N,P Ligands

A Ligand Composed of Dinitrogen and Methyldiphenylphosphane in a Cationic Molybdenum Complex**

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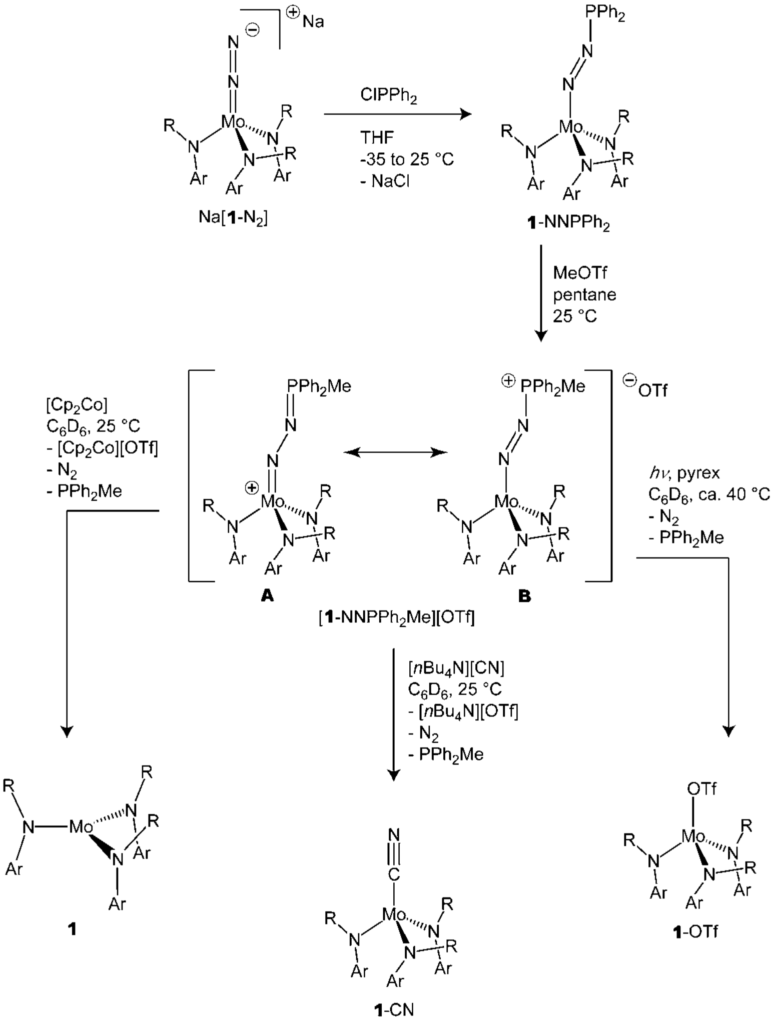
It is well recognized that a reactive chemical fragment, which in its free state may be fleeting, not isolable, and difficult to observe, may sometimes be stabilized or trapped in an isolable form by coordination to a transition-metal center. Herein we report a unique ligand made of N_2 and PPh_2Me, which is stabilized in a cationic molybdenum complex. It does not seem likely that such a "diazophosphorane" $NNPR_3$ ligand[1] would be obtained simply by addition of PR_3 to a terminal metal–N_2 complex, because the β-N (terminal) atom of coordinated N_2 typically is at least moderately nucleophilic. Furthermore, the $NNPR_3$ moiety is expected to be thermodynamically unstable in view of the great stability of N_2 and PR_3. To the best of our knowledge, the diazophosphorane $NNPR_3$ unit has not been identified previously as a ligand in spite of the prevalent use of tertiary phosphines as ligands in N_2 coordination chemistry. However, the $NNPR_3$ moiety is found as a chemical fragment in some known phosphorus–nitrogen compounds such as $R_2C{=}N{-}N{=}PR_3$, $[R{-}N{=}N{-}PR_3]^+$, $CN{-}N{=}PR_3$, and $[NNNPR_3]^+$.[1,2]

