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Mixed Dinitrogen–Organocyanamide Complexes of Molybdenum(0) and Their Protic Conversion into Hydrazide and Amidoazavinylidene Derivatives

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Organocyanamides, $N{\equiv}CNR_2$ (R = Me or Et), react with *trans*-$[Mo(N_2)_2(dppe)_2]$ (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$), in THF, to give the first mixed molybdenum dinitrogen–cyanamide complexes *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$ (R = Me **2a** or Et **2b**) which are selectively protonated at N_2 by HBF_4 to yield the hydrazide(2–) complexes *trans*-$[Mo(NNH_2)(NCNR_2)(dppe)_2][BF_4]_2$ (R = Me, **3a**, or Et, **3b**). On treatment with $Ag[BF_4]$, oxidation and metal fluorination occur, and the ligating cyanamide undergoes an unprecedented β-protonation at the unsaturated C atom to form *trans*-$[MoF(NCHNR_2)(dppe)_2][BF_4]_2$ (R = Me, **4a**, or Et, **4b**) compounds which present the novel amidoazavinylidene (or amidomethyleneamide) ligands. Complexes **4** are also formed from the corresponding compounds **3**, with liberation of ammonia and hydrazine. The crystal structure of **2b** was determined by single-crystal X-ray diffraction analysis which indicates that the N atom of the amide group has a trigonal planar geometry.

Introduction

Cyanamides, $N{\equiv}CNR_2$ (R = H, alkyl or aryl), can be regarded as amino-functionalized nitriles, but despite the well developed coordination chemistry of organonitriles[1,2] and of the biological and synthetic interest of such species [in particular cyanamide itself, $N{\equiv}CNH_2$, and its dimeric form, cyanoguanidine, $NCNC(NH_2)_2$],[3−8] only scarce examples of reactions of cyanamide ligands have been reported, and the study of their activation by coordination to a transition metal center still remains virtually unexplored, as well as the effect of the amino moiety on the reactivity of the cyano group. Insertion into a metal−carbon multiple bond,[9−13] metathesis with a metal−metal triple bond,[14] nucleophilic addition of an oxime[15] or of an alcohol (in this case to cyanoguanidine)[16] to form a five- or six-membered azametallacycle, respectively, and dehydrogenation of $NCNH_2$ followed by electrophilic addition[17,18] or deprotonation or deamination (of cyanoguanidine)[19] are the most significant reactions reported so far.

In this study, we have searched for an unprecedented type of cyanamide reactivity by ligation to an electron-rich transition metal center, *trans*-$\{Mo(dppe)_2\}$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which is able[20,21] to ligate dinitrogen and activate

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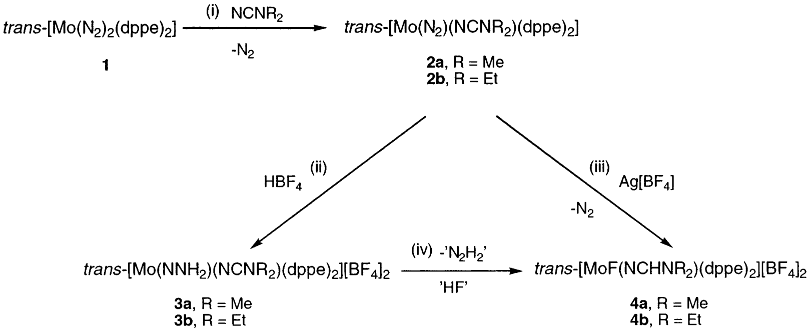
Scheme 1. Formation of the Mixed Dinitrogen−Cyanamide Complexes and Derived Hydrazide(2−) and Amidoazavinylidene Compounds



it toward electrophilic attack. For this purpose, we have prepared the first mixed cyanamide−dinitrogen complexes of molybdenum, *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$ (R = Me, **2a**, or Et, **2b**), and studied their protic reactions, what has also allowed a comparison between the behaviors of the cyanamide and dinitrogen (as well as of nitrile) ligands activated by a common metal center. In particular, the first electrophilic addition has been achieved to the cyano group of a cyanamide ligand which, however, behaves as a weaker base than dinitrogen and an organonitrile. The electrophilic addition reaction (which has previously been observed for nitriles,[22−29] isocyanides,[30−41] cyanide,[32,34,41−46] alkyne-derived species,[38−41,47−53] or phosphaalkynes[47,54,55] when ligating the above or a related N_2-binding phosphinic transition metal center) has thus been extended for the first time to cyanamide ligands.

Results and Discussion

Mixed Dinitrogen−Organocyanamide Complexes. Treatment of a THF solution of the dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$ (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$), at room temperature, with an excess (10-fold molar ratio) of the appropriate organocyanamide, $N{\equiv}CNR_2$ (R = Me or Et), leads to the formation [reaction i, Scheme 1] of the corresponding monocyanamide complexes *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$ (R = Me, **2a**, or Et, **2b**) which have been isolated, after ca. 3 h, in high yield (ca. 80−85%), as a brick (**2a**) or dark red (**2b**) solid. These complexes represent the first mixed dinitrogen−cyanamide complexes of molybdenum and relate to the dinitrogen−organonitrile compounds *trans*-$[Mo(N_2)(NCR)(dppe)_2]$ (R = alkyl or aryl) prepared by Hidai et al.[56] by an identical route. The mixed rhenium *mer*-$[ReCl(N_2)(NCNR_2)(PMePh_2)_3]$ complexes have already been prepared,[57] but their reactions have not yet been reported.

