Protonation and Methylation of Zerovalent Molybdenum Complexes of the Types *trans*-[Mo(CNR)(L)($Ph_2PCH_2CH_2PPh_2$)$_2$] (R = Ph or Bu^n; L = N_2, CO, or Nitrile) and *trans*-[Mo(CO)(L′)($Ph_2PCH_2CH_2PPh_2$)$_2$] (L′ = N_2 or Nitrile) To Give Carbyne or Hydrido Complexes[1]

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Treatment of *trans*-[Mo(CNPh)(N_2)(dppe)$_2$] with aqueous HBF_4 afforded an aminocarbyne complex, which was isolated as *trans*-[Mo(≡CNHPh)(O=CMe_2)(dppe)$_2$][BF_4] (**7**) after crystallization of the crude product from acetone−hexane, whereas the reaction of *trans*-[Mo(CNBu^n)(N_2)(dppe)$_2$] with [Me_2OH][BF_4] resulted in the formation of the aminocarbene complex with an agostic α-C−H bond, *trans*-[MoF(CHNHBu^n)(dppe)$_2$][BF_4]. Analogous treatment of *trans*-[Mo(CNR)(L)(dppe)$_2$] (R = Ph, Bu^n; L = *p*-$MeOC_6H_4CN$, CO (**4**)) with [Me_2OH][BF_4] gave aminocarbyne complexes *trans*-[Mo(≡CNHR)(NCC_6H_4OMe-*p*)(dppe)$_2$][BF_4] and *cis*-[Mo(≡CNHR)(CO)(dppe)$_2$][BF_4] (**10**). In solution at room temperature, the latter complexes gradually isomerized to the hydrido complexes [MoH(CNR)(CO)(dppe)$_2$][BF_4] (**12**). Related aminocarbyne complexes *cis*-[Mo(≡CNMeR)(CO)(dppe)$_2$][BF_4] (**13**) were obtained from the reactions of **4** with [Me_3O][BF_4]. For comparison, carbonyl complexes *trans*-[Mo(CO)(N_2)(dppe)$_2$] and *trans*-[Mo(CO)(*p*-$MeOC_6H_4CN$)(dppe)$_2$] were allowed to react with aqueous HBF_4, which revealed the formation of the hydrido complexes [MoH(CO)(H_2O)(dppe)$_2$][BF_4] (**14**) and [MoH(CO)(*p*-$MeOC_6H_4CN$)(dppe)$_2$][BF_4] (**15**), respectively. The X-ray analyses were undertaken to determine the detailed structures for **7**, **10a** (R = Ph), **12a** (R = Ph), **13b** (R = Bu^n), **14**·THF, and **15**·Et_2O.

Introduction

Previous studies in this and other laboratories about the reactivities of Mo and W dinitrogen complexes of the type [M(N_2)$_2$(**P**)$_4$] (M = Mo, W; **P** = tertiary phosphine) have shown that the coordinated N_2 in these complexes is susceptible to the electrophilic attack by protons to be converted into a hydrazido(2−) ligand (NNH_2) and/or nitrogen hydrides, i.e., NH_3 and less commonly N_2H_4, depending on the nature of the proton source and the ancillary ligand **P** along with the reaction conditions.[2] These findings are of great importance owing to their possible relevance to the mechanism for a biological N_2 fixation in nitrogenase that still remains to be elucidated.[3] Hence, reactivities of other nitrogenase substrates such as isocyanides and nitriles bound to the {M(**P**)$_4$} chromophore have also been attracting considerable interest. In contrast to the biological catalysis of nitrogenase, which reduces MeNC into methane, methylamine, and dimethylamine together with a small amount of ethylene and ethane[3b] and transforms the nitriles RCN (R = Me, Et, Pr^n) into the alkanes RCH_3 and ammonia,[4] the reactions of the isocyanide complexes *trans*-[M($CNMe$)$_2$(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) with 2 equiv of acid such as [Et_2-OH][BF_4] and HCl have been shown to give the alkyne complexes *trans*-[MX(η^2-MeHNC≡CNHMe)(dppe)$_2$]$^+$ (X = F, Cl) via the aminocarbyne species *trans*-[M(≡C-NHMe)$_2$(dppe)$_2$]$^{2+}$ generated by the protonation at the isocyanide N atoms,[5] while the protonation of the dinitrogen−nitrile complexes *trans*-[M(N_2)(NCR)(dppe)$_2$]

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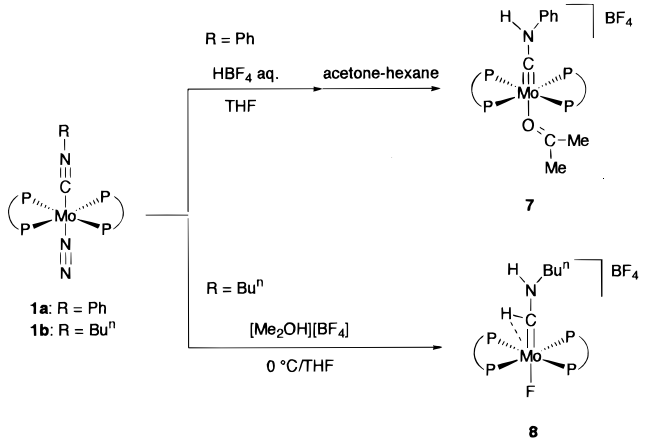
(R = Me, aryl) with excess amounts of aqueous HCl and HBF_4 has turned out to occur at the nitrile carbon to give the imido complexes *trans*-$[MX(\equiv NCH_2R)(dppe)_2]^+$ (X = Cl, F).[6] However, reactions of protic acids with these M(0) complexes tend to be significantly affected by subtle factors, which result in the formation of more diversified products. Thus, treatment of *trans*-$[M(N_2)(NCPr^n)(dppe)_2]$ with H_2SO_4 in THF at 0 °C was reported to cause the protonation at the N_2 ligand, affording $[M(NNH_2)(NCPr^n)(dppe)_2]^{2+}$.[7] On the other hand, it has been observed that hydrido complexes $[MH(CNR)_2(dppe)_2]^+$ and hydridoaminocarbyne complexes $[MH(\equiv CNHR)(CNR)(dppe)_2]^{2+}$ are formed from the reactions of *trans*-$[M(CNR)_2(dppe)_2]$ with acids under certain controlled conditions.[8] Formation of the former hydridobis(isocyanide) complexes is reminiscent of the reaction of *trans*-$[W(N_2)_2(dppe)_2]$ with HCl in THF giving the hydridobis(dinitrogen) complex $[WH(N_2)_2(dppe)_2]^+$.[9] Interestingly, the reactions of the dinitrogen−nitrile complexes with the other electrophiles such as PhCOCl[10] and Me_3SiI[11] occur rather at the N_2 ligand to give the diazenido (MNNCOPh, $MNNSiMe_3$) complexes or the hydrazido(2−) (MNNHCOPh, $MNNHSiMe_3$) complexes resulting from the successive protonation of the produced diazenido species by adventitious HX (X = Cl, I).

In the preceding papers,[12] we have reported that a range of isocyanide−dinitrogen complexes *trans*-$[Mo(CNR)(N_2)(dppe)_2]$ (**1**; R = alkyl, aryl) can readily be prepared from the reactions of *trans*-$[Mo(N_2)_2(dppe)_2]$ (**2**) with corresponding benzaldehyde imines PhCH=NR. Furthermore, a series of isocyanide complexes *trans*-$[Mo(CNR)(L)(dppe)_2]$ (L = nitrile (**3**), CO(**4**), isocyanide, and H_2) are available from **1** through subsequent replacement of the N_2 ligand by L. Now we have investigated the protonation reactions of a series of Mo(0) complexes containing one or two nitrogenase substrates as the ligand. In this paper, we wish to summarize the results of this study, demonstrating which site in complexes **3** and **4** as well as the previously reported carbonyl complexes *trans*-$[Mo(CO)(L')(dppe)_2]$ (L′ = N_2 (**5**),[13] nitrile (**6**)[14]) is more susceptible to protonation.

