Synthesis and Characterization of Molybdenum Complexes Containing Diphosphine Ligands of the Type $(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$ ($Ar = C_6H_4X$). Electronic Control of η^2-Dihydrogen versus Dihydride Coordination in $MoH_2(CO)\{(RCH_2)_2PC_2H_4P(CH_2R)_2\}_2$ ($R = Me, Pr^i, C_6H_4X$) and Implications on the Reaction Coordinate for H_2 Cleavage

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The bis(dinitrogen)molybdenum complexes *trans*-$Mo(N_2)_2\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ ($Ar = C_6H_5$ (**1a**), C_6H_4-*m*-Me (**1b**), C_6H_4-*o*-Me (**1c**), C_6H_4-*p*-Me (**1d**), C_6H_4-*o*-F (**1e**), C_6H_4-*m*-F (**1f**) C_6H_4-*p*-F (**1g**), C_6H_4-*m*-OMe (**1h**), C_6H_4-*p*-OMe (**1i**)) are prepared by reduction of $MoCl_5$ with magnesium under a dinitrogen atmosphere in the presence of the appropriate diphosphine ligand. Treatment of **1a** and **1b** with ethyl acetate in refluxing benzene under argon affords the formally 16-electron complexes $Mo(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ ($Ar = C_6H_5$ (**2a**), C_6H_4-*m*-Me (**2b**)), which are shown by ^1H NMR spectroscopy to contain an agostic Mo••H–C interaction between the molybdenum and an ortho aryl hydrogen atom. Complexes **2a** and **2b** react readily with small molecules H_2, N_2, and SO_2 to give the adducts *trans*-$Mo(L)(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ ($L = \eta^2$-H_2, $Ar = C_6H_5$ (**3a**), C_6H_4-*m*-Me (**3b**); $L = N_2$, $Ar = C_6H_5$ (**4a**), C_6H_4-*m*-Me (**4b**); $L = SO_2$, $Ar = C_6H_5$ (**5a**), C_6H_4-*m*-Me (**5b**)). In contrast to the dihydride formulation in $MoH_2(CO)\{(RCH_2)_2PC_2H_4P(CH_2R)_2\}_2$ ($R = Me, Pr^i$), the η^2-H_2 coordination in **3a** and **3b** is unambiguously established by IR, NMR, and neutron scattering spectroscopies and a single-crystal X-ray diffraction analysis of **3b**. Thus, electronic control of η^2-dihydrogen versus dihydride coordination has been achieved in complexes of the type $MoH_2(CO)\{(RCH_2)_2PC_2H_4P(CH_2R)_2\}_2$, an η^2-dihydrogen complex being formed when R is an electron-withdrawing aryl group, whereas a dihydride is formed when R is an electron-donating alkyl group. The spectroscopic data for **3a** and **3b** indicate that they exist exclusively as η^2-dihydrogen complexes with a normal H–H distance both in solution and in the solid state, and so neither an elongated H–H bond nor an η^2-dihydrogen/dihydride tautomeric equilibrium has been observed although the π-basicity of the metal center appears to be very close to the point where the H–H bond cleavage is expected to occur. This supports the suggestion that the reaction coordinate for H_2 cleavage in the molybdenum–diphosphine system is rather flat and shows relatively little change in the H–H distance until relatively precipitous cleavage of the H–H bond. Crystallographic data for **3b**: monoclinic, space group *C2/c*, $a = 26.782(5)$ Å, $b = 9.365(2)$ Å, $c = 25.399(5)$ Å, $\beta = 111.75(3)°$, $V = 5921(5)$ Å^3, $Z = 4$, and $R = 0.058$. Crystallographic data for **4a**: monoclinic, space group *C2/c*, $a = 23.644(5)$ Å, $b = 13.558(3)$ Å, $c = 17.525(4)$ Å, $\beta = 108.97(3)°$, $V = 5313(4)$ Å^3, $Z = 4$, and $R = 0.034$.

Introduction

Recent years have witnessed considerable interest in transition-metal η^2-dihydrogen complexes[1] since these complexes represent intermediates or transition states in the oxidative addition/reductive elimination of dihydrogen at transition-metal centers, which is a fundamental step in a number of important catalytic processes such as hydrogenation, hydrogenolysis, and hydroformylation. The η^2-dihydrogen coordination not only is of fundamental interest from a structural point of view but also has significant implications for the H–H bond activation process in transition-metal-catalyzed transformations involving dihydrogen. In this respect, η^2-dihydrogen complexes have been found to be involved in the mechanistic pathway in homogeneous catalysis including hydrogenation of alkenes[2] and alkynes,[3] hydrogenation of ketones,[4] hydrosilylation of alkynes,[5] dehydrogenation of alcohols,[6] dimerization of alkynes,[7] and H/D isotopic exchange.[8] Furthermore, the establishment of η^2-dihydrogen coordination has opened up the possibility of activating dihydrogen without oxidative addition. For example, it has been demonstrated that coordinated dihydrogen, especially in cationic complexes, can be highly activated toward heterolytic cleavage as a result of the depletion of the electron density of the H–H bond by $H_2(\sigma)$ to $M(d_\sigma)$ donation.[9]

The bonding model for η^2-dihydrogen coordination can be described in terms of two components: donation of electron

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density from the bonding orbital of H_2 into an empty d_σ orbital of the metal and back-donation of electron density from a filled d_π orbital of the metal into the σ^*-antibonding orbital of H_2.[10] The $H_2(\sigma)$ to $M(d_\sigma)$ donation weakens but does not break the H−H bond because the resulting three-center−two-electron (3c−2e) orbital has bonding character over all three centers. On the other hand, the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation populates the σ^*-antibonding orbital of H_2 and thus can break the H−H bond if the back-donation is sufficiently strong.

One of the major goals of our research has been to map out the reaction coordinate for H−H bond cleavage at transition-metal centers and to sort out the electronic and steric factors that control the relative stability of η^2-dihydrogen versus dihydride coordination.[1a,11] One strategy to achieve this goal has been to vary ancillary ligands and hence π-back-bonding capability of the metal center. For example, increasing the basicity of ancillary ligands should promote $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation and thereby ultimately lead to cleavage of the H−H bond. An excellent system for such a study is $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ in which the electronic and steric properties of the diphosphine ligand can be varied in a systematic way by changing the substituents on the phosphorus donor atoms. Our previous work[12] has shown that the binding mode of dihydrogen depends primarily on the basicity of the diphosphine ligand. For R = phenyl, the compound contains an η^2-H_2 ligand in a typical six-coordinate octahedral structure with the midpoint of the H−H bond occupying one coordination site, but for the more electron-donating substituents R = ethyl and isobutyl, the complex exists as a seven-coordinate dihydride with a pentagonal bipyramidal structure. This was the first evidence that electronic rather than steric factors are more critical in stabilizing η^2-dihydrogen versus dihydride coordination and that increasing $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation leads to H−H bond cleavage.

It is quite obvious that, in the molybdenum−diphosphine system, complexes containing diphosphine ligands with intermediate basicities need to be synthesized in order to further define the factors affecting the relative stability of η^2-dihydrogen versus dihydride coordination and to map out the reaction coordinate for H−H bond cleavage. The diphosphine ligands of the type $(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$ ($Ar = C_6H_4X$) seem to be suitable for this purpose because these ligands should have basicities intermediate between those of $Et_2PC_2H_4PEt_2$ (depe) and $Ph_2PC_2H_4PPh_2$ (dppe) as expected on inductive grounds and on the basis of the basicity order $PEt_3 > P(CH_2Ph)_3 > PPh_3$.[13] In this paper, we report the synthesis and characterization of some new molybdenum complexes containing diphosphine ligands of this type. Of particular interest are *trans*-$Mo(\eta^2\text{-}H_2)(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ ($Ar = C_6H_5$ (**3a**), C_6H_4-*m*-Me (**3b**)), in which the η^2-dihydrogen coordination has been unambiguously established. This differs from the previously observed dihydride formation in $MoH_2(CO)\{(RCH_2)_2PC_2H_4P(CH_2R)_2\}_2$ (R = Me, Pr^i).[12] Thus, electronic control of η^2-dihydrogen coordination versus dihydride formation has been achieved in a series of complexes of the general type $MoH_2(CO)\{(RCH_2)_2PC_2H_4P(CH_2R)_2\}_2$, wherein the coordination mode of dihydrogen is determined by the nature of R such that an η^2-dihydrogen complex is formed when R is an electron-withdrawing aryl group, whereas a dihydride is formed when R is an electron-donating alkyl group.

Results and Discussion

Ligand Preparation. A series of unsubstituted and substituted benzyl diphosphine ligands of the type $(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$ ($Ar = C_6H_4X$) are conveniently synthesized by reacting $Cl_2PC_2H_4PCl_2$ with Grignard reagents in diethyl ether (eq 1). The Grignard reagents used are either commercially available or readily prepared in situ by reacting benzyl chlorides with magnesium in diethyl ether. When the benzyl chloride contains an activating substituent such as OMe in the phenyl ring, the coupling of the benzyl chloride to give a bibenzyl can be a significant side reaction in the preparation of the Grignard reagent. This problem can be substantially mitigated by using magnesium powder instead of magnesium turnings and using I_2 as a catalyst. The diphosphine ligands

$$Cl_2PC_2H_4PCl_2 + ArCH_2MgCl \xrightarrow{Et_2O} (ArCH_2)_2PC_2H_4P(CH_2Ar)_2 \quad (1)$$

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prepared according to eq 1 are isolated in high yields as either white crystalline solids or colorless viscous liquids at room temperature. They are moderately air-sensitive in solution, but the solids can be handled in air for a short period of time.

The $^{31}P\{^1H\}$ NMR spectra of these diphosphines show only a slight variation of the chemical shift with the nature of the aromatic substituents, with electron-donating substituents causing small upfield shifts. However, there is no simple correlation between chemical shifts and any Hammett substituent constants. The two methylene protons in each of the equivalent benzyl groups are diastereotopic because there is no plane of symmetry bisecting the CH_2 unit of a benzyl group. An analogous effect has been previously observed for $(Bu^tCH_2)_2PC_2H_4P(CH_2Bu^t)_2$.[14] As a result, the benzylic protons (CH_2Ar) give an AB pattern in ^1H NMR with geminal $^2J_{HH}$ coupling constants of 13−14 Hz. It is somewhat surprising that the $^2J_{PH}$ couplings from the phosphorus to the benzylic protons are too small to be observed.

Synthesis of *trans*-$Mo(N_2)_2\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_4X). A series of bis(dinitrogen)molybdenum complexes of the type *trans*-$Mo(N_2)_2\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_5 (**1a**), C_6H_4-*m*-Me (**1b**), C_6H_4-*o*-Me (**1c**), C_6H_4-*p*-Me (**1d**), C_6H_4-*o*-F (**1e**), C_6H_4-*m*-F (**1f**), C_6H_4-*p*-F (**1g**), C_6H_4-*m*-OMe (**1h**), C_6H_4-*p*-OMe (**1i**)) are prepared by the reduction of $MoCl_5$ with magnesium turnings in THF under a dinitrogen atmosphere in the presence of the appropriate diphosphine ligand (eq 2). These new bis(dinitrogen) complexes

$$MoCl_5 + (ArCH_2)_2PC_2H_4P(CH_2Ar)_2 + Mg \xrightarrow[N_2]{THF} \textit{trans}\text{-}Mo(N_2)_2\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2 \quad (2)$$

are isolated as yellow or orange solids. They are only slightly air-sensitive in the solid state but are readily oxidized in solution by air.