Complexes **2** have strong IR bands assigned to $\nu(N{\equiv}N)$ at ca. 1900 cm^{-1} and to $\nu(N{\equiv}C)$ at ca. 2190 cm^{-1}. The former value is slightly lower than that, 1975 cm^{-1}, displayed

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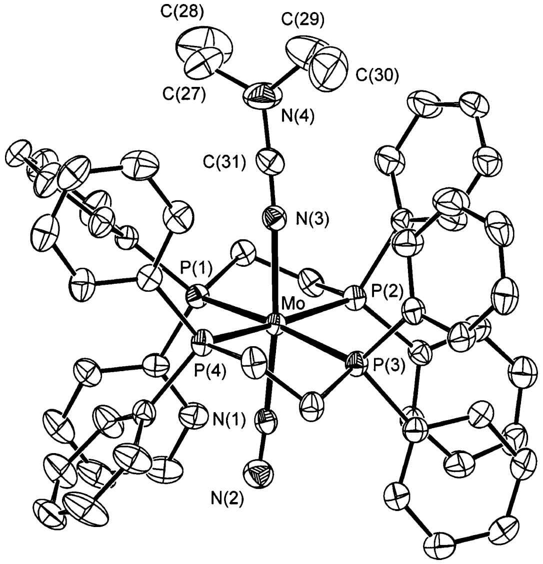


Figure 1. Molecular structure of the complex *trans*-[Mo(N_2)($NCNEt_2$)(dppe)$_2$], **2b**, with ellipsoids at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex *trans*-[Mo(N_2)($NCNEt_2$)(dppe)$_2$], **2b**[a]

Mo−N(1)	1.994(4)	N(3)−Mo−P(1)	84.04(12)
Mo−N(3)	2.151(4)	N(3)−Mo−P(2)	85.53(12)
Mo−P(1)	2.4479(14)	N(3)−Mo−P(3)	102.19(12)
Mo−P(2)	2.4361(15)	N(3)−Mo−P(4)	90.34(12)
Mo−P(3)	2.4393(14)	P(1)−Mo−P(2)	80.85(5)
Mo−P(4)	2.4601(16)	P(2)−Mo−P(3)	96.63(5)
N(1)−N(2)	1.084(8)	P(3)−Mo−P(4)	80.07(5)
N(3)−C(31)	1.142(8)	P(1)−Mo−P(4)	102.98(5)
C(31)−N(4)	1.334(9)	P(1)−Mo−P(3)	173.14(5)
N(4)−C(27)	1.423(14)	P(2)−Mo−P(4)	174.07(5)
C(27)−C(28)	1.418(18)	Mo−N(1)−N(2)	177.4(5)
N(4)−C(29)	1.419(14)	Mo−N(3)−C(31)	173.1(5)
C(29)−C(30)	1.396(18)	N(3)−C(31)−N(4)	178.0(7)
N(1)−Mo−N(3)	173.37(18)	C(31)−N(4)−C(27)	122.1(7)
N(1)−Mo−P(1)	89.99(13)	N(4)−C(27)−C(28)	112.4(10)
N(1)−Mo−P(2)	96.39(13)	C(31)−N(4)−C(29)	122.2(7)
N(1)−Mo−P(3)	83.93(13)	N(4)−C(29)−C(30)	114.1(10)
N(1)−Mo−P(4)	88.18(13)	C(27)−N(4)−C(29)	115.8(8)

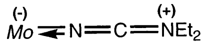
[a] esd's in parentheses.

by the parent bis(dinitrogen) complex **1**, and the latter, ν(N≡C), is shifted to a lower wavenumber (by ca. 25 cm^{-1}) in comparison with that exhibited by the free organocyanamide, as a result of the strong π-electron releasing ability of the electron-rich Mo(0) site. Complexes **2** are unstable in air and also commonly undergo significant decomposition in solution, even under N_2, which precludes a reliablecollection of NMR data in the usual deuterated solvents. In agreement with the lability of the N_2 ligand, their FAB$^+$-MS spectra, run in nitrobenzyl alcohol matrixes, do not show the corresponding molecular ions ([M$^+$]), although the fragments derived from loss of N_2, i.e., [M − N_2]$^+$, are clearly observed at *m*/*z* 964 (**2a**) or 992 (**2b**).

Their formulation was authenticated by a single-crystal X-ray diffraction analysis of diethylcyanamide complex **2b** whose molecular structure is depicted in Figure 1, and selected bond lengths and angles are listed in Table 1. The Mo atom exhibits octahedral-type coordination, with the four P atoms in the equatorial positions, whereas the apical positions are occupied by the terminal N atoms of the *trans* dinitrogen and cyanamide ligands which present linear coordinations.

The Mo−N bond length for the N_2 ligand, 1.994(4) Å, is comparable with that, 2.014(5) Å,[58] of the bis(dinitrogen) complex *trans*-[Mo(N_2)$_2$(dppe)$_2$], **1**, but marginally shorter than those for the mixed carbonyl complexes *trans*-[Mo(N_2)(CO)(dppe)$_2$], 2.068(12) Å,[59] and *trans*-[Mo(N_2)(CO){($PhCH_2$)$_2CH_2CH_2P$(CH_2Ph)$_2$}$_2$], 2.090(3) Å,[60] in accord with the strong competition of CO for the metal d$_\pi$ electron density. The Mo−N distance for the $NCNEt_2$ ligand, 2.151(4) Å, is identical to that, 2.168(6) Å,[61] in [Mo_2($OCH_2{}^tBu$)$_6$(μ-C_4Me_4)($NCNEt_2$)]. The N≡N and N≡C bond lengths, 1.084(8) and 1.142(8) Å, respectively, are similar to those of the free ligands [1.0976(1) Å[62] for N_2 and 1.1609(16) Å[63a] for the related dimethylcyanamide, $NCNMe_2$].

The N atom of the amide group, N(4), has a trigonal planar geometry [the N(4), C(27), C(29), C(31) and N(3) atoms are coplanar] rather than a pyramidal one, indicating a significant contribution of the canonical form (**a**).



$$\overset{(-)}{Mo} \leftarrow N{=}C{=}\overset{(+)}{N}Et_2$$

a

The trigonal planar geometry has also been reported for other complexes such as [Cr($NCNEt_2$)(CO)$_5$],[64] *trans*-[Fe($NCNEt_2$)$_2$(depe)$_2$][BF_4]$_2$ (depe = $Et_2PCH_2CH_2PEt_2$),[65] *trans*-[Pt(CF_3)($NCNEt_2$)(PPh_3)$_2$][BF_4],[66] or *cis*-[Pt($NCNEt_2$)$_2$(PPh_3)$_2$][BF_4]$_2$,[15] whereas the pyramidal one is displayed by *mer*-[$ReCl_2$($NCNEt_2$)($PMePh_2$)$_3$][67] and by the uncoordinated $NCNMe_2$.[63]

Hydrazide(2−) and Amidoazavinylidene Complexes. Treatment of a THF solution of the mixed dinitrogen−cyanamide complexes *trans*-[Mo(N_2)($NCNR_2$)(dppe)$_2$] (R = Me **2a** or Et **2b**), at low temperature (−60 °C), with HBF_4 (a diluted diethyl ether solution [Et_2OH][BF_4] added dropwise, ca. 4.5 molar ratio of acid relative to the complex),

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resulted [reaction ii, Scheme 1] in the formation of a pale green precipitate of the corresponding hydrazide(2−) products *trans*-$[Mo(NNH_2)(NCNR_2)(dppe)_2][BF_4]_2$ (R = Me, **3a**, or Et, **3b**), which were isolated in good yield (ca. 62−66%).