Results and Discussion

Protonation of Isocyanide−Dinitrogen Complexes 1. Protonation of the bis(dinitrogen) complex **2** by aqueous HBF_4 in THF has already been reported by this group to proceed at the terminal N atom of one N_2 ligand, affording the doubly protonated product *trans*-$[MoF(NNH_2)(dppe)_2][BF_4]$.[15] Now we have found that the analogous treatment of the isocyanide−dinitrogen complex **1a** (R = Ph) results in the formation of an aminocarbyne complex; that is, monoprotonation occurs not at the N_2 ligand but at the isocyanide N atom. There is precedent that the addition of electrophiles to electron-rich isocyanide complexes results in the formation of aminocarbyne complexes.[16] Molecular orbital calculations on the related d^6 electron-rich Re isocyanide complex $[ReCl(CNH)(H_2PCH_2CH_2PH_2)_2]$ were carried out previously, which demonstrated that a negative charge is accumulated on the Cl and N atoms and the reaction with the electrophile gives the product of N attack, that is, the thermodynamically favored aminocarbyne complex.[17] The product was isolated as the acetone adduct *trans*-$[Mo(\equiv CNHPh)(Me_2CO)(dppe)_2][BF_4]$ (**7**) after recrystallization of the yet uncharacterizable crude product[18] from acetone/hexane (Scheme 1). The IR spectrum of **7** shows a weak band at 3308 cm^{-1} attributable to ν(NH), which shifted to 2427 cm^{-1} for the deuterium analogue. In the ^1H NMR spectrum, however, the resonance due to the amino proton was not assignable presumably because of its overlapping with the phenyl resonances. The trans geometry around the Mo was implicated by its ^{31}P NMR spectrum exhibiting only one singlet at 60.5 ppm.

Scheme 1



Detailed structure of **7** has been determined by the X-ray crystallography. An ORTEP drawing and the important bond distances and angles are shown in Figure 1 and Table 1, respectively. Complex **7** has an octahedral configuration with the aminocarbyne and acetone ligands in mutually trans positions. For the aminocarbyne ligand, the Mo−C−N linkage is essentially linear (176.8(3)°). The short Mo−C distance

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(18) The crude product probably contains a H_2O molecule at the site trans to the aminocarbyne ligands, although full characterization was unsuccessful.

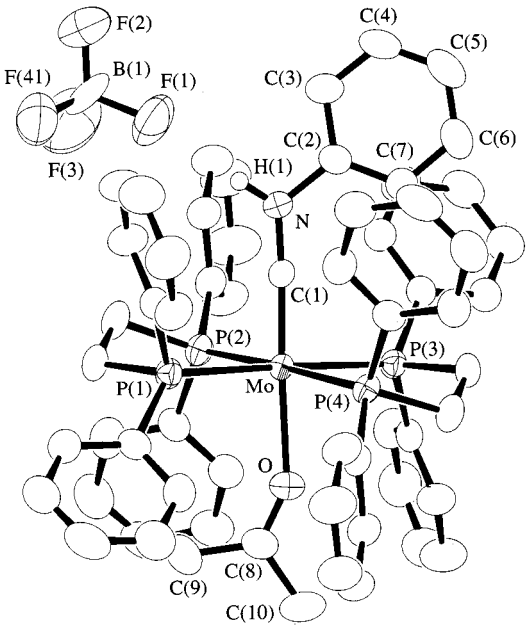


Figure 1. ORTEP drawing of **7**. Hydrogen atoms are omitted for clarity except for the amino proton H(1), having hydrogen-bonding interaction with F(1).

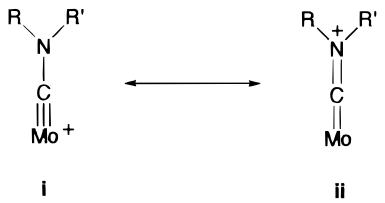
Table 1. Selected Bond Distances and Angles in 7

(a) Bond Distances (Å)			
Mo−P(1)	2.520(1)	Mo−P(2)	2.473(1)
Mo−P(3)	2.522(1)	Mo−P(4)	2.526(1)
Mo−O	2.310(3)	Mo−C(1)	1.808(4)
O−C(8)	1.226(5)	C(1)−N	1.345(5)
N−H(1)	0.90	F(1)−H(1)	2.12
(b) Bond Angles (deg)			
P(1)−Mo−P(2)	80.70(4)	P(1)−Mo−P(3)	178.32(5)
P(1)−Mo−P(4)	100.16(4)	P(1)−Mo−O	92.94(9)
P(1)−Mo−C(1)	89.2(1)	P(2)−Mo−P(3)	98.92(4)
P(2)−Mo−P(4)	177.63(6)	P(2)−Mo−O	94.64(8)
P(2)−Mo−C(1)	87.4(1)	P(3)−Mo−P(4)	80.16(4)
P(3)−Mo−O	85.45(9)	P(3)−Mo−C(1)	92.5(1)
P(4)−Mo−O	83.12(7)	P(4)−Mo−C(1)	94.8(1)
O−Mo−C(1)	177.3(2)	Mo−O−C(8)	152.0(3)
Mo−C(1)−N	176.8(3)	C(1)−N−C(2)	125.3(4)
C(1)−N−H(1)	126.0	C(2)−N−H(1)	108.0
F(1)−H(1)−N	149.0		

at 1.808(4) Å is diagnostic of the Mo−C multiple bonding, which is comparable to those in the other carbyne complexes,[16a] e.g., $[Mo(\equiv CNEt_2)(CO)_3(\mu\text{-}I)]_2$ (1.80(2) Å)[19] and $[CpMo(\equiv CCH_2CMe_3)(P(OMe)_3)_2]$ (1.796(2) Å; Cp = η^5-C_5H_5).[20] The bond angles around the N atom (125.3(4)°, 126°, and 108°) are indicative of its sp^2 character, which is consistent with the C(1)−N bond length at 1.345(5) Å, being much shorter than the typical C−N single bond distance of 1.47 Å. These structural features of the aminocarbyne ligand may be interpreted in terms of the delocalization of electron density from the N p orbital by interaction with a p orbital on the carbyne C atom as described by the two extreme structures **i** and **ii** shown in Chart 1.[21]

The acetone ligand is bound to the Mo atom in an η^1 manner as commonly observed for the ketone complexes.

Chart 1



The C−O distance at 1.226(5) Å is typical of that of the C=O double bond and comparable to those in the other σ-bound acetone ligands for, for example, $[Rh(=C=C=CPh_2)(Me_2CO)(PPr^i_3)_2][PF_6]$ (1.216(3) Å)[22] and $[Ru\{C(=CHPh)OCMeO\}(Me_2CO)(CO)(PPr^i_3)_2][BF_4]$ (1.235(10) Å).[23]

Protonation of the Bu^nNC complex **1b** with aqueous HBF_4 under the conditions employed above did not give any characterizable products. However, protonation by the use of $[Me_2OH][BF_4]$ at 0 °C proceeded cleanly, leading to the formation of the product protonated at both the N and C atoms, *trans*-$[MoF(CHNHBu^n)(dppe)_2][BF_4]$ (**8**) (Scheme 1). Differences in the reactivity between **1a** and **1b** are well comparable to those in $PhNH_2$ and Bu^nNH_2 arising from the stronger electron-donating ability of the Bu^n group than the Ph group. In this reaction, the second protonation seems to be so rapid that the monoprotonated product could not be detected; the ^1H NMR spectrum of the reaction mixture of **1b** with an equimolar amount of $[Me_2OH][BF_4]$ showed the presence of only **8** and unreacted **1b**. In contrast, the reaction of **1a** with $[Me_2OH][BF_4]$ was somehow elusive, and no tractable compounds were obtained from the reaction mixture.

