N−N Bond Cleavage of Organohydrazines by Molybdenum(II) and Tungsten(II) Complexes Containing a Linear Tetraphosphine Ligand. Formation of Nitrido or Imido Complexes and Their Reactivities

Daisuke Watanabe, Sumie Gondo, Hidetake Seino, and Yasushi Mizobe*

Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan

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The Mo(II) tetraphosphine−dihalide complexes [MoX_2(κ^4-**P4**)] (X = Cl (**2a**), Br (**2b**); **P4** = *meso*-*o*-C_6H_4($PPhCH_2CH_2PPh_2$)$_2$) having uncommon trigonal-prismatic geometry cleaved the N−N bond in Me_2NNH_2 and $PhNHNH_2$ at room temperature to form the nitrido complexes *trans*-[MoX(N)(κ^4-**P4**)] (X = Cl (**3a**), Br (**3b**)). In contrast, similar reactions of the W(II) congener [WBr_2(κ^4-**P4**)] afforded the imido complex *trans*-[WBr(NH)(κ^4-**P4**)]$^+$ (**4c**$^+$), which was isolated as a PF_6 or BPh_4 salt. Addition of HBF_4 converted **3** into the imido complexes *trans*-[MoX(NH)(κ^4-**P4**)][BF_4] (X = Cl (**4a**[BF_4]), Br (**4b**[BF_4])), while deprotonation of **4a**$^+$ and **4b**$^+$ by NEt_3 readily regenerated **3a** and **3b**. At elevated temperatures, **2a** also reacted with RNHNHR (R = Me, Ph), giving the corresponding organoimido complexes *trans*-[MoCl(NR)(κ^4-**P4**)][PF_6] (**6**[PF_6]) after anion metathesis with K[PF_6]. The mechanism has been proposed for the N−N bond cleavage, which involves the proton shift in the end-on coordinated organohydrazine followed by the two-electron reduction by the M(II) center to give the M(IV) imido complex and the amine. The nitrido ligand in **3a** is susceptible to electrophilic attack by methyl trifluoromethanesulfonate to form **6**[CF_3SO_3] (R = Me), while reactions of **3a** with acid chlorides RCOCl (R = Me, Ph, *p*-tolyl (Tol)) afforded the neutral acylimido complexes *cis*,*mer*-[$MoCl_2$(NCOR)(κ^3-**P4**)] (**7**). Treatment of **7** with K[PF_6] yielded the cationic complexes *trans*-[MoCl(NCOR)(κ^4-**P4**)][PF_6] (**8**[PF_6]). On the other hand, imido complex **4a**[BF_4] smoothly reacted with isocyanates RNCO (R = Ph, Tol) in the presence of a catalytic amount of Et_3N to give the carbamoylimido complexes *trans*-[MoCl(NCONHR)-(κ^4-**P4**)][BF_4] (**9**[BF_4]), and the thiocarbamoyl analogue *trans*-[MoCl(NCSNHPh)(κ^4-**P4**)][PF_6] (**10**[PF_6]) was also obtained from **4a**[PF_6] and PhNCS. Although hydrolysis of **7** (R = Tol) in a THF/aqueous KOH mixture resulted in the formation of *p*-toluamide only in low yield, reduction of the same complex with $NaBH_4$ and $LiAlH_4$ generated *p*-toluamide and 4-methylbenzylamine, respectively, in moderate yields. Molecular structures of **3a**, **4a**[BF_4], **4c**[BPh_4], **6**[PF_6] (R = Me), **6**[BF_4] (R = Ph), **7** (R = Me), **8**[PF_6] (R = Me), and **9**[BF_4] (R = Tol) were determined crystallographically.

Introduction

Reduction of dinitrogen into ammonia under mild conditions by the use of transition metal complexes has been attracting much attention in relation to biological and industrial nitrogen fixation. Extensive studies for more than 40 years have demonstrated that ligating N_2 can readily be converted into ammonia for a considerable number of N_2 complexes.[1,2] However, the complexes for which the reduction mechanism is rationally demonstrated by isolating the fully characterized intermediate stages are still limited. Molybdenum and tungsten complexes with tertiary phosphine co-ligands[3] and those with triamidoamine co-ligands[4] are quite noteworthy in that these can readily undergo protonation at their N_2 ligand to give a series of protonated nitrogenous ligands as well as free ammonia. These reactions involve the step in which the N−N single bond of intermediary hydrazidium ligand M=N−NH_3^+ is cleaved to give ammonia and the nitrido species M≡N. In relation to these and biological N_2-fixing systems, reductive cleavage of the N−N bonds in hydrazines has also been investigated previously, and several transition metal complexes are known to promote this transformation stoichiometrically[5,6] or catalytically,[7,8] in certain cases of which the metal species catalyze the disproportionation of hydrazine into ammonia and N_2. As for many stoichiometric reaction systems, formation of not only the nitrido but also the

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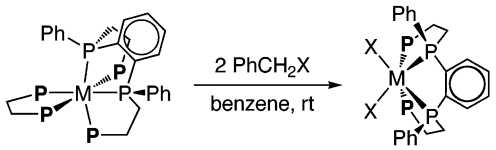
imido and amido complexes has also been confirmed. However, the well-defined bond cleavage reactions of organohydrazines by Mo and W phosphine complexes have not yet been documented.

We have reported previously the synthesis of new Mo(0) and W(0) complexes with the linear tetraphosphine ligand *meso*-*o*-$C_6H_4(PPhCH_2CH_2PPh_2)_2$ (**P4**), [M(dppe)(κ^4-**P4**)] (**1**; M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$),[9] and recent studies have disclosed the conversion of **1** into a series of complexes containing the **P4** ligand. Interestingly, the **P4** ligand in these complexes has turned out to display the binding features characteristic of its unique structure. Thus, coordination by three five-membered chelate rings is highly strained with the P−M−P angles much smaller than 90°, resulting in the facile dissociation of one or two outer P atoms to take a κ^3- or κ^2-coordination mode.[10] Furthermore, uncommon geometry around the metal center sometimes emerges. For example, M(II) dihalide complexes [MX_2(κ^4-**P4**)] (**2**; MX = MoCl (**2a**), MoBr (**2b**), WBr (**2c**)) obtained from the reaction of **1** with 2 equiv of $PhCH_2X$ have a trigonal-prismatic structure with one of three side rectangles capped by the κ^4-**P4** ligand (eq 1),[11] which presents



1 (M = Mo, W)

(**P** = PPh_2)

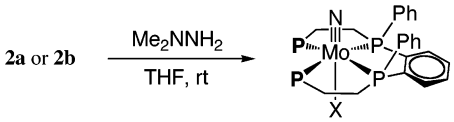
	M	X
2a	Mo	Cl
2b	Mo	Br
2c	W	Br

(1)

a sharp contrast to an octahedral geometry observed for all the other known *trans*-[MX_2(tertiary phosphine)$_4$] (M = Mo, W; X = halogen). Probably due to this unusual structure and/or facile dissociation of P atom(s), complexes **2** have been found to show much higher reactivities toward diazoalkanes than the related complexes *trans*-[MX_2(dppe)$_2$]. We have therefore investigated further the reactions of these dihalide complexes **2** with organo-nitrogenous compounds, viz., organohydrazines.

Results and Discussion

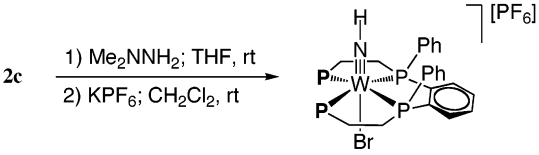
1. Formation of Nitrido and Imido Complexes via N−N Bond Cleavage of Mono- or 1,1-Disubstituted Hydrazines. The Mo(II) dichloro complex **2a** smoothly reacted with Me_2NNH_2 at room temperature in THF to form the Mo(IV) nitrido complex *trans*-[MoCl(N)(κ^4-**P4**)] (**3a**), which was extracted from the evaporated reaction mixture residue with benzene and isolated from benzene/hexane as orange-red crystals in 92% yield (eq 2). A similar procedure using the dibromo



3a (X = Cl)
3b (X = Br)

(2)

analogue **2b** instead of **2a** also afforded the nitrido complex *trans*-[MoBr(N)(κ^4-**P4**)] (**3b**) in satisfactory yield. By contrast, analogous reaction of the W complex **2c** with Me_2NNH_2 did not give the corresponding nitrido complex but a pink precipitate insoluble in benzene or THF. Although further purification of this crude solid was also hampered by its low solubility in other common solvents including CH_2Cl_2 and MeCN, crystallization from CH_2Cl_2/ether became possible after treatment of this solid with K[PF_6], leading to successful isolation of the W(IV) imido complex *trans*-[WBr(NH)(κ^4-**P4**)][PF_6] (**4c**[PF_6]) as purple crystals in 59% yield (eq 3). The initial precipitate was identified



4c[PF_6]

(3)

as the Br salt **4c**Br from its NMR spectra, comparable to those of **4c**[PF_6]. Reactions of **2a** and **2c** with excess $PhNHNH_2$ also afforded **3a** and **4c**$^+$, respectively, and GLC analysis confirmed the concurrent formation of $PhNH_2$ (∼1.0 mol per mol of **2**). These results might suggest that one metal center cleaves the N−N bond of hydrazine stoichiometrically and that the nitrido and imido ligands originate from the NH_2 group in organohydrazines.

We have also examined the reactions of **2** with unsubstituted hydrazine, but these appeared to proceed in a different way. The nitrido or imido complexes above were scarcely formed, and a much larger than a stoichiometric amount of N_2H_4 was consumed in these reactions. For instance, when **2a** was allowed to react with 10 equiv of N_2H_4 in THF at room temperature for 24 h, formation of 12.1 equiv of NH_3 and 3.0 equiv of N_2 was observed. It is likely that certain metal species catalyze disproportionation of N_2H_4 to form NH_3 and N_2 in a 4:1 molar ratio, but we have not yet been able to fully characterize the complexes present in this reaction system.

The Mo nitrido complexes **3a** and **3b** readily underwent protonation by HBF_4 at the N atoms to form the corresponding Mo(IV) imido complexes *trans*-[MoX(NH)(κ^4-**P4**)][BF_4] (X = Cl (**4a**$^+$), Br (**4b**$^+$)) (Scheme 1). It was also confirmed that treatment of these imido complexes with bases (e.g., Et_3N, Me_2NNH_2) regenerated the parent nitrido complexes. In sharp contrast, deprotonation from the W complex **4c**$^+$ did not take place by amines or hydrazines, and reactions with stronger bases such as $KN(SiMe_3)_2$ or *n*-BuLi did not proceed cleanly. These

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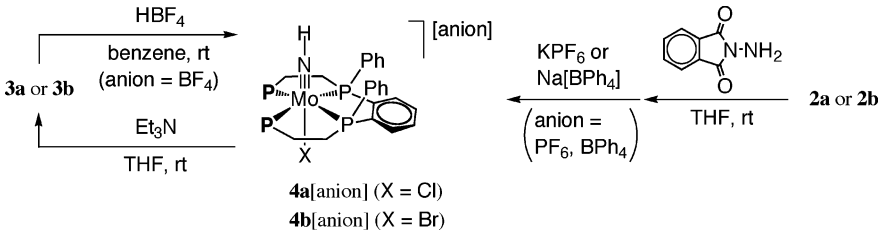
Scheme 1



results may be explained by the lower acidity of the imido ligand bound to the less-electron-withdrawing W(IV) center as compared to that in the Mo(IV) complex. In the reactions of **2** (M = Mo) with organohydrazines, due to the presence of concomitantly formed amine and/or excess hydrazine, the deprotonation products, viz., nitrido complexes, presumably become the major product. Hence the reactions using stoichiometric amounts of organohydrazines, which are converted to less basic products after N−N cleavage, might lead to the direct isolation of imido complexes even in the case of Mo. Indeed, reactions of **2a** and **2b** with 1.1 equiv of *N*-aminophthalimide proceeded very slowly (over ∼10 days) in THF at room temperature, from which were obtained the salts of cationic imido complexes **4a**$^+$ and **4b**$^+$ after anion metathesis with K[PF_6] or Na[BPh_4].