The IR spectra of **1a−i** in Nujol mulls show an intense absorption band in the range of 1907−1960 cm^{-1} assignable to the $\nu(N_2)$ stretching vibration and indicative of a trans configuration about the molybdenum atom. The $^{31}P\{^1H\}$ NMR spectra of complexes **1a−i** exhibit only a single resonance, which indicates the presence of four equivalent phosphorus atoms and thus confirms the trans configuration. The complexes $Mo(N_2)_2(Me_2PC_2H_4PMe_2)_2$[15] and $Mo(N_2)_2(Ph_2PCH{=}CHPPh_2)_2$[16] are perhaps the only examples of bis(dinitrogen)molybdenum complexes with diphosphine ligands that can also exist as the cis isomers, which give an A_2B_2 spin system in their $^{31}P\{^1H\}$ NMR spectra.

The $\nu(N_2)$ stretching frequencies of 1907−1960 cm^{-1} for **1a−i** are lower than the $\nu(N_2)$ (1976 cm^{-1}) observed for *trans*-$Mo(N_2)_2(dppe)_2$ (dppe = $Ph_2PC_2H_4PPh_2$).[17] This is consistent with the higher basicities of $(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$ as compared to that of dppe since it is generally believed that $\nu(N_2)$ is mainly determined by $M(d_\pi)$ to $N_2(\pi^*)$ back-donation.[18] However, it is surprising that the $\nu(N_2)$ stretching frequencies of some of the complexes **1a−i** are even lower than those observed for complexes of the type $Mo(N_2)_2(R_2PC_2H_4PR_2)_2$ (R = alkyl) which contain very basic alkyl diphosphine ligands. For example, complexes **1a** has a $\nu(N_2)$ band at 1935 cm^{-1}, which is significantly lower than 1947 cm^{-1} for *trans*-$Mo(N_2)_2(Bu^i{}_2PC_2H_4PBu^i{}_2)_2$[12c] and 1960 cm^{-1} for *trans*-$Mo(N_2)_2(Me_2PC_2H_4PMe_2)_2$.[15] Clearly, there is no unequivocal correlation between $\nu(N_2)$ stretching frequencies and diphosphine basicities in these bis(dinitrogen)molybdenum complexes.

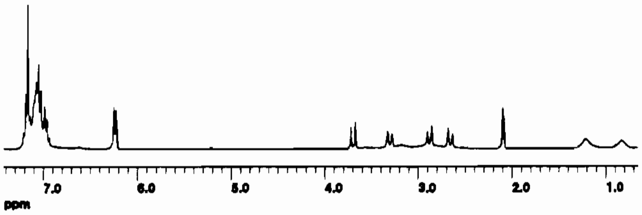

Figure 1. ^1H NMR spectrum (250 MHz, 298 K) of $Mo(CO)\{(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (**2a**) in $C_6D_5CD_3$. The quintet resonance at δ 2.09 is due to residual solvent protons.

Synthesis and Characterization of Agostic Complexes $Mo(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_5(2a), C_6H_4-*m*-Me (2b)). In a procedure similar to that used previously for the synthesis of $Mo(CO)(dppe)_2$,[12] the formally 16-electron complexes $Mo(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_5 (**2a**), C_6H_4-*m*-Me (**2b**)) are prepared by the reactions of the bis(dinitrogen)molybdenum complexes **1a** and **1b** with ethyl acetate in refluxing benzene under argon (eq 3). Like other formally

$$\textit{trans}\text{-}Mo(N_2)_2\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2 + \\ Ar = C_6H_5\ (\mathbf{1a}),\ C_6H_4\text{-}\textit{m}\text{-}Me\ (\mathbf{1b}) \\ CH_3COOEt \xrightarrow[\text{reflux, 40 min}]{\text{benzene, argon}} \\ Mo(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2 \quad (3) \\ Ar = C_6H_5\ (\mathbf{2a}),\ C_6H_4\text{-}\textit{m}\text{-}Me\ (\mathbf{2b})$$

16-electron molybdenum and tungsten complexes,[12,19] complexes **2a** and **2b** are intensely colored, deep purple in the solid state, and dark-red in solution. They are highly air-sensitive both in the solid state and in solution. Crystals of **2a** and **2b** were invariably twinned and were not suitable for an X-ray crystallographic analysis.

The IR spectra (Nujol mull) of **2a** and **2b** show strong $\nu(CO)$ bands at 1696 and 1700 cm^{-1}, respectively, which are lower than that (1723 cm^{-1}) reported for $Mo(CO)(dppe)_2$[12] and are consistent with the higher basicity of $(ArCH_2)_2PCH_2CH_2P(CH_2Ar)_2$ as compared with that of dppe. However, it is surprising that the $\nu(CO)$ stretching frequencies of **2a** and **2b** are even lower than those (1748 and 1725 cm^{-1}) reported for $Mo(CO)(R_2PCH_2CH_2PR_2)_2$ (R = Et, Bu^i)[12] which contain more basic alkyl diphosphine ligands. Obviously, factors other than diphosphine basicities are also important determinants of $\nu(CO)$. The stretching bands of the Mo⋅⋅H−C interactions in **2a** and **2b** cannot be located. However, these bands are expected to be weak and accordingly are not a reliable probe of agostic interactions.[20]

The ^1H NMR spectrum of **2a** in $C_6D_5CD_3$ at 298 K (Figure 1) shows two broad multiplet resonances for the methylene

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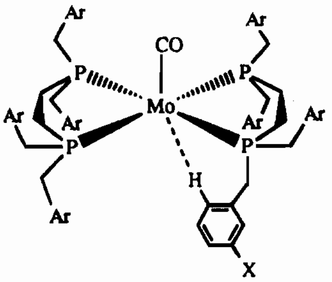
groups linking the phosphorus donors, four doublet resonances with geminal $^2J_{HH}$ coupling for the benzylic protons (CH_2Ph), and a complex region at δ 6.9−7.2 for the phenyl protons. In addition, there is a doublet resonance at δ 6.24 ($^3J_{HH}$ = 6.6 Hz), which is significantly upfield from the phenyl resonances and integrates as eight protons against the CH_2Ph or PCH_2-PCH_2P protons. This resonance smoothly disappears after treatment of **2a** with H_2, N_2, or SO_2 to give adducts (*vide infra*). When the sample is cooled, this resonance broadens and then disappears at 183 K into the baseline of the spectrum. The $^{31}P\{NMR\}$ spectrum of **2a** in $C_6D_5CD_3$ at 298 K shows a single resonance at δ 64.23, which becomes a broad resonance ($\omega_{1/2} \approx$ 82 Hz) upon cooling to 183 K, suggesting the onset of decoalescence. On the basis of these observations and similar ones for **2b** (*vide infra*), we propose an octahedral structure for **2a** and **2b** in which the otherwise vacant coordination site trans to the CO ligand is occupied by an ortho aryl hydrogen which forms an agostic Mo••H−C interaction. This structure is essentially similar to that established for Mo(CO)(dppe)$_2$ by an X-ray crystallographic analysis.[19a] The ^1H NMR resonance at δ 6.24 for **2a** can be assigned to the stereochemically nonrigid agostic hydrogen which undergoes rapid exchange with some other ortho phenyl hydrogens. Since the barrier to inversion at phosphorus for coordinated phosphine ligands is usually quite high,[21] the agostic Mo••H−C interaction can be formed only with the ortho hydrogens of those aryl groups that are oriented downward and thus *anti* to the CO ligand relative to the equatorial plane defined by the molybdenum and four phosphorus atoms. The dynamic exchange process accounts for the intensity of eight protons for the doublet resonance at δ 6.24. This average resonance is upfield from other phenyl resonances because an agostic hydrogen in a non-d^0 system usually resonates substantially upfield from tetramethylsilane.[20]



X = H (**2a**), CH_3 (**2b**)
Ar = C_6H_5 (**2a**), C_6H_4-*m*-Me (**2b**)

The variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of **2b** in $C_6D_5CD_3$ are quite similar to those of **2a**. In the ^1NMR spectrum at 298 K, the doublet resonances at δ 6.28 observed for **2a** shifts further upfield to δ 5.46 ($^3J_{HH}$ = 7.1 Hz) for **2b** and integrates as only four protons. As is the case for **2a**, this resonance completely disappears after addition of H_2, N_2, or SO_2 to **2b** to yield adducts and, upon cooling, broadens and ultimately disappears at 183 K into the baseline. The $^{31}P\{NMR\}$ spectrum of **2b** at 298 K shows a single resonance at δ 63.72 which becomes a broad feature ($\omega_{1/2} \approx$ 85 Hz) upon cooling to 183 K. On the basis of these observations, we propose that **2b** adopts an octahedral structure entirely analogous to that for **2a** and that the ^1H NMR resonance at δ 5.46 can be assigned to the fluxional agostic hydrogen. Because only the sterically less encumbered ortho aryl hydrogens, *i.e.*, those *para* to the methyl group, are capable of forming the agostic Mo••H−C interaction, the proton resonance at δ 5.46 has an intensity of four protons as contrasted to that of eight protons for the corresponding resonance in **2a**. In addition, since the agostic hydrogen exchanges with only three ortho hydrogens in **2b**, whereas it does so with seven in **2a**, the average resonance for **2b** is more upfield than that for **2a**.

It is interesting to compare the fluxionality involving the agostic hydrogen in **2a** and **2b** with that in Mo(CO)(dppe)$_2$. The X-ray crystal structure of Mo(CO)(dppe)$_2$ reveals an extremely weak agostic interaction with a rather long Mo••H distance of 2.98 Å.[19a] Surprisingly, it was recently reported that the upfield region of the ^1H NMR spectrum of Mo(CO)-(dppe)$_2$ in C_6D_6 at room temperature shows a singlet resonance at δ −0.25 with the intensity of one proton and assignable to the agostic hydrogen which does not exchange with other ortho phenyl hydrogens at room temperature.[19e] The seemingly high barrier to the fluxionality in Mo(CO)(dppe)$_2$ may suggest the presence of a strong agostic Mo••H−C interaction, which is contradictory to the long Mo••H distance revealed by X-ray crystallography. However, if the solution structure is indeed rigid, one would expect to see the inequivalence of the four phosphorus atoms in the $^{31}P\{^1H\}$ NMR spectrum, and the ^1H NMR resonance due to the agostic hydrogen would exhibit vicinal $^3J_{HH}$ coupling, albeit somewhat reduced, to the adjacent phenyl hydrogen. We have been unable to reproduce the reported observation of the agostic hydrogen resonance in Mo-(CO)(dppe)$_2$. In fact, we found that the $^{31}P\{^1H\}$ spectrum of Mo(CO)(dppe)$_2$ in C_6D_6 at 298 K displays only a single resonance at δ 78.71, which is more consistent with a fluxional solution structure.