Appearance of the four P atoms as one doublet in the $^{31}P\{^1H\}$ NMR spectrum is indicative of the trans structure for **8**, where the observed J_{P-F} value of 30 Hz is in good agreement with those of related Mo complexes of the type *trans*-$[MoF(E)(dppe)_2]^+$ (E = NNH_2, 30 Hz;[15] E = NN=CHEt, 30 Hz[24]). In the ^1H NMR spectrum, two new resonances each integrating for one proton appeared. One of these signals observed as a broad singlet at 3.15 ppm may be assigned to the NH proton. The other peak at −7.25 ppm, at a glance, seems to be attributable to the hydride (MoH) rather than the carbene proton (Mo=CH−), since the carbene proton is expected to resonate generally in a much lower field, e.g., 10−18 ppm.[25] However, the observed peak is correlated to the NH proton with the coupling constant of as large as 7.8 Hz, and furthermore the coupling of this resonance with the P atoms by J_{P-H} = 10.7 Hz seems to be too small to be assigned as that of the hydride bound to the Mo center (vide supra). In addition, the ^{13}C NMR spectrum showed the α-C resonance at 203.2 ppm, which split into a doublet with J_{C-H} = 61 Hz in the coupled spectrum. From these NMR data, it may be concluded that **1b** has a carbene ligand with an α-C−H agostic bond, as demonstrated for, for example,

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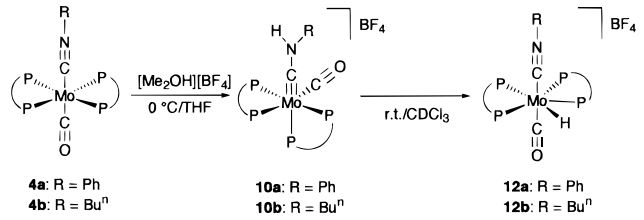
(25) Torraca, K. E.; Ghiviriga, I.; McElwee-White, L. *Organometallics* **1999**, *18*, 2262.

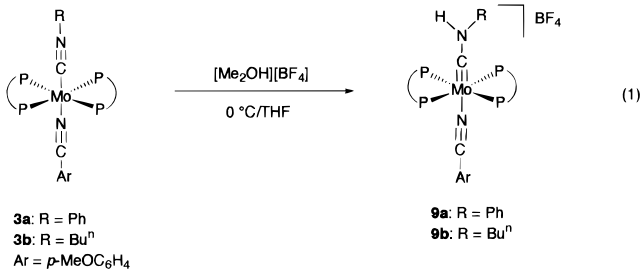
Scheme 2



$[CpMo(CHBu^n)(CO)(P(OPh)_3)]^+$,[25] *cis,trans*-$[W(CHR)Cl_2(CO)(PMe_3)_2]$ (R = Ph,[26] Bu^t [27]), *trans*-$[WCl(CHBu^t)(PMe_3)_4]^+$,[28] and *trans*-$[WMe(CHC_6H_4Me)\{PPh(CH_2CH_2PPh_2)_2\}(CO)]^+$.[29] The J_{C-H} values for such protons are reported to fall in the range 45−90 Hz, which are significantly smaller than those for the common, nonagostic methylidene protons (110−130 Hz).[29]

Formation of an aminocarbene complex from the reaction of an isocyanide complex with excess acid is precedented. For example, $[Mo(CNBu^t)_6]$ reacts with an excess of CF_3COOH at −78 °C to give $[Mo(=CHNHBu^t)(CNBu^t)_5][OCOCF_3]_2$. However, the NMR data for this complex clearly showed the absence of any agostic interaction between the α-C−H bond and the Mo center.[30]

Protonation of Isocyanide−Nitrile Complexes *trans*-[Mo(CNR)(NCC$_6$H$_4$OMe-*p*)(dppe)$_2$] (3). The reactions of **3** with $[Me_2OH][BF_4]$ in THF at 0 °C gave the monoprotonated products *trans*-$[Mo(\equiv CNHR)(NCC_6H_4OMe\text{-}p)(dppe)_2][BF_4]$ (R = Ph (**9a**), Bu^n (**9b**)) (eq 1). Only one singlet was observed in the ^{31}P NMR



spectra, while two characteristic bands appeared in the IR spectra, one being assignable to $\nu(C\equiv N)$ of the coordinated nitrile and the other to $\nu(NH)$. These data indicate that the protonation takes place at the isocyanide N atom to give the aminocarbyne ligand, which occupies the site trans to the nitrile ligand still intact after the reaction. The $\nu(C\equiv N)$ values of 2225 and 2226 cm^{-1} observed for **9a** and **9b**, respectively, are slightly higher than that of a free *p*-$MeOC_6H_4CN$ (2217 cm^{-1}).

Protonation of Isocyanide−Carbonyl Complexes 4. Protonation reactions of **4a** (R = Ph) and **4b** (R = Bu^n) with $[Me_2OH][BF_4]$ in THF at 0 °C both afforded the aminocarbyne complexes *cis*-$[Mo(\equiv CNHR)(CO)(dppe)_2][BF_4]$ (**10**) in moderate yields (Scheme 2). In the

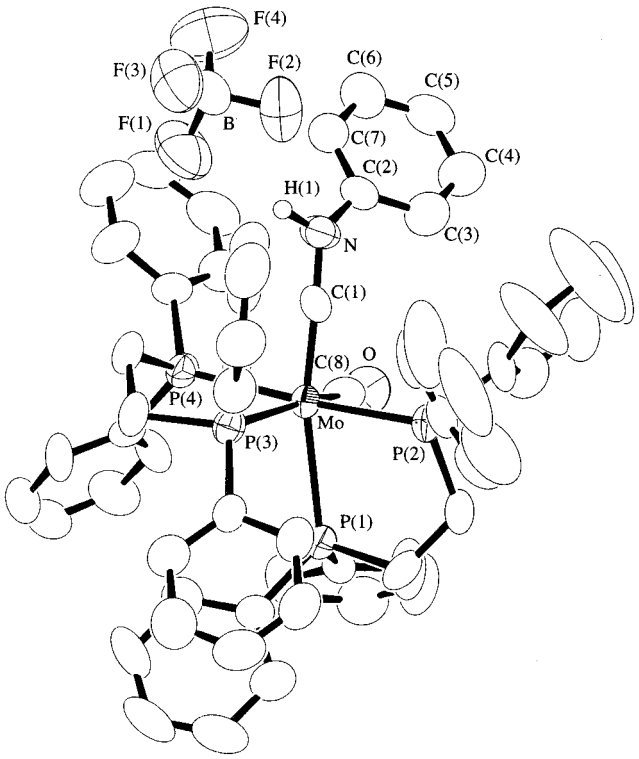


Figure 2. ORTEP drawing of **10a**. Hydrogen atoms are omitted for clarity except for the amino proton H(1), having hydrogen-bonding interaction with F(1) and F(2).

Table 2. Selected Bond Distances and Angles in 10a

(a) Bond Distances (Å)			
Mo−P(1)	2.664(3)	Mo−P(2)	2.478(3)
Mo−P(3)	2.589(3)	Mo−P(4)	2.474(3)
Mo−C(1)	1.812(10)	Mo−C(8)	1.95(1)
C(8)−O	1.154(10)	C(1)−N	1.32(1)
N−H(1)	1.0(1)	F(1)−H(1)	2.2(1)
F(2)−H(1)	2.3(1)		
(b) Bond Angles (deg)			
P(1)−Mo−P(2)	78.66(9)	P(1)−Mo−P(3)	91.53(9)
P(1)−Mo−P(4)	105.86(9)	P(1)−Mo−C(1)	166.6(3)
P(1)−Mo−C(8)	82.2(3)	P(2)−Mo−P(3)	98.53(10)
P(2)−Mo−P(4)	174.90(10)	P(2)−Mo−C(1)	92.6(3)
P(2)−Mo−C(8)	92.1(3)	P(3)−Mo−P(4)	79.16(9)
P(3)−Mo−C(1)	99.9(3)	P(3)−Mo−C(8)	166.4(3)
P(4)−Mo−C(1)	83.4(3)	P(4)−Mo−C(8)	90.9(3)
C(1)−Mo−C(8)	88.0(4)	Mo−C(1)−N	173.3(8)
Mo−C(8)−O	178.6(10)	C(1)−N−C(2)	124.1(10)
C(1)−N−H(1)	110.0(7)	F(1)−H(1)−N	157.0(10)
F(2)−H(1)−N	134.0(9)		

IR spectra of **10**, the intense bands assignable to $\nu(C\equiv O)$ appeared together with the weak $\nu(NH)$ bands, indicating that the protonation occurs on the isocyanide N atom with the CO ligand intact. On the basis of the ^{31}P NMR spectra exhibiting four resonances with the same intensities, the cis structure has been implicated for **10**.

