Main-Group Chemistry

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# Metal-Free Activation of Hydrogen, Carbon Dioxide, and Ammonia by the Open-Shell Singlet Biradicaloid [P(μ-NTer)]$_2$

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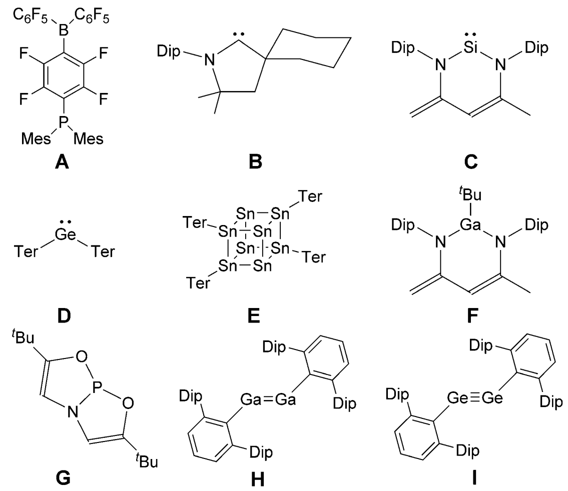
***Abstract:*** *The Group 15 open-shell singlet biradicaloid [P(μ-NTer)]$_2$ (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl) was utilized in the activation of stable small molecules. Fast reactions with $H_2$, $CO_2$, and $NH_3$ were observed. Dihydrogen easily added to [P(μ-NTer)]$_2$, yielding [HP(μ-NTer)]$_2$ under ambient conditions whereas reversible release of molecular hydrogen was observed at slightly elevated temperatures ($T > 60$ °C). As [P(μ-NTer)]$_2$ is a species with phosphorus in the unusual formal oxidation state +II, it is capable of reducing carbon dioxide to afford a zwitterionic compound, [OP(μ-NTer)$_2$P], and carbon monoxide. The reaction of [P(μ-NTer)]$_2$ with ammonia led to the formation of an azadiphosphiridine after rearrangements of the central $P_2N_2$ heterocycle.*

The activation of small molecules such as dihydrogen,[1] carbon dioxide,[2] and ammonia[3] is of great relevance with respect to many chemical reactions, especially for catalytic transformations with readily available starting materials. Most commonly, transition-metal complexes can fulfil the required activation step of those relatively stable small molecules. However, progress in main-group chemistry in the last decade has enabled similar reactivity without transition-metal complexes by utilizing new concepts such as frustrated Lewis pairs (FLPs),[2] low-valent species with open coordination sites,[4] N-heterocyclic carbenes,[5,6] persistent radicals[7] and biradicals,[8,9] or main-group compounds with multiple bonds.[10] The cognition of main-group elements as transition-metal mimics was brought forth by Power.[11] The first use of frustrated Lewis pairs (species **A** in Scheme 1) to activate dihydrogen was demonstrated by Stephan et al. in 2006. Several main-group-element-based FLPs readily activate E−H or E=O bonds (E = main-group element).[12–14] By now, research on FLPs has already taken this class of compounds to the level of catalytic transformations.[1,15] Among the first examples of highly reactive main-group species that are able to activate stable molecules were carbenes (**B**, Scheme 1), featuring electron-rich, two-coordinate carbon centers.[5,6] Several carbenes can split dihydrogen or ammonia at such a single carbon center.[16,17] The heavier Group 14 homologues, silylenes and germylenes, were also investigated; for example, Müller et al. reported on the activation of dihydrogen whereas Roesky et al. investigated the addition of ammonia to silylenes.[18,19] Even germylenes, for example, $Ter_2Ge$ (**D**), are able to activate ammonia.[20] Power et al. could show that a more complex tin cluster is able to stoichiometrically react with dihydrogen (**E**).[21] Another interesting example is the activation of $PH_3$ and $AsH_3$ at a silylene, which was investigated by Driess et al. (**C**, Scheme 1).[22,23] Aldridge and co-workers elegantly demonstrated the activation of $H_2$ and $NH_3$ and the reduction of carbon dioxide employing an electron-poor gallium center (**F**).[24] Recently, the use of geometrically restrained $P^{III}$ centers in the activation of small molecules has been investigated by Radosevich et al. (**G**)[25,26] and, with a different backbone, by the groups of Aldridge and Goicoechea.[27] The groups of Power and Linti described the activation of $H_2$ and $NH_3$ by dimeric (**H**)[28] and monomeric[29] $Ga^I$ species.



*Scheme 1.* Selected examples of classes of main-group compounds known to activate $H_2$, $NH_3$, or $CO_2$. Dip = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl, Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl.

