DOI: 10.1002/ejic.200600084

Synthesis and Molecular Structure of [Cp*Ta(Ph)(P_6Ph_5)]: A Terminal Phosphinidene Complex of the $(P_6Ph_5)^{3-}$ Ligand (Cp* = C_5Me_5)

Robert Wolf[a] and Evamarie Hey-Hawkins*[a]

Keywords: Tantalum / Phosphorus / P ligands / Oligophosphanes / Phosphinidene complexes

The terminal phosphanyl phosphinidene complex [Cp*Ta(Ph)(P_6Ph_5)] (**2**) has been isolated in 16% yield from the reaction of [Cp*$TaCl_4$] with 2 equiv. $Na_2(P_4Ph_4)$ and displays an η^4-bound $(P_6Ph_5)^{3-}$ ligand according to X-ray crystallography and ^{31}P NMR spectroscopy.

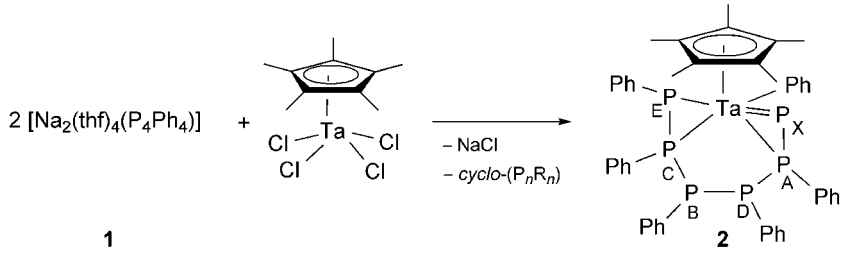
Terminal phosphinidene complexes [$L_nM(PR)$] are of much current interest due to their versatile reactivity and interesting bonding properties.[1,2] In this respect, phosphanyl phosphinidene complexes [$L_nM(PPR_2)$] are a particularly attractive subclass, as the phosphanyl group may or may not be involved in coordination.[3] The first representatives were described only recently.[4,5]

During our studies on the coordination chemistry of oligophosphanediide anions $(P_nR_n)^{2-}$ (n = 2–4)[6–9] we could show that, in spite of its highly reducing nature,[9] the $(P_4Ph_4)^{2-}$ dianion remains intact in the transmetalation reaction of 2 equiv. of [$CuCl(PCyp_3)_2$] (Cyp = *cyclo*-C_5H_9) with $Na_2(P_4Ph_4)$ (**1**).[10] While this was an example of a successful transmetalation with a valence-electron-rich late-transition-metal halide,[11] we wished to extend the scope of this reaction to early transition-metal halides as well. Herein, we report the surprising result of the reaction of **1** with [Cp*$TaCl_4$] (Cp* = C_5Me_5). This led to the isolation of [Cp*Ta(Ph)(P_6Ph_5)] (**2**), which not only contains an unprecedented oligophosphanide ligand $(P_6Ph_5)^{3-}$, but is also a rare example of a terminal phosphanyl phosphinidene complex of tantalum.

Complex **2** could be isolated in low, though reproducible, yield (16%) from the 2:1 reaction of **1** with [Cp*$TaCl_4$] (Scheme 1). An X-ray crystal structure analysis[12] of **2** revealed a mononuclear complex in which a trianionic $(P_6Ph_5)^{3-}$ ligand binds in an η^4 fashion to the metal center (Figure 1). The coordination sphere of tantalum is completed by an η^5-coordinated pentamethylcyclopentadienyl ligand and an η^1-bound phenyl ligand. Remarkably, the Ta–P bond of the "naked" phosphorus atom P1 is significantly shorter than the remaining Ta–P distances [d(Ta1–P1) = 2.416(2), d(Ta1–P2) = 2.528(2), d(Ta1–P5) = 2.561(2), d(Ta1–P6) = 2.659(2) Å], and this indicates multiple-bond character of the Ta–P1 bond. Nevertheless, it is longer than the Ta–P bonds in the phosphinidene-bridged Ta complexes [{Cp*TaCl(μ-PR)}$_2$] [R = Cy, *t*Bu, Ph, Mes, 2,4,6-*i*$Pr_3C_6H_2$; d(Ta–P) = 2.317(6)–2.358(3) Å][13,14] and the terminal phosphinidene complexes [N{$CH_2CH_2N(SiMe_3)$}$_3$Ta=PCy] [d(Ta–P) = 2.145(7) Å][2a] and [(*t*$Bu_3SiO)_3$Ta=PPh] [d(Ta–P) = 2.317(4) Å].[2b] The Ta–P distance of the other terminal phosphorus atom of the chain (P6) is much longer [d(Ta1–P6) = 2.659(2) Å]. It is in the upper range of the values found in other terminal phosphanido complexes of tantalum [d(Ta–P) = 2.390–2.595(3) Å].[14,15] The pyramidal coordination of P6 (sum of bond angles around P6: 301.3°) indicates that it acts as a one-electron donor to the metal center, which is also in accordance with the 18-electron rule (vide infra). The remaining Ta–P distances are in the known range for phosphane complexes of tantalum.[16,17] The Ta–C distance of the *ipso*-carbon atom of the η^1-coordinated phenyl ligand [d(Ta1–C1) = 2.230(7) Å] is similar to those found in other cyclopentadienyl-substituted phenyl complexes of tantalum.[18] While the P–P bond lengths of P2 to P6 are in the range of single bonds [d(P2–P3, P3–P4, P4–P5, P5–P6) = 2.133(3)–2.213(3) Å],[19] the P–P bond involving the naked phosphorus atom is distinctly shorter [d(P1–P2) = 2.096(3) Å]. Similarly short P–P bonds have been observed in other phosphanyl phosphinidene complexes[4] and also in diphosphene complexes.[20] In fact, the geometry of the (PPPh) unit in **2** closely resembles that in the recently described Nb phosphanyl phosphinidene complexes [Nb{N(R)R^1}$_3$(PPR^2_2)] (R^1 = 3,5-$Me_2C_6H_3$, R = neopentyl, R^2 = Ph, *t*Bu).[4c]

