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Azide-Analogous Organophosphorus Chemistry: RNP_2 as a Ligand and P_2 Source

*Lothar Weber**

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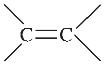
One of the most important developments in the field of phosphorus chemistry since the 1970s has been the study of compounds of trivalent phosphorus that contain pπ–pπ bonds. Derivatives with double and triple bonds involving phosphorus have enriched the fields of organic, inorganic, and organometallic chemistry enormously.[1] The diagonal relationship of the elements carbon and phosphorus, as well as the isolobal concept have provided a rationale for understanding new structures and reaction patterns. These concepts have also been extremely useful in the design of new compounds. Electrocyclic reactions (for example, Diels–Alder additions) of molecules with double bonds, such as alkenes (**A**), phosphaalkenes (**B**), and diphosphenes (**C**), are important for the selective construction of acyclic, cyclic, and polycyclic molecules.[2] The related series of molecules with triple bonds comprises alkynes (**D**), phosphaalkynes (**E**), and the diphosphorus molecule (**F**).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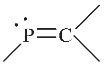
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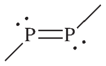
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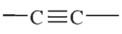
D


E


F

Nearly a century after the first preparation of ethyne, $HC\equiv CH$, by Wöhler (in 1862), Gier reported the synthesis of the unstable methylidynephosphane molecule, $HC\equiv P$, from PH_3 in the electric arc between two graphite electrodes (in 1961).[3] The synthesis of the first kinetically stable (at room temperature) phosphaalkyne, $t\mathrm{Bu}C\equiv P$, by Becker et al.[4] was a milestone and served as impetus for the explosive development of the organic and organometallic chemistry of such triple-bond systems.[5] The door to a plethora of novel ring and cage compounds, such as tetraphosphacubanes,[6] 1,3,5-triphosphabenzenes,[7] and oligophosphacyclopentadienyl complexes,[8] was suddenly wide open. Remarkable recent results in this area are the synthesis of the borate anion $[(CF_3)_3BC\equiv P]^-$, which features a phosphaethynide unit,[9] and of the complex $[(Ph_2PCH_2CH_2PPh_2)_2Ru(H)(C\equiv P)]$, which features a terminal phosphaethynyl ligand.[10,11]

N_2 is the only known allotrope of nitrogen. In contrast, the P_4 tetrahedron is the only species present in phosphorus melts and in the gas phase of phosphorus at temperatures up to 1100 K. At higher temperatures, the dissociation equilibrium $P_4 \rightleftarrows 2\,P_2$ gains relevance. Unlike the inert N_2 molecule, the higher congener P_2 is extremely reactive, preventing its use as a laboratory chemical in synthesis. Analogously to phosphinidene (RP) chemistry,[12] compounds that release P_2 in the presence of suitable reactants under mild conditions are desirable. There is only one known process in which a P_2 unit is transferred from white phosphorus to an organic molecule, lithium(trimethylsilyl)diazomethanide, under mild conditions to afford a 1,2,3,4-diazadiphosphole.[13]

Transition-metal complexes with P_2 ligands have been well studied. In nearly all cases, these complexes are produced by the metal-assisted degradation of white phosphorus, often under forcing conditions. This synthesis method generally leads to mixtures of complexes with different P_x ligands ($x \leq 12$).[14] A P_2 unit has never been transferred from such a complex to an organic molecule.[15]

The search for a P_2-transfer reagent came to an end when Cummins et al. reported the synthesis of $[(\eta^2\text{-Mes*NPP})Nb(NNpAr)_3]$ (**4**; Mes* = 2,4,6-$t\mathrm{Bu}_3C_6H_2$, Np = $CH_2C(CH_3)_3$, Ar = 3,5-$Me_2C_6H_3$).[16] Reaction of the niobaaziridine hydride **1** with white phosphorus provided the μ-η^2:η^2-P_2-diniobium complex **2** (Scheme 1). Complex **2** was then reductively cleaved by sodium amalgam in tetrahydrofuran (THF) to afford salt **3**, which features a phosphidoniobium anion. Treatment of **3** with the chloroiminophosphane ClP=NMes* reported by Niecke et al.[17] led to complex **4** with a η^2-P=P=NMes* ligand, which can formally be regarded as a diphosphorus-substituted organic azide.