As hinted at by the structures of these known compounds, we suggest that the $NNPR_3$ moiety has the potential for stabilization by binding with a metal center at its N-terminus. This study presents a rational construction of the surprising $NNPR_3$ ligand by stepwise functionalization of dinitrogen coordinated to a formally d^2 molybdenum center.[3] The X-ray structural analysis, as well as topological charge density analysis based on density functional calculations, indicate that the diazophosphorane ligand is stabilized effectively by equal contributions from the two following limiting resonance structures: (triorganophosphoranylidene)hydrazido(2−) $[\mathrm{Mo}]^+({=}N{-}N{=}PR_3)$ and (triorganophosphonio)diazenido $[\mathrm{Mo}](N{=}N{-}^{+}PR_3)$; these are shown as **A** and **B**, respectively, in Scheme 1.



Scheme 1. Synthesis of [1-$NNPPh_2Me$][OTf], resonance structures, and reactivity. R = *t*Bu, Ar = 3,5-dimethylphenyl.

The anionic end-on dinitrogen complex $[(N_2)\mathrm{Mo}\{N(t\mathrm{Bu})\mathrm{Ar}\}_3]^{1-}$ $[\mathbf{1}\text{-}N_2]^-$ ($\mathrm{Ar} = 3,5\text{-}Me_2C_6H_3$), which is conveniently obtained as its sodium salt by the reaction of $[\mathrm{Mo}\{N(t\mathrm{Bu})\mathrm{Ar}\}_3]$ (**1**) with excess Na/Hg under 1 atm N_2,[4] was derivatized smoothly by reaction with Ph_2PCl in THF to afford the diphenylphosphinodiazenido complex **1**-$NNPPh_2$.[5] The $^{31}P\{^1H\}$ NMR signal of **1**-$NNPPh_2$ appears at $\delta = 67.3$ ppm as a singlet in C_6D_6. Monitoring of the reaction in C_6D_6 or $[D_8]$THF showed two major by-products: $[\mathrm{Mo}\{N(t\mathrm{Bu})\mathrm{Ar}\}_3]$ (**1**) and Ph_2PPPh_2, with additional formation of $[\mathrm{ClMo}\{N(t\mathrm{Bu})\mathrm{Ar}\}_3]$[5] in small quantities. The molar ratio of **1**-$NNPPh_2$/Ph_2PPPh_2 in C_6D_6 after 1 h at 23 °C was 78/22. The

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orange complex **1**-NNPPh$_2$ was isolated in 10% yield after repeated recrystallization from pentane at −35 °C. The low yield of isolated **1**-NNPPh$_2$ was due in part to the spontaneous decomposition of **1**-NNPPh$_2$ to [Mo{N(*t*Bu)Ar}$_3$],[6] Ph$_2$PPPh$_2$, and N$_2$ during the recrystallization. The structure of **1**-NNPPh$_2$ was determined by X-ray structure analysis (Figure 1). The N4–N5 (1.261(4) Å) and N5–P1 (1.736(4) Å) lengths are consistent with a N=N double bond and N–P single bond, respectively. Complex **1**-NNPPh$_2$ can thus be formulated as the phosphinodiazenido derivative [(Ph$_2$P–N=N)Mo{N(*t*Bu)Ar}$_3$].[7] The Mo1-N4-N5-P1 skeleton is bent at the N5 atom (N4-N5-P1 122.6(3)°). The Mo1–N4 length (1.753(3) Å) and Mo1-N4-N5 angle (171.1(3)°) are similar to those found for the related trimethylsilyldiazenido complex [(Me$_3$Si-N=N)Mo{N(*t*Bu)Ar}$_3$].[4] Strong multiple bonding between the α-N atom and Mo in these systems is indicated by the short bond length, the linear bond angle, and the isolobal relationship with nitrosyl complexes such as [(ON)Mo{N(*t*Bu)Ar}$_3$].[8] Because of the isolobal relationship between the quartet ground state Mo{N(*t*Bu)Ar}$_3$ fragment[6] and a ground state N atom, we recognize that nitrosyl [(ON)Mo{N(*t*Bu)Ar}$_3$] is isolobal with the triatomic N$_2$O molecule: both systems share a stable $(\pi_0)^4(\pi_1)^4$ configuration across linear MoNO and NNO moieties, respectively.