The reaction is related to the known[68] protonation at one of the N_2 ligands in *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W) to give, on loss of the other N_2 and metal fluorination, the hydrazide(2−) products $[MF(NNH_2)(dppe)_2][BF_4]$, but in the case of complexes **2**, the stronger coordination ability of the organocyanamide, in comparison with dinitrogen, allows its retention in the metal coordination sphere. To the best of our knowledge, there are only two more examples in the literature of isolated hydrazide(2−) complexes which result from protonation of coordinated N_2 to NNH_2(2−) occurring without loss of a ligand: *trans*-$[M(NNH_2)(NC^nPr)(dppe)_2][HSO_4]_2$ (M = Mo or W)[69a] and *fac*-$[Mo(NNH_2)\{PhP(CH_2CH_2PPh_2)_2\}(Me_2PCH_2PMe_2)][CF_3SO_3]_2$.[69b] In the present case, the protonation of N_2 at complexes **2** to yield NNH_2(2−) in **3** with resulting metal oxidation leads to a significant increase (by ca. 40 cm^{-1}) of the IR $\nu(N{\equiv}C)$ of the organocyanamide ligand [2231 (**3a**) or 2225 (**3b**) cm^{-1}] which becomes even higher (by ca. 15 cm^{-1}) than the value of the corresponding free species. This indicates that, in contrast to complexes **2** of Mo(0), in the Mo(IV) complexes **3** the organocyanamide ligand behaves as a predominant σ-donor and not as an effective π-acceptor.

In complexes **3**, the hydrazide(2−) ligand is clearly detected by its strong IR band at 1618 cm^{-1} due to $\delta(NH_2)$, and the $\nu(NH_2)$ medium intensity bands in the 3418−3237 cm^{-1} range. Particularly, the presence of the bending mode is consistent with both hydrogen atoms attached to the same nitrogen atom. In their ^1H NMR spectra (CD_2Cl_2), broad resonances at δ 7.00 (**3a**) or 6.83 (**3b**), which disappear upon deuteriation, are assigned to NNH_2. In fact, these shifts support the hydrazide formulation, NNH_2, rather than the diazene one, NHNH, for which the NH protons resonance should occur as two distinct multiplets at significantly lower fields;[70] furthermore, ready H/D exchange upon addition of D_2O is a common feature for several hydrazide(2−) complexes.[68a] The expected ^1H and ^{13}C NMR resonances of the organocyanamides have also been unambiguously identified, and, e.g., for **3a**, the methyl-protons resonance occurs as a singlet at δ 2.02 whereas the cyano-carbon resonance is a singlet at δ 130.02 (or 129.72 for **3b**).

In the FAB^+-MS spectra of complexes **3**, the molecular ions ($[M^+]$) are not detected, but the fragments derived from NNH_2 loss $[M - NNH_2]^+$ [*m*/*z* 964 (**3a**) or 992 (**3b**)] and metal fluorination $[M - NNH_2 + F]^+$ [*m*/*z* 983 (**3a**) or 1011 (**3b**)] are clearly observed with the expected isotopic patterns. These observations suggest that the NNH_2 ligand exhibits a significant lability, being readily displaced by fluoride, at least in FAB conditions. Interestingly, this behavior is consistent with that observed in solution (see in a following paragraph).

The formation of complexes **3** involves β-protonation at the N_2 ligand in the mixed dinitrogen−organocyanamide parent complexes **2**. Hence, the commonly inert N_2 ligand is more susceptible to protonation than the organocyanamide co-ligand in compounds **2**, and the proton addition occurs selectively at the former. Although a similar reaction was reported[69a] between *trans*-$[M(N_2)(NC^nPr)(dppe)_2]$ (M = Mo or W) and H_2SO_4 to give $[M(NNH_2)(NC^nPr)(dppe)_2][HSO_4]_2$, these behaviors contrast sharply with those observed[28,29] for the reactions of HBF_4, HCl, or HBr with the series *trans*-$[M(N_2)(NCR)(dppe)_2]$ (HBF_4: M = Mo, R = Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*, Me;[28] M = W, R = Me.[29] HCl: M = Mo or W, R = Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*, Me.[28] HBr: M = Mo, R = Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*, Me[28]) in which the organonitrile undergoes double protonation at the cyano-carbon, with formation, on N_2 loss, of the imido-complexes *trans*-$[MX(NCH_2R)(dppe)_2]^+$ (X = F, Cl, or Br). Therefore, although such protonations appear to depend on the nature of the acid, the reactions with HBF_4 suggest that those ligands can be ordered as follows according to their Brönsted basicity: NCR > N_2 > $NCNR_2$. The ligating organocyanamides appear to behave as the weakest bases despite the strong overall (resonance/inductive) electron-donor character of the NR_2 group. Although this character could enhance the nucleophilicity of the adjacent cyano-group, the effect appears to be transmitted to the metal (see above form **a**), thus promoting its π-electron release to the N_2 ligand which is in *trans* position to the cyanamide.

Nevertheless, the organocyanamide in complexes **2** is also activated toward protonation and treatment of a THF solution of **2a** or **2b**, at low temperature (−80 °C), with $Ag[BF_4]$, followed by diethyl ether addition, affords [reaction iii, Scheme 1] *trans*-$[MoF(NCHNR_2)(dppe)_2][BF_4]_2$ (R = Me **4a** or Et **4b**) which were isolated in a considerable yield (ca. 65%) as a greenish yellow (**4a**) or dark yellow (**4b**) solid. To the best of our knowledge, these products present the previously unknown amidoazavinylidene (or amidomethyleneamide) ligand $N{=}CHNR_2$ (R = Me or Et) formally derived from protonation at the cyano-C atom of the organocyanamide, an unprecedented reaction of this species which, thus, is shown to be susceptible to protonation similarly to an organonitrile (NCR) when activated by the electron-rich metal center in the described[28,29] *trans*-$[M(N_2)(NCR)(dppe)_2]$ (M = Mo or W) complexes. This type of reaction was first reported[22−24] for *trans*- or *cis*-$[ReCl(NCR)(dppe)_2]$ which, on reaction with HBF_4, generate the azavinylidene (or methyleneamide) complexes *trans*- or *cis*-$[ReCl(NCHR)(dppe)_2][BF_4]$, and parallels the behavior observed for other unsaturated species, such as isocyanides,[30−41] vinylidenes,[49] or phenylallene,[48,52,53] ligating the $\{ReCl(dppe)_2\}$ or $\{M(dppe)_2\}$ (M = Mo or W) metal sites.