The structure of **10a** (R = Ph) has been fully characterized by the X-ray analysis. An ORTEP drawing is depicted in Figure 2, while the important bond distances and angles are summarized in Table 2. For the aminocarbyne ligand in **10a**, the Mo−C−N linkage is essentially linear (173.3(8)°), and the Mo−C and C−N distances at 1.812(10) and 1.32(1) Å are comparable to those in **7**. It is to be noted that in the closely related alkylidyne complex *cis*-$[Mo(\equiv CCH_2Ph)(CO)(dppe)_2]$-

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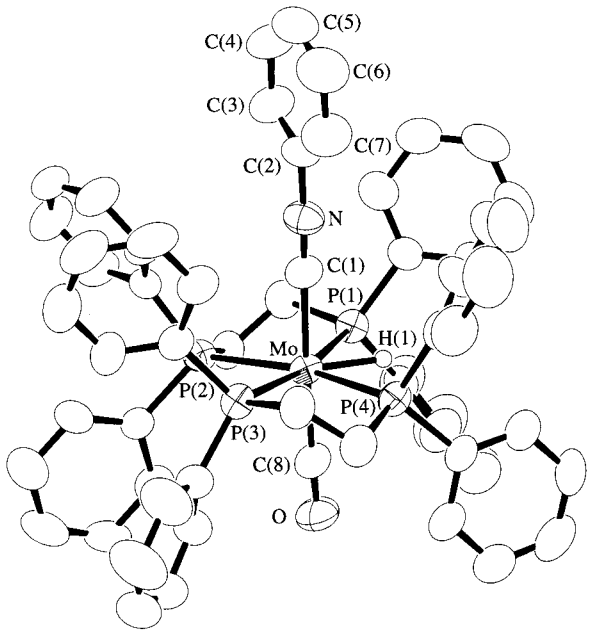


Figure 3. ORTEP drawing of the cation in **12a**. Hydrogen atoms are omitted for clarity except for the hydride H(1).

$[BF_4]$ (**11**)[31] the Mo−$C_{carbyne}$ distance (1.768(8) Å) is considerably shorter than that in **10a**. This may be explained by the significant contribution of the resonance structure **ii** shown in Chart 1 for the aminocarbyne complex **10a**. The fact that the ν(C≡O) bands appeared at 1893 and 1910 cm^{-1} for **10a** and **11**, respectively, indicates the stronger electron-donating ability of the Mo center toward the CO ligand in **10a** than that in **11**. This is also consistent with the significant contribution of structure **ii**, where the donation of lone-pair electron density occurs from the N atom toward the metal center.

Complexes **10** have proved to be unstable in solution at room temperature. Thus, **10** dissolved in $CDCl_3$ are gradually converted into hydridoisocyanide complexes $[MoH(CNR)(CO)(dppe)_2][BF_4]$ (**12**) (Scheme 2). As expected, this isomerization turned out to be much enhanced by the addition of $[Me_2OH][BF_4]$. Migration of the proton from the aminocarbyne ligand to the metal center was invoked previously to explain the formation of $[MH(CNMe)_2(dppe)_2]^+$ from the reaction of *trans*-$[M(CNMe)_2(dppe)_2]$ and $[Et_2OH][BF_4]$ via the presumed intermediate *trans*-$[M(\equiv CNHMe)(CNMe)(dppe)_2]^+$.[8a]

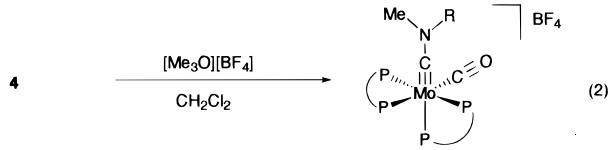
The structure of **12a** (R = Ph) has been determined in detail by X-ray analysis (Figure 3 and Table 3). Complex **12a** has a pentagonal bypyramidal structure with the CO and PhNC ligands occupying the apical positions. The hydride was unequivocally found in the Fourier map, which lies on the basal plane between the P(1) and P(4) atoms (d(Mo−H) = 1.63(7) Å). Bonding parameters in the CO and PhNC ligands are unexceptional. The IR spectrum of **12a** shows the intense bands at 2061 and 1861 cm^{-1} assignable to ν(C≡N) and ν(C≡O), respectively, which are shifted to the considerably higher region than those of the parent Mo(0) complex **4a** (ν(C≡N), 2017 and 1991; ν(C≡O), 1812 cm^{-1}).[12a] The ^{31}P NMR spectrum of **12a** exhibits two

Table 3. Selected Bond Distances and Angles in 12a

(a) Bond Distances (Å)			
Mo−P(1)	2.475(2)	Mo−P(2)	2.565(2)
Mo−P(3)	2.570(2)	Mo−P(4)	2.471(2)
Mo−C(1)	2.094(6)	Mo−C(8)	1.977(7)
C(8)−O	1.157(7)	C(1)−N	1.163(7)
Mo−H(1)	1.63(7)		
(b) Bond Angles (deg)			
P(1)−Mo−P(2)	78.70(6)	P(1)−Mo−P(3)	168.60(6)
P(1)−Mo−P(4)	112.12(6)	P(1)−Mo−C(1)	87.8(2)
P(1)−Mo−C(8)	88.9(2)	P(2)−Mo−P(3)	91.35(6)
P(2)−Mo−P(4)	168.38(6)	P(2)−Mo−C(1)	93.5(2)
P(2)−Mo−C(8)	87.5(2)	P(3)−Mo−P(4)	78.28(6)
P(3)−Mo−C(1)	87.2(2)	P(3)−Mo−C(8)	96.3(2)
P(4)−Mo−C(1)	91.2(2)	P(4)−Mo−C(8)	88.4(2)
C(1)−Mo−C(8)	176.3(3)	Mo−C(1)−N	178.4(6)
Mo−C(8)−O	178.6(6)	C(1)−N−C(2)	177.5(7)
P(1)−Mo−H(1)	50.0(2)	P(4)−Mo−H(1)	61.0(2)

broad resonances with the same intensities, while the ^{1}H NMR spectrum shows a high-field resonance characteristic of the hydride proton, which splits into a triplet of triplets at low temperatures. These spectral data are consistent with the solid structure clarified by the X-ray diffraction. Complex **12b** also exhibited the analogous spectral feature.

Methylation of Isocyanide−Carbonyl Complexes 4. Complexes **4** reacted with $[Me_3O][BF_4]$ in CH_2Cl_2 at room temperature to give the aminocarbyne complexes *cis*-$[Mo(\equiv CNMeR)(CO)(dppe)_2][BF_4]$ (**13**) in moderate yields (eq 2). Isolation of any characterizable products



(2)

13a: R = Ph
13b: R = Bu^n

failed by the analogous treatment of **1** with $[Me_3O][BF_4]$. It is interesting to note that $[Mo(CNBu^t)_6]$ is susceptible to electrophilic attack by MeOTf[29] and alkyl halides[32] at the α-carbon atom to give η^2-iminoacyl complexes $[Mo(\eta^2\text{-}Bu^tNCR)(CNBu^t)_5]^+$ (R = Me, $PhCH_2$). Spectroscopic data for **13** are indicative of the cis structure, as manifested for the related CNHR complexes **10**, which has been confirmed by X-ray analysis of the Bu^n complex **13b**.