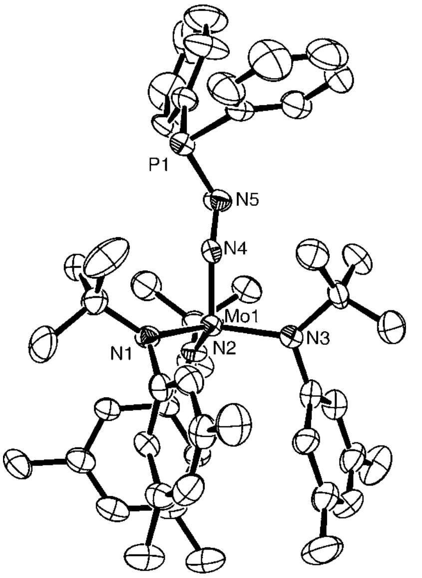

Figure 1. Molecular structure of **1**-NNPPh$_2$ with thermal ellipsoids drawn at the 50% probability level.

Treatment of **1**-NNPPh$_2$ with MeOTf (1 equiv) in C$_6$D$_6$ rapidly provided the triflate salt [(Ph$_2$MePNN)Mo{N(*t*Bu)Ar}$_3$][OTf] [**1**-NNPPh$_2$Me][OTf] of the desired cation, in essentially quantitative fashion at ambient temperature. No N-methylated product was observed, even when excess MeOTf was employed. In contrast, it has been reported that the reaction of Na[**1**-N$_2$] with MeOTf (2 equiv) afforded the doubly N-methylated product [(Me$_2$NN)Mo{N(*t*Bu)Ar}$_3$][OTf].[4] The yellow-orange complex [**1**-NNPPh$_2$Me][OTf] was isolated in 41% yield from Na[**1**-N$_2$] without purification of the intermediate **1**-NNPPh$_2$. The ^{1}H NMR resonance for the PPh$_2$(C*H*$_3$) moiety in [**1**-NNPPh$_2$Me][OTf] appears at δ = 3.03 ppm as a doublet ($^2J_{\mathrm{PH}}$ = 13 Hz). The ^{31}P{^{1}H} NMR spectrum of [**1**-NNPPh$_2$Me][OTf] shows a singlet at δ = 20.0 ppm. The structure of [**1**-NNPPh$_2$Me][OTf] was determined in a single-crystal X-ray diffraction study (Figure 2). The Mo1-N4-N5 angle (166.7(2)°) and N4-N5-P1 angle (129.2(2)°) in [**1**-NNPPh$_2$Me][OTf] differ only slightly from corresponding angles in **1**-NNPPh$_2$ (Figure 1). The system is thus still close to linear at the α-N atom and rather bent at the β-N atom. However, the N5–P1 interatomic distance (1.626(3) Å) is 0.11 Å shorter than the corresponding distance in **1**-NNPPh$_2$ (1.736(4) Å), and is similar to that found in a typical iminophosphorane (e.g. 1.602 Å for Ph-N=PPh$_3$).[9] Note also that the N4–N5 (1.299(3) Å) bond length is increased relative to **1**-NNPPh$_2$; in other words, greater activation of the N$_2$ unit has been triggered by the methylation reaction, although the N4–N5 distance in [**1**-NNPPh$_2$Me][OTf] is still considerably shorter than that observed for phosphoranylidene hydrazone systems such as Ph$_3$P=N–N=CPh$_2$ (N–N = 1.388 Å).[10] Of further interest: the Mo1–N4 (1.739(2) Å) bond length in [**1**-NNPPh$_2$Me][OTf] is slightly shorter than that found for precursor **1**-NNPPh$_2$.

