DOI: 10.1002/ange.200604736

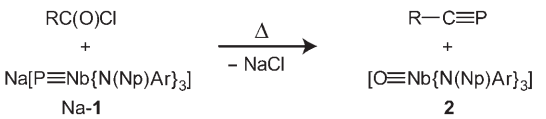
VIP Terminal Phosphide Complexes

A Terminal Nitride-to-Phosphide Conversion Sequence Followed by Tungsten Phosphide Functionalization Using a Diphenylphosphenium Synthon**

*Alexander R. Fox, Christopher R. Clough, Nicholas A. Piro, and Christopher C. Cummins**

Dedicated to Professor Philip P. Power

The terminal, anionic niobium phosphide (P^{3-}) complex Na[P≡Nb(N[Np]Ar)$_3$] (Na-**1**; Np = neopentyl, Ar = 3,5-$Me_2C_6H_3$) has served as a platform for the construction of multiply bonded, phosphorus-containing moieties as both complexed ligands and free entities.[1–5] Exemplifying the latter is the synthesis of phosphaalkynes (RC≡P) and [O≡Nb{N(Np)Ar}$_3$] (**2**) by treatment of Na-**1** with acid chlorides (RC(O)Cl), a reaction [Eq. (1)] that proceeds with NaCl



(1)

elimination and formation of a thermally unstable yet isolable metallacyclic acylphosphinidene intermediate of the form [{RC(O)P}Nb{N(Np)Ar}$_3$].[5] We envisioned that a similar method could be employed to synthesize new transition-metal phosphide complexes, given the availability of a suitable reaction partner for Na-**1**. We recently reported an attractive candidate for this application: the tungsten oxide/chloride complex, [O(Cl)W{N(*i*Pr)Ar}$_3$] (**3**).[6] In a reaction similar to Equation (1), complex **3** is prepared by treating the corresponding nitride complex [N≡W{N(*i*Pr)Ar}$_3$] (**4**) with pivaloyl chloride (*t*BuC(O)Cl), and is quantitatively obtained as a blood-red, highly lipophilic solid of sufficient purity for further synthetic studies. We hypothesized that in the presence of Na-**1**, **3** would behave as an "inorganic acid chloride", engaging Na-**1** by elimination of NaCl. With subsequent intermetal exchange of P and O ligands, the known oxidoniobium complex **2** would be generated as well as a new terminal phosphide complex [P≡W{N(*i*Pr)Ar}$_3$] (**5**). Several examples of installing multiply bonded ligands (oxide, imide, and alkylidene) by intermetal ligand exchange have been reported;[7–16] herein, we extend this concept to the terminal phosphide functional group.

Our hypothesis was tested by treating a yellow-orange, ethereal solution of Na-**1** with a red, ethereal solution of **3** at −35 °C, following in situ preparation of **3** from **4** and removal of *t*BuCN. Upon stirring for two hours at 22 °C, an orange-brown, homogeneous solution was obtained. Following solvent removal under reduced pressure the product mixture was dissolved in C_6D_6. The ^{1}H NMR spectrum of the product mixture revealed clean formation of **2** and a single, new isopropylanilide ligand environment. The ^{31}P{^{1}H} NMR spectrum contained only one feature, a singlet at very low field strength ($\delta = 1021$ ppm), flanked by a pair of satellites ($^1J_{PW} = 193$ Hz), consistent with a terminal phosphide ligand coupled to a ^{183}W nucleus ($I = 1/2$, 14.3 % natural abundance).[17] Separation of **5** from NaCl was trivial; however, separation of **5** from coproduct **2** at first proved difficult, owing to their similar solubility properties. This was initially overcome by applying the Pasteur method,[18] whereby mixtures of crystalline **2** and **5** were manually separated.