It appears that the stability of the agostic complexes of the type Mo(CO){$(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$}$_2$ (Ar = C_6H_4X) is remarkably sensitive to both the nature and position of the aromatic substituent X. Although a wide range of the bis(dinitrogen)molybdenum complexes **1a**−**i** have been prepared, so far we have been able to synthesize only complexes **2a** and **2b** with X = H and *m*-Me, respectively, from **1a** and **1b** according to eq 3. Attempts to prepare similar agostic complexes by reacting **1c**−**i** with ethyl acetate in refluxing benzene under argon have invariably failed. In all cases, a mixture of intractable products were obtained. It is possible that the desired agostic complexes were first formed, but rapidly decomposed under the reaction conditions. Because substitution of a fluorine for a hydrogen should not have any significant steric effects, the failure of complexes **1e**−**g** to give stable agostic complexes is probably due to electronic effects. The position of the aromatic substituent X is also critical because, in contrast to **1b** which contains *meta* methyl groups and gives the stable agostic complex **2b** according to eq 3, isomeric complexes **1c** and **1d**, which contain *ortho* and *para* methyl groups, respectively, do not yield isolable agostic complexes. This is more likely due to steric effects than due to any electronic effects. The importance of steric effects on the stability of the agostic Mo••H−C interaction is also manifested by the selective binding of the sterically less hindered ortho hydrogen in **2b** as described above.

Coordination of H_2, N_2, and SO_2 to Mo(CO){$(ArCH_2)_2$-$PC_2H_4P(CH_2Ar)_2$}$_2$ (Ar = C_6H_5 (2a), C_6H_4-*m*-Me (2b)). Addition of small molecules H_2, N_2, or SO_2 to solutions of **2a** and **2b** in toluene results in the displacement of the weak agostic Mo••H−C interaction and formation of the adducts *trans*-Mo-(L)(CO){$(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$}$_2$ (L = η^2-H_2, Ar = C_6H_5 (**3a**), C_6H_4-*m*-Me (**3b**); L = N_2, Ar = C_6H_5 (**4a**), C_6H_4-*m*-Me (**4b**); L = SO_2, Ar = C_6H_5 (**5a**), C_6H_4-*m*-Me (**5b**)) (eq 4). These reactions are very rapid and are accompanied by characteristic color changes from dark red to yellow or orange.

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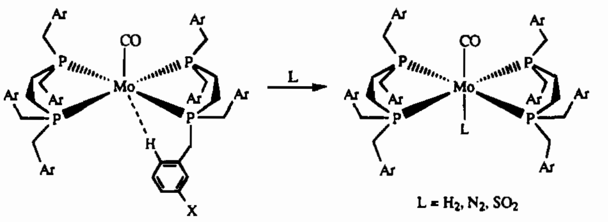

(4)

The resulting adducts are isolated as yellow or orange solids in high yields. Complex **3a** is insoluble in all common solvents except benzene and toluene in which it is only sparingly soluble, whereas other adducts are reasonably soluble in benzene and toluene. Satisfactory NMR spectra of **3a** were obtained only with a supersaturated solution prepared in situ by exposing a solution of **2a** in $C_6D_5CD_3$ to H_2 and carefully avoiding disturbance of the solution. The addition of SO_2 in eq 4 is irreversible, whereas addition of H_2 or N_2 is reversible and thus samples of **3** or **4** for NMR and IR studies must be prepared and kept under an H_2 or N_2 atmosphere. Loss of N_2 from the dinitrogen complexes **4a** and **4b** is slow in the solid state but facile in solution under vacuum. Loss of H_2 from the η^2-dihydrogen complexes **3a** and **3b** occurs both in solution and in the solid state. Thus, exposure of solutions or finely ground solids of **3a** and **3b** to a dynamic vacuum regenerates **2a** and **2b** quantitatively. In fact, complexes **2a** and **2b** are best isolated and purified by conversion to the much less soluble η^2-dihydrogen complexes **3a** and **3b** and then removal of dihydrogen in a dynamic vacuum.

The $^{31}P\{^1H\}$ NMR spectra of all the adducts **3**−**5** are temperature independent in the range of 193−298 K and display only a single resonance, which indicates the presence of four equivalent phosphorus atoms and thus a trans orientation of the ligand L relative to the CO ligand. The IR spectra of the dinitrogen adducts **4a** and **4b** in Nujol mulls show strong $\nu(N_2)$ absorptions at 2062 and 2063 cm^{-1}, respectively. The IR spectra of the SO_2 adducts **5a** and **5b** in Nujol mulls show two ν(SO) bands at 1180 and 1041 cm^{-1} for **5a** and 1184 and 1042 cm^{-1} for **5b**. This suggests a planar $Mo(\eta^1\text{-}SO_2)$ binding mode for these adducts which is typically found for an electrophilic metal fragment capable of π-back-donation.[22] The ν(CO) bands of the SO_2 adducts **5a** and **5b** appear at 1880 and 1874 cm^{-1}, respectively. These ν(CO) stretching frequencies are considerably higher than those for the corresponding dinitrogen adducts **4a** (1784 cm^{-1}) and **4b** (1786 cm^{-1}), suggesting that SO_2 is overall a better π-acceptor than is N_2 in these cases.

IR spectra of the η^2-dihydrogen complexes **3a** and **3b** in Nujol mulls exhibit $\delta(MoH_2)$ deformation modes at 432 and 421 cm^{-1}, respectively. This feature is absent for the D_2 isotopomers of **3a** and **3b**. Complex **3a** also displays a partially obscured underlying feature at 907 cm^{-1}, which shifts to 677 cm^{-1} for the D_2 isotopomer of **3a** and so is probably assignable to the symmetric stretching mode $\nu_s(MoH_2)$. Other vibration modes expected for $Mo(\eta^2\text{-}H_2)$ binding[1a] are not observable in the IR, probably due to obscuration by the diphosphine ligand absorptions. However, a broad band at 2640 cm^{-1} in the inelastic neutron scattering differential spectrum[1h] for **3a** may be identified with ν(HH). This frequency is essentially identical to the 2650 cm^{-1} observed by IR in $Mo(\eta^2\text{-}H_2)(CO)(dppe)_2$. No bands that can be assigned to the vibrational modes of a dihydride complex are observed for **3a** and **3b**. The ν(CO) bands of **3a** and **3b** appear at 1751 and 1757 cm^{-1}, respectively, and are substantially higher than those for the corresponding agostic precursors **2a** (1696 cm^{-1}) and **2b** (1700 cm^{-1}). This suggests that there is greater $Mo(d_\pi)$ to $H_2(\sigma^*)$ back-donation in η^2-H_2 coordination as compared to $Mo(d_\pi)$ to C−H (σ^*) back-donation in the agostic Mo···H−C interactions.

Variable-temperature solution ^1H and $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** in $C_6D_5CD_3$ indicate that the η^2-H_2 binding mode observed in the solid state by IR is also maintained in solution. In contrast to the temperature-dependent $^{31}P\{^1H\}$ NMR spectra observed for seven-coordinate dihydride complexes of the type $MH_2(CO)(R_2PC_2H_4PR_2)_2$ (M = Mo, R = Et, Bu^i; M = W, R = Ph) which adopts a pentagonal bipyramidal structure[12b,c,19e,f] the $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** are temperature independent (193−298 K) and show only a single resonance. This is consistent with a six-coordinate octahedral structure with C_{4v} symmetry in which the η^2-H_2 ligand is trans to the CO ligand. The hydride region of he ^1H NMR spectra of **3a** and **3b** at 298 K shows a broad resonance (δ −5.38, $\omega_{1/2} \approx 66$ Hz) which can be assigned to the η^2-H_2 ligand. The line width of the resonance increases with decrease in temperature. If the H_2 atmosphere is removed under vacuum and replaced by argon, the η^2-H_2 resonance disappears with concomitant appearance of the resonance due to the agostic Mo···H−C interaction (supra infra). The hydride region of the ^1H NMR spectra of the η^2-HD isotopomers of **3a** and **3b**, generated in situ by exposing solution of **2a** and **2b** in $C_6D_5CD_3$ to HD, displays a 1:1:1 triplet at δ −5.41 with a $^1J_{HD}$ coupling constant of 30 Hz for the η^2-HD ligand. The $^1J_{HD}$ value is somewhat smaller than the 34 Hz observed for $Mo(\eta^2\text{-}H_2)(CO)(dppe)_2$. The IR and ^{31}P and ^1H NMR spectra of **3a** and **3b** show no evidence for the presence of an equilibrium dihydride tautomer as observed for $W(\eta^2\text{-}H_2)(CO)_3(PR_3)_2$ in solution by NMR and IR.[12a,19c] This is perhaps surprising in view of the fact that the former contain only one strongly π-accepting CO ligand whereas the latter contain three and the general observation that replacement of a σ-donating phosphine ligand by a π-accepting CO ligand reduces the π-basicity of the metal center and thus favors η^2-dihydrogen over dihydride coordination.[1] The higher energy of the d_π orbitals of the tungsten complexes compared to those of the molybdenum complexes is no doubt an overriding factor.

The presence of an η^2-H_2 ligand in **3b** is also confirmed by the ^1H NMR spin−lattice relaxation times (T_1) of the hydride resonance which were measured in $C_6D_5CD_3$ at 250 MHz by the inversion-recovery method using a standard 180°−τ−90° pulse sequence.[23] The exceedingly low solubility of **3a** precludes T_1 measurements. The T_1 values for **3b** at various temperatures are given in the Experimental Section, and a plot of ln T_1 vs $1/T$ gives a V-shaped curve, as predicted by theory.[23] The V-shaped curve rules out the presence of a dihydride tautomer which is in fast equilibrium with the η^2-dihydrogen tautomer, because distortion of the ln T_1 vs $1/T$ plot would be expected for a tautomeric equilibrium where the concentration ratio of the two tautomers should usually be temperature dependent.[9d,19c,d,24−27] Since the molecule of **3b** has a very high

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Table 1. Crystallographic Data for *trans*-Mo(η^2-H_2)(CO){(*m*-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-*m*-$Me)_2\}_2$ (**3b**) and *trans*-Mo(N_2)(CO){$(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (**4a**)

	3b	**4a**
empirical formula	$C_{69}H_{82}MoOP_4$	$C_{61}H_{64}MoN_2OP_4$
fw	1147.24	1061.02
crystal system	monoclinic	monoclinic
space group	*C2/c*	*C2/c*
a, Å	26.782(5)	23.644(5)
b, Å	9.365(2)	13.558(3)
c, Å	25.399(5)	17.525(4)
α, deg	90.00	90.00
β, deg	111.75(3)	108.97(3)
γ, deg	90.00	90.00
V, $Å^3$	5921(5)	5313(4)
Z	4	4
ϱ(calcd), g cm^{-3}	1.287	1.326
μ(Mo Kα), cm^{-1}	3.73	4.11
min/max transm coeff	0.70−0.94	0.86−0.89
T, K	203	203
R^a	5.81	3.37
$R_w{}^b$	7.97	5.36

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

molecular weight and so a relatively large moment of inertia, T_1 minimizes at a relatively high temperature (273 K). From the minimum T_1 value of 10 ms, assuming a ±20% error[28] in T_1 measurements and rapid rotation of the η^2-H_2 ligand around the Mo−H_2 axis, an H−H distance of 0.85 ± 0.03 Å may be calculated for the η^2-H_2 ligand.[29] This calculated H−H distance is comparable with 0.80−0.85 Å determined for Mo(η^2-H_2)(CO)(dppe)$_2$ by neutron diffraction.[12c] In addition, measurements of the dipolar couplings of the η^2-H_2 ligand in **3a** and **3b** by solid-state ^1H NMR[30] have yielded an H−H distance of 0.87 ± 0.01 Å[31] which is in excellent agreement with that obtained from the solution T_1 measurements.