The formation of complexes **4a** or **4b** by reaction of the Mo(0) complexes **2a** or **2b** with $Ag[BF_4]$ involves metal oxidation by Ag^+, with resulting loss of the labile N_2 ligand,

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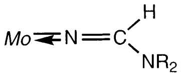
nucleophilic attack by $[BF_4]^-$ at the metal leading to fluorination, and protonation of the ligating $NCNR_2$ which occurs even without the deliberate addition of an acid. Traces of moisture in the solvents used and/or in the hygroscopic silver salt conceivably constitute the proton source, although a radical process (involving the THF solvent as the hydrogen source) cannot be ruled out. Preliminary cyclic voltammetric experiments, at low temperature, in dried $[NBu_4][BF_4]$/THF show that complexes **4a** or **4b** are only formed upon oxidation of the corresponding **2a** or **2b** parent complexes. The protonation occurs selectively at the ligated cyano-group rather than at the amide part of the $NCNR_2$ ligand, being consistent with the relevance of the activating role of the metal on the former group and also with the shown VB form (**a**) with a positive charge localized at the amide N atom.

Complexes **4** are also formed by slow spontaneous decomposition in $CHCl_3$ or CH_2Cl_2 solution of the corresponding hydrazide(2−) compounds *trans*-$[Mo(NNH_2)(NCNR_2)(dppe)_2][BF_4]_2$, **3a** or **3b**, with formal loss of N_2H_2 and addition of "HF" [reaction iv, Scheme 1], thus somehow paralleling the behavior of the latter complexes in FAB$^+$-MS conditions (see previous description). This conversion was monitored by ^1H and ^{31}P-$\{^1H\}$ NMR in $CDCl_3$ and also accounts for the isolation (in greater amounts for extended reaction times) of **4a** and **4b** from the mother liquor in the synthesis of **3a** or **3b** by reaction of HBF_4 with *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$, **2a** or **2b**. The **3** → **4** conversion also leads to the formation of ammonia and hydrazine (molar yields of ca. 8.5 and 2.5%, respectively, relative to the metal or to NNH_2), the formation of ammonia being highly promoted (above 40% yield) by the addition of a catalytic amount of HBF_4 (0.10 HBF_4/complex molar ratio).

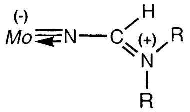
Reaction iv (Scheme 1) can alternatively be viewed as formally involving an intramolecular prototropic shift from the ligating NNH_2(2−) to the cyanamide ligand, followed by displacement of the resulting diazenide (NNH^-) by fluoride. However, the driving forces are not clearly envisaged for these processes which, moreover, do not appear to have a precedent, although a proton transfer between β-ketonitrile species has been reported[27,28] for the $\{Mo(dppe)_2\}$ metal center, on treatment of *trans*-$[Mo(N_2)_2(dppe)_2]$, **1**, with an excess of $N{\equiv}CCH_2COR$ to afford the (alkyleneamido)(nitrile−enolato) complexes *trans*-$[Mo(NCHCH_2COR)(NCCHCOR)(dppe)_2]$ which further convert into nitride products. Hence, the mode of conversion of the NNH_2 ligand in complexes **3** into N_2H_4 and NH_3 could not be elucidated.

Decomposition reactions of hydrazide(2−) ligands have been reported only scantly and are not yet well understood. They are dependent on a variety of factors and can lead namely to hydride ligands (with N_2 loss)[69b] or, in an acid catalyzed process, to bridging hydrazide(3−), $(N{-}NH)^{3-}$, or bridging hydrazide(4−), $(N{-}N)^{4-}$, ligands.[71]

In complexes **4a** and **4b**, the amidoazavinylidene ligands have been clearly identified by ^{13}C and ^1H NMR and IR spectroscopies and can be represented, in a VB formalism, as a hybrid of the canonical forms (**b**) and (**c**), corresponding to formal 3- or 5-electron donors (the latter with an imido character) and conferring the 16- or 18-electron configuration to the metal center, respectively.



b



c

The methylene-carbon N*C*HNR$_2$ resonance, in the ^{13}C-$\{^1H\}$ NMR spectra, is a singlet at δ 162.54 (**4a**) or 162.32 (**4b**), which splits in the expected doublet ($J_{CH} \approx 200$ Hz) in the ^1H-undecoupled spectra and falls within the chemical shift range, δ 157−169, known[72] for the amidinium species $[H(R^1)NC(R^2){=}NR^3(R^4)]^+$. The other carbon nuclei of the $NCHNR_2$ ligands resonate as expected, e.g., for **4a** as two singlets, in the ^{13}C-$\{^1H\}$ NMR spectra, at δ 44.27 and 37.64, which, in the ^1H-undecoupled spectra, split into quartets ($J_{CH} \approx 145$ Hz). The nonequivalency of the two R groups (also observed in the ^1H NMR spectra, as well as for **4b**) in the $NCHNR_2$ ligand indicate some restricted rotation of the amide group around the $C{-}NR_2$ bond, suggesting a significant contribution of the VB form (**c**) with a $C{=}NR_2$ double bond character. Formamidinium ions, $[H(R^1)NCH{=}NR^2(R^3)]^+$, also exhibit a restricted rotation around the C=N bond.[72]

In the ^1H NMR spectra, although the NC*H*NR$_2$ resonance was not clearly identified, $^1H{-}^{13}C$ HETCOR experiments allowed its unambiguous identification at δ 7.29 (**4a**) or 7.37 (**4b**), i.e., comparable with those commonly observed[72] for the formyl C*H*=N proton resonance of formamidinium ions (δ 7.43−8.43) or of formamidines $R^1N{=}CHNR^2(R^3)$ (δ 7.13−7.61).