A more efficient method of separating **5** from coproduct **2** was achieved by in situ conversion of **2** to the bistriflate complex [(TfO)$_2$Nb{N(Np)Ar}$_3$] (**6**, Tf = CF_3SO_2),[5] a complex that is only sparingly soluble in common hydrocarbon solvents. Accordingly, treatment of a 1:1 mixture of **2** and **5** in Et_2O with neat triflic anhydride (Tf_2O, 1 equiv) at room temperature resulted in a color change from orange-brown to yellow-brown over several minutes as a yellow precipitate formed. Following solvent removal under reduced pressure, the product mixture was dissolved in C_6D_6. The ^{1}H NMR spectrum of the product mixture revealed clean and selective production of **6**, with **5** remaining unperturbed. The ^{31}P{^{1}H} NMR spectrum displayed only the downfield signal associated with **5**, thus confirming its role as a spectator in this reaction. Thus, a one-pot procedure for the synthesis and isolation of **5** was achieved wherein precipitate **6** is separated simply by filtration (Scheme 1). By this method, spectroscopically pure **6** was isolated in 92 % yield as a golden precipitate, and spectroscopically pure **5** was isolated as orange blocks in 66 % yield following overnight crystallization from Et_2O at −35 °C.[19]

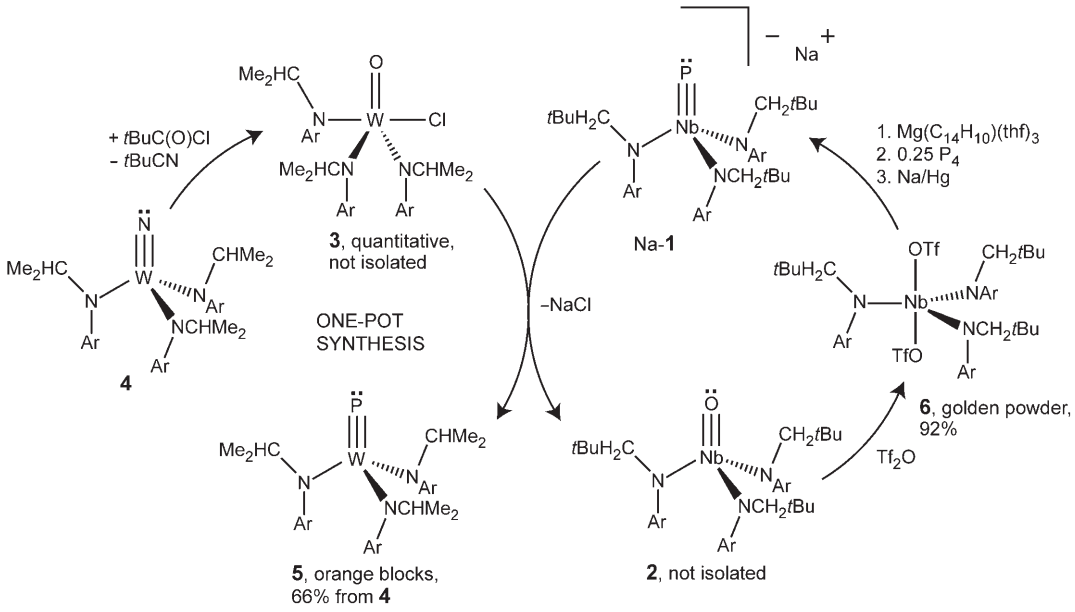
X-ray structural analysis of **5** confirmed its monomeric formulation and the terminal coordination of the phosphide ligand (Figure 1). In the solid state, **5** is found to be isostructural to its molybdenum congener [P≡Mo{N(*i*Pr)Ar}$_3$],[20] crystallizing in the orthorhombic space group

[*] A. R. Fox, C. R. Clough, N. A. Piro, C. C. Cummins
Department of Chemistry, Room 6-435
Massachusetts Institute of Technology
77 Massachusetts Ave., Cambridge, MA 02139-4307 (USA)
Fax: (+1) 617-258-5700
E-mail: ccummins@mit.edu

[**] We gratefully acknowledge the U.S. National Science Foundation (CHE-0316823) for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1.

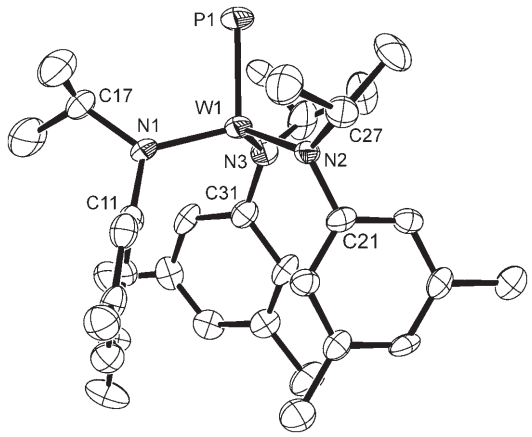


Figure 1. ORTEP rendering of **5** (one of two independent molecules shown, ellipsoids set at 50%). Selected bond lengths [Å] and angles [°]: W1-P1 2.119(3), W1-N 1.939 av; P1-W1-N 104.4 av.