X-ray Crystal Structures of *trans*-Mo(η^2-H_2)(CO){(*m*-Me-$C_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-*m*-Me)$_2\}_2$ (3b) and *trans*-Mo-(N_2)(CO){$(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (4a). Crystals of **3b** and **4a** suitable for X-ray crystallography were grown from benzene/hexane under an atmosphere of dihydrogen and dinitrogen, respectively. A summary of crystallographic data is given in Table 1. ORTEP drawings are given in Figures 2 and 3, and selected bond lengths and angles are given in Tables 2 and 3.

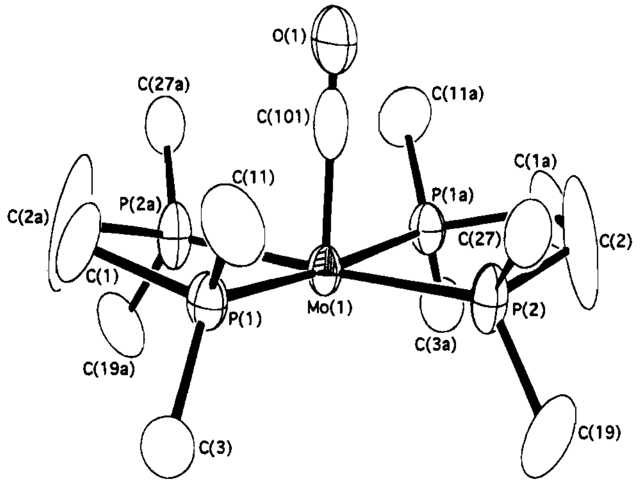

Figure 2. ORTEP drawing of *trans*-Mo(η^2-H_2)(CO){(*m*-$MeC_6H_4CH_2)_2$-$PC_2H_4PCH_2C_6H_4$-*m*-Me)$_2\}_2$ (**3b**). The *m*-tolyl groups in the diphosphine ligands are omitted for clarity.

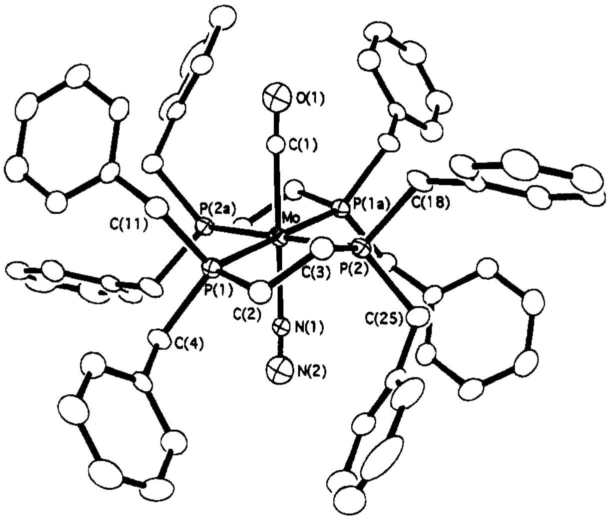

Figure 3. ORTEP drawing of *trans*-Mo(N_2)(CO){$(C_6H_5CH_2)_2PC_2H_4P$-$(CH_2C_6H_5)_2\}_2$ (**4a**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-Mo(η^2-H_2)(CO){(*m*-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-*m*-Me)$_2\}_2$ (**3b**)

	Bond Lengths		
Mo(1)−P(1)	2.423(2)	Mo(1)−P(1A)	2.423(2)
Mo(1)−P(2)	2.418(1)	Mo(1)−P(2A)	2.418(1)
Mo(1)−C(101)	1.948(13)	C(101)−O(1)	1.080(15)
P(1)- -C(1)	1.845(6)	P(1)−C(3)	1.865(7)
P(1)−C(11)	1.861(8)	P(2)−C(2)	1.829(10)
P(2)−C(19)	1.857(8)	P(2)−C(27)	1.846(7)
	Bond Angles		
P(1)−Mo(1)−P(2A)	80.4(1)	P(2)−Mo(1)−P(1A)	80.4(1)
P(1)−Mo(1)−P(2)	99.5(1)	P(1A)−Mo(1)−P(2A)	99.5(1)
P(1)−Mo(1)−P(1A)	174.7(1)	P(2)−Mo(1)−P(2A)	177.0(1)
P(1)−Mo(1)−C(101)	87.4(1)	P(1A)−Mo(1)−C(101)	87.4(1)
P(2)−Mo(1)−C(101)	88.5(1)	P(2A)−Mo(1)−C(101)	88.5(1)
Mo(1)−C(101)−O(1)	180.0(1)	Mo(1)−P(1)−C(1)	108.8(2)
Mo(1)−P(1)−C(3)	123.7(2)	Mo(1)−P(1)−C(11)	117.5(3)
C(1)−P(1)−C(3)	102.7(3)	C(1)−P(1)−C(11)	101.1(3)
C(3)−P(1)−C(11)	99.9(3)	Mo(1)−P(2)−C(2)	108.8(2)
Mo(1)−P(2)−C(19)	122.1(2)	Mo(1)−P(2)−C(27)	119.4(2)
C(2)−P(2)−C(19)	97.7(5)	C(2)−P(2)−C(27)	102.6(4)
C(19)−P(2)−C(27)	102.6(3)		

If the η^2-H_2 ligand, which was not located in the difference Fourier maps, is disregarded, the crystal structure of **3b** (Figure 2) shows a distorted square pyramidal coordination geometry around the molybdenum center with the carbonyl group occupying the apical position. The η^2-H_2 ligand probably occupies the otherwise vacant coordination site trans to the carbonyl group. This is evidenced by the fact that the diphosphine ligands

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$Mo(N_2)(CO)\{(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (**4a**)

Bond Lengths

Mo−P(1)	2.433(1)	Mo−P(1A)	2.433(1)
Mo−P(2)	2.452(1)	Mo−P(2A)	2.452(1)
Mo−C(1)	2.090(3)	Mo−N(1)	2.090(3)
C(1)−O(1)	1.037(4)	N(1)−N(2)	1.037(4)
P(1)−C(2)	1.852(3)	P(1)−C(4)	1.865(3)
P(1)−C(11)	1.867(3)	P(2)−C(3)	1.854(2)
P(2)−C(18)	1.864(3)	P(2)−C(25)	1.866(3)

Bond Angles

P(1)−Mo−P(2)	80.5(1)	P(1A)−Mo−P(2A)	80.5(1)
P(1)−Mo−P(2A)	99.5(1)	P(2)−Mo−P(1A)	99.5(1)
P(1)−Mo−P(1A)	180.0(1)	P(2)−Mo−P(2A)	180.0(1)
P(1)−Mo−C(1)	91.1(1)	P(1A)−Mo−C(1)	88.9(1)
P(2)−Mo−C(1)	84.8(1)	P(2A)−Mo−C(1)	95.2(1)
P(1)−Mo−N(1)	91.1(1)	P(1A)−Mo−N(1)	88.9(1)
P(2)−Mo−N(1)	84.8(1)	P(2A)−Mo−N(1)	95.2(1)
Mo−C(1)−O(1)	176.3(3)	Mo−N(1)−N(2)	176.3(3)
Mo−P(1)−C(2)	110.3(1)	Mo−P(1)−C(4)	119.2(1)
Mo−P(1)−C(11)	121.0(1)	C(2)−P(1)−C(4)	101.5(1)
C(2)−P(1)−C(11)	97.1(1)	C(4)−P(1)−C(11)	103.9(1)
Mo−P(2)−C(3)	108.5(1)	Mo−P(2)−C(18)	116.6(1)
Mo−P(2)−C(25)	124.3(1)	C(3)−P(2)−C(18)	102.1(1)
C(3)−P(2)−C(25)	103.3(1)	C(18)−P(2)−C(25)	99.4(1)

bend away from the "vacant" site toward the carbonyl group, since they would bend toward the coordination site if it is empty. Theoretical calculations[12c,34] suggest that the bending of phosphine ligands away from the coordination site of H_2 causes a hybridization of the metal d-orbitals toward H_2 in order to reduce the antibonding influence of the phosphine, which results in an increase in the strength of H_2 coordination.

The pseudo-square-planar arrangement of the diphosphine ligands in **3b** leads to quite uniform Mo−P distances of 2.418(1)−2.423(2) Å and large trans P−Mo−P angles of 174.7(1) and 177.0(1)°. The averaged Mo−P distance of 2.421(2) Å in **3b** is only slightly shorter than that of 2.438(2) Å found in *trans*-$Mo(\eta^2\text{-}H_2)(CO)(dppe)_2$,[12c] whereas the averaged bite angles of the chelating diphosphine ligands in both compounds are essentially identical (80.4(1)°). The Mo−C(101) (carbonyl) distance in **3b** is 1.948(13) Å, which is essentially equal to the value of 1.933(5) Å found in *trans*-$Mo(\eta^2\text{-}H_2))(CO)(dppe)_2$.[12c]

The crystal structure of **4a** (Figure 3) is that of an octahedron with the carbonyl and dinitrogen groups being trans to each other. There is a disorder between the carbonyl and dinitrogen ligands. As a result, the difference Fourier maps of the final structure without these ligands did not reveal distinct positions for the two ligand types at each site. Therefore, a single ligand was refined with a 50/50 occupancy of C/N and O/N atoms. The averaged bite angle (80.5(1)°) of the diphosphine ligands is almost identical to that in **3b**, whereas the averaged Mo−P distance of 2.442(1) Å is only slightly longer than that of 2.421(2) Å in the latter compound.

Inelastic Neutron Scattering Studies of H_2 Rotation in *trans*-$Mo(\eta^2\text{-}H_2)(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_5 (3a), C_6H_4-*m*-CH_3 (3b)). One of the useful probes of nonclassical η^2-H_2 coordination in the solid state has been the observation of rotational tunneling transitions by inelastic neutron scattering (INS) studies.[1h] We have therefore collected INS data on the two H_2 complexes **3a** and **3b**. The difference vibrational spectra (complex with H_2 ligand *minus* complex with D_2 ligand) for **3a** and **3b** were obtained on the FDS instrument at the Los Alamos Neutron Scattering Center, and the rotational tunneling spectrum for **3b** was obtained on the MIBEMOL spectrometer at the Laboratoire Léon Brillouin of the CE-Saclay (Saclay, France). The rotational transitions from the INS data were analyzed with a model of rotation with one angular degree of freedom in a double-minimum potential, only the first term V_2 in the Fourier expansion of this potential being used. The rotational constant B was taken to be 45 cm^{-1} on the basis of the H−H distance of 0.85 Å obtained in the NMR studies described above. The rotational transitions and the barrier heights V_2 for H_2 rotation for **3a** and **3b** are listed in Table 4, along with previous results[12c] on two closely related compounds, *trans*-$Mo(\eta^2\text{-}H_2)(CO)(dppe)_2{\cdot}4.5C_6D_6$ (**6a**) and *trans*-$Mo(\eta^2\text{-}H_2)(CO)(dppe)_2{\cdot}2C_6D_5CD_3$ (**6b**). The barriers observed for **3a** and **3b** are 0.65 and 0.53 kcal mol^{-1}, respectively, which are comparable to the values of 0.61 and 0.48 kcal mol^{-1} for **6a** and **6b**. These complexes show the lowest barriers to H_2 rotation that have been measured to date,[1h] attributable to the 4-fold symmetry of the ligands in the plane parallel to that of H_2 rotation.[12c]

Table 4. Rotational Transitions (0−1, 0−2) and 2-Fold Barrier Heights (V_2) for H_2 Rotation in Molybdenuym η^2-Dihydrogen Complexes

complex	0−1, cm^{-1}	0−2, cm^{-1}	V_2, kcal mol^{-1}
3a	12[a]	122	0.65
3b	15	112	0.53
6a	13		0.61
6b	17		0.48

[a] Calculated frequency value.