2. Characterization of the Nitrido and Imido Complexes. Single-crystal X-ray diffraction studies were carried out to determine the structural details. Molecular structures of the nitrido complex **3a** and the imido complex **4a**[BF_4] are depicted in Figures 1 and 2, respectively. In both complexes, the Mo centers adopt severely distorted octahedral geometry with mutually trans N and Cl atoms, and four P atoms of the **P4** ligand occupy the remaining equatorial sites. The phenyl groups attached to the inner P atoms are directed syn to the nitrogenous ligand. The Mo−N distance in the nitrido complex **3a** at 1.667(3) Å is characteristic of a Mo−N triple bond and somewhat shorter than those in *trans*-[MoCl(N)(depe)$_2$] (depe = $Et_2PCH_2CH_2PEt_2$), at 1.684(5)−1.722(5) Å,[12] and *trans*-[Mo(L)(N)(dppe)$_2$] (L = N_3,[13] NCCH=COPh,[14] NCC(CN)COMe[15]), at 1.70−1.79 Å. The ν(Mo≡N) values at 994 and 997 cm^{-1} for **3a** and **3b**, respectively, are almost comparable to those at 970−1000 cm^{-1} for the other precedent Mo(IV)−nitrido complexes.[12,14−17] In the cationic imido complex **4a**$^+$, the Mo−N bond is elongated to 1.712(4) Å from that of the nitrido complex **3a**, which is a value typical of the 2σ- and 4π-electron-donating imido ligand.[13,17,18] This assignment is consistent with the finding that the imido group has an almost linear Mo−N−H bond (176(1)°). The N−Mo−Cl linkages in both **3a** and **4a**$^+$ are essentially linear. However, their Mo−Cl distances at 2.7851(9) Å for **3a** and 2.523(1) Å for **4a**$^+$ differ significantly, indicating that trans influence of the nitrido ligand is much stronger than that of the imido ligand. Bonding parameters associated with the **P4** ligand are essentially identical between **3a** and **4a**$^+$. Thus, in each structure the Mo−P distances for the inner P atoms are much shorter than those for the outer ones. Since the P−Mo−P angles in the five-membered chelate rings are in the range 78−81°, the remaining cisoid P(1)−Mo−P(4) angles of 118.9(2)° for **3a** and 112.71(4)° for **4a**$^+$ are widened considerably from ideal 90°. To compress the P(1)−Mo−P(4) angles, all Mo−P bonds in **3a** and **4a**$^+$ are tilted away from the N atoms, as shown by the obtuse N−Mo−P angles. For instance, average values of the four N−Mo−P angles are 98.7(1)° for **3a** as compared to 90.2(6)−95.2(2)° for the above *trans*-[Mo(L)(N)(dppe)$_2$].

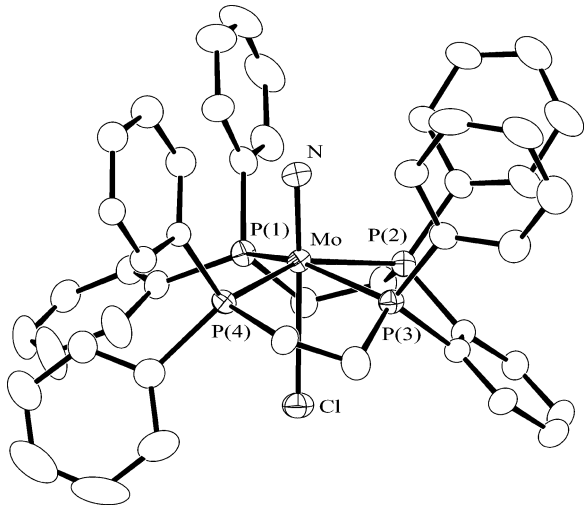


Figure 1. Molecular structure of **3a**. Hydrogen atoms and the minor components of the disordered groups are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg) (P* = P(1)−P(4)): Mo−Cl, 2.7851(9); Mo−P(1), 2.518(1); Mo−P(2), 2.4388(9); Mo−P(3), 2.432(1); Mo−P(4), 2.525(7); Mo−N, 1.667(3); N−Mo−Cl, 177.9(1); Cl−Mo−P*, 80.80(3)−82.8(1); N−Mo−P*, 95.5(2)−100.61(9); P(1)−Mo−P(2), 78.38(3); P(2)−Mo−P(3), 78.05(3); P(3)−Mo(1)−P(4), 79.6(2); P(1)−Mo−P(3), 152.18(3); P(2)−Mo−P(4), 154.3(2); P(1)−Mo−P(4), 118.9(2).

As depicted in Figure 3, the crystal strucuture of the cation in **4c**[BPh_4] is quite similar to that of **4a**$^+$. Bonding parameters of the imido ligand are not exceptional in comparison with other W(IV) complexes.[13,19] It has been found that one of the phenyl groups in the BPh_4 anion is interacting with the imido hydrogen in a NH−π fashion, with the shortest H···C distance being 2.60(9) Å.

As is consistent with the crystal structures of pseudo-C_s symmetry, each of **3** and **4**$^+$ exhibits two $^{31}P\{^1H\}$ signals assignable to the outer and inner P atoms. These are mutually coupling in an AA′XX′ pattern (see Experimental Section for

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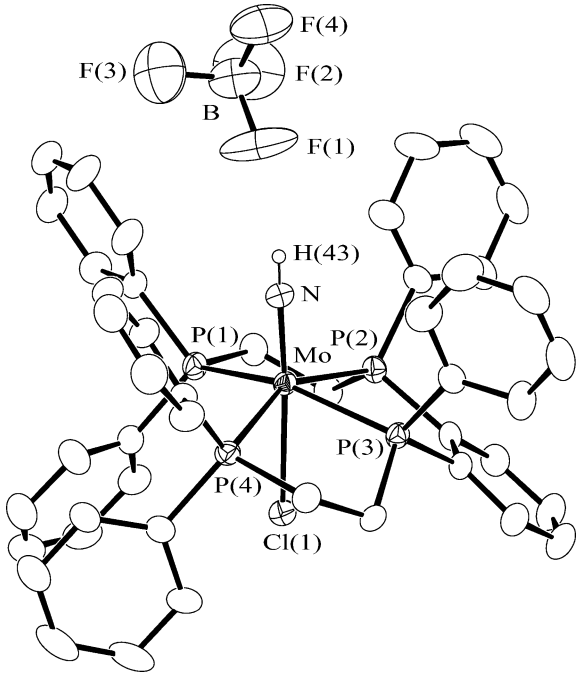

Figure 2. Molecular structure of **4a**[BF_4]. Hydrogen atoms in the **P4** ligand are omitted for clarity. Thermal ellipsoids of non-hydrogen atoms are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo−Cl(1), 2.523(1); Mo−P(1), 2.533(1); Mo−P(2), 2.453(1); Mo−P(3), 2.455(1); Mo−P(4), 2.535(1); Mo−N, 1.712(4); N−H(43), 0.77(4); F(1)···H(43), 2.13-(4); N−Mo−Cl(1), 175.8(1); Cl(1)−Mo−P, 78.76(4)−80.78(4); N−Mo−P, 98.1(1)−103.7(1); P(1)−Mo−P(2), 80.60(4); P(2)−Mo−P(3), 79.16(4); P(3)−Mo−P(4), 79.91(3); P(1)−Mo−P(3), 153.01(4); P(2)−Mo−P(4), 153.13(3); P(1)−Mo−P(4), 112.71(4); Mo−N−H(43), 176(1).

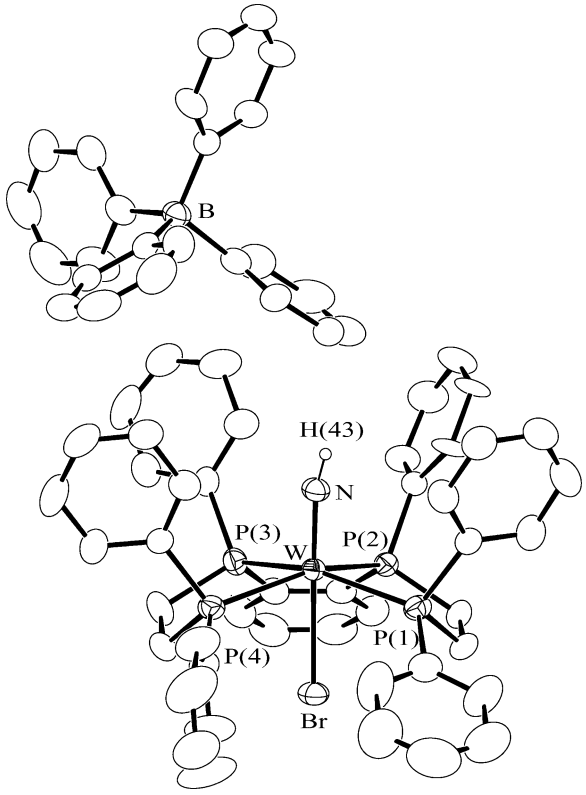

Figure 3. Molecular structure of **4c**[BPh_4]. Hydrogen atoms except for the imido N-H and the minor components of the disordered groups are omitted for clarity. Thermal ellipsoids of non-hydrogen atoms are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): W−Br, 2.6994(8); W−P(1), 2.520(1); W−P(2), 2.433(1); W−P(3), 2.445(1); W−P(4), 2.523(2); W−N, 1.725(5); N−H(43), 0.82(9); N−W−Br, 178.2(2); Br−W−P, 78.91(4)−80.94(4); N−W−P, 99.3(2)−101.5(2); P(1)−W−P(2), 78.64(4); P(2)−W−P(3), 79.92(4); P(3)−W−P(4), 78.02(4); P(1)−W−P(3), 153.36(5); P(2)−W−P(4), 151.70(4); P(1)−W−P(4), 116.04(5); W−N−H(43), 166(5). The nearest N−H···C contact to the BPh_4 anion is 2.60(9) Å.

details), and the signal at larger δ value is attributable to the inner P atoms.[20] In the ^{1}H NMR spectrum, a broad peak observed in the range δ 4.0−4.7 for the Mo complexes **4a**$^+$ and **4b**$^+$ and δ 6.2−6.4 for the W complex **4c**$^+$ is assignable to the imido proton. These chemical shifts are slightly affected by the nature of the counteranion. It is noteworthy that most imido NH signals of the previously reported Mo(IV) and W(IV) complexes are obscured or appear at δ 7−10[17,21,22] except for that at δ 5.53 for *cis,trans*-[WCl_2(NH)(PMe_2Ph)$_2$(C_2H_2)].[19] In the IR spectra of the solid samples of **4**$^+$, the ν(N−H) values are in the ordinary range 3100−3400 cm^{-1},[16a−c,17,19,21] where the influence of the counteranion is clearly observed: the ν(N−H) frequencies decrease in the order of the anion PF_6 > BPh_4 > BF_4 (e.g., 3292, 3235, and 3203 cm^{-1}, respectively, for **4a**$^+$). This tendency may be ascribed to the interaction of the imido hydrogen with the counteranion. Hydrogen bonding is apparently present in the X-ray structure of **4a**[BF_4] ((N−)H···F = 2.13(4) Å), and some contact exists in **4c**[BPh_4] as described above, which is also the case in the isomorphous **4a**[BPh_4].[23] In addition, preliminary crystallographic analysis of **4c**[PF_6] indicates the absence of any interaction between the imido ligand and the PF_6 anion.[23] In these series, the ν(N−H) values of the W complexes are higher by >40 cm^{-1} than those of the Mo complexes, which is consistent with the less protic nature of the former.