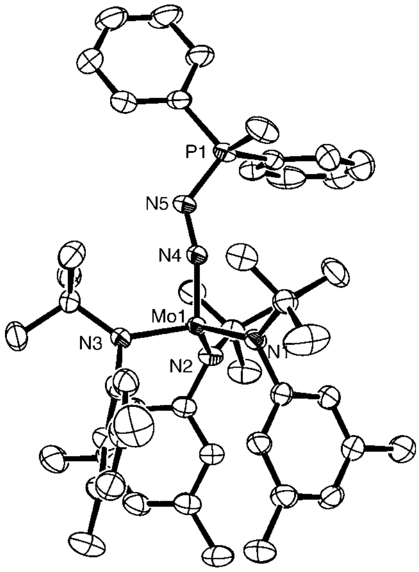

Figure 2. Molecular structure of cation [**1**-NNPPh$_2$Me]$^+$ with thermal ellipsoids drawn at the 50% probability level. The triflate counteranion is not shown.

The isolated salt [**1**-NNPPh$_2$Me][OTf] is stable in C$_6$D$_6$ solution in the dark for several days at ambient temperature and even at 50 °C for one day. Interestingly, degradation of the NNPPh$_2$Me ligand was observed when [**1**-NNPPh$_2$Me][OTf] was photoirradiated (Rayonet RPR-2537 Å lamps, Pyrex tube) in C$_6$D$_6$. After irradiation for 1 h at ca. 40 °C, approximately 50% of [**1**-NNPPh$_2$Me][OTf] was converted into the triflate complex [Mo{N(*t*Bu)Ar}$_3$(OTf)] (**1**-OTf) and PPh$_2$Me (ca. 90% based on the consumption of [**1**-NNPPh$_2$Me][OTf]) and presumably N$_2$. The purple triflate complex **1**-OTf was identified by an independent synthesis, that is, oxidation of [Mo{N(*t*Bu)Ar}$_3$] with AgOTf or [Cp$_2$Fe][OTf]. The reaction of [**1**-NNPPh$_2$Me][OTf] with [*n*Bu$_4$N][CN] in C$_6$D$_6$ upon mixing afforded [(NC)Mo{N(*t*Bu)Ar}$_3$] (**1**-CN)[11] and PPh$_2$Me + N$_2$ almost quantitatively (Scheme 1). Treatment of [**1**-NNPPh$_2$Me][OTf] with cobaltocene (1 equiv) in C$_6$D$_6$ gave [Mo{N(*t*Bu)Ar}$_3$] (**1**) and PPh$_2$Me + N$_2$ again in almost quantitative yield. Thus, as expected, the fragile NNPPh$_2$Me ligand in [**1**-NNPPh$_2$Me][OTf] is subject to facile fragmentation to its PPh$_2$Me and N$_2$ components under exposure to some chemical or physical stimuli (Scheme 1).

To gain insight into the electronic structure of [**1**-NNPPh$_2$Me][OTf] we performed density functional calculations (ADF 2004.01, BP86/TZ2P) on the model compounds [(H$_2$PNN)Mo(NH$_2$)$_3$] (**1**′-NNPH$_2$) and [(H$_3$PNN)Mo(NH$_2$)$_3$]$^+$ ([**1**′-NNPH$_3$]$^+$).[12] A topological charge density analysis[13] was carried out with aid of the Xaim program,[14] based on the calculated charge density distributions. The electronic charge density value found at the (3,−1) critical point (ρ_b) of the N−N bond in [**1**′-NNPH$_3$]$^+$ ($0.4016\,e\,a_0^{-3}$) was lower than that in **1**′-NNPH$_2$ ($0.4586\,e\,a_0^{-3}$). The calculated bond order (n) is 1.6 for [**1**′-NNPH$_3$]$^+$ (cf. 1.9 for **1**′-NNPH$_2$); this estimation is derived from Bader's linear correlation between ρ_b values and N−N bond order (n).[13] These data indicate that the N−N bond in the cationic [Mo](NNPR$_3$) complex is intermediate between a single and a double bond.[15] The information obtained from computational analysis, combined with the experimental structural data, reveal that the bonding in cation [**1**-NNPPh$_2$Me]$^+$ is characterized by resonance between the hydrazido(2-) form **A** and the diazenido form **B** (Scheme 1). A similar pair of resonance structures was proposed in connection with the particular diazenylphosphonium salt [4-Et$_2$NC$_6$H$_4$NNPPh$_3$][BF$_4$] and its short P−N bond length (1.648 Å).[16]