Inspection of Table 4 shows no obvious correlation between phosphine basicity and the barrier height. For example, **3a** and **3b** contain phosphines with similar basicity but show significantly different barriers. Theoretical calculations suggest that the degree of the distortion of the MoP_4 skeleton, caused by electronic and steric effects or even by crystal packing and/or solvation effects, can significantly affect the barrier for H_2 rotation.[12c] This has been clearly demonstrated for **6a** and **6b**, which contain the same diphosphine but have different solvation and slightly different arrangements of the MoP_4 skeleton, leading to different barriers. Therefore, any attempted correlation of barrier height with phosphine basicity will be thwarted by the sensitivity of the barrier to distortion of the MoP_4 skeleton.

Electronic Control of η^2-Dihydrogen vs Dihydride Coordination in the Series $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ and Implications on the Reaction Coordinate for H_2 Cleavage. Theoretical investigations of the metal-H_2 interaction suggest that although both the $H_2(\sigma)$ to $M(d_\sigma)$ donation and the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation will weaken the H−H bond and strengthen the M−H bond, it is the degree of the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation that controls H−H bond cleavage by populating the σ^*-antibonding orbital of H_2.[10] The molybdenum−diphosphine system is well suited for evaluating electronic and steric effects of the ancillary ligands on the relative stability of η^2-dihydrogen versus dihydride coordination.

Steric and electronic effects of tertiary phosphine ligands in transition-metal complexes has been relatively well studied.[13] The steric effects have been evaluated in terms of the ligand cone angle, θ. Several electronic parameters, notably the frequency of the A_1 mode of $\nu(CO)$ in $Ni(CO)_3(PR_3)$, have been used as a measure of Lewis basicity. Our previous work[12] has established the η^2-dihydrogen coordination in $Mo(\eta^2\text{-}H_2)(CO)(dppe)_2$ in contrast to the dihydride formation in $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i). Since dppe and $Bu^i{}_2PC_2H_4PBu^i{}_2$ are expected to have similar steric bulk (cf. PPh_3 and $PBu^i{}_3$, which have very similar cone angles: 145 and 143°[13]) but different basicities, the relative stability of η^2-dihydrogen versus

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dihydride coordination in $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ is clearly dominated by the basicity of the diphosphine ligand. The diphosphine basicity controls the degree of $Mo(d_\pi)$ to $H_2(\sigma^*)$ back-donation and thus H−H bond cleavage. On the other hand, the relative insensitivity of the structure to steric effects is manifested by the fact that similar dihydride structures are found for complexes containing the diphosphine ligands depe and $Bu^i_2PC_2H_4PBu^i_2$ which have similar basicities but different steric bulk (cf. PEt_3 and PBu^i_3, which have rather different cone angles: 132 and 143°[13]).

The present work has established η^2-dihydrogen coordination in **3a** and **3b**. The calculated cone angle of 165° for $P(CH_2Ph)_3$ is substantially larger than 143° for PBu^i_3.[13] Assuming that the bulkiness of the corresponding diphosphine ligands follows the same order, it would appear that the structural change from η^2-dihydrogen to dihydride coordination on going from **3a** or **3b** to $MoH_2(CO)(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i) may involve both electronic and steric effects. Nevertheless, it has been shown that under steric constraints the cone angles of phosphines and phosphites with large internal degrees of freedom can dramatically decrease from the values calculated from the static models.[13] Indeed, as a consequence of the ability of the flexible benzyl group to adopt a conformation that mitigates the interligand repulsion, the effective cone angle of $P(CH_2Ph)_3$ has been found to be 142°,[32] which is essentially the same as the cone angle (143°) for PBu^i_3. On this basis and in view of the steric crowdedness of the molybdenum−diphosphine system, the steric bulk of the diphosphine ligands in **3a** and **3b** is probably very close to that of $Bu^i_2PC_2H_4PBu^i_2$. Thus, it is the lower basicity of the diphosphine ligands in **3a** and **3b** as compared to that of $Bu^i_2PCH_2CH_2PBu^i_2$ that appears to be responsible for the change in the dihydrogen binding mode upon varying the diphosphine ligand.

The π-basicity of a metal fragment can be probed by the position of $\nu(N_2)$ for the dinitrogen complex because $v(N_2)$ is mainly determined by $M(d_\pi)$ to $N_2(\pi^*)$ back-donation.[18] A more π-basic metal fragment should give a lower $\nu(N_2)$ in the dinitrogen complex and also shows a higher tendency to cleave the H−H bond of dihydrogen to give a dihydride complex. Since many η^2-H_2 complexes have an octahedral d^6 configuration, and the binding site for H_2 also accomodates N_2, Morris et al.[33] have proposed a correlation between the preferred binding mode of H_2 and the $v(N_2)$ stretching frequency for the corresponding octahedral d^6 dinitrogen complex: a stable η^2-H_2 complex is formed when $\nu(N_2)$ falls in the range 2060−2150 cm^{-1}, a dihydride is formed when $\nu(N_2)$ is lower than 2060 cm^{-1}, and a thermally unstable η^2-H_2 complex, which undergoes irreversible H_2 loss, is formed if $\nu(N_2)$ is higher than 2150 cm^{-1}.

The $\nu(N_2)$ frequencies for *trans*-$Mo(N_2)(CO)(R_2PC_2H_4PR_2)_2$ complexes in Nujol mulls decrease with increasing electron-donating ability of R in the order R = Ph (2095) > $CH_2C_6H_5$ (2062) ≈ $CH_2C_6H_4$-*m*-Me (2063) > Et (2050) > Bu^i (2040). This suggests that the basicity of the diphosphine ligand controls the π-basicity of the metal center, which in turn affects the $\nu(N_2)$. The $\nu(N_2)$ values for **4a** and **4b** lie very near the 2060 cm^{-1} borderline value between η^2-dihydrogen and dihydride complexes and thus do not allow a reliable prediction of the binding mode of dihydrogen in **3a** and **3b**. In contrast, the positions of $\nu(N_2)$ for *trans*-$Mo(N_2)(CO)(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i) clearly fall in the range where dihydride complexes are expected to be found. It is noteworthy that going from R = Et and Bu^i to R = $CH_2C_6H_5$ and $CH_2C_6H_4$-*m*-Me causes only a very small shift (12−23 cm^{-1}) in $\nu(N_2)$, merely corresponding to a small perturbation of the π-basicity of the metal center. However, even this "fine tuning" causes a structural change from an η^2-dihydrogen complex to a dihydride species.

The somewhat lower $^1J_{HD}$ value of 30 Hz for **3a** and **3b** compared with that of 34 Hz for $Mo(\eta^2\text{-}H_2)(CO)(dppe)_2$[12] may indicate a slightly more activated η^2-H_2 ligand in **3a** and **3b**. This, combined with the fact that the $\nu(N_2)$ values for **4a** and **4b** are very near the borderline value between η^2-dihydrogen and dihydride complexes, suggests that the π-basicity of the metal center in **3a** and **3b** is very close to that required for H−H bond cleavage. However, spectroscopic data for **3a** and **3b** indicate that they exist exclusively as η^2-dihydrogen complexes both in solution and in the solid state. Both the solution ^1H NMR T_1 measurements and solid-state ^1H NMR studies give an H−H distance of ca. 0.86 Å which is surprisingly similar to those determined for other unstreched η^2-H_2 complexes.[1] Thus, neither an elongated H−H bond nor an η^2-dihydrogen/dihydride tautomeric equilibrium has been observed in **3a** and **3b** despite the fact that the π-basicity of the metal center seems to be perilously close to the point where H−H bond cleavage should occur.

The results presented above lend support to our previous suggestion[12c] that the reaction coordinate for oxidative addition of H_2 in the molybdenum−diphosphine system is rather flat until very close to the precipitous cleavage of the H−H bond, i.e., there is relatively little change in the H−H distance until bond rupture is quite imminent, presumably at a point where increasing $Mo(d_\pi)$ to $H_2(\sigma^*)$ back-donation can no longer be tolerated without H−H bond lengthening. At this point, only a very small increase in $Mo(d_\pi)$ to $H_2(\sigma^*)$ back-donation is needed for the H−H bond cleavage to occur. This behavior has been likened to the breaking of a taught rope instead of the breaking of an elastic rubber band.[12c] Similar behavior has been found for the oxidative addition of C−H bonds.[35] Therefore, it appears that the search for H−H bond lengthening and/or η^2-dihydrogen/dihydride tautomeric equilibrium in the molybdenum−diphosphine system is no easy task and perhaps requires even finer tuning of the π-basicity of the metal fragment than the present study has done.

It is interesting to compare our system with that of Morris, $[MH(\eta^2\text{-}H_2)(R_2PC_2H_4PR_2)]^+$ (M = Fe, Ru).[36] In the latter system, no H−H bond cleavage has been observed when R is varied in a similar way. This apparently indicates either that the reaction coordinate for H−H bond activation is much more elastic than in the molybdenum system or that the H−H bond is further away from the point of cleavage on the reaction coordinate. A plausible rationalization would be that the presence of the positive charge on the complex probably stabilizes η^2-dihydrogen over dihydride coordination by reducing $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation,[1] and additionally, the placement of a highly trans-influencing terminal hydride ligand trans to the η^2-dihydrogen ligand may well make the system more elastic.

Conclusion

We have synthesized and characterized a number of new molybdenum complexes containing the substituted and unsub-

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stituted benzyl diphosphine ligands of the type $(ArCH_2)_2PC_2H_4P(CH_2Ar)_2$ (Ar = C_6H_4X) which have basicities intermediate between those of dppe and depe. The stability of the agostic complexes of the type $Mo(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_4X)) has been found to depend markedly on both the nature and position of the aromatic substituent X. The coordination mode adopted by dihydrogen in a series of $MoH_2(CO)\{(RCH_2)_2PC_2H_4P(CH_2R)_2\}_2$ complexes is determined by the nature of R, an η^2-dihydrogen complex being formed when R is an electron-withdrawing aryl group, whereas a dihydride is formed when R is an electron-donating alkyl group. Thus, the dominant factor controlling the relative stability of η^2-dihydrogen versus dihydride coordination is the basicity of the diphosphine ligand. This fits closely with the bonding and activation model of dihydrogen which suggests that the degree of the $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation controls H−H bond cleavage by populating the σ^*-antibonding orbital of H_2.