3. N−N Bond Cleavage of 1,2-Disubstituted Hydrazines to Form the Organoimido Complexes. Since the nitrido and imido ligands in **3** and **4**$^+$ originate from the NH_2 group in mono- and 1,1-disubstituted hydrazines, reactions of **2** with 1,2-disubstituted hydrazines may provide N-substituted imido complexes. It has turned out that in contrast to mono- and 1,1-disubstituted hydrazines, which smoothly reacted with **2** at room temperature, the reaction of PhNHNHPh with the Mo complex **2a** required much more severe conditions, viz., in toluene at reflux. The major product present in the resulting blue-green solution was characterized as the neutral phenylimido complex *cis,mer*-[$MoCl_2$(NPh)(κ^3-**P4**)] (**5y**) by ^{1}H and ^{31}P{^{1}H} NMR spectra (Scheme 2). Thus, the latter spectrum showed four resonances due to four inequivalent P nuclei, including one signal at δ −10.2, which is characteristic of a dissociated outer

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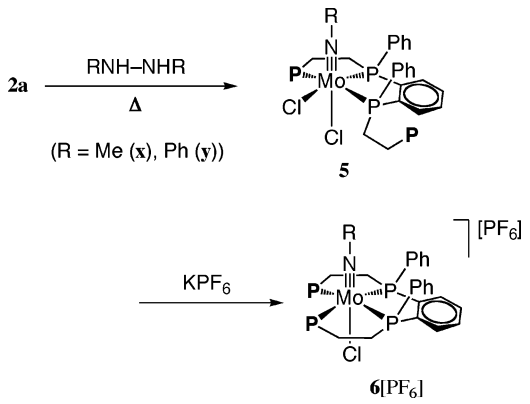
(23) Crystallographic data for **4a**[BPh_4]·0.4(CH_2Cl_2)·0.5(Et_2O): $C_{72.4}H_{68.8}BCl_{1.8}NMoO_{0.5}P_4$, fw = 1255.41, space group $P2_1/a$ (no. 14), a = 21.084(5) Å, b = 13.910(3) Å, c = 23.044(5) Å, β = 107.850(1)°, V = 6433(3) Å^3, Z = 4, ρ_{calcd} = 1.296 g cm^{-3}, μ = 0.421 mm^{-1}, R_1 = 0.075 (5478 reflections with $F_o^2 > 2\sigma(F_o^2)$) and wR_2 = 0.226 (15 127 all unique reflections) for 837 parameters. For **4c**[PF_6]·0.6(CH_2Cl_2): $C_{46.6}H_{44.2}BrCl_{1.4}F_6NP_5W$, fw = 1200.52, space group $P2_1/c$ (no. 14), a = 14.514(3) Å, b = 15.950(3) Å, c = 22.629(5) Å, β = 108.174(1)°, V = 4977(2) Å^3, Z = 4, ρ_{calcd} = 1.602 g cm^{-3}, μ = 3.420 mm^{-1}, R_1 = 0.053 (6237 reflections with $F_o^2 > 2\sigma(F_o^2)$) and wR_2 = 0.159 (11 478 all unique reflections) for 624 parameters.

Scheme 2



P atom. Although purification of **5y** was unsuccessful, treatment with K[PF_6] transformed **5y** into the cationic complex *trans*-[MoCl(NPh)(κ^4-**P4**)][PF_6] (**6y**[PF_6]), which was isolated as pure brown crystals in 38% yield. The reaction of **2a** with MeNHNHMe, which was generated in situ from its bis(hydrochloride) salt and Et_3N, proceeded at 60 °C to form the methylimido complex *cis*,*mer*-[$MoCl_2$(NMe)(κ^3-**P4**)] (**5x**) and after analogous anion metathesis with K[PF_6] *trans*-[MoCl(NMe)(κ^4-**P4**)][PF_6] (**6x**[PF_6]) was obtained as red crystals in 63% yield. Reactions of the W complex **2c** with 1,2-disubstituted hydrazines were also examined under forcing conditions but resulted in the formation of an intractable mixture containing only a small amount of the expected W organoimido complexes, if any.

Molecular structures of both **6x**[PF_6] and **6y**[BF_4] have been fully determined by X-ray crystallography as shown in Figures 4 and 5, respectively. Coordination geometries of both complexes are esssentially identical with that of **4a**$^+$ except for the organic substituents bound to the N atom. The Mo−N−C linkages are bent slightly by 10.2(3)° and 12.5(3)° toward the direction of the *o*-phenylene group in **P4** probably due to intramolecular steric repulsion against the phenyl groups bound to the outer P atoms in **P4**. The Mo−N distances are comparable to that of **4a**$^+$ and other reported values for organoimido ligands bound to Mo(IV).[15,24−27]

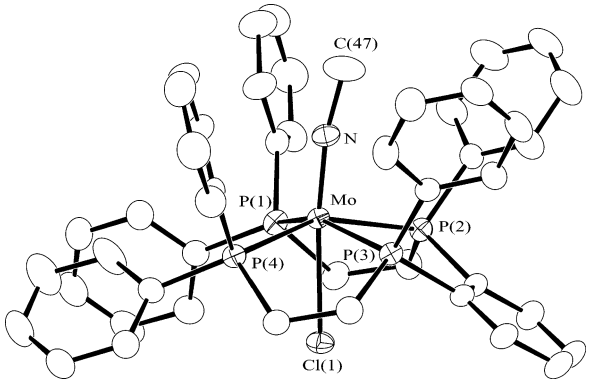


Figure 4. Molecular structure of the cationic part of **6x**[PF_6]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo−Cl(1), 2.5414(7); Mo−P(1), 2.5423(8); Mo−P(2), 2.4377(7); Mo−P(3), 2.4341(7); Mo−P(4), 2.5384(7); Mo−N, 1.710(3); N−C(47), 1.436(5); N−Mo−Cl(1), 173.65(9); Cl(1)−Mo−P, 79.18(3)−80.03(3); N−Mo−P, 95.57(8)−103.80(8); P(1)−Mo−P(2), 78.74(2); P(2)−Mo−P(3), 80.53(2); P(3)−Mo−P(4), 79.05(2); P(1)−Mo−P(3), 152.98(3); P(2)−Mo−P(4), 152.79(3); P(1)−Mo−P(4), 113.77(3); Mo−N−C(47), 169.8(3).

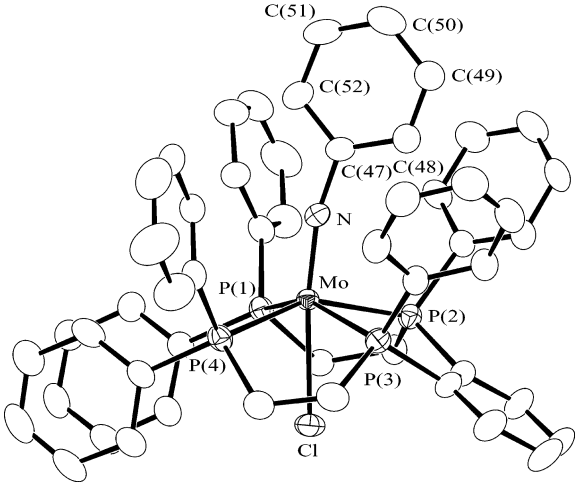


Figure 5. Molecular structure of the cationic part of **6y**[BF_4]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo−Cl, 2.553(1); Mo−P(1), 2.531(2); Mo−P(2), 2.435(2); Mo−P(3), 2.430(1); Mo−P(4), 2.524(2); Mo−N, 1.733(3); N−C(47), 1.426(5); N−Mo−Cl, 172.5(1); Cl−Mo−P, 75.86(4)−78.58(5); N−Mo−P, 97.2(1)−106.2(1); P(1)−Mo−P(2), 79.71(6); P(2)−Mo−P(3), 80.91(5); P(3)−Mo−P(4), 79.81(5); P(1)−Mo−P(3), 150.77(5); P(2)−Mo−P(4), 151.59(4); P(1)−Mo−P(4), 108.61(4); Mo−N−C(47), 167.5(3).

On the basis of the above results, plausible mechanisms for the N−N bond cleavage of organohydrazines by **2** are illustrated in Scheme 3. At first, the 16-electron M(II) center undergoes coordination of hydrazine by the sterically less hindered N atom. Hydrazidium ligand is formed via intramolecular 1,2-H shift accompanied by dissociation of X or one of the PPh_2 groups in **P4**. Then, electron donation from the M(II) center causes reductive N−N bond cleavage to generate 1 equiv of the amine and M−N multiple bond formation, affording the M(IV) imido complex such as **4**$^+$, **6**$^+$, and **5**. Deprotonation of the imido ligand in **4**$^+$ (R^3 = H) may provide the nitrido complex **3**, but the equilibrium exists in this step between **4**$^+$ and coexisting amine or excess hydrazine as described above. Such interconversions between nitrido and imido ligands by proton tranfer are well precedented.[12,16a−c,17,21,22,28]

The above pathways of N−N bond cleavage are quite parallel to what proceeds on the dialkylhydrazido(2−) complexes *trans*-[$M^{IV}Br(NNR_2)(dppe)_2$]$^+$ (M = Mo, W; R = alkyl) derived from the dinitrogen complexes *trans*-[$M(N_2)_2(dppe)_2$].[29,30] Two-electron reduction of these affords the neutral complexes [$M^{II}(NNR_2)(dppe)_2$], which causes N−N bond cleavage upon

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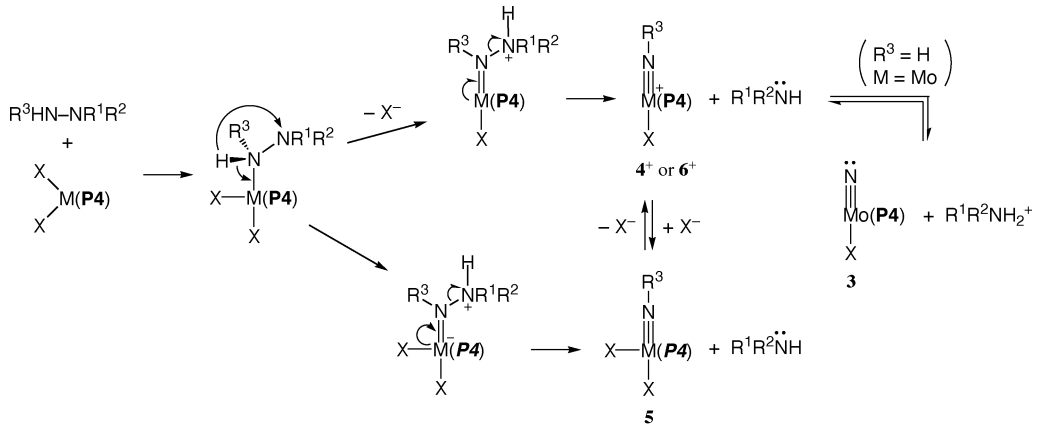
Scheme 3[a]



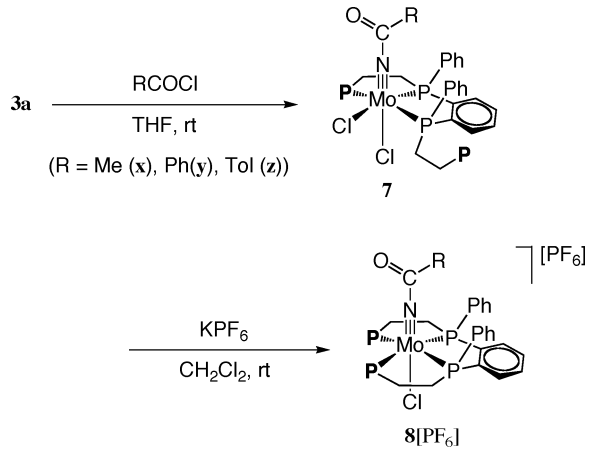
[a] "***P4***" represents the κ^3-coordination mode.