In summary, this work demonstrates that the remarkable ligand NNPR$_3$ composed of dinitrogen and methyldiphenylphosphane can be obtained and is understandable in the context of a cationic molybdenum system. Because one-electron reduction of cation [**1**-NNPPh$_2$Me]$^+$ leads to fragmentation to the three known molecules PPh$_2$Me, N$_2$, and [Mo{N(*t*Bu)Ar}$_3$] (**1**), it may be said that this remarkable three-component system is bound together entirely by the absence of a single electron.

Experimental Section

1-NNPPh$_2$: A solution of Na[**1**-N$_2$] (500 mg, 0.740 mmol) in THF (6 mL) was combined with a solution of Ph$_2$PCl (133 μL, 0.740 mmol) in THF (2 mL) at −35 °C. After the reaction mixture had been stirred for 5 min, THF solvent was removed in vacuo. Then pentane (10 mL) was added, the mixture was filtered through Celite, and pentane was removed in vacuo. Repeated recrystallization from pentane gave analytically pure **1**-NNPPh$_2$ (62.8 mg, 10 % yield). ^{1}H NMR (C$_6$D$_6$): $\delta = 8.01$ (t, $J = 7.2$ Hz, 4H), 7.25 (t, $J = 8.4$ Hz, 4H), 7.10 (t, $J = 7.2$ Hz, 2H), 6.64 (s, 3H), 6.03 (s, 6H), 2.04 (s, 18H), 1.53 (s, 27H); ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 67.3$ (s); Elemental analysis calcd C 68.80, H 7.70, N 8.36: found: C 69.03, H 8.19, N 7.96. Crystallographic data for **1**-NNPPh$_2$: C$_{48}$H$_{64}$N$_5$PMo, $M = 837.97$, space group $P2_1/c$, $a = 22.6095(19)$, $b = 10.5661(9)$, $c = 19.4732(16)$ Å; $\beta = 94.183(2)°$, $V = 4639.6(7)$ Å^3, $Z = 4$, $F(000) = 1776$, $\rho_{\mathrm{calcd}} = 1.20\ \mathrm{g\,cm^{-3}}$, 542 parameters refined with 7280 reflections with $I > 2\sigma(I)$ to $R = 0.0516$.