$P2_12_12_1$ with two independent molecules per asymmetric unit. The W–P bond lengths of the two independent molecules (2.119(3), 2.122(3) Å) agree well with metal–phosphide bond lengths observed in previously reported terminal phosphide complexes.[20–24]

Previously reported routes to terminal phosphide complexes include metathesis of phosphaalkynes with $[W_2(OtBu)_6]$,[25–27] ancillary-ligand exchange at an existing terminal metal phosphide moiety,[14] activation of P_4 to yield complexed phosphide as a terminal ligand either directly or via intermediate bimetallic complexes containing μ-P_1 or μ:η^2,η^2-P_2 ligands,[2,5,20,21,28,29] and by treating $[(N_3N)WCl]$ ($N_3N = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) with either LiP(H)Ph (2 equiv) or $LiP(SiMe_3)_2$ (2 equiv).[22,30] Complete intermetal exchange of a phosphide ligand represents a new addition to this list. Increasing the attractiveness of the method described herein is the fact that **6** can be easily converted to the niobaziridine–hydride complex $[Nb(H)\{\eta^2\text{-}tBu(H)C{=}NAr\}\{N(Np)Ar\}_2]$,[31] from which the niobium phosphide reagent Na-**1** is ultimately derived (Scheme 1, right).[5]

DFT calculations were performed on a heterobimetallic model intermediate in order to further our understanding of the process by which **1** and **3** combine to exchange phosphide and oxide ligands.[19] The optimized structure of the model intermediate $[\{Ph(Me)N\}_3Nb(\mu\text{-}O)(\mu\text{-}P)W\{N(iPr)Ar\}_3]$ contains an unsymmetrical $\{Nb(\mu\text{-}O)(\mu\text{-}P)W\}$ core (Figure 2). The short W–P bond length (2.22 Å) and long W–O bond length (2.05 Å) are suggestive of an already significant W–P multiple-bond interaction and near complete transfer of the oxide ligand to the niobium center. Moreover, collapse of this model intermediate to the corresponding oxidoniobium complex $[O{\equiv}Nb\{N(Me)Ph\}_3]$ and **5** is calculated to be exothermic by 22 kcal mol^{-1}. Attempts to observe such an

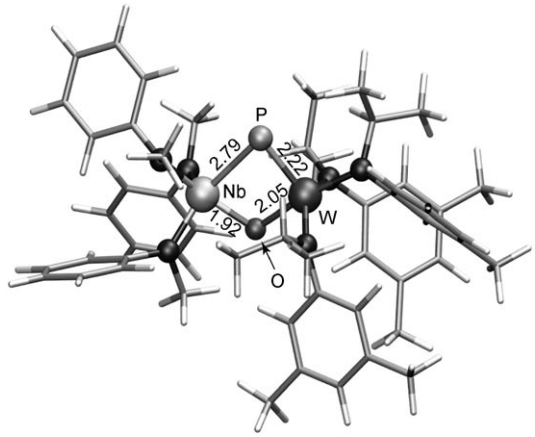
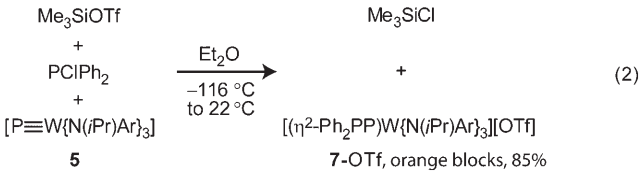


Figure 2. Optimized structure of model intermediate $[\{Ph(Me)N\}_3Nb(\mu\text{-}O)(\mu\text{-}P)W\{N(iPr)Ar\}_3]$. Selected bond lengths shown in Å.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

intermediate by low-temperature $^{31}P\{^1H\}$ NMR spectroscopy were unsuccessful.[32]