IR data also corroborate the shown conjugated representation of the amidoazavinylidene ligands. In fact, the very strong band (KBr pellet) at 1616 (**4a**) or 1586 (**4b**) cm^{-1} falls in the commonly observed range (1658−1582 cm^{-1})[72] for ν(N=C) of conjugated amidines, whereas no band that could be assigned to this stretching mode was exhibited by other phosphinic compounds[22,27,73] with nonconjugated azavinylidene ligands, NCHR (R = alkyl or aryl). In addition, the medium/strong bands at 1330 (**4a**) or 1319 (**4b**) cm^{-1} can tentatively be assigned to ν(MoN) since these wavenumbers are close to those known (1300−1100 cm^{-1})[74] for metal−imide vibrations.

The presence of the fluoride ligand in complexes **4** was proved by the typical doublet ($^2J_{PF} \approx 38$ Hz) resonance (δ ca. −104) shown by the ^{31}P-$\{^1H\}$ NMR spectra and the quintet resonance, with an identical coupling constant, in the ^{19}F NMR spectra, observed at δ −38.81 (**4a**) or −37.20 (**4b**). The molecular ions for both complexes were detected in their FAB$^+$-MS spectra [m/z = 984 (**4a**) or 1012 (**4b**)].

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Final Remarks

This study demonstrates that organocyanamides ($N{\equiv}CNR_2$) are susceptible to activation toward electrophilic attack at the cyano-group, upon coordination to a suitable transition metal center, by achieving the first example of NC-protonation of such ligands to produce the previously unreported amidoazavinylidene (or amidomethyleneamide) species, $M{=}N{=}CHNR_2$. Hence, organocyanamides can behave like organonitriles ($N{\equiv}CR$) and dinitrogen, which, when ligating the same or the isoelectronic metal sites $\{M(dppe)_2\}^{n+}$ ($n = 0$, M = Mo or W; $n = 1$, M = Re), are protonated to the corresponding azavinylidene (or methyleneamide), $M{=}N{=}CHR$, or diazenide $M{=}N{=}NH$ species.

However, the NR_2 amide group confers to $NCNR_2$ and derived species distinct electronic properties from those of the corresponding NCR and derivatives. In particular, the organocyanamide ligands at the *trans*-$\{Mo(dppe)_2\}$ site behave as weaker Brönsted bases than NCR and N_2 and promote the activation (toward protonation) of N_2 in *trans* position. Moreover, the π-electron release of the amide group favors the π-electron donor ability of the organocyanamides and derived amidoazavinylidene ligands, enhancing the formation of metal−nitrogen multiple bonds with imide character. These features of organocyanamides deserve further exploration, namely toward the search for novel multiple metal−nitrogen bonded ligands and new forms of reactivity.

Experimental Section

Generalities. Solvents were dried and degassed by standard techniques. All reactions were performed under an inert atmosphere (argon) which was also always used when handling the unstable complexes **2a** and **2b** and the hygroscopic $Ag[BF_4]$ salt. *trans*-$[Mo(N_2)_2(dppe)_2]$ was prepared according to a published method,[75] and the other reagents were used as purchased (Aldrich). Hydrazine[76] and ammonia[77] tests were performed according to published methods. All the preparations (see following paragraphs), including those of compounds **4**, have been repeated and gave reproducible results.

Infrared spectra were recorded on a BioRad Excalibur FTS 3000MX FTIR spectrophotometer; wavenumbers are in cm^{-1}. Abbreviations: vs = strong, s = strong, m = medium, br = broad. NMR spectra were obtained on a Varian Unity 300 spectrometer; δ values are in ppm relative to $SiMe_4$ (^1H or ^{13}C), $P(OMe)_3$ (^{31}P), or $CFCl_3$ (^{19}F). In the ^{13}C NMR data, assignments and coupling constants common to the ^{13}C-$\{^1H\}$ NMR spectra are not repeated. Coupling constants are in hertz. Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, m = complex multiplet, br = broad, dt = doublet of triplets, dm = doublet of complex multiplets, tq = triplet of quartets, tm = triplet of complex multiplets, qt = quartet of triplets, qm = quartet of complex multiplets. The FAB-MS spectra were run on a Trio 2000 mass spectrometer. The samples were dispersed in a 3-nitrobenzyl alcohol (NBA) liquid matrix and then bombarded with an 8 keV (ca. 1.28×10^{-15} J) xenon fast atoms beam. Data system acquisition was calibrated with CsI. The calculation of theoretical isotopic patterns was performed by using a computer program[78] taking into account the natural abundance of the various isotopes. The *m*/*z* values were calculated using the ^{98}Mo isotope. The elemental analyses were done by the Laboratório de Análises of the Instituto Superior Técnico.

Preparation of the Complexes. *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$ (R = Me, 2a, or Et, 2b). A THF solution (20 cm^3) of *trans*-$[Mo(N_2)_2(dppe)_2]$, **1**, (0.100 g, 0.105 mmol) was treated with the appropriate organocyanamide $NCNR_2$ [85.0 μL, 1.05 mmol (R = Me) or 124 μL, 1.06 mmol (R = Et)] and stirred for ~3−5 h, at 25 °C, until dark red. Concentration in vacuo followed by slow dropwise addition of *n*-pentane led to the precipitation of complex **2a** or **2b** as a microcrystalline brick (**2a**) or dark red (**2b**) solid which was separated by filtration, washed with *n*-pentane, and dried in vacuo (ca. 0.083 g, 80%, **2a**, or ca. 0.090 g, 84%, **2b**, yield). One of the crystals of **2b** was analyzed by X-ray diffraction. Once isolated from the mother liquor, compounds **2a** and **2b** display a pronounced instability even in the solid state and always have to be handled under argon. Moreover, attempted recrystallization resulted in partial decomposition. These difficulties prevented reliable elemental analyses (ca. 2% C off the expected value). Although in degassed C_6D_6 solutions their stability was sufficient to collect ^1H and ^{31}P-$\{^1H\}$ NMR data, no valuable ^{13}C NMR spectra could be obtained due to decomposition during the required long acquisition time. Low temperature ^{13}C NMR studies were prevented by the high freezing point of this solvent and by the low solubility of the compounds in toluene at low temperature.

Complex 2a. IR (KBr pellet): 2190 [s, $\nu(N{\equiv}C)$], 1890 [vs, $\nu(N{\equiv}N)$]. NMR (298 K): ^1H (C_6D_6), δ 7.6−6.8 [m, 40 H, C_6H_5 (dppe)], 2.6−2.2 [m, 8 H, CH_2 (dppe)], 1.49 [s, 6 H, $NCN(CH_3)_2$]; ^{31}P-$\{^1H\}$ (C_6D_6), δ −72.3 s. FAB$^+$-MS: *m*/*z* 964 ($[M - N_2]^+$), 908 ($[M - N_2 - CNMe_2]^+$).