Spectroscopic data for *trans*-$Mo(\eta^2\text{-}H_2)(CO)\{(ArCH_2)_2PC_2H_4P(CH_2Ar)_2\}_2$ (Ar = C_6H_5 (**3a**), C_6H_4-*m*-CH_3 (**3b**)) indicate that these complexes exist exclusively as η^2-dihydrogen complexes with a normal H−H distance both in solution and in the solid state. Neither an elongated H−H bond nor an η^2-dihydrogen/dihydride tautomeric equilibrium has been observed despite the apparent nearness of the π-basicity of the metal center to the point where the H−H bond cleavage is expected to occur. These results support our previous suggestion that the reaction coordinate for H−H bond cleavage in the molybdenum−diphosphine system is rather flat; i.e., relatively little change in the H−H distance takes place until very close to precipitous cleavage of the H−H bond. Thus, the search for H−H bond lengthening and/or η^2-dihydrogen/dihydride equilibrium in the molybdenum−diphosphine system seems to require even finer tuning of the π-basicity of the metal fragment than the present study has done. This might be achievable by variation of the substituents on the phosphorus atoms and/or by variation of the chelate ring size to adjust the electron donor/acceptor properties of the diphosphine ligand.

Experimental Section

General Procedures. All manipulations were performed either under a helium atmosphere in a Vacuum Atmospheres glovebox or under an argon atmosphere using standard Schlenk techniques unless otherwise specified. Solvents were distilled from sodium benzophenone ketyl and stored under argon over 4-Å molecular sieves. Magnesium turnings and powder were dried by flame heating in vacuo. All deuterated NMR solvents were passed through a column of activated alumina immediately prior to use.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AF-250 spectrometer at 250.13 and 101.26 MHz, respectively; ^1H chemical shifts were referenced to the residual solvent resonance relative to TMS; ^{31}P chemical shifts were referenced to external 85% H_3PO_4. The ^1H NMR T_1 measurements were carried out at 250 MHz by the inversion−recovery method using a standard 180°−τ−90° pulse sequences.[23] Infrared spectra were recorded on a BioRad FTS-40 FT-IR spectrometer as Nujol mulls between KBr plates unless otherwise specified. Elemental analyses were performed using a Perkin-Elmer PE2400 CHN elemental analyzer.

$(PhCH_2)_2PC_2H_4P(CH_2Ph)_2$. A solution of $Cl_2PC_2H_4PCl_2$ (15.0 g, 64.5 mmol) in diethyl ether (100 mL) was added dropwise over 1 h to a solution of $PhCH_2MgCl$ (Aldrich, 1.0 M in Et_2O, 400 mL, 400 mmol) which was cooled in a NaCl−ice bath. The mixture was stirred at room temperature overnight. Toluene (150 mL) was added, and the excess Grignard reagent was hydrolyzed at 0 °C by slow addition of a saturated NH_4Cl solution (250 mL). The organic layer was siphoned from the reaction flask under argon via a stainless steel cannula, and the aqueous layer was extrated with additional toluene (2 × 100 mL). The combined organic layer was dried over anhydrous Na_2SO_4 for 2 h and then filtered. The filtrate was concentrated to ca. 100 mL, and absolute EtOH (200 mL) was added. The resulted white solid was filtered off, washed with EtOH (4 × 20 mL), and dried in vacuo. Yield: 22.9 g (78%). Anal. Calcd for $C_{30}H_{32}P_2$: C, 79.28; H, 7.10. Found: C, 78.82; H, 7.16. ^1H NMR (CD_2Cl_2): δ 7.06−7.27 (m, 20 H, Ph), 2.76 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ph), 2.67 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ph), 1.26 (br m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −12.61 (s).

$(m\text{-}MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}m\text{-}Me)_2$. A solution of *m*-$MeC_6H_4CH_2Cl$ (16.8 g, 119 mmol) in diethyl ether (35 mL) was added dropwise over 1 h to a suspension of magnesium turnings (3.19 g, 131 mmol) in diethyl ether (85 mL). The mixture was stirred for 2 h and then filtered to give a greenish solution of *m*-$MeC_6H_4CH_2MgCl$. A solution of $Cl_2PC_2H_4PCl_2$ (4.61 g, 19.9 mmol) in diethyl ether (40 mL) was then added dropwise over 1 h to the Grignard solution which was cooled in a NaCl−ice bath, and the mixture was stirred at room temperature overnight. Workup of the reaction mixture in a manner similar to that described above gave a colorless viscous liquid. Yield: 9.6 g (95%). Anal. Calcd for $C_{34}H_{40}P_2$: C, 79.98; H, 7.90. Found: C, 79.51; H, 7.69. ^1H NMR (CD_2Cl_2): δ 7.14 (t, $^3J_{HH}$ = 7.7 Hz, 4 H, Ar), 6.98 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, Ar), 6.93 (s, 4 H, Ar), 6.89 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, Ar), 2.73 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ar), 2.64 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ar), 2.30 (s, 12 H, Me), 1.31 (br m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.01 (s).

$(o\text{-}MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}o\text{-}Me)_2$. *o*-$MeC_6H_4CH_2MgCl$, which was prepared from *o*-$MeC_6H_4CH_2Cl$ (11.1 g, 78.6 mmol), magnesium turnings (3.19 g, 131 mmol), and I_2 (0.20 g, 0.8 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (3.02 g, 13.1 mmol) as described above. Workup of the reaction mixture gave a white solid. Yield: 5.8 g (87%). Anal. Calcd for $C_{34}H_{40}P_2$: C, 79.98; H, 7.90. Found: C, 80.32; H, 8.16. ^1H NMR (CD_2Cl_2): δ 7.00−7.17 (m, 20 H, Ar), 2.76 (br s, 8 H, CH_2Ar), 2.23 (s, 12 H, Me), 1.45 (m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −20.04 (s).

$(p\text{-}MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}p\text{-}Me)_2$. *p*-$MeC_6H_4CH_2MgCl$, which was prepared from *p*-$MeC_6H_4CH_2Cl$ (16.8 g, 119 mmol) and magnesium turnings (3.19 g, 131 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (4.61 g, 19.9 mmol) as described above. Workup of the reaction mixture gave a white solid. Yield: 9.8 g (96%). Anal. Calcd for $C_{34}H_{40}P_2$: C, 79.98; H, 7.90. Found: C, 79.65; H, 7.93. ^1H NMR (CD_2Cl_2): δ 7.06 (d, $^3J_{HH}$ = 7.9 Hz, 8 H, Ar), 6.96 (d, $^3J_{HH}$ = 7.9 Hz, 8 H, Ar), 2.70 ($^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ar), 2.61 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ar), 2.30 (s, 12 H, Me), 1.27 (br m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −14.12 (s).

$(o\text{-}FC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}o\text{-}F)_2$. *o*-$FC_6H_4CH_2MgCl$, which was prepared from *o*-F-$C_6H_4CH_2Cl$ (12.2 g, 84.1 mmol) and magnesium turnings (2.35 g, 96.7 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (3.26 g, 14.0 mmol) as described above. Workup of the reaction mixture gave a white solid. Yield: 4.6 g (62%). Anal. Calcd for $C_{30}H_{28}F_4P_2$: C, 68.44; H, 5.36. Found: C, 68.43; H, 5.41. ^1H NMR (CD_2Cl_2): δ 6.96 (m, 4 H, Ar), 6.70 (m, 12 H, Ar), 2.66 (br s, 8 H, CH_2Ar), 1.42 (br m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.06 (s).

$(m\text{-}FC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}m\text{-}F)_2$. *m*-$FC_6H_4CH_2MgCl$, which was prepared from *m*-$FC_6H_4CH_2Cl$ (12.3 g, 85.1 mmol) and magnesium turnings (2.27 g, 93.4 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (3.29 g, 14.2 mmol) as described above. Workup of the reaction mixture gave a white solid. Yield: 6.3 g (84%). Anal. Calcd for $C_{30}H_{28}F_4P_2$: C, 68.44; H, 5.36. Found: C, 68.12; H, 5.52. ^1H NMR (CD_2Cl_2): δ 7.17−7.26 (m, 4 H, Ar), 6.80−6.92 (m, 12 H, Ar), 2.76 (d, $^2J_{HH}$ = 13.2 Hz, 4 H, CH_2Ar), 2.68 (d, $^2J_{HH}$ = 13.2 Hz, 4 H, CH_2Ar), 1.29 (m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −12.56 (s).

$(p\text{-}FC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}p\text{-}F)_2$. *p*-$FC_6H_4CH_2MgCl$, which was prepared from *p*-$FC_6H_4CH_2Cl$ (17.26 g, 119 mmol) and magnesium turnings (3.19 g, 131 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (4.61 g, 19.9 mmol) as described above. Workup of the reaction mixture gave a white solid. Yield: 6.2 g (59%). Anal. Calcd for $C_{30}H_{28}F_4P_2$: C, 68.44; H, 5.36. Found: C, 68.17; H, 5.36. ^1H NMR (CD_2Cl_2): δ 7.04 (m, 8 H, Ar), 6.94 (m, 8 H, Ar), 2.72 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ar), 2.63 (d, $^2J_{HH}$ = 13.5 Hz, 4 H, CH_2Ar), 1.26 (br m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.16 (s).

$(m\text{-}MeOC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4\text{-}m\text{-}OMe)_2$. *m*-$MeOC_6H_4CH_2MgCl$, which was prepared from *m*-$MeOC_6H_4CH_2Cl$ (11.9 g, 75.7 mmol), magnesium turnings (6.0 g, 247 mmol), and I_2 (0.30 g, 1.2 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (2.92 g, 12.6 mmol) as described above. Workup of the reaction mixture gave a viscous oil. Yield: 6.4 g (88%). Anal. Calcd for $C_{34}H_{40}O_4P_2$: C, 71.07; H, 7.02. Found: C, 70.92; H, 6.94. ^{1}H NMR (CD_2Cl_2): δ 7.14 (t, $^3J_{HH} = 7.9$ Hz, 4 H, Ar), 6.65−6.72 (m, 12 H, Ar), 3.75 (s, 12 H, O*Me*), 2.73 (d, $^2J_{HH} = 13.4$ Hz, 4 H, C*H*$_2$Ar), 2.65 (d, $^2J_{HH} = 13.4$ Hz, 4 H, C*H*$_2$Ar), 1.31 (m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.31 (s).

(p-$MeOC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$p$-$OMe)_2$. p-$MeOC_6H_4CH_2$-MgCl, which was prepared from p-$MeOC_6H_4CH_2Cl$ (11.6 g, 73.8 mmol), magnesium powder (50 mesh, 6.0 g, 247 mmol), and I_2 (0.25 g, 0.98 mmol), was reacted with $Cl_2PC_2H_4PCl_2$ (2.84 g, 12.3 mmol) as described above. Workup of the reaction mixture gave a viscous oil. Yield: 5.4 g (76%). Anal. Calcd for $C_{34}H_{40}O_4P_2$: C, 71.07; H, 7.02. Found: C, 70.72; H, 6.81. ^{1}H NMR (CD_2Cl_2): δ 7.01 (d, $^3J_{HH} = 8.4$ Hz, 8 H, Ar), 6.80 (d, $^3J_{HH} = 8.4$ Hz, 8 H, Ar), 3.77 (s, 12 H, O*Me*), 2.70 (d, $^2J_{HH} = 13.7$ Hz, 4 H, C*H*$_2$Ar), 2.62 (d, $^2J_{HH} = 13.7$ Hz, 4 H, C*H*$_2$Ar), 1.30 (m, 4 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.86 (s).