Already in 2005, in a seminal report by Power et al., digermyne **I** was shown to react with $H_2$. Furthermore, the heavy Group 14 analogues of alkynes were reported to activate $CO_2$[30,31] and 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO).[32,33] In these reactions, the surprisingly high reactivity of digermynes was attributed to the significant extent of biradical character in these systems,[34,35] which was also suggested for digallene **H**.[36–38] Biradicaloid[39] Group 15

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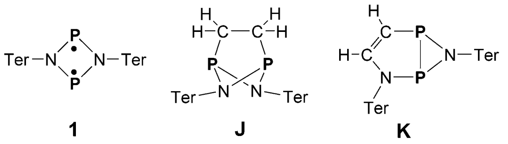
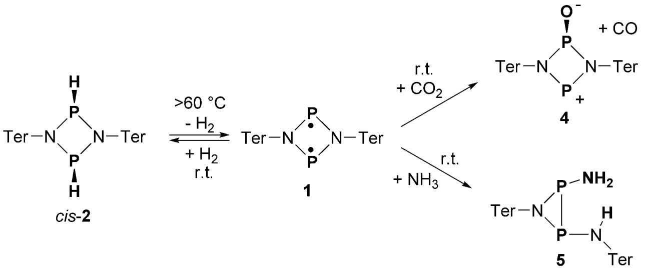
species have been in the focus of our interest for several years and were shown to readily react with several molecules with main-group-element multiple bonds, affording, for example, [2.1.1]bicyclic species (**J**)[40–43] or, in the activation of alkynes, [3.1.0]heterobicycles (**K**, Scheme 2) after rearrangement.[44] Herein, we report on the reactivity of the diphosphadiazanediyl [P(μ-NTer)]$_2$ (**1**, Scheme 2) towards gaseous dihydrogen, carbon dioxide, and ammonia under ambient conditions.



***Scheme 2.*** The singlet biradicaloid diphosphadiazanediyl **1** and some of its activation products of ethylene and acetylene.

Earlier investigations had shown that biradicaloid **1** can be prepared on gram scale and that it is highly reactive, but stable in solution and in the solid state under argon atmosphere.[40] Treatment of an orange solution of biradicaloid **1** in benzene with dihydrogen at room temperature readily led to the formation of a colorless solution within one minute. After concentrating the solution, colorless crystals of the diphosphadiazane *cis*-[HP(μ-NTer)]$_2$ (**2**) were obtained in good yields (60–70 %, Scheme 3). Interestingly, $^{31}$P NMR experiments indicated the presence of only one isomer of **2**. This is in contrast to the previously reported reaction of **1** with iodine, which afforded both *cis* and *trans* isomers and is therefore expected to proceed by a different mechanism.[45] The $^{31}$P NMR resonance of **2** was observed as an AA′XX′ pattern centered at 193.9 ppm (Figure 1, left; for sections of the $^{1}$H NMR spectra, see the Supporting Information, Figure S1). Comparison with computed data enabled the identification of **2** as *cis*-[HP(μ-NTer)]$_2$ (calcd $\delta(^{31}P)$: 186 (*cis*), 210 ppm (*trans*)). The $J_{PH}$ coupling constant of −128.5 Hz is rather small for a $^{1}J$ coupling constant (NaPH$_2$: −155 Hz).[46]



***Scheme 3.*** Reaction of [P(μ-NTer)]$_2$ (**1**) with H$_2$, CO$_2$, and NH$_3$.

The $\nu_{P-H}$ stretching modes at 2040 (out-of-phase) and 2092 cm$^{-1}$ (in-phase) are, to the best of our knowledge, found at the lowest energy for $\nu_{P-H}$ vibrations observed thus far (Figure 1, right; typically, $\nu_{P-H} = 2200$–$2500$ cm$^{-1}$, for [Ph$_3$PH]Br: 2180 cm$^{-1}$).[47] The presence of *cis*-[HP(μ-NTer)]$_2$ (**2**) in the solid state was unequivocally confirmed by single-crystal X-ray studies, which revealed a slightly puckered P$_2$N$_2$ ring (dihedral angle −13.2(1)°) with two P atoms in trigonal-pyramidal arrangements and strongly polarized P–N single bonds (Figure 2).