Complex 2b. IR (KBr pellet): 2187 [m, $\nu(N{\equiv}C)$], 1910 [vs, $\nu(N{\equiv}N)$]. NMR (298 K): ^1H (C_6D_6), δ 7.6−6.8 [m, 40 H, C_6H_5 (dppe)], 2.45 [m, 4 H, CH_2 (dppe)], 2.30 [m, 4 H, CH_2 (dppe)], 1.84 [q, 4 H, J_{HH} 7.2, $NCN(CH_2CH_3)_2$], 0.26 [t, 6 H, J_{HH} 7.2, $NCN(CH_2CH_3)_2$]; ^{31}P-$\{^1H\}$ (C_6D_6), δ −72.2 s. FAB$^+$-MS: *m*/*z* 992 ($[M - N_2]^+$), 908 ($[M - N_2 - CNEt_2]^+$).

***trans*-$[Mo(NNH_2)(NCNR_2)(dppe)_2][BF_4]_2$ (R = Me, 3a, or Et, 3b).** To a stirred THF solution (20 cm^3) of *trans*-$[Mo(N_2)(NCNR_2)(dppe)_2]$ [0.090 g, 0.091 mmol (**2a**) or 0.088 mmol (**2b**)], cooled at −60 °C, was added dropwise a 1:11 diluted diethyl ether solution of $[Et_2OH][BF_4]$ 85% [0.650 cm^3, 0.401 mmol (**2a**) or 0.620 cm^3, 0.383 mmol (**2b**)]. The solution color turned greenish brown, and after 1 h, the temperature was allowed to rise to −30 °C, leading to the formation of a light green solid. After 4 h at −30 °C, with stirring, the solution was allowed to reach room temperature, and after 1 h at this temperature, the pale green solid of **3a** or **3b** was separated by filtration, washed with diethyl ether, and dried in vacuo [ca. 0.066 g, 62% yield (**3a**) or ca. 0.070 g, 66% yield (**3b**)]. Concentration of the mother liquor in vacuo and addition of Et_2O led to the precipitation of a mixture of **4a** or **4b** (see following paragraphs) with *trans*-$[MoFO(dppe)_2][BF_4]$, the latter identified by comparing the IR and NMR (^1H, ^{31}P-$\{^1H\}$,and ^{19}F) data with those reported[79] for the known compound.

Complex 3a. IR (KBr pellet): 3416, 3321 and 3238 [m, br, $\nu(NH_2)$], 2231 [vs, $\nu(N{\equiv}C)$], 1618 [s, $\delta(NH_2)$], 1150−1000 [vs,

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br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.51 [t, 4 H, J_{HH} 7.2, H_p (dppe)], 7.49 [t, 4 H, J_{HH} 6.9, H_p' (dppe)], [7.41 t, 8 H, J_{HH} 7.3, H_m (dppe)], 7.29 [t, 8 H, J_{HH} 7.6, H_m' (dppe)], 7.23 [m, 8 H, H_o (dppe)], 7.00 (s, br, 2 H, disappears on addition of D$_2$O, NNH_2), 6.96 [m, 8 H, H_o' (dppe)], 3.03 [m, 4 H, CH_2 (dppe)], 2.81 [m, 4 H, CH_2 (dppe)], 2.02 [s, 6 H, NCN(CH_3)$_2$]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −90.0 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 132.68 [qnt, virtual J_{CP} 2.6, C_o (dppe)], 132.62 [qnt, virtual J_{CP} 2.7, C_o' (dppe)], 131.90 [s, C_p (dppe)], 131.73 [s, C_p' (dppe)], 131.58 [qnt, virtual J_{CP} 9.7, C_i (dppe)], 130.85 [qnt, virtual J_{CP} 9.7, C_i' (dppe)], 130.05 [qnt, virtual J_{CP} 2.3, C_m (dppe)], 130.02 (s, NCNMe$_2$), 129.84 [qnt, virtual J_{CP} 2.2, C_m' (dppe)], 39.11 [s, NCN(CH$_3$)$_2$], 27.21 [qnt, virtual J_{CP} 9.7, CH$_2$ (dppe)]; ^{13}C (CD$_2$Cl$_2$), δ 132.68 (dm, J_{CH} 160.7), 132.62 (dm, J_{CH} 160.7), 131.90 (dt, J_{CH} 162.9, $^2J_{CH}$ 6.8), 131.73 (dt, J_{CH} 163.0, $^2J_{CH}$ 7.0), 131.58, 130.85, 130.05 (dm, J_{CH} 163.0), 130.02, 129.84 (dm, J_{CH} 163.0), 39.11 (q, J_{CH} 143.2), 27.21 (tm, J_{CH} 131.5). FAB$^+$-MS: *m*/*z* 983 ([M − NNH$_2$ + F]$^+$), 964 ([M − NNH$_2$]$^+$). FAB$^-$-MS: *m*/*z* 87 ([BF$_4$]$^-$). (Found: C, 52.6; H, 4.7; N, 4.2%. C$_{55}$H$_{56}$N$_4$B$_2$F$_8$MoP$_4$·HBF$_4$ requires C, 52.7; H, 4.6; N, 4.5%.)