An ORTEP drawing of the cation in **13b** is shown in Figure 4, while selected bond distances and angles are listed in Table 4. The structure of **13b** is quite analogous to that of **10a**. Thus, the aminocarbyne and CO ligands occupy the mutually cis positions, and in the aminocarbyne ligand the Mo−C−N linkage is almost linear (173.7(6)°). However, the Mo−C distance at 1.843(7) Å is slightly longer and the $C_{carbyne}$−N distance at 1.305(8) Å is a little shorter than the corresponding bond distances of 1.812(10) and 1.32(1) Å, respectively, in **10a**. These differences may be explained by the greater contribution of the structure **ii** for **13b** with the strongly electron-donating NBu^nMe group than for **10a** with the NHPh moiety. The almost planar geometry around the

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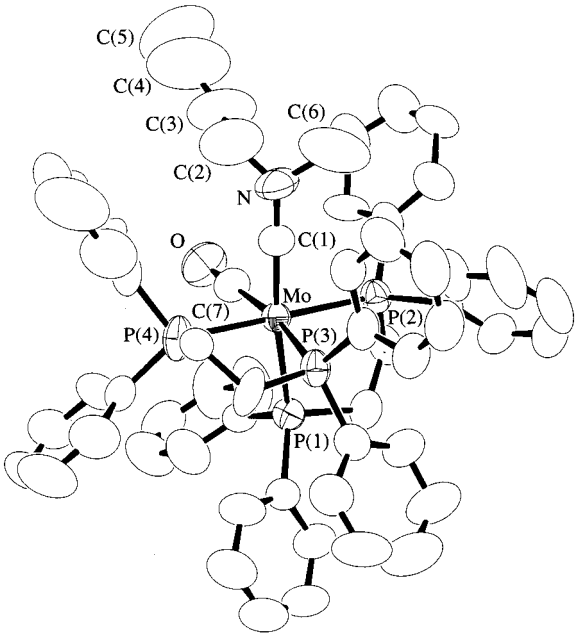


Figure 4. ORTEP drawing of the cation in **13b**. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances and Angles in 13b

	(a) Bond Distances (Å)		
Mo−P(1)	2.664(2)	Mo−P(2)	2.501(2)
Mo−P(3)	2.589(2)	Mo−P(4)	2.502(2)
Mo−C(1)	1.843(7)	Mo−C(7)	1.950(7)
C(7)−O	1.169(7)	C(1)−N	1.305(8)
	(b) Bond Angles (deg)		
P(1)−Mo−P(2)	78.82(6)	P(1)−Mo−P(3)	95.36(6)
P(1)−Mo−P(4)	102.32(7)	P(1)−Mo−C(1)	165.3(2)
P(1)−Mo−C(7)	83.9(2)	P(2)−Mo−P(3)	99.15(6)
P(2)−Mo−P(4)	177.92(7)	P(2)−Mo−C(1)	89.4(2)
P(2)−Mo−C(7)	91.2(2)	P(3)−Mo−P(4)	79.05(6)
P(3)−Mo−C(1)	95.2(2)	P(3)−Mo−C(7)	169.3(2)
P(4)−Mo−C(1)	89.7(2)	P(4)−Mo−C(7)	90.7(2)
C(1)−Mo−C(7)	87.6(3)	Mo−C(1)−N	173.7(6)
Mo−C(7)−O	177.5(6)	C(1)−N−C(2)	129.5(8)
C(1)−N−C(6)	121.0(8)	C(2)−N−C(6)	106.3(9)

N atom is observed also in **13b**, with C−N−C angles of 129.5(8)°, 121.0(8)°, and 106.3(9)°.

Protonation of Carbonyl−Dinitrogen Complex 5 and Carbonyl−Nitrile Complex 6. Relevant to the reaction of isocyanide−carbonyl complexes **4** with [Me_2-OH][BF_4], our study has been extended further to clarify the details of the protonation reactions of other Mo(0) carbonyl complexes. As for the related reaction of *cis*-[$Mo(CO)_2(dppe)_2$] with acids, the hydrido complex [MoH-$(CO)_2(dppe)_2$][SO_3F], having a monocapped octahedral structure, was formed by treatment with HSO_3F,[33] whereas the paramagnetic complexes *trans*-[$Mo(CO)_2$-$(dppe)_2$]X (X = BF_4, HSO_4) were obtained from the reaction with [Et_2OH][BF_4] and H_2SO_4.[34]

Now we have found that treatment of **5** with aqueous HBF_4 in THF at room temperature results in the loss of the coordinated N_2 to give the hydrido complex [MoH-$(CO)(OH_2)(dppe)_2$][BF_4] (**14**) (eq 3), whose structure has been determined unambiguously by X-ray analysis

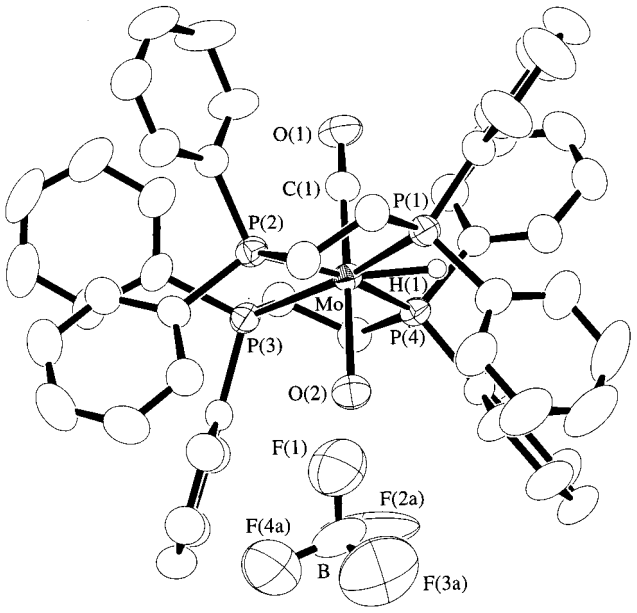
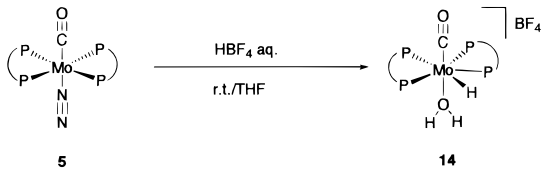


Figure 5. ORTEP drawing of **14**. Hydrogen atoms are omitted for clarity except for the hydride H(1).

Table 5. Selected Bond Distances and Angles in 14

	(a) Bond Distances (Å)		
Mo−P(1)	2.453(1)	Mo−P(2)	2.575(2)
Mo−P(3)	2.516(1)	Mo−P(4)	2.426(1)
Mo−O(2)	2.330(6)	Mo−C(1)	1.857(5)
C(1)−O(1)	1.175(5)	Mo−H(1)	1.63(5)
	(b) Bond Angles (deg)		
P(1)−Mo−P(2)	77.47(5)	P(1)−Mo−P(3)	167.61(5)
P(1)−Mo−P(4)	114.33(5)	P(1)−Mo−O(2)	88.68(9)
P(1)−Mo−C(1)	93.1(2)	P(2)−Mo−P(3)	90.17(4)
P(2)−Mo−P(4)	168.10(5)	P(2)−Mo−O(2)	83.0(1)
P(2)−Mo−C(1)	97.5(2)	P(3)−Mo−P(4)	78.05(4)
P(3)−Mo−O(2)	90.63(9)	P(3)−Mo−C(1)	87.7(2)
P(4)−Mo−O(2)	95.3(1)	P(4)−Mo−C(1)	83.9(2)
O(2)−Mo−C(1)	178.2(2)	Mo−C(1)−O(1)	176.5(4)
P(1)−Mo−H(1)	53.0(1)	P(4)−Mo−H(1)	60.0(1)

(Figure 5 and Table 5). No intermediate stages, e.g., a hydroxycarbyne complex, were detected. Complex **14**



(3)

has a pentagonal bipyramidal geometry with the CO and H_2O ligands in the apical positions. The hydride was located between the P(1) and P(4) atoms, with the Mo−H distance at 1.63(5) Å. Complex **14** shows a strong ν(C≡O) band at 1776 cm^{-1} in its IR spectrum, which is lower than the values for [$Mo(CO)(dppe)_2$] (1807 cm^{-1}) and **5** (1812 and 1789 cm^{-1}).[13] The exceptionally low ν(C≡O) value observed for the CO ligand in **14** suggests the extremely electron-donating nature of the [MoH-$(OH_2)(dppe)_2$]$^+$ moiety toward the CO ligand, having no other π-acidic ligands but the good donor ligand H_2O in the trans position.