protonation to produce the M(IV) imido complexes and NHR_2. The hydrazidium complexes $[M^{II}(L)(NNHR_2)(dppe)_2]^+$ as the intermediate stage have been detected. In a similar way, chemical reduction of the (1-pyridinio)imido complexes *cis,trans*-$[WCl_2(NNC_5H_{5-n}R_n)(PMe_2Ph)_2(L)]$ (R = alkyl; L = CO, C_2H_2) in the presence of proton source is known to yield smoothly the imido complexes *cis,trans*-$[WCl_2(NH)(PMe_2Ph)_2(L)]$ and pyridines $NC_5H_{5-n}R_n$.[19] With respect to the formation of the organoimido ligand via cleavage of the N−N bond on the single metal center, it has been reported that decomposition[31] or halogenation[32] of $[(CO)_5W\{NPhNPhC(OMe)Me\}]$ gives $[(CO)_5W(NPh)]$ or $[(CO)_2W(NPh)X_2]_2$, respectively, together with PhN═C(OMe)Me. Disproportionation of two RCONHNHR′ into a NR′ and a R′N═NCOR ligand on Mo(IV) complexes has also been precedented.[33]

Finally, it should be emphasized that the closely related *trans*-$[MoBr_2(dppe)_2]$ did not show any reactivities toward hydrazine compounds. The remarkably higher reactivity of **2** is presumably ascribable to the presence of the electronically less stable metal center with the sterically less congested reaction site arising from their unusual trigonal-prismatic structure.

4. Preparation of the Organoimido Complexes by the Reactions with Electrophiles. The terminal nitrido ligand is presumed to be susceptible to electrophilic attack due to the presence of lone-pair electrons, and reactivities toward not only proton but also carbon electrophiles have been widely investigated.[16c,22,24b,c,34−40] Since the nitrido ligand in **3** is readily protonated to form the imido ligand, the N atom in **3** is assumed to be of significantly nucleophilic character. As expected, **3a** rapidly reacted with methyl triflate at room temperature to give the methylimido complex **6x**$[CF_3SO_3]$ in 71% yield. However, reactions of **3** with alkyl halides afforded only mixtures of several uncharacterized products.

Scheme 4



On the other hand, reactions of **3** with various acid chlorides RCOCl proceeded smoothly at room temperature, yielding the acylimido complexes *cis,mer*-$[MoCl_2(NCOR)(\kappa^3$-**P4**$)]$ (R = Me (**7x**), Ph (**7y**), Tol (**7z**); Tol = *p*-tolyl) in satisfactory yields (Scheme 4). As observed for **5**, treatment with KPF_6 in CH_2Cl_2 at room temperature converted **7** into the corresponding cationic complexes *trans*-$[MoCl(NCOR)(\kappa^4$-**P4**$)][PF_6]$ (**8**$[PF_6]$). IR spectra of both **7** and **8**$[PF_6]$ show strong ν(C═O) bands at 1640−1700 cm^{-1}, which are comparable to those of previously reported acylimido complexes.[22,36−39,40d,41]

X-ray crystallography has been undertaken to compare the structures of acetylimido complexes **7x** and **8x**$[PF_6]$. As depicted in Figures 6 and 7, respectively, there is no significant difference between the structures of acetylimido ligands in these two, which are featured by a linear Mo−N−C array and a trigonal planar,

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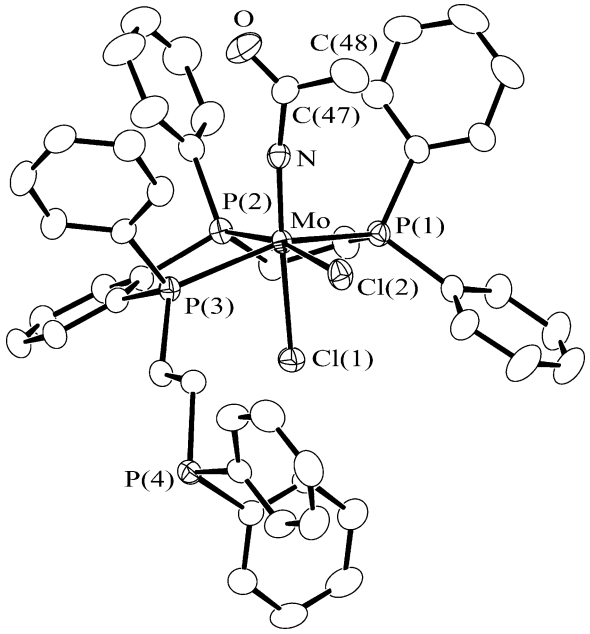


Figure 6. Molecular structure of **7x**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo−Cl(1), 2.484(1); Mo−Cl(2), 2.512(1); Mo−P(1); 2.490(1); Mo−P(2), 2.408(1); Mo−P(3), 2.5115(9); Mo−N, 1.749(3); N−C(47), 1.382(6); O(1)−C(47), 1.189(7); C(47)−C(48), 1.488(7); Cl(1)−Mo−Cl(2), 90.18(4); N−Mo−Cl(1), 174.1(1); N−Mo−Cl(2), 93.4(1); Cl(1)−Mo−P(1), 77.81(3); Cl(1)−Mo−P(2), 80.44(4); Cl(1)−Mo−P(3), 79.08(3); Cl(2)−Mo−P(1), 101.66(4); Cl(2)−Mo−P(2), 169.91(4); Cl(2)−Mo−P(3), 93.95(3); N−Mo−P(1), 96.9(1); N−Mo−P(2), 96.2(1); N−Mo−P(3), 105.3(1); P(1)−Mo−P(2), 80.12(4); P(2)−Mo−P(3), 80.70(3); P(1)−Mo−P(3), 152.03(3); Mo−N−C(47), 171.3(3); O(1)−C(47)−N, 122.5(4); O(1)−C(47)−C(48), 122.8(5); N−C(47)−C(48), 114.6(4).

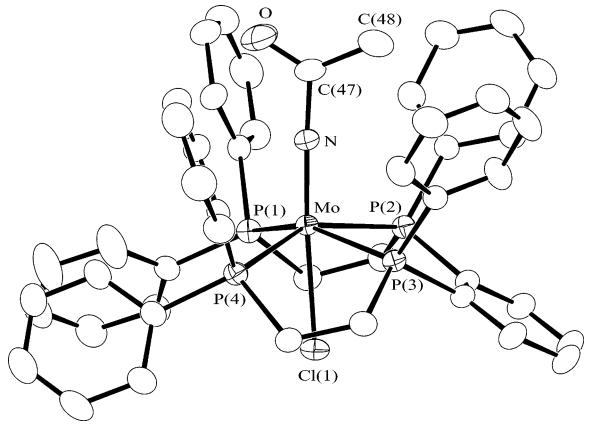
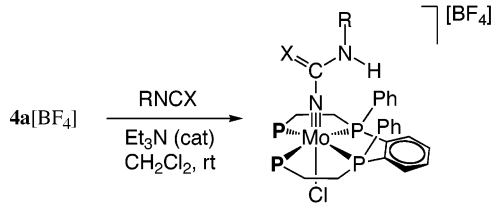


Figure 7. Molecular structure of the cationic part of **8x**[PF_6]. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo−Cl(1), 2.5298(9); Mo−P(1), 2.5434(8); Mo−P(2), 2.4447(8); Mo−P(3), 2.4469(8); Mo−P(4), 2.5425(8); Mo−N, 1.737(3); N−C(47), 1.414(5); O−C(47), 1.209(5); C(47)−C(48), 1.456(6); N−Mo−Cl(1), 176.37(9); Cl(1)−Mo−P, 78.43(3)−79.17(3); N−Mo−P, 98.20(9)−103.20(8); P(1)−Mo−P(2), 78.94(3); P(2)−Mo−P(3), 80.36(3); P(3)−Mo−P(4), 79.06(3); P(1)−Mo−P(3), 151.67(3); P(2)−Mo−P(4), 152.62(3); P(1)−Mo−P(4), 112.84(3); Mo−N−C(47), 177.2(3); N−C(47)−O, 118.3(4); N−C(47)−C(48), 116.8(4); O−C(47)−C(48), 124.9(4).

sp^2-hybridized C(47).[40b−d,41−43] The Mo−N and N−C bond lengths are almost comparable to those in the methyl- and phenylimido complexes **6**$^+$. In **7x**, the **P4** ligand coordinates in a tridentate fashion to the octahedral Mo center in a meridional fashion with one of the outer P atoms dissociated. The acetylimido and one of two chlorido ligands are mutually trans, and the former resides at the same side with the phenyl groups bound to the inner P atoms. The cis N−Mo−P angles are widened to 96.2(1)−105.3(1)° as observed in **3**, **4**$^+$, and **6**$^+$ (vide supra). The coordination geometry of **8x**$^+$ is essentially the same as those of the *trans*-κ^4-**P4** imido complexes **4**$^+$ and **6**$^+$. In the ^{1}H NMR spectra, a considerable high-field shift of the acetyl signals is observed for **7x** (δ 0.48) and especially for **8x**$^+$ (δ −0.12) probably due to the shielding effect by the phenyl groups in **P4**, which are surrounding the acetylimido ligand.

Although treatment of **3a** with organic isocyanates resulted in recovery of **3a**, imido complex **4a**[BF_4] did react with RNCO to give the carbamoylimido complexes *trans*-[MoCl(NCONHR)(κ^4-**P4**)][BF_4] (R = Ph (**9y**[BF_4]), Tol (**9z**[BF_4])) in moderate yields (eq 4). These reactions did take place at room temperature



(4)

9y[BF_4] (R = Ph, X = O)
9z[BF_4] (R = Tol, X = O)
10y[BF_4] (R = Ph, X = S)

in CH_2Cl_2 but were much accelerated by addition of a catalytic amount of Et_3N (∼20 mol %). Since the imido N atom in **4a**$^+$ lacks the lone-pair electrons as a result of their donation to the Mo center, it is assumed that the nitrido complex **3a** generated in situ might be the active species also in this reaction, and here its adduct with RNCO undergoes rapid protonation to form stable **9**$^+$. Under similar conditions, **4a**[PF_6] also reacted with isothiocyanate PhNCS, yielding *trans*-[MoCl(NCSNHPh)(κ^4-**P4**)][PF_6] (**10y**[PF_6]). For **9y**[BF_4], the IR spectrum exhibits the characteristic bands for the −C(O)NH− moiety (ν(N−H) at 3381, amide I at 1681, and amide II at 1511 cm^{-1}), and the ^{1}H NMR signal of the amide proton appears at δ 3.62 as a broad peak. Thiocarbamoylimido complex **10y**[PF_6] shows ν(C═S) at 1096 cm^{-1}.

The molecular structure of **9z**[BF_4] has been determined unambiguously by X-ray crystallography as shown in Figure 8. The structure of the {MoCl(κ^4-**P4**)} chromophore is not exceptional in comparison with other imido complexes described above. The carbamoylimido ligand is almost planar, in which the Mo−N distance of 1.746(3) Å and the Mo−N−C angle of 177.1(3)° are comparable to those of the above imido ligands. With respect to the C(47)−N(2) bond, the *p*-tolyl group bound to N(2) is located trans to the imido N(1) atom, avoiding repulsion against the **P4** ligand. The short C(47)−N(2) bond length of 1.345(5) Å indicates the existence of π-bonding to some extent by contribution of the resonance structure **I** in Chart 1. In contrast, the long C(47)−N(1) distance, at 1.411(5) Å, reflects the absence of π-donation from the imido N atom to the carbonyl C atom represented by **II**.