Initial reactivity studies of **5** revealed its low nucleophilic character, exemplified by a lack of reaction with Me_3SiOTf (1 equiv) in Et_2O, CH_2Cl_2, or C_6D_6 for extended periods and at elevated temperatures. We were, however, able to productively exploit this observation with the construction of an η^2-bound phosphanylphosphinidene complex.[33–37] Accordingly, thawing solutions of **5** and Me_3SiOTf (1 equiv) in Et_2O and $PClPh_2$ in Et_2O were combined and allowed to stir for 3 h [Eq. (2)]. Over this time, the solution warmed to 22 °C and an



orange solid slowly precipitated. Recrystallization of the precipitate from THF/*n*-pentane at −35 °C provided the cationic, orange diphenylphosphanylphosphinidene complex $[(\eta^2\text{-}Ph_2PP)W\{N(iPr)Ar\}_3][OTf]$ (**7**-OTf), in 85% yield.[19] Formation of **7**-OTf likely proceeds by the reaction of weakly nucleophilic **5** with an electrophilic phosphenium species generated by the reaction of Me_3SiOTf and $PClPh_2$.[38] The synthesis of **7**-OTf through Me_3SiCl elimination closely relates to the synthesis of the Group 5 η^2-phosphanylphosphinidene complexes $[(\eta^2\text{-}R_2PP)Nb\{N(Np)Ar\}_3]$ (**8**, R = *t*Bu; **9**, R = Ph),[2,39] and complements the work of Fritz and coworkers with their synthesis of Group 10 η^2-phosphanylphosphinidene complexes by tBu_2PP group transfer.[40,41]

The $^{31}P\{^1H\}$ NMR spectrum of **7**-OTf in $CDCl_3$ contains two sets of doublets located at $\delta = 331.8$ (P_α, phosphinidene) and 6.7 ppm (P_β, phosphanyl) with a large $^1J_{PP}$ coupling constant (428 Hz) that is suggestive of multiple bonding between the phosphorus centers.[42] Additionally, satellites due to coupling between ^{183}W and ^{31}P are observed for P_β ($^1J_{WP} = 72$ Hz). Though such satellites are not resolved for P_α, the W–P_α coupling constant cannot exceed the magnitude of the base width of the $^{31}P_\alpha$ NMR peak (44 Hz). Such remarkably low values for J_{PW} may reflect low participation of the phosphorus-based s orbitals in the W–P interactions.[22]

Salt **7**-OTf crystallizes in the triclinic space group $P\bar{1}$, with three THF molecules of crystallization. The solid-state structure of **7**-OTf shows the η^2 interaction of the Ph_2PP fragment with the tungsten center (Figure 3). No close contacts are observed between the complex cation and triflate anion in **7**-OTf. The W1–P1 bond length (2.3312(9) Å) and W1–P2 bond length (2.4981(9) Å) in **7**-OTf are both approximately 0.09 Å shorter than analogous bond lengths observed in the related neutral complex **9**. The P1–P2 bond length (2.0873(12) Å) in **7**-OTf is approximately 0.014 Å longer than the analogous length observed in **9**, and is approximately 0.12 Å shorter that expected for a P–P single bond.[43] This further supports the view that the Ph_2PP ligand in **7**-OTf possesses multiple-bond character. Taken together, the spectral and structural features of **7**-OTf point to a view of the

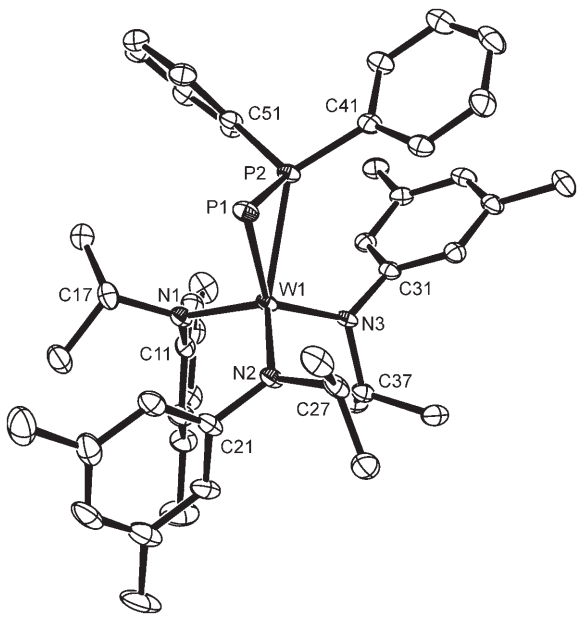


Figure 3. ORTEP rendering of complex cation **7** (ellipsoids set at 50%). Selected bond lengths [Å] and angles [°]: W1-P1 2.3312(9), W1-P2 2.4981(9), P1-P2 2.0973(12); W1-P1-P2 60.60(3), P1-P2-W1 60.32(3).

bonding situation as that of a doubly bonded phosphanylphosphinidene ligand complexed to a formally d^2 tungsten(IV) center according to the standard Dewar–Chatt–Duncanson model of π complexation.