Treatment of the carbonyl−nitrile complex *trans*-[Mo-$(CO)(NCC_6H_4OMe$-*p*$)(dppe)_2$] (**6**) with aqueous HBF_4 also afforded the hydrido complex [$MoH(CO)(NCC_6H_4$-OMe-*p*$)(dppe)_2$][BF_4] (**15**) in high yield (eq 4). In contrast

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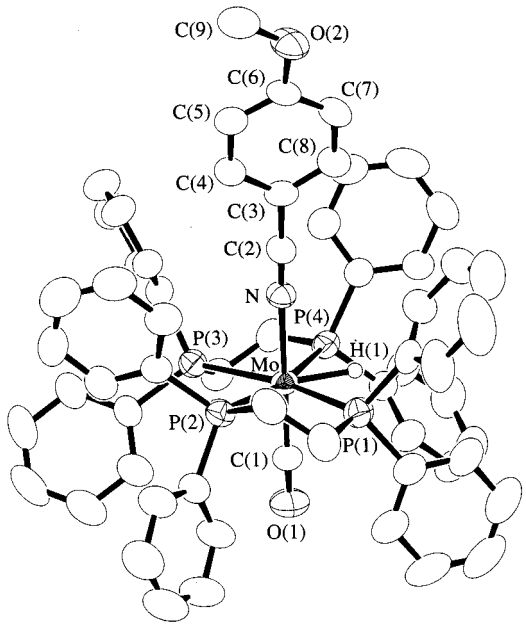
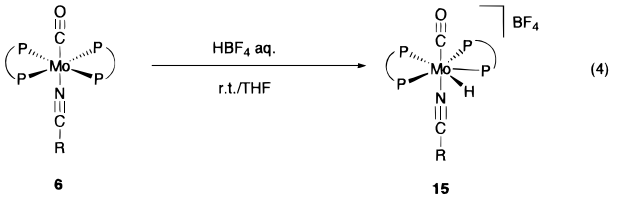


Figure 6. ORTEP drawing of the cation in **15**. Hydrogen atoms are omitted for clarity except for the hydride H(1).

Table 6. Selected Bond Distances and Angles in 15

	(a) Bond Distances (Å)		
Mo−P(1)	2.464(2)	Mo−P(2)	2.567(2)
Mo−P(3)	2.550(2)	Mo−P(4)	2.438(2)
Mo−N	2.190(4)	Mo−C(1)	1.892(5)
C(1)−O(1)	1.181(6)	N−C(2)	1.131(6)
Mo−H(1)	1.64(3)		
	(b) Bond Angles (deg)		
P(1)−Mo−P(2)	77.61(5)	P(1)−Mo−P(3)	167.94(5)
P(1)−Mo−P(4)	114.49(5)	P(1)−Mo−N	90.4(1)
P(1)−Mo−C(1)	91.2(2)	P(2)−Mo−P(3)	90.73(5)
P(2)−Mo−P(4)	167.49(5)	P(2)−Mo−N	85.2(1)
P(2)−Mo−C(1)	96.8(2)	P(3)−Mo−P(4)	77.34(5)
P(3)−Mo−N	91.7(1)	P(3)−Mo−C(1)	87.0(2)
P(4)−Mo−N	91.3(1)	P(4)−Mo−C(1)	86.5(2)
N−Mo−C(1)	177.6(2)	Mo−N−C(2)	177.7(5)
Mo−C(1)−O(1)	175.8(5)	N−C(2)−C(3)	176.0(6)
P(1)−Mo−H(1)	59.0(1)	P(4)−Mo−H(1)	55.0(1)

to the reaction of the dinitrogen−nitrile complex *trans*-$[Mo(N_2)(NCR)(dppe)_2]$ with HBF_4, giving *trans*-$[MoF(NCH_2R)(dppe)_2]^+$ (vide supra), the protonation of **6** occurs at the metal center without loss of both the CO and nitrile ligands. The structure of **15** has also been



(4)

characterized by X-ray crystallography, which is depicted in Figure 6 and Table 6. The geometry around the Mo in **15** is also a pentagonal bipyramid, with the CO and nitrile ligands occupying the apical positions. The hydride was found on the basal plane between the P(1) and P(4) atoms, which is consistent with the low-temperature ^1H and ^{31}P NMR spectra showing a triplet of triplets at −4.45 ppm due to the hydride proton and two broad signals with the same intensities assigned to the dppe ligands, respectively. The IR spectrum exhibiting two characteristic bands at 2217 and 1796 cm^{-1} due to ν(N≡C) and ν(C≡O) are in agreement with the structure determined by the X-ray analysis. It is to be noted that **6** shows ν(N≡C) and ν(C≡O) bands at 2155 and 1767 cm^{-1}.[14]

Concluding Remarks

The present study on the protonation reaction of the Mo(0) complexes containing one or two nitrogenase substrates as the ligand has disclosed that on treatment with either $[Me_2OH][BF_4]$ or aqueous HBF_4, a series of isocyanide complexes *trans*-$[Mo(CNR)(L)(dppe)_2]$ with $L = N_2$, *p*-$MeOC_6H_4CN$, and CO undergoes protonation at the isocyanide N atom to give the aminocarbyne complexes except for **1b** ($R = Bu^n$, $L = N_2$), the latter of which is susceptible to attack at both the α-C and N atom in the *n*-butylisocyanide ligand, affording the carbene complex with an agostic α-C−H bond, **8**. In the aminocarbyne and carbene complexes obtained here, both the nitrile and CO ligands are still intact for **9** and **10**, whereas the coordinated N_2 in **1** is lost in the products **7** and **8**. However, the aminocarbyne complexes **10** with the CO ligand are unstable in a solution state at room temperature and are converted into the hydridoisocyanide complexes **12**. The methylation of the isocaynide−carbonyl complexes **4** with $[Me_3O][BF_4]$ proceeds similarly to give the stable aminocarbyne complexes **13**. By contrast, the carbonyl complexes *trans*-$[Mo(CO)(L)(dppe)_2]$ ($L = N_2$, *p*-$MeOC_6H_4CN$) reacted with aqueous HBF_4 to afford the hydrido complexes **14** and **15**, with a loss of the N_2 ligand for the former and a retention of the nitrile ligand for the latter, respectively.

Experimental Section

General Considerations. All manipulations were done under an atmosphere of N_2 except for those stated otherwise. IR and NMR spectra were recorded on a JASCO FT/IR-420 spectrometer at room temperature and on JEOL EX-270 or LA-400 spectrometers at 20 °C, respectively. The signals due to the aromatic protons are omitted from the ^1H NMR data shown below. Elemental analyses were carried out with a Perkin-Elmer 2400 series II CHN analyzer. Amounts of solvating molecules in the products were determined by X-ray crystallography, NMR measurements, and/or GLC analysis. Complexes **1**, **3**, **4**,[12] **5**,[13] and **6**[14] were prepared according to the literature methods, whereas aqueous HBF_4, $[Me_2OH][BF_4]$, and $[Me_3O][BF_4]$ were commercially obtained and used as received.

Preparation of 7. To a suspension of **1a**·$2C_6H_6$ (223 mg, 0.217 mmol) in THF (2 mL) was added an aqueous HBF_4 solution (42%, 0.3 mL). A yellow solid immediately precipitated, which was filtered off and redissolved in acetone. Addition of hexane to the solution afforded orange crystals of **7** (162 mg, 65% yield). Anal. Calcd for $C_{62}H_{60}NOBF_4P_4Mo$: C, 65.22; H, 5.30; N, 1.23. Found: C, 65.26; H, 5.44; N, 1.15. IR (KBr): ν(NH), 3308; ν(C═O), 1673; ν(CN), 1495 cm^{-1}. ^1H NMR (acetone-d_6): δ 2.8−3.0 (m, 8H, PCH_2), 2.04 (s, 6H, Me_2C═O). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 60.5 (s).