5. Liberation of Organonitrogen Compounds from the Organoimido Complex. Nitrido and imido complexes not only

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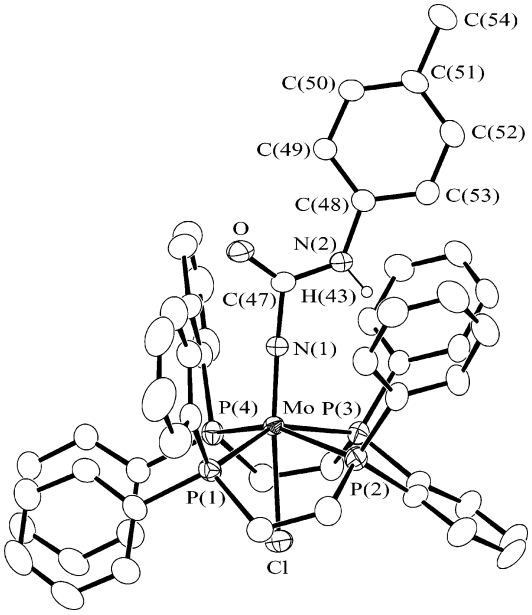
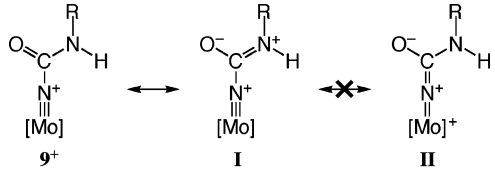


Figure 8. Molecular structure of the cationic part of **9z**[BF_4]. Hydrogen atoms except for the N-H moiety are omitted for clarity. Thermal ellipsoids of non-hydrogen atoms are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Mo−Cl, 2.529(1); Mo−P(1), 2.525(1); Mo−P(2), 2.428(1), Mo−P(3), 2.440(1); Mo−P(4), 2.529(1); Mo−N(1), 1.746(3); N(1)−C(47), 1.411(5); O−C(47), 1.204(5); N(2)−C(47), 1.345(5); N(2)−C(48), 1.409(4); N(2)−H(43), 0.86(4); N(1)−Mo−Cl, 174.88(9); Cl−Mo−P, 77.37(4)−78.89(4); N(1)−Mo−P, 97.9(1)−104.7(1); P(1)−Mo−P(2), 79.94(4); P(2)−Mo−P(3), 80.87(4); P(3)−Mo−P(4), 79.72(5); P(1)−Mo−P(3), 151.31(3); P(2)−Mo−P(4), 152.59(4); P(1)−Mo−P(4), 109.49(4); Mo−N(1)−C(47), 177.1(3); N(1)−C(47)−O, 121.8(4); N(2)−C(47)−O, 126.4(4); N(1)−C(47)−N(2), 111.9(3); C(47)−N(2)−C(48), 127.3(3); C(47)−N(2)−H(43), 108(2); C(48)−N(2)−H(43), 118(2).

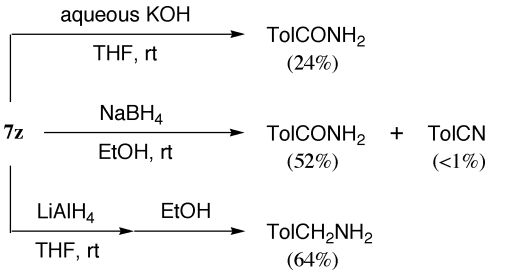
Chart 1



[Mo] = [MoCl(κ⁴-**P4**)]

represent the important intermediate stages in the N_2-fixing cycle but are utilizable as nitrogen sources for organic synthesis. For instance, some nitrido complexes of Mn and Ru serve as N atom-transfer reagents, attaining aziridination of alkenes or amination of silyl enol ethers.[36,44,45] Recently, it has been shown that a series of d^0 nitrido complexes with amido ancillary ligands $[M(N)(NRAr)_3]^{n-}$ (M = Nb: $n = 1$; Mo and W: $n = 0$; R = alkyl; Ar = 3,5-$C_6H_3Me_2$) react with acyl halides to produce nitriles via transient formation of an acylimido ligand.[40c−e] Incorporation of N atoms into organic compounds has also been investigated in detail by using the nitrido complex *trans*-[MoCl(N)(dppe)$_2$], closely related to **3**. Alkylation at the nitrido ligand in this complex provides various organoimido complexes, and the following electrolytic reduction[24,46] or deprotonation[24c,47]

Scheme 5[a]



[a] Yields of the organic compounds are presented in parentheses.

gives primary amines or nitriles, respectively. To demonstrate a utility for the nitrido complex **3** in organic synthesis, we have examined liberation of organonitrogen compounds from the toluoylimido complex **7z**.

In contrast to the above d^0 acylimido−amido complexes liberating nitriles readily, **7z** was stable even under refluxing conditions in toluene. However, when **7z** was treated with aqueous KOH in THF to hydrolyze the Mo−N bond, Tol-$CONH_2$ was produced although the yield was not satisfactory (24% after 1 h; Scheme 5). Since all the starting complex was consumed, the low yield of amide is probably due to the hydrolysis of the amide group, which was implied by the finding that a similar reaction conducted in EtOH generated a significant amount of TolCOOEt.

Versatility of hydride reagents in the cleavage of the Mo−N multiple bond has previously been demonstrated in the reactions of the pyrrolylimido complex *trans*-[MoF{N(1-pyrrolyl)}(dppe)$_2$]$^+$ to yield *N*-aminopyrrole, pyrrole, and ammonia.[48] As expected, treatment of **7z** with an excess amount of $NaBH_4$ in EtOH at room temperature improved the yield of $TolCONH_2$ to 52%, and neither TolCOOEt nor $TolCH_2NH_2$ was detected in the reaction mixtures. On the other hand, reaction of **7z** with excess $LiAlH_4$ in THF gave $TolCH_2NH_2$ in 64% yield after quenching by EtOH. In both reaction mixtures, several Mo−**P4** complexes were present, but their isolation and characterization were not successful.

Experimental Section

General Comments. All manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by common procedures and distilled under nitrogen before use. Complexes **2** were prepared according to literature methods.[11] Other reagents were commercially available and used as received.

^1H and $^{31}P\{^1H\}$ NMR spectra (400 MHz) were recorded on a JEOL alpha-400 spectrometer at 20 °C, and chemical shifts were referenced to those of residual solvent impurity resonances for ^1H (C_6D_6 at 7.16, CD_2Cl_2 at 5.32, and acetone-d_6 at 2.09) or external 85% H_3PO_4 for ^{31}P. The coupling systems of $^{31}P\{^1H\}$ NMR spectra were analyzed by simulations using the gNMR program package.[49] IR spectra were recorded on a JASCO FT/IR-420 spectrometer, and elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer. GC-MS and GLC measurements were performed on a Shimadzu GC-MS QP-5050 spectrometer and GC-14B gas

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chromatographs equipped with CBP1 or CBP10 fused silica capillary columns (25 m × ϕ 0.25 mm). HPLC analyses were carried out on a Shimadzu Prominence system equipped with a UV−vis detector and a HRC-SIL packed column (15 cm × ϕ 4.6 mm) using *n*-hexane/EtOH (85:15) as eluent.

Preparation of *trans*-[MoCl(N)(κ^4-P4)] (3a). To a green suspension of **2a** (740 mg, 0.840 mmol) in THF (50 mL) was added 1,1-dimethylhydrazine (100 μL, 1.32 mmol), and the mixture was stirred at room temperature for 90 min. Volatiles were removed from the resulting orange-red solution under reduced pressure, and the residue was extracted with benzene (40 mL). Addition of hexane to the concentrated benzene extract afforded orange-red crystals of **3a**·0.5(C_6H_6) (664 mg, 92% yield). ^{1}H NMR (C_6D_6): δ 2.05−2.25, 2.35−2.55, 2.75−2.95, 3.35−3.55 (m, 2H each, PCH_2), 6.75−7.15 (m, 20H, aromatic H), 7.45−7.6 (m, 6H, aromatic H), 7.75−7.85, 8.55−8.65 (m, 4H each, aromatic H). ^{31}P{^{1}H} NMR (C_6D_6): δ 66.5, 101.9 (AA′XX′ pattern: $J_{AX} = 6$, $J_{AX'} = 94$, $J_{AA'} = 23$, $J_{XX'} = 12$ Hz). IR (KBr, cm^{-1}): 994 (ν(Mo≡N)). Anal. Calcd for $C_{49}H_{45}ClMoNP_4$: C, 65.16; H, 5.02; N, 1.55. Found: C, 65.67; H, 5.12; N, 1.37.

Preparation of *trans*-[MoBr(N)(κ^4-P4)] (3b). This complex was obtained similarly from **2b** (980 mg, 1.00 mmol) and 1,1-dimethylhydrazine (114 μL, 1.50 mmol) as reddish-orange microcrystals (728 mg, 80% yield). ^{1}H NMR (C_6D_6): δ 2.10−2.3, 2.35−2.55, 2.8−3.0, 3.45−3.65 (m, 2H each, PCH_2), 6.75−7.15 (m, 20H, aromatic H), 7.5−7.7 (m, 6H, aromatic H), 7.75−7.85, 8.50−8.60 (m, 4H each, aromatic H). ^{31}P{^{1}H} NMR (C_6D_6): δ 64.1, 101.5 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 96$ Hz). IR (KBr, cm^{-1}): 997 (ν(Mo≡N)). Anal. Calcd for $C_{46}H_{42}BrMoNP_4$: C, 60.81; H, 4.66; N, 1.54. Found: C, 60.61; H, 4.95; N, 1.47.

Reaction of 2a with Phenylhydrazine. A mixture of **2a** (82 mg, 0.093 mmol) and phenylhydrazine (28 μL, 0.28 mmol) in THF (5 mL) was stirred at room temperature for 24 h. After evaporation of solvent from the resulting orange-red solution, extraction with benzene followed by crystallization by adding hexane to the extract gave crystals of **3a**·0.5(C_6H_6) (41 mg, 48% yield). In a different run using **2a** (33 mg, 0.037 mmol) and phenylhydrazine (21 mg, 0.19 mmol), the formation of 103 mol % of aniline per **2a** was confirmed by GC-MS and GLC analyses.

Preparation of *trans*-[WBr(NH)(κ^4-P4)][PF$_6$] (4c[PF$_6$]). 1,1-Dimethylhydrazine (11 μL, 0.15 mmol) was added to a green suspension of **2c**·0.5(C_6H_6) (107 mg, 0.098 mmol) in THF (5 mL). After the mixture was stirred at room temperature for 60 min, the resultant pink suspension was evaporated to dryness under reduced pressure, and then the residual solid was washed with benzene (8 mL). The remaining pink solid was stirred with KPF_6 (92 mg, 0.50 mmol) in CH_2Cl_2 (8 mL) for 24 h at room temperature and then filtered. Addition of diethyl ether to the concentrated filtrate formed efflorescent purple crystals, which were filtered off and throughly dried under vacuum, giving **4c**[PF_6] (66 mg, 59% yield). ^{1}H NMR (CD_2Cl_2): δ 2.85−3.35 (m, 6H, PCH_2), 2.35−3.60 (m, 2H, PCH_2), 6.37 (br, 1H, NH), 6.95−7.25 (m, 20H, aromatic H), 7.35−7.5 (m, 6H, aromatic H), 7.65−7.75 (m, 2H, aromatic H), 7.80−7.85 (m, 4H, aromatic H), 7.90−8.00 (m, 2H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.6 ($J_{W-P} = 317$ Hz), 82.1 ($J_{W-P} = 273$ Hz) (AA′XX′ pattern with ^{183}W satellites: $J_{AX} = 26$, $J_{AX'} = 121$, $J_{AA'} = 14$, $J_{XX'} = 3$ Hz). IR (KBr, cm^{-1}): 3338 (ν(N−H)). Anal. Calcd for $C_{46}H_{43}BrF_6NP_5W$: C, 48.36; H, 3.79; N, 1.23. Found: C, 48.62; H, 4.21; N, 0.98.