By analogy to the chemistry of organic azides, which release nitrene fragments (RN) with the elimination of N_2, it was anticipated that complex **4** might release a P_2 unit with the transfer of the resulting nitrene to the metal. Accordingly, the thermolysis of **4** at 65 °C in neat 1,3-cyclohexadiene led to the smooth and quantitative formation of the imidoniobium complex **5** and the tetracycle **6** (Scheme 2). The intermediates in this transformation could not be detected spectroscopically. The reaction follows first order kinetics with respect

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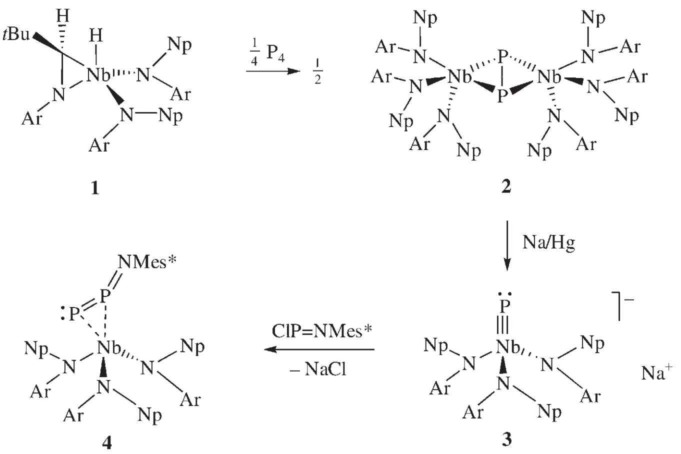
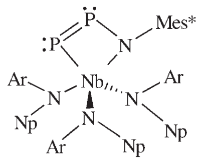
[*] Prof. Dr. L. Weber
Fakultät für Chemie
Universität Bielefeld
Universitätsstrasse 25, 33615 Bielefeld
(Germany)
Fax: (+49) 521-106-6146
E-mail: lothar.weber@uni-bielefeld.de



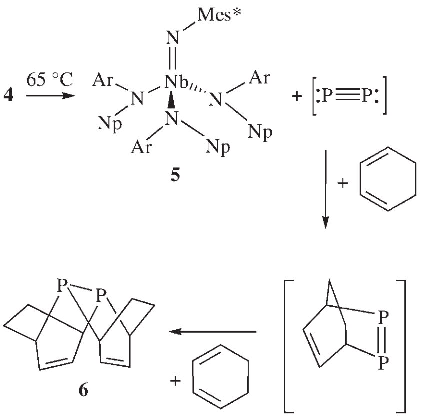
Scheme 1.

to **4** and may involve the isomer **4′**, in which an Nb–N interaction involving the PPNMes* ligand occurs.

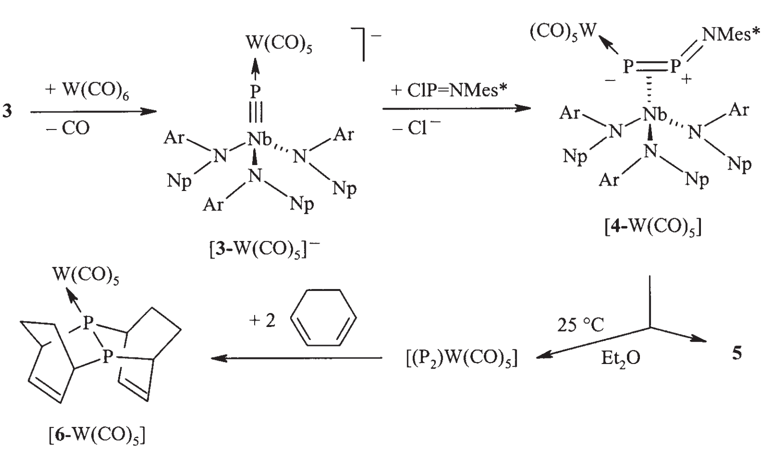


4'