Preparation of 8. A suspension of **1b** (77 mg, 0.075 mmol) in THF (3 mL) was treated with $[Me_2OH][BF_4]$ (18 μL, 0.15 mmol) at 0 °C. After stirring for 2 h, ether was added to the reaction mixture. A yellow solid deposited, which was filtered off and crystallized from CH_2Cl_2−ether at 0 °C to give orange crystals of **8** (41 mg, 49% yield). Anal. Calcd for $C_{57}H_{59}NBF_5P_4Mo$: C, 63.17; H, 5.49; N, 1.29. Found: C, 63.09; H, 5.38; N,

1.54. IR (KBr): ν(NH), 3360 and 3300; ν(CN), 1526 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −7.25 (d quin, J_{H-H} = 7.8 Hz, J_{H-P} = 10.7 Hz, 1H, MoCH), 0.50 (m, 2H, NCH_2CH_2), 0.55−0.7 (m, 5H, CH_2CH_3), 1.91 (br quar, 2H, J = 6.8 Hz, NCH_2), 3.15 (br, 1H, NH), 2.5−2.8 (m, 8H, PCH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 48.6 (d, J_{P-F} = 30 Hz). ^{13}C NMR (CD_2Cl_2): δ 203.2 (J_{C-P} = 13 Hz (quin), J_{C-F} = 67 Hz (d), J_{C-H} = 61 Hz (d), MoC).

Preparation of 9a·1/2CH_2Cl_2. Into a solution of **3a**·1/2C_6H_6 (80 mg, 0.068 mmol) in THF (3 mL) was added [Me_2OH][BF_4] (18 μL, 0.148 mmol) at −30 °C under Ar. After stirring for 2 h at 0 °C, ether was added to precipitate a solid, which was filtered off and recrystallized from CH_2Cl_2−ether to give **9a**·1/2CH_2Cl_2 as orange crystals (62 mg, 73% yield). Anal. Calcd for $C_{67.5}H_{62}N_2OBClF_4P_4Mo$: C, 64.38; H, 4.96; N, 2.22. Found: C, 64.28; H, 5.10; N, 2.24. IR (KBr): ν(C≡N), 2225; ν(NH), 3282 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.90 (s, 3H, MeO), 5.05 (br, 1H, NH), 2.3−2.7 (m, 8H, PCH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 65.0 (s).

Preparation of 9b. This complex was obtained in 61% yield as orange crystals from **3b** by a method similar to that for preparing **9a**. Anal. Calcd for $C_{65}H_{65}N_2OBF_4P_4Mo$: C, 65.23; H, 5.47; N, 2.34. Found: C, 64.60; H, 5.43; N, 2.30. IR (KBr): ν(C≡N), 2226; ν(NH), 3294 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 0.7 (m, 3H, CH_3), 0.8−0.9 (m, 4H, $CH_2CH_2CH_3$), 2.3−2.7 (m, 10H, $NHCH_2$ and PCH_2), 3.83 (s, 3H, MeO), 3.65 (br, 1H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 66.8 (s).

Preparation of 10a. To a suspension of **4a** (86 mg, 0.084 mmol) in THF (3 mL) was added [Me_2OH][BF_4] (21 μL, 0.17 mmol) at 0 °C. After stirring for 2 h at this temperature, ether was added to deposit the orange solid, which was filtered off and recrystallized from CH_2Cl_2−ether at −20 °C, affording orange crystals of **10a** (38 mg, 42%). Anal. Calcd for $C_{60}H_{54}NOBF_4P_4Mo$: C, 64.82; H, 4.90; N, 1.26. Found: C, 64.22; H, 4.88; N, 1.42. IR (KBr): ν(NH), 3239; ν(C≡O), 1893; ν(CN), 1502 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.9−3.4 (m, 8H, PCH_2), 6.60 (br s, 1H, NH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.8 (ddd, J = 23, 15, and 3 Hz, 1P), 40.8 (dd, J = 24 and 14 Hz, 1P), 50.5 (dd, J = 84 and 24 Hz, 1P), 57.7 (ddd, J = 84, 23, and 3 Hz, 1P).

Preparation of 10b·1/2CH_2Cl_2. This complex was obtained as yellow crystals in 62% yield from **4b** by a method similar to that for **10a**. Anal. Calcd for $C_{58.5}H_{59}NOBClF_4P_4Mo$: C, 61.95; H, 5.24; N, 1.23. Found: C, 62.35; H, 5.21; N, 1.16. IR (KBr): ν(NH), 3253; ν(C≡O), 1854; ν(CN), 1533 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.64 (t, 3H, J = 7.1 Hz, CH_3), 0.78 (sex, J = 7.1 Hz, 2H, CH_2CH_3), 0.85−1.05 (m, 2H, NCH_2CH_2), 1.8−3.2 (m, 10H, NCH_2 and PCH_2), 6.35 (br s, 1H, NH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 26.6 (ddd, J = 24, 12, and 3 Hz), 39.6 (ddd, J = 24, 12, and 3 Hz), 55.4 (ddd, J = 87, 24, and 3 Hz), 59.7 (ddd, J = 87, 24, and 3 Hz).

Preparation of 12a. A CH_2Cl_2 solution of **10a** (27 mg, 9.925 mmol) was left for 31 h at 20 °C. Addition of ether to the resulting solution gave pale yellow crystals of **12a** (15 mg, 56% yield). Anal. Calcd for $C_{60}H_{54}NOBF_4P_4Mo$: C, 64.82; H, 4.90; N, 1.26. Found: C, 64.69; H, 5.31; N, 1.33. IR (KBr): ν(N≡C), 2061; ν(C≡O), 1861 cm^{-1}. ^{1}H NMR ($CDCl_3$, 20 °C): δ −5.35 (m, 1H, MoH), 2.4−2.8 (m, 8H, PCH_2). ^{1}H NMR (THF-d_8, −43 °C): δ −5.46 (tt, J_{P-H} = 70.2 and 12.7 Hz, 1H, MoH). ^{1}H NMR (THF-d_8, 47 °C): δ −5.23 (quin, J_{P-H} = 42.1 Hz, 1H, MoH). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 54−58 and 79−83 (br, 2P each).

Formation of 12b. Isomerization of **10b** into **12b** in a $CDCl_3$ solution was monitored by NMR spectra, which revealed the formation of **12b** in 95% after 8.5 h. IR (KBr): ν(NC), 2113; ν(CO), 1833 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −5.54 (pseudo quin, J_{H-P} = 42 Hz, 1H, MoH), 0.65 (t, J = 7.1 Hz, 3H, CH_3), 0.7−0.9 (m, 4H, $CH_2CH_2CH_3$), 2.4−2.8 (m, 10H, NCH_2 and PCH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 52−60 and 77−84 (br, 2P each).

Preparation of 13a. Complex **4a** (61 mg, 0.059 mmol) dissolved in CH_2Cl_2 (3 mL) was treated with [Me_3O][BF_4] (17 mg, 0.12 mmol) at room temperature. After stirring for 20 h, ether was added to the resulting solution, affording **13a** as pale red microcrystals (29 mg, 43% yield). Anal. Calcd for $C_{61}H_{56}NOBF_4P_4Mo$: C, 65.08; H, 5.01; N, 1.24. Found: C, 64.63; H, 5.07; N, 1.23. IR (KBr): ν(C≡O), 1859; ν(CN), 1506 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.6−1.8 (m, 3H, PCH_2), 1.86 (s, 3H, NMe), 2.1−2.4 (m, 3H, PCH_2), 2.85 and 3.55 (m, 1H each, PCH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.1 (br t, J = 22 Hz, 1P), 34.2 (br td, J = 21 and 5 Hz, 1P), 50.5 (ddd, J = 84, 23, and 5 Hz, 1P), and 56.8 (dd, J = 84 and 20 Hz, 1P).