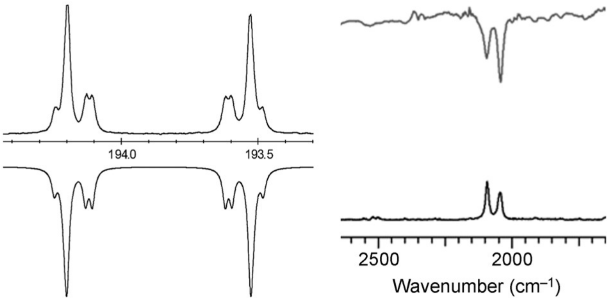


***Figure 1.*** Left: $^{31}$P NMR spectrum of *cis*-**2** (top: measured, bottom: simulated; $J_{PP'} = 22.1$, $^{1}J_{PH} = -128.5$, $^{3}J_{PH'} = 6.3$, $^{4}J_{HH'} = 5.9$ Hz). Right: The $\nu_{P-H}$ sections of the IR (top) and Raman spectra (bottom).

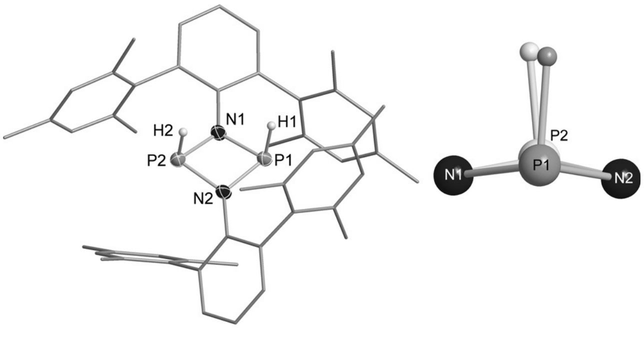


***Figure 2.*** Left: Molecular structure of **2**. Thermal ellipsoids set at 50 % probability (123 K). Selected bond lengths [Å] and angles [°]: P1–N2 1.696(2), P1–N1 1.768(2), P2–N1 1.732(2), P2–N2 1.740(2); N2-P1-N1 80.7(1), N1-P2-N2 80.5(1). Right: View along the P–P axis showing the puckered P$_2$N$_2$ core.

Diphosphadiazane **2** is not long-term stable even under argon atmosphere at room temperature as it slowly releases molecular hydrogen. For example, as shown by $^{31}$P NMR spectroscopy, approximately 90 % of **2** and 10 % of the biradicaloid **1** (singlet at $\delta = 276.4$ ppm) were detected after six months. In an NMR experiment, heating of **2** in solution led to the formation of **1** only above 60 °C, but this, too, only to a small extent within hours of heating. Interestingly, the addition of alkynes to **2** did not afford hydrogen transfer to the alkyne but led to expulsion of dihydrogen and formation of [3.1.0]bicyclic azadiphosphiridines (species **J** in Scheme 2), which has been observed for the reaction of **1** with alkynes as well.[48]

Computations at the M062X/aug-cc-pvtz level of theory for the model compound [P(μ-NPh)]$_2$ (**1Ph**) to determine the mechanism indicated a low activation barrier (17.9 kcal mol$^{-1}$, TS1) for the 1,2-addition of dihydrogen at both P radical centers in an exergonic process (−7.8 kcal mol$^{-1}$, Figure 3). It is interesting to note that the reverse reaction requires a higher activation energy (25.7 kcal mol$^{-1}$), which nicely explains the dihydrogen release at elevated temperatures. The

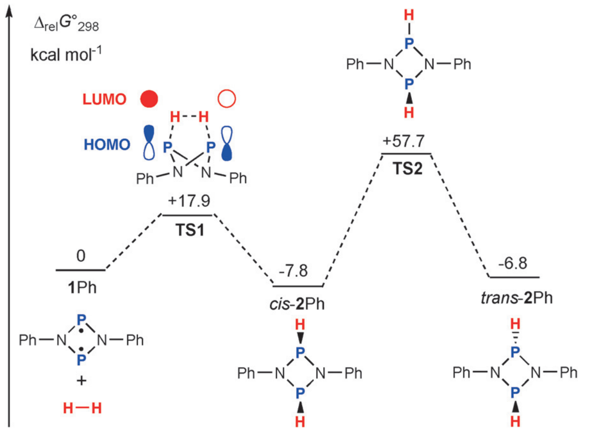


*Figure 3.* $H_2$ activation: Computed transition states (TSs) and activation barriers for the formation of **2** (*cis*) and the isomerization to the *trans* isomer (phenyl-substituted model compounds, M062X/aug-cc-pvtz).

exclusive formation of the *cis* isomer can be explained by the interaction of the transannular antibonding HOMO (of biradicaloid **1**) with the antibonding σ* LUMO (of $H_2$) when the two species approach each other (Figure 3) and the rather large barrier (57.7 kcal mol$^{-1}$, TS2) for the isomerization process. Hence, *cis*-**2**Ph is both the thermodynamically and kinetically favored product, which is in accord with the experimental data recorded for *cis*-**2**.