***trans*-$Mo(N_2)_2\{(PhCH_2)_2PC_2H_4P(CH_2Ph)_2\}$ (1a).** $MoCl_5$ (0.98 g, 3.59 mmol), $(PhCH_2)_2PC_2H_4P(CH_2Ph)_2$ (4.91 g, 10.80 mmol), and magnesium turnings (4.91 g, 201 mmol) were combined in a flask and kept under an atmosphere of dinitrogen. The flask was cooled in an ice-bath, and THF (50 mL) precooled to 0 °C was added to the flask under dinitrogen. The mixture was then vigorously stirred at room temperature under dinitrogen for 16 h. The solvent was removed in vacuo. The residue was extracted with hot toluene (70 °C) (2 × 50 mL) and filtered through Celite to give a dark brown solution, which was evaporated to dryness. The brown residue was triturated with diethyl ether (3 × 50 mL), and the dark supernatant was removed by siphonage via a stainless steel cannula. The remaining solid was extracted with toluene (2 × 50 mL) and filtered through Celite. The orange filtrate was concentrated in vacuo to ca. 5 mL, and hexane (50 mL) was added. The orange solid was filtered off, washed with methanol (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuo. Yield: 2.5 g (65%). Anal. Calcd for $C_{60}H_{64}MoN_4P_4$: C, 67.93; H, 6.08; N, 5.28. Found: C, 67.68; H, 5.89; N, 5.35. IR (Nujol): $\nu(N_2)$ 1935 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.00−710 (m, 40 H, Ph), 3.40 (d, 2J_{HH} = 13.8 Hz, 8 H, C*H*$_2$Ph), 3.08 (d, $^2J_{HH} = 13.8$ Hz, 8 H, C*H*$_2$Ph), 0.97 (br m, 8 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.45 (s).

Compounds **1b−h** were prepared analogously to **1a** and their analytical and spectroscopic data are given below.

***trans*-$Mo(N_2)_2\{(m$-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$m$-$Me)_2\}$ (1b).** Yield: 35%. Anal. Calcd for $C_{68}H_{80}MoN_4P_4$: C, 69.62; H, 6.89; N, 4.78. Found: C, 69.28; H, 6.99; N, 4.62. IR (Nujol): $\nu(N_2)$ 1939 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.12 (t, $^3J_{HH} = 7.4$ Hz, 8 H, Ar), 7.06 (d, $^3J_{HH} = 7.4$ Hz, 8 H, Ar), 6.96 (s, 8 H, Ar), 6.90 (d, $^3J_{HH} = 7.4$ Hz, 8 H, Ar), 3.48 (d, $^2J_{HH} = 13.9$ Hz, 8 H, C*H*$_2$Ar), 3.16 (d, $^2J_{HH} = 13.9$ Hz, 8 H, C*H*$_2$Ar), 2.17 (s, 24 H, Me), 1.04 (br m, 8 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.71 (s).

***trans*-$Mo(N_2)_2\{(o$-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$o$-$Me)_2\}$ (1c).** Yield: 26%. Anal. Calcd for $C_{68}H_{80}MoN_4P_4$: C, 69.62; H, 6.89; N, 4.78. Found: C, 68.98; H, 6.79; N, 4.43. IR (Nujol): $\nu(N_2)$ 1936 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.9−7.3 (m, Ar), 3.68 (d, $^2J_{HH} = 14.2$ Hz, C*H*$_2$Ar), 3.60 (d, $^2J_{HH} = 14.2$ Hz, C*H*$_2$Ar), 2.00 (s, Me), 1.33 (br m, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.76 (s).

***trans*-$Mo(N_2)_2\{(p$-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$p$-$Me)_2\}$ (1d).** Yield: 35%. Anal. Calcd for $C_{68}H_{80}MoN_4P_4$: C, 69.62; H, 6.89; N, 4.78. Found: C, 69.82; H, 6.88; N, 4.40. IR (Nujol): $\nu(N_2)$ 1929 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$): δ 6.9−7.1 (m, Ar), 3.41 (d, $^2J_{HH} = 13.7$ Hz, C*H*$_2$Ar), 3.07 (d, $^2J_{HH} = 13.7$ Hz, C*H*$_2$Ar), 2.16 (s, Me), 0.99 (br m, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 57.76 (s).

***trans*-$Mo(N_2)_2\{(o$-$FC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$o$-$F)_2\}$ (1e).** Yield: 31%. Anal. Calcd for $C_{60}H_{56}F_8MoN_4P_4$: C, 59.81; H, 4.68; N, 4.65. Found: C, 59.59; H, 4.59; N, 4.12. IR (Nujol): $\nu(N_2)$ 1960 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.7−7.1 (m, 32 H, Ar), 3.56 (d, $^2J_{HH} = 14.2$ Hz, 8 H, C*H*$_2$Ar), 3.47 (d, $^2J_{HH} = 14.2$ Hz, 8 H, C*H*$_2$Ar), 1.45 (br m, 8 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 57.90 (s).

***trans*-$Mo(N_2)_2\{(m$-$FC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$m$-$F)_2\}$ (1f).** Yield: 48%. Anal. Calcd for $C_{60}H_{56}F_8MoN_4P_4$: C, 59.81; H, 4.68; N, 4.65. Found: C, 59.84; H, 4.78; N, 3.95. IR (Nujol): $\nu(N_2)$ 1941 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.6−7.0 (m, 32 H, Ar), 3.15 (d, $^2J_{HH} = 13.9$ Hz, 8 H, C*H*$_2$Ar), 2.85 (d, $^2J_{HH} = 13.9$ Hz, 8 H, C*H*$_2$Ar), 0.78 (br m, 8 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.16 (s).

***trans*-$Mo(N_2)_2\{(p$-$FC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$p$-$F)_2\}$ (1g).** Yield: 49%. Anal. Calcd for $C_{60}H_{56}F_8MoN_4P_4$: C, 59.81; H, 4.68; N, 4.65. Found: C, 59.82; H, 4.37; N, 4.34. IR (Nujol): $\nu(N_2)$ 1933 cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.02 (br s, 16 H, Ar), 6.99 (br s, 16 H, Ar), 3.33 (d, $^2J_{HH} = 14.1$ Hz, 8 H, C*H*$_2$Ar), 3.12 (d, $^2J_{HH} = 14.1$ Hz, 8 H, C*H*$_2$Ar), 0.89 (br m, 8 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 55.52 (s).

***trans*-$Mo(N_2)_2\{(m$-$MeOC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$m$-$OMe)_2\}$ (1h).** Yield: 35%. Anal. Calcd for $C_{68}H_{80}MoN_4O_8P_4$: C, 62.77; H, 6.20; N, 4.31. Found: C, 62.61; H, 6.09; N, 3.97. IR (Nujol): $\nu(N_2)$ 1927 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.07 (t, $^3J_{HH} = 7.6$ Hz, 8 H, Ar), 6.85 (s, 8 H, Ar), 6.81 (d, $^3J_{HH} = 7.6$ Hz, 8 H, Ar), 6.66 (d, $^3J_{HH} = 7.6$ Hz, 8 H, Ar), 3.44 (d, $^2J_{HH} = 13.4$ Hz, 8 H, C*H*$_2$Ar), 3.39 (s, 24 H, Me), 3.13 (d, $^2J_{HH} = 13.4$ Hz, 8 H, C*H*$_2$Ar), 1.04 (br m, 8 H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.71 (s).

***trans*-$Mo(N_2)_2\{(p$-$MeOC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$p$-$OMe)_2\}$ (1i).** (p-$MeOC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$p$-$OMe)_2$ (5.40 g, 20.9 mmol), $MoCl_5$ (0.86 g, 3.13 mmol), and magnesium turnings (5.4 g, 222 mmol) were reacted in THF (50 mL) under dinitrogen for 16 h as described above for **1a**. Under gentle swirling, the supernatant suspension was decanted from the magnesium turnings which remained at the bottom of flask. The pale-yellow solid was filtered off, washed with diethyl ether (3 × 30 mL), and dried in vacuo. Yield: 1.82 g (45%). IR (Nujol): $\nu(N_2) = 1907$ cm^{-1}. This compound is insoluble in all common organic solvents and thus precludes characterization by NMR.

***trans*-$Mo(\eta^2$-$H_2)(CO)\{(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (3a).** *trans*-$Mo(N_2)_2\{(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (**1a**) (1.50 g, 1.41 mmol) and ethyl acetate (2.2 mL, 22.5 mmol) were refluxed for 30 min in benzene (20 mL) with a slow stream of argon sweeping through the flask and exiting through the reflux condenser. The dark red solution was evaporated to dryness in vacuo. The residue was suspended in hexane (35 mL) and stirred under H_2 for 40 min. The yellow solid was filtered off, washed with H_2-saturated hexane (20 mL), and dried in a stream of H_2. Yield: 1.10 g (69%). Anal. Calcd for $C_{61}H_{66}MoOP_4$: C, 70.80; H, 6.43. Found: C, 70.37; H, 6.29. IR (Nujol): ν(CO) 1751 cm^{-1}; $\nu_s(MoH_2)$ 907 cm^{-1}; $\delta(MoH_2)$ 432 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$): δ 7.0−7.2 (m, Ph), 2.9−3.2 (m, C*H*$_2$Ph), 0.93 (m, PCH_2CH_2P), −5.38 (br, $\omega_{1/2} \approx 67$ Hz, $Mo(\eta^2$-$H_2)$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_5$): δ 66.44 (s). The D_2 isotopomer of **3a** was prepared similarly. IR of the D_2 isotopomer in Nujol mull: ν(CO) 1747 cm^{-1}; $\nu_s(MoD_2)$ 677 cm^{-1}.

***trans*-$Mo(\eta^2$-$H_2)(CO)\{(m$-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$m$-$Me)_2\}_2$ (3b).** This compound was prepared analogously to **3a** in 79% yield. Anal. Calcd for $C_{69}H_{82}MoOP_4$: C, 72.24; H, 7.20. Found: C, 71.89; H, 7.11. IR (Nujol): ν(CO) 1757 cm^{-1}; $\delta(MoH_2)$ 421 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$): δ 6.80−7.20 (m, Ar), 3.1−3.3 (m, C*H*$_2$Ph), 2.18 (s, Me), 1.10 (m, PCH_2CH_2P), −5.38 (br, $\omega_{1/2} \approx 65$ Hz, $Mo(\eta^2$-$H_2)$). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ 66.05 (s). Variable-temperature ^{1}H NMR T_1 relaxation times of the η^2-H_2 resonance: 233 K, 17 ms; 243 K, 14 ms; 253 K, 12 ms; 263 K, 11 ms; 273 K, 10 ms; 283 K, 11 ms; 298 K, 13 ms. The D_2 isotopomer of **3b** was prepared similarly. IR of the D_2 isotopomer in Nujol mull: ν(CO) 1752 cm^{-1}.