Reaction of 2c with Phenylhydrazine. A mixture of **2c**·0.5(C_6H_6) (49 mg, 0.044 mmol) and phenylhydrazine (14 μL, 0.14 mmol) in THF (4 mL) was stirred at room temperature for 24 h. GC-MS and GLC analyses of the liquid phase confirmed the formation of aniline (1.02 equiv to **2c**). The deposited pink solid was filtered off and stirred with KPF_6 (25 mg, 0.14 mmol) in CH_2Cl_2 (5 mL). Crystals of **4c**[PF_6] were obtained by addition of diethyl ether to the filtered solution (10 mg, 20% yield). Anion metathesis with Na[BPh_4] in CH_2Cl_2 followed by crystallization from CH_2Cl_2/diethyl ether afforded efflorescent purple crystals of **4c**[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O), which lost the solvating molecules under vacuum. ^{1}H NMR (CD_2Cl_2): δ 2.8−3.2 (m, 6H, PCH_2), 2.4−3.65 (m, 2H, PCH_2), 6.22 (br, 1H, NH), 6.80−7.55 (m, 46H, aromatic H), 7.7−8.0 (m, 8H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.5, 82.0 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 147$ Hz). IR (KBr, cm^{-1}): 3295 (ν(N−H)). Anal. Calcd for $C_{70}H_{63}BBrNP_4W$: C, 63.85; H, 4.82; N, 1.06. Found: C, 63.42; H, 4.96; N, 0.95.

Formation of *trans*-[MoCl(NH)(κ^4-P4)][BF$_4$] (4a[BF$_4$]) by Protonation of 3a with HBF$_4$. To a solution of **3a** (301 mg, 0.35 mmol) in benzene (25 mL) was added 54% HBF_4 in diethyl ether (58 μL, 0.42 mmol) at room temperature with stirring. After 70 min, the deposited pink solid of **4a**[BF_4]·0.25(C_6H_6) was filtered off, washed successively with benzene (15 mL) and diethyl ether (15 mL), and then dried under vacuum (309 mg, 91% yield). ^{1}H NMR (CD_2Cl_2): δ 2.85−3.10 (m, 6H, PCH_2), 3.25−3.45 (m, 2H, PCH_2), 4.62 (br, 1H, NH), 7.00−7.35 (m, 20H, aromatic H), 7.5−7.6 (m, 6H, aromatic H), 7.75−7.80 (m, 2H, aromatic H), 7.90−8.05 (m, 6H, aromatic H), 7.35 (s, 1.5H, 0.25C_6H_6). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.8, 92.3 (AA′XX′ pattern: $J_{AX} = 5$, $J_{AX'} = 129$, $J_{AA'} = 22$, $J_{XX'} = 9$ Hz). IR (KBr, cm^{-1}): 3203 (ν(N−H)). Anal. Calcd for $C_{47.5}H_{44.5}BClF_4MoNP_4$: C, 58.73; H, 4.62; N, 1.44. Found: C, 58.83; H, 4.63; N, 1.39. Single crystals for X-ray analysis were obtained by recrystallization from CH_2Cl_2/Et_2O as purple crystals of **4a**[BF_4]·0.25(CH_2Cl_2)·0.25(Et_2O). Anal. Calcd for $C_{47.25}H_{46}BCl_{1.5}F_4MoNO_{0.25}P_4$: C, 57.23; H, 4.68; N, 1.41. Found: C, 57.63; H, 4.54; N, 1.47.

Preparation of *trans*-[MoBr(NH)(κ^4-P4)][BF$_4$] (4b[BF$_4$]). This compound was prepared according to a method similar to that for **4a**[BF_4] by starting from **3b** (36 mg, 0.040 mmol) and 54% HBF_4 in diethyl ether (6.6 μL, 0.048 mmol) and obtained as a pink solid of **4b**[BF_4]·0.25(C_6H_6) (12 mg, 29% yield). ^{1}H NMR (CD_2Cl_2): δ 2.70−3.20 (m, 6H, PCH_2), 3.35−3.6 (m, 2H, PCH_2), 4.67 (br, 1H, NH), 6.85−7.30 (m, 20H, aromatic H), 7.5−7.6 (m, 6H, aromatic H), 7.75−7.8 (m, 2H, aromatic H), 7.9−8.05 (m, 6H, aromatic H), 7.35 (s, 1.5H, 0.25C_6H_6). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 53.8, 91.9 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 127$ Hz). IR (KBr, cm^{-1}): 3197 (ν(N−H)). Anal. Calcd for $C_{47.5}H_{44.5}BBrF_4MoNP_4$: C, 56.16; H, 4.42; N, 1.38. Found: C, 56.47; H, 4.39; N, 1.47.

Reaction of 4a[BF$_4$] with Et$_3$N. Triethylamine (20 μL, 0.14 mmol) was added to a stirred mixture of **4a**[BF_4] (48 mg, 0.049 mmol) in THF (5 mL) at room temperature. The pink suspension immediately turned to an orange solution, NMR measurement of which revealed the formation of **3a**.

Reaction of 2a with *N*-Aminophthalimide. A mixture of **2a** (50 mg, 0.056 mmol) and *N*-aminophthalimide (10 mg, 0.061 mmol) in THF (5 mL) was stirred at room temperature for 240 h. The resulting pink solid was filtered off, washed with THF and diethyl ether, and then stirred with KPF_6 (30 mg, 0.16 mmol) in CH_2Cl_2 for 24 h. Addition of diethyl ether to the filtered product solution formed purple crystals of **4a**[PF_6] (19 mg, 34% yield). ^{1}H NMR (CD_2Cl_2): δ 4.28 (br, 1H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.7, 92.3 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 134$ Hz). IR (KBr): ν(N−H) 3292 cm^{-1}. Anal. Calcd for $C_{46}H_{43}ClF_6MoNP_5$: C, 54.70; H, 4.29; N, 1.39. Found: C, 54.38; H, 4.17; N, 1.37. By a similar method, purple crystals of **4a**[BPh_4] (36 mg, 24% yield) were obtained from **2a** (112 mg, 0.126 mmol) and *N*-aminophthalimide (23 mg, 0.14 mmol), using Na[BPh_4] (57 mg, 0.52 mmol) instead of KPF_6. ^{1}H NMR (CD_2Cl_2): δ 4.06 (br, 1H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.6, 92.2 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 134$ Hz). IR (KBr, cm^{-1}): 3235 (ν(N−H)). Anal. Calcd for $C_{70}H_{63}BClMoNP_4$: C, 70.99; H, 5.36; N, 1.18. Found: C, 70.63; H, 5.22; N, 1.06.

Preparation of 4b[PF$_6$] and 4b[BPh$_4$]. Each compound was prepared according to a method similar to that for the corresponding salt of **4a**$^+$ by starting from **2b**, *N*-aminophthalimide, and an

appropriate source of anion. **4b**[PF_6]: 32% yield as purple crystals. ^{1}H NMR (CD_2Cl_2): δ 4.29 (br, 1H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 53.5, 91.6 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 127$ Hz). IR (KBr, cm^{-1}): 3279 (ν(N−H)). Anal. Calcd for $C_{46}H_{43}ClF_6MoNP_5$: C, 52.39; H, 4.11; N, 1.33. Found: C, 52.28; H, 4.06; N, 1.26. **4b**[BPh_4]: 40% yield as purple crystals. ^{1}H NMR (CD_2Cl_2): δ 4.04 (br, 1H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 53.2, 91.5 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 127$ Hz). IR (KBr, cm^{-1}): 3231 (ν(N−H)). Anal. Calcd for $C_{70}H_{63}BClMoNP_4$: C, 68.42; H, 5.17; N, 1.14. Found: C, 68.34; H, 5.13; N, 1.00.

Preparation of *trans*-[MoCl(NMe)(κ^4-P4)][PF_6] (6x[PF_6]). To a mixture of **2a** (44 mg, 0.050 mmol) and 1,2-dimethylhydrazine bis(hydrochloride) (10 mg, 0.075 mmol) were added THF (5 mL) and Et_3N (21 μL, 0.15 mmol), and the mixture was stirred at 60 °C for 90 min. NMR measurement of the resulting brown solution showed the presence of a single product, whose spectrum is diagnostic of *cis,mer*-[$MoCl_2$(NMe)(κ^3-**P4**)] (**5x**). Volatiles were removed under reduced pressure, and KPF_6 (47 mg, 0.26 mmol) and CH_2Cl_2 (5 mL) were added to the residue. After stirring for 48 h at room temperature, the mixture was filtered. Addition of diethyl ether to the filtrate afforded red crystals of **6x**[PF_6]·CH_2Cl_2 (35 mg, 63% yield). **5x**: ^{1}H NMR (C_6D_6): δ 1.18 (br dt, $J_{PH} = 4.2$, 2.9 Hz, 3H, Me). ^{31}P{^{1}H} NMR (C_6D_6): δ −10.3 (d, $J_{PP} = 32$ Hz), 50.3 (d, $J_{PP} = 194$ Hz), 53.8 (ddd, $J_{PP} = 194$, 32, 5 Hz), 105.5 (d, $J_{PP} = 5$ Hz). **6x**[PF_6]·CH_2Cl_2: ^{1}H NMR (CD_2Cl_2): δ 1.48 (quin, $J_{PH} = 3.2$ Hz, 3H, Me), 3.0−3.35 (m, 8H, PCH_2), 6.8−6.9 (m, 4H, aromatic H), 7.0−7.35 (m, 16H, aromatic H), 7.55−7.60, 7.80−7.85 (m, 6H each, aromatic H), 8.0−8.05 (m, 2H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.0, 93.8 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 141$ Hz). Anal. Calcd for $C_{48}H_{47}Cl_3F_6MoNP_5$: C, 51.98; H, 3.72; N, 1.01. Found: C, 52.09; H, 4.24; N, 0.98.

Preparation of *trans*-[MoCl(NPh)(κ^4-P4)][PF_6] (6y[PF_6]). A mixture of **2a** (45 mg, 0.051 mmol) and 1,2-diphenylhydrazine (14 mg, 0.075 mmol) in toluene (5 mL) was refluxed for 90 min. The sole product in the resulting blue-green solution was characterized as *cis,mer*-[$MoCl_2$(NPh)(κ^3-**P4**)] (**5y**) from the NMR spectra. After evaporation of the solvent in vacuo, the residue was stirred with KPF_6 (46 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) at room temperature for 24 h. The mixture was filtered, and the filtrate was evaporated to dryness. After addition of THF (5 mL) and Et_3N (7 μL, 0.051 mmol), the mixture was stirred for 1 h, evaporated again, and washed three times with benzene (5 mL). Recrystallization of the residue from CH_2Cl_2/diethyl ether gave brown crystals of **6y**[PF_6] (21 mg, 38% yield). **5y**: ^{1}H NMR (C_6D_6): δ 5.91 (d, $J = 7.6$ Hz, 2H, *o*-H in NPh), 6.39 (br t, $J = 8.0$ Hz, 2H, *m*-H in NPh). ^{31}P{^{1}H} NMR (C_6D_6): δ −10.2 (d, $J_{PP} = 37$ Hz), 52.9 (d, $J_{PP} = 196$ Hz), 54.4 (ddd, $J_{PP} = 196$, 37, 6 Hz), 103.2 (d, $J_{PP} = 6$ Hz). **6y**[PF_6]: ^{1}H NMR (CD_2Cl_2): δ 3.0−3.5 (m, 8H, PCH_2), 5.22 (d, $J = 7.3$ Hz, 2H, *o*-H in NPh), 6.50 (dd, $J = 8.3$, 7.3 Hz, 2H, *m*-H in NPh), 6.85−7.6 (m, 27H, aromatic H), 7.8−7.9 (m, 6H, aromatic H), 8.0−8.1 (m, 2H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.0, 93.8 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 138$ Hz). Anal. Calcd for $C_{52}H_{47}ClF_6MoNP_5$: C, 57.50; H, 4.31; N, 1.29. Found: C, 56.87; H, 4.36; N, 1.23. Single crystals of **6y**[BF_4] suitable for X-ray crystallographic study were obtained by anion metathesis with $NaBF_4$ followed by crystallization from $ClCH_2CH_2Cl$/diethyl ether.