In a second series of experiments, a benzene solution of **1** was treated with a constant flow of carbon dioxide, which again resulted in an immediate color change, but this time from orange to red by formation of the zwitterionic species **4** and CO (Scheme 3).[49] Red crystals of **4** could be isolated in moderate yield (25 %) after concentrating the reaction mixture. X-ray structure determination revealed an almost planar $P_2N_2$ ring (Figure 4, deviation from planarity 6°) with one exocyclic oxygen atom attached to one phosphorus atom and a very short P–O bond (P2–O1 1.477(2) Å). This P–O bond is considerably shorter than the sum of the covalent radii for a single bond, but is in accord with a strongly polarized double bond ($\Sigma r_{cov}(P{-}O) = 1.72$, $\Sigma r_{cov}(P{=}O) = 1.48$ Å, corrected according to the Schomaker–Stevenson equation).[50,51] Moreover, the P2–N bonds (1.877(2), 1.963(2) Å) are significantly longer than the P1–N bonds (1.626(2), 1.627(2) Å) and the sum of the covalent radii for a single bond ($\Sigma r_{cov}(P{-}N) = 1.76$, $\Sigma r_{cov}(P{=}N) = 1.52$ Å).[50,51] The $^{31}$P NMR data (AB spin system, $\delta = 335.0$, 196.6 ppm, $J_{PP} = 52.0$ Hz; calcd $\delta = 350$, 196 ppm)[52] are in agreement with this structural motif and compare very well with hitherto known cationic species, for example, $[ClP(\mu\text{-}N^tBu)_2P]^+$ ($\delta = 176.6$, 365.7 ppm, $J_{PP} = 73.2$ Hz),[53] $[ClP(\mu\text{-}NTer)_2P]^+$ ($\delta = 203.6$, 366.6 ppm, $J_{PP} = 53.0$ Hz) and $[N_3P(\mu\text{-}NTer)_2P]^+$ ($\delta = 197.0$, 349.3 ppm, $J$ not resolved).[54] As depicted in Figure 5, both thermodynamics and kinetics clearly favor the 1,2 side-on addition of $CO_2$ at both P atoms forming intermediate **3**Ph, which releases CO upon forming the final product **4**Ph. In the first reaction step (Figure 5), the intermediate formation of the 1,2 side-on addition product **3**Ph rather than the 1,3 side-on product can be explained by the interaction of the transannular antibonding HOMO (of biradicaloid **1**Ph) with the antibonding π* LUMO (of $CO_2$), which, for symmetry reasons, only allows the 1,2- but not the 1,3-addition.[55]

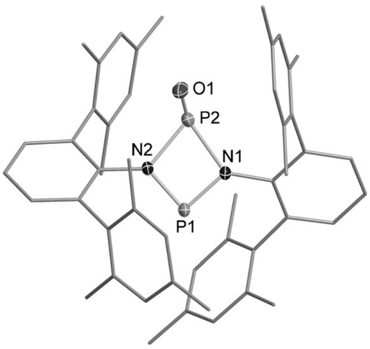


*Figure 4.* Molecular structure of **4**. Thermal ellipsoids set at 50 % probability (173 K). Selected bond lengths [Å] and angles [°]: P1–N1 1.626(2), P1–N2 1.627(2), P1–P2 2.6895(8), P2–O1 1.477(2), P2–N2 1.877(2), P2–N1 1.963(2); N1-P1-N2 89.50(8), O1-P2-P1 115.20(8), N2-P2-N1 73.20(7).

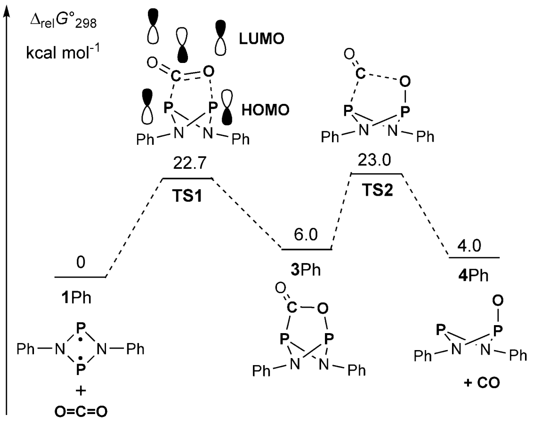


*Figure 5.* $CO_2$ activation: Computed transition states and activation barriers for the formation of intermediate **3**Ph and the final product **4**Ph upon CO release (phenyl-substituted model compounds, M062X/aug-cc-pvtz).