Phosphinidene species are known to be markedly stabilized by coordination to a [W(CO)$_5$] fragment.[12] The transfer of a P_2 unit from **4** to two equivalents of 1,3-cyclohexadiene was facilitated by a similar approach. The starting material [**3**-W(CO)$_5$]$^-$ was treated with ClP=NMes* to form [**4**-W(CO)$_5$], which was then treated with a slight excess of 1,3-cyclohexadiene in diethyl ether at 25 °C to give the adduct [**6**-W(CO)$_5$] (Scheme 3). The P_2 unit is apparently stabilized through complexation, which prolongs the lifetime of the fragment and makes the use of a large excess of the diene unnecessary. The first-order kinetics of the reaction indicates that the extrusion of [(P_2)W(CO)$_5$] from [**4**-W(CO)$_5$] is the rate determining step.



Scheme 2.



Scheme 3.

Apart from raising fundamental questions about the mechanism and scope of this novel P_2 chemistry in solution, the realization of a clean P_2 transfer to a 1,3-diene opens a promising route to polycyclic diphosphanes, which are of interest as ligands in homogenous catalysis.

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[1] *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**.

[2] Review: R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 157–219.

[3] T. E. Gier, *J. Am. Chem. Soc.* **1961**, *83*, 1769–1770.

[4] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1981**, *36*, 16–19.

[5] a) M. Regitz, P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 58–111; b) L. Weber, *Adv. Organomet. Chem.* **1997**, *41*, 1–67.

[6] T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter, M. Regitz, *Angew. Chem.* **1989**, *101*, 1035–1037; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1013–1015.

[7] a) P. Binger, S. Leininger, J. Stannek, B. Gabor, M. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411–2414; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227–2230; b) F. Tabellion, A. Nachbaur, S. Leininger, C. Peters, M. Regitz, F. Preuss, *Angew. Chem.* **1998**, *110*, 1318–1321; *Angew. Chem. Int. Ed.* **1998**, *37*, 1233–1235.

[8] K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester **1998**, pp. 258–358.

[9] M. Finze, E. Bernhardt, H. Willner, C. W. Lehmann, *Angew. Chem.* **2004**, *116*, 4254–4257; *Angew. Chem. Int. Ed.* **2004**, *43*, 4160–4163.

[10] J. C. Cordaro, D. Stein, H. Rüegger, H. Grützmacher, *Angew. Chem.* **2006**, *118*, 6305–6308; *Angew. Chem. Int. Ed.* **2006**, *45*, 6159–6162.

[11] See the Highlight: R. J. Angelici, *Angew. Chem.*, DOI: 10.1002/ange.200603724; *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200603724.

[12] a) Review: F. Mathey in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 33–47; b) Review: R. Streubel, *Coord. Chem.*

Rev. **2002**, *227*, 175 – 192; c) L. Weber, G. Noveski, U. Lassahn, H.-G. Stammler, B. Neumann, *Eur. J. Inorg. Chem.* **2005**, 1940 – 1946.

[13] C. Charrier, N. Maigrot, L. Ricard, P. Le Floch, F. Mathey, *Angew. Chem.* **1996**, *108*, 2282 – 2283; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2133 – 2134.

[14] Review: M. Ehses, A. Romerosa, M. Peruzzini, *Top. Curr. Chem.* **2002**, *220*, 107 – 140.

[15] See however: $[W_2(OiPr)_6(py)_2 + [Co_2(\mu\text{-}P_2)(CO)_6] \rightarrow [W_2(OiPr)_6(py)(\mu\text{-}P_2)] + \ldots$; M. H. Chisholm, K. Folting, J. C. Huffman, J. J. Koh, *Polyhedron* **1985**, *4*, 893 – 895.

[16] N. A. Piro, J. S. Figueroa, J. T. McKellar C. C. Cummins, *Science* **2006**, *313*, 1276 – 1279.

[17] E. Niecke, M. Nieger, F. Reichert, *Angew. Chem.* **1988**, *100*, 1781 – 1782; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1715 – 1716.

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