Complex 3b. IR (KBr pellet): 3418, 3317 and 3237 [m, br, ν(NH$_2$)], 2225 [vs, ν(N≡C)], 1618 [s, δ(NH$_2$)], 1150−1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.52 [t, 4 H, J_{HH} 6.9, H_p (dppe)], 7.50 [t, 4 H, J_{HH} 6.9, H_p' (dppe)], 7.40 [t, 8 H, J_{HH} 7.5, H_m' (dppe)], 7.30 [t, 8 H, J_{HH} 7.2, H_m (dppe)], 7.16 [m, 8 H, H_o' (dppe)], 6.99 [m, 8 H, H_o (dppe)], 6.83 (s, br, 2 H, disappears on addition of D$_2$O, NNH_2), 3.00 [m, 4 H, CH_2 (dppe)], 2.84 [m, 4 H, CH_2 (dppe)], 2.29 [q, 4 H, J_{HH} 7.3, NCN(CH_2CH$_3$)$_2$], 0.65 [t, 6 H, J_{HH} 7.3, NCN(CH$_2$CH_3)$_2$]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −90.8 s; ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 132.68 [qnt, virtual J_{CP} 2.7, C_o (dppe)], 132.43 [qnt, virtual J_{CP} 2.8, C_o' (dppe)], 131.88 [s, C_p + C_p' (dppe)], 131.45 [qnt, virtual J_{CP} 9.7, C_i (dppe)], 130.93 [qnt, virtual J_{CP} 9.7, C_i' (dppe)], 130.08 [qnt, virtual J_{CP} 2.2, C_m (dppe)], 129.93 [qnt, virtual J_{CP} 2.2, C_m' (dppe)], 129.72 (s, NCNEt$_2$), 45.01 [s, NCN(CH$_2$CH$_3$)$_2$], 27.01 [qnt, virtual J_{CP} 9.8, CH$_2$ (dppe)], 13.20 [s, NCN(CH$_2$$CH_3$)$_2$]; ^{13}C (CD$_2Cl_2$), δ 132.68 (dm, J_{CH} 165.0), 132.43 (dm, J_{CH} 165.0), 131.88 (dt, J_{CH} 163.6, $^2J_{CH}$ 7.3), 131.45, 130.93, 130.08 (dm, J_{CH} 165.4), 129.93 (dm, J_{CH} 165.4), 129.72, 45.01 (tq, J_{CH} 145.0, $^2J_{CH}$ 3.7), 27.01 (tm, J_{CH} 134.6), 13.20 (qt, J_{CH} 128.2, $^2J_{CH}$ 2.8). FAB$^+$-MS: *m*/*z* 1011 ([M − NNH$_2$ + F]$^+$), 992 ([M − NNH$_2$]$^+$). FAB$^-$-MS: *m*/*z* 87 ([BF$_4$]$^-$). (Found: C, 56.4; H, 4.9; N, 4.0%. C$_{57}$H$_{60}$N$_4$B$_2$F$_8$MoP$_4$·$^1/_4$HBF$_4$ requires C, 56.3; H, 5.0; N, 4.6%.)

***trans*-[MoF(NCHNR$_2$)(dppe)$_2$][BF$_4$]$_2$ (R = Me, 4a, or Et, 4b).** A stirred THF solution (25 cm^3) of *trans*-[Mo(N$_2$)(NCNR$_2$)(dppe)$_2$] [0.100 g, 0.101 mmol (**2a**) or 0.0981 mmol (**2b**)], cooled at −80 °C, was treated with a THF solution of Ag[BF$_4$] [0.201 or 0.195 mmol (in the cases of **2a** or **2b**, respectively); 3.9 cm^3 or 3.8 cm^3, accordingly, of a 0.0514 M solution]. There occurred an immediate formation of a fine and dark precipitate of silver metal, and the system was left with stirring for 2 h at −70 to −50 °C, then left to warm to −30 °C (the solution color became greenish brown or orangish brown, respectively) and maintained at this temperature for ca. 2 h. It was then left to reach room temperature, and after 1 h, always with stirring, the solution was filtered through Celite and concentrated in vacuo. Dropwise addition of diethyl ether resulted in the precipitation of a greenish yellow or dark yellow solid of **4a** or **4b**, respectively, which was separated by filtration, washed with diethyl ether, and dried in vacuo [ca. 0.075 g, 64% yield (**4a**) or 0.076 g, 65% yield (**4b**)]. Complexes **4** are also formed upon slow decomposition of the corresponding compounds **3** in solution (see following paragraphs).

Complex 4a. IR (KBr pellet): 1616 [vs, ν(N=C)], 1330 [m, ν(MoN)], 1120−1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.52 [t, 4 H, J_{HH} 7.3, H_p (dppe)], 7.42 [t, 4 H, J_{HH} 7.2, H_p' (dppe)], 7.34 [t, 8 H, J_{HH} 7.8, H_m (dppe)], 7.29 [cross-peak detected by HETCOR, NCHNMe$_2$], 7.20 [t, 8 H, J_{HH} 7.5, H_m' (dppe)], 7.12 [m, 8 H, H_o' (dppe)], 7.03 [m, 8 H, H_o (dppe)], 3.49 [m, 4 H, CH_2 (dppe)], 3.17 [m, 4 H, CH_2 (dppe)], 2.71 [s, 3 H, NCHN(CH_3^{A})$_2$], 0.62 [s, 3 H, NCHN(CH_3^{B})$_2$]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −103.9 (d, J_{PF} 37.5); ^{19}F (CD$_2$Cl$_2$), δ −38.81 (qnt, 1 F, $^2J_{FP}$ 38.1, MoF^-), −151.46 (s, 8 F, B$F_4$$^-$); ^{13}C-{^{1}H} (CD$_2Cl_2$), δ 162.54 [s, N$C$HNMe$_2$], 132.88 [m, C_o + C_o' (dppe)], 131.89 [s, C_p (dppe)], 130.95 [s, C_p' (dppe)], 130.24 [qnt, virtual J_{CP} 2.2, C_m (dppe)], 129.26 [qnt, virtual J_{CP} 2.2, C_m' (dppe)], 44.26 [s, NCHN(CH$_3$^{A})$_2$], 37.64 [s, NCHN(CH$_3$^{B})$_2$], 29.84 [qnt, virtual J_{CP} 9.5, CH$_2$ (dppe)]; ^{13}C (CD$_2$Cl$_2$), δ 162.54 (d, J_{CH} 200.8), 132.88 (dm, J_{CH} 162.7), 131.89 (dt, J_{CH} 163.5, $^2J_{CH}$ 7.3), 130.95 (dt, J_{CH} 162.3, $^2J_{CH}$ 7.0), 130.24 (dm, J_{CH} 163.0), 129.26 (dm, J_{CH} 163.6), 44.26 (q, J_{CH} 145.7), 37.64 (q, J_{CH} 145.1), 29.84 (tm, J_{CH} 131.5). FAB$^+$-MS: *m*/*z* 984 ([M]$^+$). FAB$^-$-MS: *m*/*z* 87 ([BF$_4$]$^-$). (Found: C, 56.2; H, 4.4; N, 2.0%. C$_{55}$H$_{55}$N$_2$B$_2$F$_9$MoP$_4$ requires C, 57.1; H, 4.8; N, 2.4%.)