In conclusion, we now provide an example of a method for installing a terminal phosphide ligand through intermetal atom exchange. It is hoped that this methodology may make available terminal phosphide complexes of metals for which they are not known; isolable terminal phosphide systems currently are limited to Nb, Mo, and W. Additionally, an otherwise weakly nucleophilic terminal phosphide complex has been functionalized by generating a reactive electrophile in its presence, thus furthering the role of terminal phosphide complexes as platforms for the synthesis of complexed, phosphorus-containing moieties.

Received: November 21, 2006
Published online: January 9, 2007

Keywords: atom transfer · multiple bonds · P ligands · phosphorus · tungsten

[1] J. S. Figueroa, C. C. Cummins, *Dalton Trans.* **2006**, 2161–2168.
[2] J. S. Figueroa, C. C. Cummins, *Angew. Chem. Int. Ed.* **2004**, *43*, 984–988; *Angew. Chem.* **2004**, *116*, 1002–1006.
[3] J. S. Figueroa, C. C. Cummins, *Angew. Chem. Int. Ed.* **2005**, *44*, 4592–4596; *Angew. Chem.* **2005**, *117*, 4668–4672.
[4] N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* **2006**, *313*, 1276–1279.
[5] J. S. Figueroa, C. C. Cummins, *J. Am. Chem. Soc.* **2004**, *126*, 13916–13917.
[6] C. R. Clough, J. B. Greco, J. S. Figueroa, P. L. Diaconescu, W. M. Davis, C. C. Cummins, *J. Am. Chem. Soc.* **2004**, *126*, 7742–7743.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[7] J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, W. J. Youngs, *J. Am. Chem. Soc.* **1980**, *102*, 4515 – 4516.
[8] J. H. Wengrovius, R. R. Schrock, *Organometallics* **1982**, *1*, 148 – 155.
[9] J. Robbins, G. C. Bazan, R. R. Schrock, *Inorg. Chem.* **1993**, *32*, 4155 – 4156.
[10] A. M. Lapointe, R. R. Schrock, *Organometallics* **1993**, *12*, 3379 – 3381.
[11] A. M. Lapointe, R. R. Schrock, W. M. Davis, *Organometallics* **1995**, *14*, 2699 – 2703.
[12] A. M. Lapointe, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1995**, *117*, 4802 – 4813.
[13] M. Jolly, J. P. Mitchell, V. C. Gibson, *J. Chem. Soc. Dalton Trans.* **1992**, 1331 – 1332.
[14] I. J. Blackmore, V. C. Gibson, A. J. Graham, M. Jolly, E. L. Marshall, B. P. Ward, *J. Chem. Soc. Dalton Trans.* **2001**, 3242 – 3243.
[15] V. C. Gibson, A. J. Graham, M. Jolly, J. P. Mitchell, *Dalton Trans.* **2003**, 4457 – 4465.
[16] A. Galindo, F. Montilla, A. Pastor, E. Carmona, E. Gutierrez-Puebla, A. Monge, C. Ruiz, *Inorg. Chem.* **1997**, *36*, 2379 – 2385.
[17] G. Wu, D. Rovnyak, M. J. A. Johnson, N. C. Zanetti, D. G. Musaev, K. Morokuma, R. R. Schrock, R. G. Griffin, C. C. Cummins, *J. Am. Chem. Soc.* **1996**, *118*, 10654 – 10655.
[18] G. L. Geison, *The Private Science of Louis Pasteur*, Princeton University Press, Princeton, **1995**, chap. 3, pp. 53 – 89.
[19] Full synthetic and spectroscopic details for all new compounds, as well as computational details, can be found in the Supporting Information. CCDC-626595 (**5**) and CCDC-626596 (**7**-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.
[20] J.-P. F. Cherry, F. H. Stephens, M. J. A. Johnson, P. L. Diaconescu, C. C. Cummins, *Inorg. Chem.* **2001**, *40*, 6860 – 6862.