Prepration of 13b. This complex was prepared by a method essentially similar to that of **13a**: pale brown crystals, yield 55%. Anal. Calcd for $C_{59}H_{60}NOBF_4P_4Mo$: C, 64.09; H, 5.47; N, 1.27. Found: C, 63.92; H, 5.48; N, 1.28. IR (KBr): ν(C≡O), 1858; ν(CN), 1550 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.7−1.2 (m, 7H, $CH_2CH_2CH_3$), 2.0−3.2 (m, 10H, NCH_2 and PCH_2), 2.06 (s, 3H, NMe). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.1 (ddd, J = 3, 15 and 24 Hz, 1P), 37.9 (dd, J = 23 and 15, 1P), 50.3 (dd, J = 85 and 24 Hz, 1P), and 58.8 (ddd, J = 3, 85 and 23 Hz, 1P).

Preparation of 14·THF. To a THF solution of **5**·1/2C_6H_6 (102 mg, 0.102 mmol) was added aqueous HBF_4 (42%, 61 mg, 0.29 mmol) at room temperature. After stirring for 0.5 h, the resultant pale yellow solution was concentrated to ca. 2.5 mL. Addition of ether gave yellow crystals of **14**·THF (88 mg, 78% yield). Anal. Calcd for $C_{57}H_{59}O_3BF_4P_4Mo$: C, 62.31; H, 5.41. Found: C, 62.37; H, 5.44. IR (KBr): ν(C≡O), 1776 cm^{-1}. ^{1}H NMR (THF-d_8, 20 °C): δ −3.7 to −2.5 (v br, 1H, MoH), 2.6−3.0 (m, 8H, PCH_2). ^{1}H NMR (THF-d_8, −73 °C): δ −3.39 (quin, J_{P-H} = 41 Hz, 1H, MoH). ^{31}P{^{1}H} NMR (THF-d_8): δ 65−69 (br).

Preparation of 15·Et_2O. To a suspension of **6** (95 mg, 0.090 mmol) in THF (3 mL) was added aqueous HBF_4 (42%, 39 mg, 0.19 mmol) under Ar, and the mixture was stirred for 2 h. By addition of ether to the resultant solution, yellow crystals of **15**·Et_2O precipitated (100 mg, 91% yield). Anal. Calcd for $C_{65}H_{66}NO_3BF_4P_4Mo$: C, 64.21; H, 5.47; N, 1.15. Found: C, 64.31; H, 5.58; N, 1.08. IR (KBr): ν(C≡N), 2217; ν(C≡O), 1796 cm^{-1}. ^{1}H NMR (THF-d_8, 20 °C): δ −4.20 (quin, J_{P-H} = 42 Hz, 1H, MoH), 2.45−2.7 and 2.8−3.05 (m, 4H each, PCH_2), 3.83 (s, 3H, MeO). ^{1}H NMR (THF-d_8, −90 °C): δ −4.45 (tt, J_{P-H} = 70.3 and 11.2 Hz, 1H, MoH). ^{31}P{^{1}H} NMR (THF-d_8): δ 66−70 (br). ^{31}P{^{1}H} NMR (THF-d_8, −90 °C): δ 53−56 and 83−86 (br).

X-ray Crystallographic Studies. Single crystals of **7**, **10a**, **12a**, **13b**, **14**·THF, and **15**·Et_2O were sealed in glass capillaries under Ar and transferred to a Rigaku AFC7R diffractometer equipped with a graphite-monochromatized Mo Kα source. Diffraction studies were done at room temperature. Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 reflections with 35° < 2θ < 40°. The intensities of three check reflections were monitored every 150 reflections during data collection, which revealed no significant decay for **10a**, **12a**, **13b**, **14**·THF, and **15**·Et_2O, but an almost linear decay for **7**, with an average 6.3% loss in intensities at the end of the data collection. Intensity data were corrected for Lorentz and polarization effects and for absorption (ψ scans), and for **7** decay correction was also applied. Details of crystal and data collection parameters are listed in Table 7.

Structure solution and refinements were carried out by using the teXsan program package.[35] The positions of the nonhydrogen atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY),[36] which were refined anisotropically by full-matrix least-squares techniques. The hydrogen atoms attached to the amino N in **7** and **10a** as well as those bound to the Mo atom in **12a**, **14**, and **15** were found from the Fourier maps, which were refined isotropically, except for the amino hydrogen in **7**. Other hydrogens were

(35) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

(36) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

Table 7. Crystallographic Data for 7, 10a, 12a, 13a, 14·THF, and 15·Et_2O

	7	**10a**	**12a**	**13a**	**14**·THF	**15**·Et_2O
formula	$C_{62}H_{60}NOBF_4P_4Mo$	$C_{60}H_{54}NOBF_4P_4Mo$	$C_{60}H_{54}NOBF_4P_4Mo$	$C_{59}H_{60}NOBF_4P_4Mo$	$C_{57}H_{59}O_3BF_4P_4Mo$	$C_{65}H_{66}NO_3BF_4P_4Mo$
fw	1141.80	1111.73	1111.73	1105.77	1098.73	1215.88
space group	*Cc* (No. 9)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	23.936(3)	12.073(7)	11.498(4)	12.258(2)	14.75(1)	11.349(5)
b (Å)	12.244(4)	22.55(2)	27.625(6)	22.932(3)	17.336(9)	14.251(4)
c (Å)	20.348(2)	19.497(9)	17.059(2)	19.710(2)	21.587(10)	18.731(5)
α (deg)	90	90	90	90	90	88.07(2)
β (deg)	109.520(8)	104.94(4)	99.95(2)	104.808(8)	110.20(4)	86.39(3)
γ (deg)	90	90	90	90	90	88.87(3)
V (Å^3)	5620(1)	5129(5)	5336(2)	5356(1)	5181(4)	3021(1)
Z	4	4	4	4	4	2
ρ_{calc} (g cm^{-3})	1.349	1.440	1.384	1.371	1.408	1.336
F(000)	2360	2288	2288	2288	2272	1260
μ_{calc} (cm^{-1})	4.02	4.38	4.21	4.19	4.35	3.81
cryst size (mm^3)	1.0 × 0.8 × 0.6	0.6 × 0.15 × 0.1	0.6 × 0.15 × 0.05	0.4 × 0.3 × 0.2	0.6 × 0.3 × 0.2	0.8 × 0.2 × 0.15
scan type	$\omega-2\theta$	$\omega-2\theta$	ω	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
2θ range (deg)	5−55	5−55	5−55	5−50	5−55	5−50
no. measd	6905	12 275	12 839	9895	12 325	11 427
no. unique	6761	11 730	12 242	9426	11 872	10 566
no. obsd	5871	3792	4716	4545	6396	5448
no. var	680	653	666	712	662	743
corrections	Lorentz−polarization; absorption (ψ scan, transmn factor: 0.9219−0.9999); decay (6.3%, linear); secondary extinction (coeff: 4.763 × 10^{-8})	Lorentz−polarization; absorption (ψ scan, transmn factor: 0.9521−0.9965)	Lorentz−polarization	Lorentz−polarization; absorption (ψ scan, transmn factor: 0.9447−0.9996)	Lorentz−polarization; absorption (ψ scan, transmn factor: 0.9379−0.9988)	Lorentz−polarization; absorption (ψ scan, transmn factor: 0.9621−0.9986)
R^a	0.030	0.058	0.048	0.047	0.047	0.044
$R_w{}^b$	0.031	0.057	0.045	0.047	0.044	0.037
GOF	1.68	1.57	1.31	1.44	1.60	1.41
residual peaks (e$^-$/Å^{-3})	0.39, −0.46	0.85, −0.89	0.40, −0.36	0.31, −0.38	0.89, −0.42	0.35, −0.33

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

placed at the calculated positions and included in the final stages of the refinements with fixed parameters.

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Supporting Information Available: Tables of atomic coordinates and equivalent thermal parameters, anisotropic thermal parameters, and extensive bond lengths and angles, together with figures with full atom-numbering schemes, for **7**, **10a**, **12a**, **13b**, **14**·THF, and **15**·Et_2O. These materials are available free of charge via the Internet at http://pubs.acs.org.

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