Complex 4b. IR (KBr pellet): 1586 [vs, ν(N=C)], 1319 [s, ν(MoN)], 1120−1000 [vs, br, ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.53 [t, 4 H, J_{HH} 7.3, H_p (dppe)], 7.41 [t, 4 H, J_{HH} 7.2, H_p' (dppe)], 7.37 [t, 9 H, J_{HH} 7.3, H_m (dppe; buried under that triplet but its cross-peak detected by HETCOR, NCHNEt$_2$], 7.18 [t, 8 H, J_{HH} 7.6, H_m' (dppe)], 7.09 [m, 16 H, H_o + H_o' (dppe)], 3.49 [m, 4 H, CH_2 (dppe)], 3.15 [q, 2 H, J_{HH} 7.0, NCHN(CH_2^{A}CH$_3$)$_2$; buried under that quartet but its cross-peak detected by HETCOR, 4 H, CH_2 (dppe)], 1.33 [q, 2 H, J_{HH} 7.3, NCHN(CH_2^{B}CH$_3$)$_2$], 0.90 [t, 3 H, J_{HH} 7.0, NCHN(CH$_2$CH_3^{A})$_2$], −0.28 [t, 3 H, J_{HH} 7.3, NCHN(CH$_2$CH_3^{B})$_2$]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ −104.3 (d, J_{PF} 37.4); ^{19}F (CD$_2$Cl$_2$), δ −37.20 (qnt, 1 F, $^2J_{FP}$ 38.1, F^-), −151.46 (s, 8 F, B$F_4$$^-$); ^{13}C-{^{1}H} (CD$_2Cl_2$), δ 162.32 (s, N$C$HNEt$_2$), 132.90 [qnt, virtual J_{CP} 2.7, C_o (dppe)], 132.44 [qnt, virtual J_{CP} 2.7, C_o' (dppe)], 132.28 [s, C_p (dppe)], 131.83 [s, C_p' (dppe)], 130.38 [qnt, virtual J_{CP} 2.1, C_m (dppe)], 129.25 [qnt, virtual J_{CP} 2.3, C_m' (dppe)], 48.56 [s, NCHN(CH$_2$^{A}CH$_3$)$_2$], 43.62 [s, NCHN(CH$_2$^{B}CH$_3$)$_2$], 29.68 [qnt, virtual J_{CP} 9.4, CH$_2$ (dppe)], 13.28 [s, NCHN(CH$_2$$CH_3$^{A})$_2$], 9.57 [s, NCHN(CH$_2$$CH_3$^{B})$_2$]; ^{13}C (CD$_2Cl_2$), δ 162.32 (d, J_{CH} 200.2), 132.90 (dm, J_{CH} 162.3), 132.44 (dm, J_{CH} 161.8), 132.28 (dt, J_{CH} 163.6, $^2J_{CH}$ 7.0), 131.83 (dt, J_{CH} 163.6, $^2J_{CH}$ 7.0), 130.38 (dm, J_{CH} 162.1), 129.25 (dm, J_{CH} 163.7), 48.56 (tm, J_{CH} 146.8), 43.62 (tm, J_{CH} 145.6), 29.68 (tm, J_{CH} 135.2), 13.28 (qt, J_{CH} 129.4, $^2J_{CH}$ 3.7), 9.57 (qt, J_{CH} 129.6, $^2J_{CH}$ 3.7). FAB$^+$-MS: *m*/*z* 1012 ([M]$^+$). FAB$^-$-MS: *m*/*z* 87 ([BF$_4$]$^-$). (Found: C, 57.0; H, 4.9; N, 2.0%. C$_{57}$H$_{59}$N$_2$B$_2$F$_9$MoP$_4$ requires C, 57.8; H, 5.0; N, 2.4%.)

Conversion of the Hydrazide(2−) Complex 3b into the Amidoazavinylidene Complex 4b. A CH$_2$Cl$_2$ (20 cm^3) solution of complex **3b** (0.025 g, 0.021 mmol) was stirred at 23 °C and regularly monitored by ^{31}P-{^{1}H} NMR and IR spectroscopies (applied to 0.50 cm^3 samples taken from that solution) until the complete disappearance of the starting complex (45 days) upon conversion into **4b** (ca. 60% yield) as the main complex product. The solution was then transferred to a separatory funnel, and the water soluble nitrogen products were repeatedly extracted by 5 × 20 cm^3 portions of distilled and deionized water. The aqueous extracts were added to a 100.0 cm^3 volumetric flask, and aliquots (5.00 cm^3) of the final water solution were analyzed for hydrazine[76] or ammonia[77] by using standard spectrophotometric methods [molar yields of 2.5% (hydrazine) or 8.5% (ammonia), relative to the starting metal complex].

An identical procedure was also followed for monitoring the **3b** → **4b** conversion in acidic media, by adding a catalytic amount (0.10 acid/complex molar ratio) of [Et$_2$OH][HBF$_4$] to the starting CH$_2$Cl$_2$ reaction solution. However, this procedure cannot be used

Table 2. Crystalographic Data for *trans*-[Mo(N_2)($NCNEt_2$)(dppe)$_2$], **2b**

chemical formula	$C_{57}H_{58}MoN_4P_4$
fw	1018.89
cryst syst	orthorhombic
space group	*Pbca*
a/Å	14.545(3)
b/Å	21.756(4)
c/Å	31.881(6)
V/Å^3	10088(3)
T/K	293
Z	8
μ(Mo Kα)/mm^{-1}	0.429
total reflns collected	2879
indep reflns	2879 (R_{int} = 0.0000)
obsd reflns [$I > 2\sigma(I)$]	2879
R indices (all data)	R1 = 0.0230 wR2 = 0.0582
final R indices [$I > 2\sigma(I)$]	R1 = 0.0230 wR2 = 0.0582

for the preparation of **4b** in view of its further decomposition in acidic medium.

Crystal Structure Determination of *trans*-[Mo(N_2)($NCNEt_2$)(dppe)$_2$] 2b. Crystals of **2b** were grown spontaneously at ca. −20 °C from the mother liquor resulting from the filtration step of the synthesis of this complex. X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a β-monochromator and using Mo Kα radiation. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were constrained to have identical U. The PROFIT program[80] was used for cell refinement and data reduction. The structure was solved by direct methods by using the SHELXS-97 package.[81] The structure refinements were carried out with SHELXL-97.[82] ORTEP representations were performed using the PLATON99 program.[83] Crystallographic data are summarized in Table 2, and selected bond lengths and angles in Table 1.

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Supporting Information Available: CIF file giving positional and thermal parameters, bond distances, and bond angles for **2b**. ^{1}H and ^{31}P-{^{1}H} NMR spectra for **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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