The standard Gibbs energy for the overall reaction (**1**Ph→**4**Ph) is slightly endergonic (4.0 kcal mol$^{-1}$) in the gas phase for the model reaction (phenyl instead of terphenyl); however, as no standard conditions were applied and the formed CO was removed constantly from the reaction mixture, the reaction is driven to product **4** in accord with the experimental observations.

Lastly, we investigated the reaction of $[P(\mu\text{-}NTer)]_2$ (**1**) with the polarized N–H bonds of ammonia. Again in a straightforward reaction, the initially orange solution of **1** turned colorless upon treatment with $NH_3$, yielding one final product (**5**) in rather good yields (50 %, Scheme 3 and Figure 6). $^{31}$P NMR control experiments of this reaction did not indicate the formation of any intermediate, indicating a rather fast reaction. Indicative for azadiphosphiridines, the $^{31}$P NMR spectrum showed a high-field-shifted AB spin

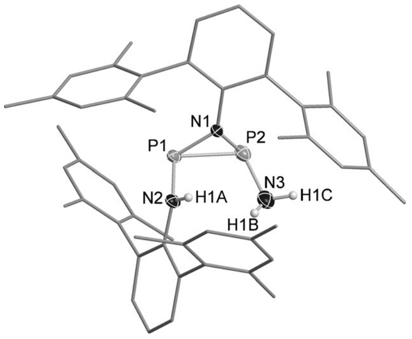


*Figure 6.* Molecular structure of **5**. Thermal ellipsoids set at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: P1–N2 1.725(2), P1–N1 1.729(2), P1–P2 2.2064(8), P2–N3 1.673(2), P2–N1 1.755(2); N1-P1-P2 51.24(6), N1-P2-P1 50.19(5), N2-P1-P2 103.07(7), N3-P2-P1 106.88(9), N2-P1-P2-N3 10.9(1).

system ($\delta = -50.7, -59.2$ ppm) with a characteristically small $^1J_{PP}$ coupling constant of $-114$ Hz.[44,56–61] The presence of an azadiphosphiridine moiety is evident from the molecular structure (Figure 6) as well, with a P–P bond length of 2.2064(8) Å, which compares well to the sum of the covalent radii ($\Sigma r_{cov}$(P–P) = 2.22 Å).[51] Three distinct $\nu_{N-H}$ modes were observed in the IR and Raman spectra, which are in nice agreement with the computations (IR: 3299, 3324, and 3384 cm$^{-1}$; Raman: 3302, 3326, and 3388 cm$^{-1}$). The bands at 3299 and 3384 cm$^{-1}$ could be assigned to the in-phase (symmetric) and out-of-phase (antisymmetric) N–H stretching modes of the primary amine functional group whereas the band at 3324 cm$^{-1}$ was assigned to the N–H stretch of the secondary amine group. Computations of the formation of model compound **5**Ph did not give a simple picture (see the Supporting Information, Table S8 and Figure S11). The initial step is the activation of an N–H bond by both P radical centers, which requires an activation energy of 25.7 kcal mol$^{-1}$, affording the *cis* isomer of an 1-amino-1,3-diphospha-2,4-diazane intermediate in an exergonic reaction ($-13.5$ kcal mol$^{-1}$). The second step is proton migration from P to N with a high activation barrier of 53.8 kcal mol$^{-1}$, which is followed by ring breaking by cleavage of a P–N bond and simultaneous formation of the azadiphosphiridine ring **5**Ph. Owing to the rather large activation barrier of the second step, we believe that the presence of excess ammonia as a proton shuttle may significantly decrease this barrier. A similar rearrangement was observed for the activation of alkynes and phosphaalkynes, which also led to the formation of [3.1.0]bicyclic azadiphoshiridines.[44]

In summary, we have shown that the singlet biradicaloid [P(μ-NTer)]$_2$ displays intriguing reactivity, enabling the activation of $H_2$, $CO_2$, and $NH_3$. These reactions are very fast even at ambient temperature, so no intermediates could be observed. Activation of $H_2$ led to the exclusive formation of *cis*-[HP(μ-NTer)]$_2$ in an almost reversible process; at elevated temperatures, $H_2$ is released, recovering biradicaloid [P(μ-NTer)]$_2$. The reaction with $CO_2$ afforded the "biradicaloid monoxide" [OP(μ-NTer)$_2$P], a zwitterionic species of interest with respect to its coordination behavior, which could not be obtained by direct reaction of [P(μ-NTer)]$_2$ with oxygen. The reaction with ammonia afforded an azadiphosphiridine scaffold after activation of an N–H bond. As a cascade of reactions is necessary to rearrange the molecule into an azadiphosphiridine, this process was not reversible.

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