$Mo(CO)\{(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (2a). A suspension of *trans*-$Mo(\eta^2$-$H_2)(CO)\{(C_6H_5CH_2)_2PC_2H_4P(CH_2C_6H_5)_2\}_2$ (**3a**) (1.00 g) in nonane (20 mL) was subject to a dynamic vacuo at 40 °C for 30 min. The resulting purple solid was filtered off, washed with hexane (2 × 20 mL), and dried in vacuo. Yield: 0.76 g (76%). Anal. Calcd for $C_{61}H_{64}MoOP_4$: C, 70.93; H, 6.25. Found: C, 70.42; H, 6.02. IR (Nujol): ν(CO) 1696 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$): δ 6.9−7.2 (m, Ph), 6.24 (d, $^3J_{HH} = 6.6$ Hz, agostic C-*H*), 3.72 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$Ph), 3.32 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$Ph), 2.90 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$Ph), 2.64 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$Ph), 1.20 (m, PCH_2CH_2P), 0.83 (m, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_5$): δ 64.23 (s).

$Mo(CO)\{(m$-$MeC_6H_4CH_2)_2PC_2H_4P(CH_2C_6H_4$-$m$-$Me)_2\}_2$ (2b). This compound was prepared analogously to **2a** in 64% yield. Anal. Calcd for $C_{69}H_{80}MoOP_4$: C, 72.36; H, 7.04. Found: C, 71.99; H, 6.95. IR (Nujol): ν(CO) 1700 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$): δ 6.8−7.1 (m, Ar), 5.46 (d, $^3J_{HH} = 7.1$ Hz, agostic C-*H*), 3.82 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$Ar), 3.44 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$Ar), 2.95 (d, $^1J_{HH} = 13.5$ Hz, C*H*$_2$-

Ar), 2.82 (d, $^1J_{\mathrm{HH}}$ = 13.5 Hz, CH_2Ar), 2.22 (s, Me), 2.02 (s, Me), 1.30 (m, PCH_2CH_2P), 0.98 (m, PCH_2CH_2P). ^{31}P{^{1}H} NMR ($C_6D_5CD_5$): δ 63.72 (s).

***trans*-Mo(N$_2$)(CO){(C$_6$H$_5$CH$_2$)$_2$PC$_2$H$_4$P(CH$_2$C$_6$H$_5$)$_2$}$_2$ (4a).** A solution of Mo(CO){($C_6H_5CH_2$)$_2$PC_2H_4P($CH_2C_6H_5$)$_2$}$_2$ (**2a**) (200 mg) in toluene (1 mL) was stirred under N_2 for 2 min during which the color of the solution changed from dark red to orange. Addition of hexane (15 mL) resulted in the precipitation of an orange solid, which was filtered off, washed with hexane (10 mL), and dried in a stream of N_2. Yield: 134 mg (67%). Anal. Calcd for $C_{61}H_{64}MoN_2OP_4$: C, 69.06; H, 6.08; N, 2.64. Found: C, 68.74; H, 6.12; N, 2.39. IR (Nujol): $\nu(N_2)$ 2062 cm^{-1}; ν(CO) 1784 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.95−7.2 (m, Ph), 3.63 (d, $^1J_{\mathrm{HH}}$ = 13.5 Hz, CH_2Ph), 3.33 (d, $^1J_{\mathrm{HH}}$ = 13.5 Hz, CH_2Ph), 3.18 (d, $^1J_{\mathrm{HH}}$ = 13.5 Hz, CH_2Ph), 2.92 (d, $^1J_{\mathrm{HH}}$ = 13.5 Hz, CH_2Ph), 1.15 (m, PCH_2CH_2P), 0.90 (m, PCH_2CH_2P). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.16 (s).

***trans*-Mo(N$_2$)(CO){(*m*-MeC$_6$H$_4$CH$_2$)$_2$PC$_2$H$_4$P(CH$_2$C$_6$H$_4$-*m*-Me)$_2$}$_2$ (4b).** This compound was prepared analogously to **4a** in 62% yield. Anal. Calcd for $C_{69}H_{80}MoN_2OP_4$: C, 70.64; H, 6.87; N, 2.44. Found: C, 70.28; H, 6.79; N, 2.15. IR (Nujol): $\nu(N_2)$ 2063 cm^{-1}; ν(CO) 1786 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.90−7.12 (m, Ar), 3.68 (d, $^1J_{\mathrm{HH}}$ = 14.1 Hz, CH_2Ar), 3.41 (d, $^1J_{\mathrm{HH}}$ = 14.1 Hz, CH_2Ar), 3.21 (d, $^1J_{\mathrm{HH}}$ = 14.1 Hz, CH_2Ar), 2.99 (d, $^1J_{\mathrm{HH}}$ = 14.1 Hz, CH_2Ar), 2.17 (s, Me) 1.23 (m, PCH_2CH_2P), 0.94 (m, PCH_2CH_2P). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.51 (s).

***trans*-Mo(SO$_2$)(CO){(C$_6$H$_5$CH$_2$)$_2$PC$_2$H$_4$P(CH$_2$C$_6$H$_5$)$_2$}$_2$ (5a).** A solution of Mo(CO){($C_6H_5CH_2$)$_2$PC_2H_4P($CH_2C_6H_5$)$_2$}$_2$ (**2a**) (200 mg) in toluene (2 mL) was stirred under SO_2 for 2 min during which the color of the solution changed from dark red to yellow. Addition of hexane (15 mL) resulted in the precipitation of a greenish yellow solid, which was filtered off, washed with hexane (10 mL), and dried in vacuo. Yield: 138 mg (65%). Anal. Calcd for $C_{61}H_{64}MoO_3P_4S$: C, 66.79; H, 5.88. Found: C, 66.63; H, 5.65. IR (Nujol): ν(CO) 1880 cm^{-1}; ν(SO) 1180, 1041 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.9−7.3 (m, Ph), 2.6−3.9 (m, CH_2Ph), 1.37 (m, PCH_2CH_2P), 0.89 (m, PCH_2CH_2P). ^{31}P{^{1}H} NMR (C_6D_6): δ 58.46 (s).

***trans*-Mo(SO$_2$)(CO){(*m*-MeC$_6$H$_4$CH$_2$)$_2$PC$_2$H$_4$P(CH$_2$C$_6$H$_4$-*m*-Me)$_2$}$_2$ (5b).** This compound was prepared analogously to **5a** in 69% yield. Anal. Calcd for $C_{69}H_{80}MoO_3P_4S$: C, 68.53; H, 6.67. Found: C, 68.17; H, 6.61. IR (Nujol): ν(CO) 1874 cm^{-1}; ν(SO) 1184, 1042 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.8−7.2 (m, Ar), 2.7−3.8 (m, CH_2Ar), 2.20 (s, Me), 2.15 (s, Me), 1.38 (m, PCH_2CH_2P), 1.05 (m, PCH_2CH_2P). ^{31}P{^{1}H} NMR (C_6D_6): δ 58.82 (s).

X-ray Crystallographic Analysis of *trans*-Mo(η^2-H$_2$)(CO){(Me-*m*-C$_6$H$_4$CH$_2$)$_2$PC$_2$H$_4$P(CH$_2$C$_6$H$_4$-*m*-Me)$_2$}$_2$ (3b). Crystals of **3b** were prepared by slow diffusion of hexane into a solution of the compound in benzene under a dihydrogen atmosphere. A crystal having the approximate dimensions of 0.23 × 0.31 × 0.40 mm was selected, mounted on a glass fiber with Apiezon "H" grease, and transferred to the goniostat cooled to −70 °C. Data were collected on a Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range 23° < 2θ < 28°. The scan rate was varied between 1.54 and 6.7°/min in 2θ. A total of 7706 reflections were collected ($-28 \le h \le +28$, $-10 \le k \le 0$, $-27 \le l \le +27$) in the range 2° < 2θ < 45° with 3861 being unique (R_{int} = 5.71%). A series of high χ (above 80°) reflections were scanned to provide the basis for an empirical absorption correction that ranged from 0.70 to 0.94. No crystal decay was evident during data collection.

The molybdenum atom position was revealed using a Patterson map and all remaining nonhydrogen atoms were located in succeeding difference Fourier maps and refined anisotropically. All hydrogen atoms (except for the η^2-dihydrogen ligand) were added to the structure factor calculations (C−H fixed at 0.96 Å), but were not refined. Difference Fourier maps did not reveal the position of the η^2-dihydrogen ligand, and it was not included in calculations. The final residuals for the full-matrix least-squares refinement were R = 5.81, R_w = 7.97, and GOF = 1.42 based on 340 refined parameters and 3010 reflections ($F > 3.0\sigma(F)$). All calculations were conducted using the SHELXTL-Plus software package.[37] The maximum and minimum peaks of the Fourier difference map corresponded to +1.49 and −0.55 e/Å^3, respectively.

X-ray Crystallographic Analysis of *trans*-Mo(N$_2$)(CO){(C$_6$H$_5$CH$_2$)$_2$PC$_2$H$_4$P(CH$_2$C$_6$H$_5$)$_2$}$_2$ (4a). Crystals of **4a** were prepared by slow diffusion of hexane into a solution of the compound in benzene under a dinitrogen atmosphere. A crystal having the approximate dimensions of 0.28 × 0.39 × 0.43 mm was selected, mounted on a glass fiber with Apiezon "H" grease, and transferred to the goniostat cooled to −70 °C. Data were collected on a Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of 25 reflections in the range 24° < 2θ < 32°. The scan rate was varied between 0.95 and 10.0°/min in 2θ. A total of 7184 reflections were collected ($-25 \le h \le +25$, $-13 \le k \le 0$, $-18 \le l \le +18$) in the range 2° < 2θ < 45° with 3446 being unique (R_{int} = 3.58%). A series of high χ (above 80°) reflections were scanned to provide the basis for an empirical absorption correction that ranged from 0.86 to 0.89. No crystal decay was evident during data collection.

The molybdenum atom position was revealed using a Patterson map and all remaining non-hydrogen atoms were located in succeeding difference Fourier maps and refined anisotropically. All hydrogen atoms were added to the structure factor calculations (C−H fixed at 0.96 Å), but were not refined. The molybdenum atom is located at a special position, necessitating disorder of the carbonyl and dinitrogen ligands. Difference Fourier maps of the final structure without these ligands did not reveal distinct positions for the two ligand types at each site, and so a single ligand was refined with a 50/50 occupancy of C/N or O/N atoms. The final residuals for the full-matrix least-squares refinement were R = 3.37, R_w = 5.36, and GOF = 1.35 based on 303 refined parameters and 3104 reflections ($F > 3.0\sigma(F)$). All calculations were conducted using the SHELXTL Plus software package.[37] The maximum and minimum peaks of the Fourier difference map corresponded to +0.51 and −37 e/Å^3, respectively.

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Supplementary Material Available: Listings of crystallographic data, positional and thermal parameters, atomic parameters of hydrogen atoms, and bond lengths and angles for **3b** and **4a** (16 pages). Ordering information is given on any current masthead page.

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(37) SHELXTL-Plus; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1988.