[21] C. E. Laplaza, W. M. Davis, C. C. Cummins, *Angew. Chem.* **1995**, *107*, 2181 – 2183; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2042 – 2044.
[22] N. C. Zanetti, R. R. Schrock, W. M. Davis, *Angew. Chem.* **1995**, *107*, 2184 – 2186; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2044 – 2046.
[23] F. H. Stephens, J. S. Figueroa, P. L. Diaconescu, C. C. Cummins, *J. Am. Chem. Soc.* **2003**, *125*, 9264 – 9265.
[24] B. P. Johnson, G. Balázs, M. Scheer, *Coord. Chem. Rev.* **2006**, *250*, 1178 – 1195.
[25] G. Becker, W. Becker, R. Knebl, H. Schmidt, U. Hildenbrand, M. Westerhausen, *Phosphorus Sulfur Silicon Relat. Elem.* **1987**, *30*, 349 – 352.
[26] M. Scheer, K. Schuster, T. A. Budzichowski, M. H. Chisholm, W. E. Streib, *J. Chem. Soc. Chem. Commun.* **1995**, 1671 – 1672.
[27] M. Scheer, P. Kramkowski, K. Schuster, *Organometallics* **1999**, *18*, 2874 – 2883.
[28] F. H. Stephens, M. J. A. Johnson, C. C. Cummins, O. P. Kryatov, S. V. Kryatov, E. V. Rybak-Akimova, J. E. McDonough, C. D. Hoff, *J. Am. Chem. Soc.* **2005**, *127*, 15191 – 15200.
[29] M. H. Chisholm, K. Folting, J. W. Pasterczyk, *Inorg. Chem.* **1988**, *27*, 3057 – 3058.
[30] M. Scheer, J. Müller, M. Häser, *Angew. Chem.* **1996**, *108*, 2637 – 2641; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2492 – 2496.
[31] J. S. Figueroa, C. C. Cummins, *J. Am. Chem. Soc.* **2003**, *125*, 4020 – 4021.
[32] Frozen solutions of **1** and **3** in Et_2O were layered in a J. Young NMR tube and allowed to thaw and mix immediately prior to insertion into an NMR probe precooled to −70 °C. No intermediate was observed in the $^{31}P\{^1H\}$ NMR spectrum: within the time that it took for the layered solutions to thaw and the sample to be inserted into the NMR probe (ca. 90 s), only the resonance for product **5** was observed, thus indicating swift and complete consumption of **1**.
[33] G. Trinquier, G. Bertrand, *Inorg. Chem.* **1985**, *24*, 3842 – 3856.
[34] S. Q. Jin, B. T. Colegrove, H. F. Schaefer, *Inorg. Chem.* **1991**, *30*, 2969 – 2977.
[35] S. Creve, K. Pierloot, M. T. Nguyen, L. G. Vanquickenborne, *Eur. J. Inorg. Chem.* **1999**, 107 – 115.
[36] S. Grigoleit, A. Alijah, A. B. Rozhenko, R. Streubel, W. W. Schoeller, *J. Organomet. Chem.* **2002**, *643*, 223 – 230.
[37] J. Olkowska-Oetzel, J. Pikies, *Appl. Organomet. Chem.* **2003**, *17*, 28 – 35.
[38] N. Burford, P. J. Ragogna, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* **2003**, *125*, 14404 – 14410.
[39] For a recent example of an early-transition-metal η^1-phosphanylphosphinidene complex, see: J. Pikies, E. Baum, E. Matern, J. Chojnacki, R. Grubba, A. Robaszkiewicz, *Chem. Commun.* **2004**, 2478 – 2479.
[40] H. Krautscheid, E. Matern, I. Kovacs, G. Fritz, J. Pikies, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1917 – 1924.
[41] H. Krautscheid, E. Matern, J. Pikies, G. Fritz, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2133 – 2135.
[42] S. Shah, J. D. Protasiewicz, *Coord. Chem. Rev.* **2000**, *210*, 181 – 201.
[43] The experimentally determined P–P interatomic distance in $P_4(g)$ is 2.21 Å. N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, **1997**, chap. 12, p. 479.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim