol). IR (KBr): $\nu(N_2)$ 2010 (m), 1923 (vs) cm^{-1}. ^{31}P NMR: cis, δ 4.5 (m, 1); trans, δ 3.3 (s, 7.2).

Electrochemistry. Cyclic voltammetry measurements were carried out in a two-compartment, three-electrode cell fitted with a Luggin probe using a Hi-Tek potentiostat, Type DT2101, a Chemical Electronics (Birtley) Ltd. waveform generator, Type 01, and a Philips PM8041 X-Y recorder. The cell was fitted with a platinum-wire working electrode, a

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(1) Reactions of Coordinated Dinitrogen. 23. Part 22: Gebreyes, K.; George, T. A.; Koczon, L. M.; Ma, L.; Shaikh, S. N.; Tisdale, R. C.; Zubieta, J. Submitted for publication in *Polyhedron*.
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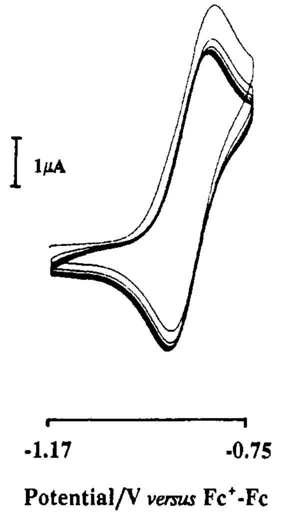

Figure 1. Cyclic voltammogram of a mixture of *trans*- (88%) and *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ in THF solution at a scan rate of 100 mV s^{-1}.

tungsten secondary electrode, and a silver-wire pseudoreference electrode. The electrolyte was 0.2 M $[NBu^n{}_4][BF_4]$ in THF solution. Potentials quoted are referenced to the ferrocenium–ferrocene (Fc^+/Fc) couple (=0.00 V; 0.535 V versus the SCE in this electrolyte).

Results and Discussion

During an attempt to prepare *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ by a published procedure[9,14] (the only obvious difference being that the reaction was run under a modest pressure of N_2 rather than a flow of N_2), an IR spectrum of the oily residue, obtained after removal of solvent following the reduction of $MoCl_3(THF)_3$ in the presence of 90% of the stoichiometric amount of PMe_2Ph, clearly showed the presence of more than one N_2-containing complex. The ^{31}P NMR spectrum of the residue indicated that the cis isomer was present in addition to the previously unreported trans isomer.[15] The isomers were effectively separated by their different solubilities in pentane; the trans isomer is very soluble while the cis is only partially soluble. The cis isomer can be purified by trituration with pentane. Light causes decomposition to occur in solution with the formation of a brown solid. The trans isomer can be purified by trituration with wet deoxygenated methanol. Extended trituration leads to decomposition. As determined by ^{31}P NMR spectroscopy, the highest purity obtained by these methods was 96% for the cis and 92% for the trans isomer. In the ^{31}P NMR spectrum of the trans isomer the six resonances arising from coupling of ^{31}P to $^{95,97}Mo$ ($I = {}^5/_2$, $J \approx 140$ Hz) were observed.[17]

The isomers slowly interconvert. Samples of cis and trans isomers were dissolved in C_6D_6 in separate NMR tubes and their ^{31}P NMR spectra monitored periodically. After 16 days at room temperature in the dark, equilibrium was reached. The equilibrium constant is 2.5 in favor of the cis isomer, corresponding to a difference of 2.2 kJ mol^{-1} in $\Delta G°$ at 23 °C. At the end of 19 days only a small amount of free PMe_2Ph was present in solution in addition to the two isomers.

The cyclic voltammogram of a sample of the trans isomer showed a reversible oxidation wave at $E°' = -0.83$ V versus the Fc^+/Fc couple. The difference in peak potentials was 85 mV. Under the same conditions *trans*-$[Mo(N_2)_2(dppe)_2]$, which has been shown to undergo one-electron, electrochemically reversible oxidation, afforded the same peak potential separation.[19] Previously, the cis isomer had been shown to be oxidized irreversibly.[20] On the first anodic scan of the cyclic voltammogram (see Figure 1) of a sample of trans isomer containing 12% cis isomer $i_{pa}/i_{pc} > 1$. In subsequent scans, i_{pa}/i_{pc} decreased rapidly until it became unity. Addition of a sample of the cis isomer to this solution caused an increase in the ratio i_{pa}/i_{pc} upon the next scan but no shift in the value of $E°'$ and no new oxidation waves in the voltammogram. Thus, in the voltammogram the irreversible oxidation of the cis isomer is superimposed upon that of the trans isomer, indicating that the isomers oxidize at similar potentials. This is surprising, considering the significant differences in redox potentials of *cis*- and *trans*-$[Mo(CO)_2(dppe)_2]$, for example.[21,22] Oxidation of *cis*-$[Mo(CO)_2(dppe)_2]$ produces the cis cation, which rapidly isomerizes to the trans cation. No redox-induced isomerization was observed. Dinitrogen is more labile in *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ than in trans complexes of molybdenum(0).[23] Loss of N_2 would appear to be even more facile in the cis-Mo(I) cation since even at low temperature oxidation is irreversible. The potential at which the trans isomer is oxidized is precisely that which would have been predicted from the values for *trans*-$[Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$ and *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$: −0.97 and −0.70 V, respectively, versus the Fc^+/Fc couple.[23] In terms of coordinating ability, PMe_2Ph can be considered to be halfway between $Et_2PCH_2CH_2PEt_2$ and $Ph_2PCH_2CH_2PPh_2$ and so the oxidation potential would be expected to occur halfway between the these two potentials, at about −0.83 V, which it does.

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Kinetics of Substitution Reactions of Binuclear Platinum(III) Pyrophosphito- and Sulfato-Bridged Complexes

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A great deal of the research on complexes containing metal–metal bonds has been concerned with structural questions, with less attention being paid to chemical reactivity.[1–7] Since binuclear platinum(III) complexes containing the pyrophosphito bridging ligand ($P_2O_5H_2{}^{2-}$) are well characterized from a structural point of view,[7] we felt that studies of their ligand-substitution reactions would be particularly useful. A specific matter that we have addressed in the $[Pt_2(pop)_4X(OH_2)]^{3-}$ (pop = $P_2O_5H_2$; X = Cl,

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