Reaction of 3a with CF_3SO_3Me. Methyl trifluoromethanesulfonate (13 μL, 0.11 mmol) was added to a benzene solution (5 mL) of **3a**·0.5(C_6H_6) (87 mg, 0.10 mmol) at room temperature. Stirring the mixture for 20 min formed a pink precipitate, which was filtered off and recrystallized from CH_2Cl_2/diethyl ether to give pink microcrystals of **6x**[CF_3SO_3]·0.5(CH_2Cl_2) (78 mg, 71% yield). ^{1}H NMR (CD_2Cl_2): δ 1.48 (quin, $J_{PH} = 3.2$ Hz, 3H, Me), 3.0−3.35 (m, 8H, PCH_2), 6.8−6.9 (m, 4H, aromatic H), 7.0−7.35 (m, 16H, aromatic H), 7.55−7.60, 7.80−7.85 (m, 6H each, aromatic H), 8.0−8.05 (m, 2H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.0, 93.8 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 141$ Hz). IR (KBr, cm^{-1}): 1265, 1149 (ν(S=O)). Anal. Calcd for $C_{48.5}H_{46}Cl_2F_3MoNO_3P_4S$: C, 54.41; H, 4.33; N, 1.31. Found: C, 54.40; H, 4.28; N, 1.09.

Preparation of *cis,mer*-[$MoCl_2$(NCOMe)(κ^3-P4)] (7x). To a solution of **3a**·0.5(C_6H_6) (86 mg, 0.10 mmol) in THF (5 mL) was added acetyl chloride (11 μL, 0.15 mmol), and the solution was stirred at room temperature for 1 h. The color of the solution changed from reddish-orange to green. Concentration of the solution in vacuo followed by addition of hexane formed green crystals of **7x**·THF (78 mg, 76% yield). ^{1}H NMR (acetone-d_6): δ 0.48 (s, 3H, Me), 2.2−4.1 (m, 8H, PCH_2), 6.95−7.25 (m, 7H, aromatic H), 7.3−7.45 (m, 11H, aromatic H), 7.5−7.7 (m, 7H, aromatic H), 7.85−7.9 (m, 2H, aromatic H), 8.0−8.3 (m, 7H, aromatic H), 1.83, 3.66 (m, 4H each, THF). ^{31}P{^{1}H} NMR (acetone-d_6): δ −11.1 (d, $J_{PP} = 41$ Hz), 47.5 (d, $J_{PP} = 182$ Hz), 56.2 (ddd, $J_{PP} = 182$, 41, 5 Hz), 93.8 (d, $J_{PP} = 5$ Hz). IR (KBr, cm^{-1}): 1673 (ν(C=O)). Anal. Calcd for $C_{52}H_{53}Cl_2MoNO_2P_4$: C, 61.55; H, 5.26; N, 1.38. Found: C, 61.91; H, 5.30; N, 1.36.

Preparation of *cis,mer*-[$MoCl_2$(NCOR)(κ^3-P4)] (R = Ph (7y), *p*-Tol (7z)). These complexes were prepared from **3a**·0.5(C_6H_6) and 1.5 equiv of the corresponding acid chlorides according to a method analogous to that for preparing **7x**. **7y**·0.5(THF): 47% yield as yellow-green crystals. ^{1}H NMR (acetone-d_6): δ 2.4−2.55 (m, 1H, PCH_2), 2.7−2.9, 3.05−3.15 (m, 2H each, PCH_2), 3.8−4.15 (m, 3H, PCH_2), 6.95−7.55 (m, 24H, aromatic H), 7.55−7.75 (m, 7H, aromatic H), 7.95−8.1 (m, 6H, aromatic H), 8.2−8.3 (m, 2H, aromatic H), 1.83, 3.66 (m, 2H each, 0.5THF). ^{31}P{^{1}H} NMR (acetone-d_6): δ −10.9 (d, $J_{PP} = 41$ Hz), 49.2 (d, $J_{PP} = 177$ Hz), 55.8 (ddd, $J_{PP} = 177$, 41, 5 Hz), 95.3 (d, $J_{PP} = 5$ Hz). IR (KBr, cm^{-1}): 1644 (ν(C=O)). Anal. Calcd for $C_{55}H_{51}Cl_2MoNO_{1.5}P_4$: C, 63.47; H, 4.94; N, 1.35. Found: C, 63.21; H, 5.09; N, 1.27. **7z**·0.5(THF): 90% yield as yellow-green crystals. ^{1}H NMR (acetone-d_6): δ 2.36 (s, 3H, Me), 2.4−2.55 (m, 1H, PCH_2), 2.7−2.9, 3.0−3.2 (m, 2H each, PCH_2), 3.8−4.15 (m, 3H, PCH_2), 6.95−7.45 (m, 23H, aromatic H), 7.55−7.75 (m, 7H, aromatic H), 7.9−8.1 (m, 6H, aromatic H), 8.25−8.35 (m, 2H, aromatic H), 1.83, 3.66 (m, 2H each, 0.5THF). ^{31}P{^{1}H} NMR (acetone-d_6): δ −10.9 (d, $J_{PP} = 41$ Hz), 49.2 (d, $J_{PP} = 179$ Hz), 55.8 (ddd, $J_{PP} = 179$, 41, 5 Hz), 95.3 (d, $J_{PP} = 5$ Hz). IR (KBr, cm^{-1}): 1642 (ν(C=O)). Anal. Calcd for $C_{56}H_{53}Cl_2MoNO_{1.5}P_4$: C, 63.77; H, 5.06; N, 1.33. Found: C, 63.49; H, 4.98; N, 1.18.

Preparation of *trans*-[MoCl(NCOMe)(κ^4-P4)][PF_6] (8x[PF_6]). A mixture of **7x**·THF (28 mg, 0.028 mmol) and KPF_6 (29 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 18 h. Filtration followed by addition of diethyl ether to the concentrated filtrate formed reddish-purple crystals of **8x**[PF_6]·CH_2Cl_2 (18 mg, 57% yield). ^{1}H NMR (CD_2Cl_2): δ −0.12 (s, 3H, Me), 3.0−3.55 (m, 8H, PCH_2), 6.95−7.35 (m, 20H, aromatic H), 7.5−7.65 (m, 6H, aromatic H), 7.85−7.9 (m, 2H, aromatic H), 7.95−8.10 (m, 6H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 56.7, 93.5 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 133$ Hz). IR (KBr, cm^{-1}): 1697 (ν(C=O)). Anal. Calcd for $C_{49}H_{47}Cl_3F_6MoNOP_5$: C, 51.76; H, 4.17; N, 1.23. Found: C, 51.88; H, 4.08; N, 1.11.

Preparation of *trans*-[MoCl(NCOR)(κ^4-P4)][PF_6] (R = Ph (8y[PF_6]), *p*-Tol (8z[PF_6])). These complexes were obtained in a manner similar to that for **8x**[PF_6] from **7y** or **7z** with excess KPF_6. **8y[PF_6]**: 51% yield as reddish-purple crystals. ^{1}H NMR (CD_2Cl_2): δ 3.0−3.6 (m, 8H, PCH_2), 6.43 (dd, $J = 8.3$, 1.0 Hz, 2H, *o*-H of COPh), 6.55 (br t, $J = 7.6$ Hz, 2H, *m*-H of COPh), 6.95−7.3 (m, 21H, aromatic H), 7.4−7.5 (m, 6H, aromatic H), 7.8−7.9 (m, 2H, aromatic H), 7.95−8.05 (m, 6H, aromatic H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 55.8, 93.4 (AA′XX′ pattern: $J_{AX} + J_{AX'} = 129$ Hz). IR (KBr, cm^{-1}): 1647 (ν(C=O)). Anal. Calcd for $C_{53}H_{47}ClF_6MoNOP_5$: C, 57.13; H, 4.25; N, 1.26. Found: C, 56.67; H, 4.14; N, 1.02. **8z[PF_6]**: 71% yield as reddish-purple crystals. ^{1}H NMR (CD_2Cl_2): δ 2.08 (s, 3H, Me), 3.0−3.6 (m, 8H, PCH_2), 6.32 (s, 4H, MeC_6H_4), 6.95−7.3 (m, 20H, aromatic H), 7.4−7.5 (m, 6H, aromatic H), 7.8−7.9 (m, 2H, aromatic H), 7.95−8.05 (m, 6H,

Table 1. Crystallographic Data for 3a·0.5(C_6H_6), 4a[BF_4]·0.25(CH_2Cl_2)·0.25(Et_2O), 4c[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O), and 6x[PF_6]·CH_2Cl_2

	3a·0.5(C_6H_6)	**4a**[BF_4]·0.25(CH_2Cl_2)·0.25(Et_2O)	**4c**[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O)	**6x**[PF_6]·CH_2Cl_2
formula	$C_{49}H_{45}ClNMoP_4$	$C_{47.25}H_{46}BCl_{1.5}F_4NMoO_{0.25}P_4$	$C_{72.95}H_{70.2}BBrCl_{0.7}NO_{0.65}P_4W$	$C_{48}H_{47}Cl_3F_6NMoP_5$
fw	903.19	991.71	1394.64	1109.06
space group	*C*2/*c* (no. 15)	*P*$\bar{1}$ (no. 2)	$P2_1/a$ (no. 14)	$P2_1/n$ (no. 14)
a, Å	31.555(7)	10.368(3)	21.378(4)	14.955(2)
b, Å	14.956(3)	10.953(3)	13.828(2)	21.017(3)
c, Å	22.808(5)	22.328(7)	23.027(4)	15.553(2)
α, deg	90	77.59(1)	90	90
β, deg	119.6042(7)	86.42(1)	107.5212(8)	90.036(2)
γ, deg	90	69.16(1)	90	90
V, Å^3	9359(3)	2314(1)	6491(2)	4889(1)
Z	8	2	4	4
ρ_{calcd}, g cm^{-3}	1.282	1.423	1.427	1.507
μ, mm^{-1}	0.506	0.558	2.570	0.653
cryst size, mm^3	0.5 × 0.4 × 0.3	0.3 × 0.15 × 0.1	0.5 × 0.4 × 0.2	0.4 × 0.4 × 0.1
transmn factor	0.629−0.859	0.744−0.946	0.489−0.598	0.727−0.937
no. of reflns unique	10 856 (R_{int} = 0.024)	10 523 (R_{int} = 0.036)	14 976 (R_{int} = 0.038)	11 274 (R_{int} = 0.029)
no. of reflns obsd[a]	8221	6144	9778	7724
no. of variables	568	601	873	624
R_1[b]	0.049	0.047	0.042	0.036
wR_2[c]	0.145	0.138	0.131	0.120
gof[d]	1.01	1.01	1.02	1.03

[a] $F_o^2 > 2\sigma(F_o^2)$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ ($w = [\sigma(F_o^2) + aF_o^2 + b]^{-1}$) for all unique data. [d] gof = $[\sum w(F_o^2 - F_c^2)^2/\{$(no. of reflns obsd) − (no. of variables)$\}]^{1/2}$.

aromatic H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 55.8, 93.4 (AA′XX′ pattern: $J_{AX} + J_{AX'}$ = 130 Hz). IR (KBr, cm^{-1}): 1642 (ν(C═O)). Anal. Calcd for $C_{54}H_{49}ClF_6MoNOP_5$: C, 57.49; H, 4.38; N, 1.24. Found: C, 57.28; H, 4.29; N, 1.19.