[**1**-NNPPh$_2$Me][OTf]: A solution of Na[**1**-N$_2$] (600 mg, 0.888 mmol) in THF (6 mL) was combined with a solution of Ph$_2$PCl (159 μL, 0.888 mmol) in THF (2 mL) at −35 °C. After the reaction mixture was stirred for 5 min, THF solvent was removed in vacuo. Then pentane (10 mL) was added, the mixture was filtered through Celite, and pentane was removed in vacuo to give a crude material containing **1**-NNPPh$_2$ (387 mg). To a pentane solution of the crude product, MeOTf (55 μL, 0.49 mmol) was added, and the mixture was stirred for 5 min. Yellow powder was immediately generated. The liquid was decanted off, and the yellow powder was washed with pentane twice, and dried in vacuo. Recrystallization from CH$_2$Cl$_2$/Et$_2$O/*n*-hexane gave yellow-orange microcrystals of [**1**-NNPPh$_2$Me][OTf] (363 mg, 41 % yield from Na[**1**-N$_2$]). ^{1}H NMR (C$_6$D$_6$): $\delta = 8.19$ (dd, $J = 13.1$ Hz, $J = 8.4$ Hz, 4H), 7.32 (m, 4H), 7.15 (overlap with solvent residuals, 2H), 6.62 (s, 3H), 5.77 (br s, 6H), 3.03 (d, $J = 13.2$ Hz, 3H), 1.97 (s, 18H), 1.16 ppm (s, 27H); ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta = 20.0$ ppm (s); FTIR (C$_6$D$_6$, KBr): $\tilde{\nu}_{\mathrm{NN}} = 1586\ \mathrm{cm^{-1}}$. Elemental analysis calcd C 59.93, H 6.74, N 6.99; found: C 59.96, H 6.78, N 6.92. Crystallographic data for [**1**-NNPPh$_2$Me][OTf]: C$_{50}$H$_{67}$N$_5$PSO$_3$F$_3$Mo, $M = 1002.07$, space group $P2_1/n$, $a = 21.3981(17)$, $b = 10.8084(8)$, $c = 22.1557(17)$ Å; $\beta = 95.1550(10)°$, $V = 5103.4(7)$ Å^3, $Z = 4$, $F(000) = 2104$, $\rho_{\mathrm{cald}} = 1.304\ \mathrm{g\,cm^{-3}}$, 577 parameters refined with 11 891 reflections with $I > 2\sigma(I)$ to $R = 0.0505$.

CCDC-258978 (**1**-NNPPh$_2$), CCDC-258979 ([**1**-NNPPh$_2$Me][OTf]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-OTf: Mo(N[*t*Bu]Ar)$_3$ (**1**, 273 mg, 0.437 mmol) was dissolved in pentane (10 mL), and AgOTf (112 mg, 0.437 mmol) was added at room temperature. The mixture was stirred vigorously for 4 h. The color of the mixture changed to deep purple. Then the mixture was filtered through Celite, and the filtrate was concentrated. Crystallization from pentane at −35 °C gave deep purple microcrystals of **1**-OTf (43.8 mg, 13 % yield). ^{1}H NMR (C$_6$D$_6$): $\delta = 6.06$ (s, 3H), 5.94 (br s, 6H), 2.11 (s, 27H), 1.86 ppm (s, 18H); Elemental analysis calcd C 57.43, H 7.03, N 5.43; found: C 57.59, H 7.12, N 5.38. An NMR monitoring experiment of the reaction of [Mo{N(*t*Bu)Ar}$_3$] with [Cp$_2$Fe][OTf] (1 equiv) in C$_6$D$_6$/[D$_8$]THF (v/v = 9/1) showed quantitative formation of **1**-OTf.

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[1] The abbreviation R which appears in some general formulas in this paper is not necessarily identical to the R = *t*Bu as in **1** and complexes derived therefrom.

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[12] ADF Program Package (release 2004.1) was used. The optimized structures showed good agreement with the metrical parameters found in the crystal structure studies of **1**-NNPPh$_2$ and [**1**-NNPPh$_2$Me][OTf], except for the N-N-P angle in [**1**′-NNPH$_3$]$^+$ which appears marginally smaller compared to that found experimentally for [**1**-NNPPh$_2$Me][OTf]. Selected structural parameters of optimized **1**′-NNPPH$_2$ and [**1**′-NNPH$_3$]$^+$: for **1**′-NNPH$_2$: Mo−N 1.757, N−N 1.243, N−P 1.770 Å; Mo-N-N 174.6, N-N-P 120.94°; for [**1**′-NNPH$_3$]$^+$: Mo−N 1.735, N−N 1.295, N−P 1.627 Å; Mo-N-N 172.8, N-N-P 121.6°.

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