Preparation of *trans*-[MoCl(NCONHPh)(κ^4-P4)][BF_4] (9y[BF_4]). To a solution of **4a**[BF_4] (38 mg, 0.039 mmol) in dichloroethane (4 mL) were added phenyl isocyanate (13 μL, 0.12 mmol) and Et_3N (1 μL, 7 μmol) at room temperature with stirring. The color of the solution turned from reddish-purple to brown during 2 h. Addition of diethyl ether to the concentrated solution gave brown crystals of **9y**[BF_4] (24 mg, 57% yield). ^1H NMR (CD_2Cl_2): δ 3.05−3.40 (m, 8H, PCH_2), 3.62 (br, 1H, NH), 6.14 (d, *J* = 7.6 Hz, 2H, *o*-H of NPh), 6.9−7.15 (m, 21H, aromatic H), 7.2−7.3 (m, 2H, aromatic H), 7.55−7.6 (m, 6H, aromatic H), 7.95−8.0 (m, 2H, aromatic H), 8.1−8.2 (m, 6H, aromatic H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.1, 93.5 (AA′XX′ pattern: $J_{AX} + J_{AX'}$ = 138 Hz). IR (KBr, cm^{-1}): 3381 (ν(N−H)), 1681 (ν(C═O)), 1511 (δ(NH)). Anal. Calcd for $C_{53}H_{48}BClF_4MoN_2OP_4$: C, 59.43; H, 4.52; N, 2.62. Found: C, 58.81; H, 4.47; N, 2.57.

Preparation of *trans*-[$MoCl_2$(NCONHTol-*p*)(κ^4-P4)][BF_4] (9z[BF_4]). This complex was obtained as brown crystals (39 mg, 74% yield) from **4a**[BF_4] (47 mg, 0.048 mmol) in a fashion analogous to that for **9y**[BF_4], where phenyl isocyanate was replaced by *p*-tolyl isocyanate (19 μL, 0.15 mmol). ^1H NMR (CD_2Cl_2): δ 2.18 (s, 3H, Me), 3.0−3.4 (m, 8H, PCH_2), 3.58 (br, 1H, NH), 6.03 (d, *J* = 8.5 Hz, 2H, MeC_6H_4), 6.8−7.15 (m, 20H, aromatic H), 7.2−7.3 (m, 2H, aromatic H), 7.55−7.6 (m, 6H, aromatic H), 7.9−8.0 (m, 2H, aromatic H), 8.1−8.2 (m, 6H, aromatic H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 57.9, 93.4 (AA′XX′ pattern: $J_{AX} + J_{AX'}$ = 138 Hz). IR (KBr, cm^{-1}): 3391 (ν(N−H)), 1678 (ν(C═O)), 1513 (δ(NH)). Anal. Calcd for $C_{54}H_{50}BClF_4MoN_2OP_4$: C, 59.77; H, 4.64; N, 2.58. Found: C, 59.70; H, 4.68; N, 2.44.

Preparation of *trans*-[MoCl(NCSNHPh)(κ^4-P4)][PF_6] (10y[PF_6]). Phenyl isothiocyanate (15 μL, 0.12 mmol) and Et_3N (1 μL, 7 μmol) were added to **4a**[PF_6] (40 mg, 0.040 mmol) dissolved in CH_2Cl_2 (4 mL), and the solution was stirred at room temperature for 24 h. The resulting red solution was concentrated, and diethyl ether was added to deposit a brown solid of **10y**[PF_6] (32 mg, 69% yield). ^1H NMR (CD_2Cl_2): δ 3.05−3.5 (m, 8H, PCH_2), 5.24 (br s, 1H, NH), 6.21 (br d, *J* = 6 Hz, 2H, *o*-H of NPh), 6.95−7.15 (m, 21H, aromatic H), 7.2−7.3 (m, 2H, aromatic H), 7.55−7.6 (m, 6H, aromatic H), 7.9−7.95 (m, 2H, aromatic H), 8.05−8.2 (m, 6H, aromatic H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 56.0, 93.7 (AA′XX′ pattern: $J_{AX} + J_{AX'}$ = 136 Hz). IR (KBr, cm^{-1}): 3348 (ν(N−H)), 1360 (δ(NH)), 1096 (ν(C═S)). Anal. Calcd for $C_{53}H_{48}ClF_6MoN_2P_5S$: C, 55.58; H, 4.22; N, 2.45. Found: C, 55.44; H, 4.26; N, 2.37.

Reaction of 7z with KOH. To a THF (5 mL) solution of **7z**·0.5THF (53 mg, 0.050 mmol) was added a 0.5 M aqueous KOH solution (1 mL, 0.5 mmol), and the mixture was stirred vigorously at room temperature for 1 h. The green solution turned to red during this period. HPLC analysis of the resultant solution confirmed the formation of *p*-TolCONH$_2$ in 24% yield.

Reaction of 7z with $NaBH_4$. A mixture of **7z**·0.5THF (42 mg, 0.040 mmol) and $NaBH_4$ (66 mg, 1.7 mmol) in EtOH (4 mL) was stirred at room temperature for 1 h. HPLC analysis of the resulting reddish-orange solution showed the formation of *p*-TolCONH$_2$ and *p*-TolCN in 52% and <1% yields, respectively.

Reaction of 7z with $LiAlH_4$. A solution of **7z**·0.5THF (42 mg, 0.040 mmol) and $LiAlH_4$ (15 mg, 0.40 mmol) in THF (4 mL) was stirred at room temperature for 1 h, and then the resulting dark green suspension was quenched by adding EtOH (4 mL). After stirring the mixture for 1 h, the liquid phase was analyzed by GLC, which revealed the formation of *p*-TolCH$_2$NH$_2$ in 64% yield.

Crystallography. Single crystals of **3a**·0.5(C_6H_6), **4a**[BF_4]·0.25(CH_2Cl_2)·0.25(Et_2O), **6x**[PF_6]·CH_2Cl_2, **6y**[BF_4], **7x**·THF, **8x**[PF_6]·CH_2Cl_2, and **9z**[BF_4] were obtained by the procedures stated above, whereas those of **4c**[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O) were used immediately after collecting from the mother liquor. These were sealed in glass capillaries under argon and mounted on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromatized Mo Kα source. Diffraction data were collected at 20 °C and processed using the CrystalClear program package.[50] All data were corrected for absorption (based on multiscans) and for Lorentz and polarization effects. Details of the X-ray diffraction study are listed in Tables 1 and 2.

Structure solution and refinements were carried out by using the CrystalStructure program package.[51] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY)[52]

(50) *CrystalClear 1.3.5*; Rigaku Corporation, 1998−2003.

(51) *CrystalStructure 3.6.0*, Crystal structure analysis package; Rigaku and Rigaku/MSC: 9009 New Trails Dr., The Woodlands, TX 77381, 2000−2004.

Table 2. Crystallographic Data for 6y[BF_4], 7x·THF, 8x[PF_6]·CH_2Cl_2, and 9z[BF_4]

	6y[BF_4]	**7x**·THF	**8x**[PF_6]·CH_2Cl_2	**9z**[BF_4]
formula	$C_{52}H_{47}BClF_4NMoP_4$	$C_{52}H_{53}Cl_2NMoO_2P_4$	$C_{49}H_{47}Cl_3F_6NMoOP_5$	$C_{54}H_{50}BClF_4N_2MoOP_4$
fw	1028.04	1014.74	1137.07	1085.09
space group	*Pna*2$_1$ (no. 33)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	*Pna*2$_1$ (no. 33)
a, Å	19.402(2)	9.602(3)	14.935(2)	19.422(3)
b, Å	17.427(2)	14.550(4)	21.363(4)	18.184(2)
c, Å	14.257(2)	17.553(5)	15.569(3)	14.219(2)
α, deg	90	98.444(5)	90	90
β, deg	90	92.608(4)	90.9925(7)	90
γ, deg	90	93.140(4)	90	90
V, Å^3	4821(1)	2418(1)	4967(1)	5022(1)
Z	4	2	4	4
ρ_{calcd}, g cm^{-3}	1.416	1.393	1.521	1.435
μ, mm^{-1}	0.512	0.554	0.647	0.498
cryst size, mm^3	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.1	0.35 × 0.15 × 0.1	0.25 × 0.25 × 0.2
transmn factor	0.690−0.858	0.715−0.946	0.714−0.937	0.882−0.905
no. of reflns unique	10 706 (R_{int} = 0.032)	11 012 (R_{int} = 0.035)	11 624 (R_{int} = 0.039)	11 853 (R_{int} = 0.038)
no. of reflns obsd[a]	7568	6109	7518	7493
no. of variables	661	612	642	667
R_1[b]	0.033	0.044	0.042	0.034
wR_2[c]	0.109	0.140	0.126	0.116
gof[d]	1.03	1.01	1.01	1.03

[a] $F_o^2 > 2\sigma(F_o^2)$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ ($w = [\sigma(F_o^2) + aF_o^2 + b]^{-1}$) for all unique data. [d] gof = $[\sum w(F_o^2 - F_c^2)^2/\{$(no. of reflns obsd) − (no. of variables)$\}]^{1/2}$.

and subsequent Fourier synthesis (DIRDIF 99).[53] These were refined by full-matrix least-squares techniques with anisotropic thermal parameters except for those stated otherwise below. Thermal ellipsoids of non-hydrogen atoms are drawn at the 30% probability level in all figures. The C−H hydrogen atoms were placed at the calculated positions and included in the final stages of the refinements with fixed parameters, while the N−H hydrogen atoms were found in difference Fourier maps and refined with isotropic parameters. The absolute structures of **6y**[BF_4] and **9z**[BF_4] were determined by refinement of Flack parameters (x = 0.26(3) and 0.15(3), respectively).[54] As for **3a**·0.5(C_6H_6), atoms in the CH_2−P(4)−Ph moiety were found in the two disordered positions with occupancies of 0.5 each, while another phenyl group was also disordered toward two orientations but with occupancies of 0.7 and 0.3. The phenyl groups of 0.5 and 0.3 occupancies in this solution were refined isotropically. In each of **4a**[BF_4]·0.25(CH_2Cl_2)·0.25(Et_2O) and **4c**[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O), the solvent molecules were found overlapping at the same site in the crystal, and these were refined isotropically with the restraints of the bond lengths and angles. Three phenyl groups in the cationic part of **4c**[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O) were located at the disordered positions in 0.55/0.45, 0.75/0.25, and 0.75/0.25 ratios, among which the C atoms of 0.25 occupancy were refined isotropically. In addition, the BF_4 anion in **6y**[BF_4] was disordered in two orientations in a 0.7/0.3 ratio.

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Supporting Information Available: Crystallographic data of **3a**·0.5(C_6H_6), **4a**[BF_4]·0.25(CH_2Cl_2)·0.25(Et_2O), **4c**[BPh_4]·0.35(CH_2Cl_2)·0.65(Et_2O), **6x**[PF_6]·CH_2Cl_2, **6y**[BF_4], **7x**·THF, **8x**[PF_6]·CH_2Cl_2, and **9z**[BF_4] in CIF format and detailed experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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