Formally, compound **2** may be regarded as an 18-electron complex with a double bond between the metal center and the unsubstituted phosphorus atom (P1) and single bonds to the other coordinating P atoms (as depicted in Scheme 1). However, alternative descriptions of the bonding situation involving a multiply bonded PPPh fragment

[a] Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany
Fax: +49-341-9739319
E-mail: hey@rz.uni-leipzig.de



Scheme 1.

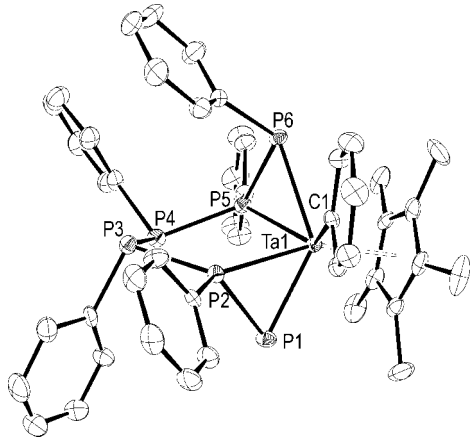


Figure 1. Solid-state molecular structure of **2**; H atoms omitted for clarity, ellipsoid probability: 30%. Selected bond lengths [Å] and angles [°]: Ta1–P1 2.416(2), Ta1–P2 2.528(2), Ta1–P5 2.561(2), Ta1–P6 2.659(2), Ta1–C1 2.230(7), av Ta–C in Cp* 2.451, P1–P2 2.096(3), P2–P3 2.213(3), P3–P4 2.185(3), P4–P5 2.211(3), P5–P6 2.133(3), C1–Ta1–P1 104.4(2), C1–Ta1–P2 78.6(2), C1–Ta1–P5 130.1(2), C1–Ta1–P6 89.6(2), P1–Ta1–P2 50.12(6), P1–Ta1–P5 93.61(7), P1–Ta1–P6 134.52(6), P2–Ta1–P5 78.55(6), P2–Ta1–P6 92.77(6), P5–Ta1–P6 48.20(6), P2–P1–Ta1 67.71(7), P5–P6–Ta1 63.50(7), P3–P2–Ta1 126.84(9), P4–P5–Ta1 118.84(9), P1–P2–P3 124.4(1), P2–P3–P4 95.7(1), P3–P4–P5 103.1(1), P4–P5–P6 129.4(1).

are equally plausible and may account for the relatively long Ta–P bond compared to other Ta phosphinidene complexes and the short bond between P1 and P2. Thus, the bonding situation is probably best described by a superposition of different mesomeric structures, as already suggested by Cummins and Pikies.[3,4,21]

The molecular composition of **2** was fully confirmed by IR spectroscopy, mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy. Notably, no P–H stretch is observed in the IR spectrum. The ^{1}H NMR spectrum shows multiplets in the region of 6.28 to 8.18 ppm for the phenyl groups and a singlet at δ = 1.81 ppm for the methyl resonances of the Cp* ligand. A characteristic low-field signal at +182.70 ppm is observed for the *ipso*-carbon atom of the Ta-bound phenyl group in the $^{13}C\{^1H,^{31}P\}$ NMR spectrum.[18,22] The $^{31}P\{^1H\}$ NMR spectrum displays a first-order ABCDEX spin system (Figure 2). No additional couplings are detected in the proton-coupled ^{31}P NMR spectrum. Only the ^1J(P–P) couplings could be assigned with certainty from the $^{31}P\{^1H\}$ NMR spectrum due to the line broadening caused by the interaction of four phosphorus nuclei (P_X, P_A, P_C, and P_E) with the ^{181}Ta nucleus. Nevertheless, this observation permits the assignment of the individual resonances (cf. Scheme 1). The striking low-field shift of the two-coordinate, "naked" P atom P_X (δ_X = +370.3, $^1J_{AX}$ = ±471 Hz) indicates multiple-bond character of the Ta–P_X bond. Its chemical shift is comparable to those observed in the related Nb complexes [Nb{N(R)-R^1}$_3$(PPR^2_2)] (R^1 = 3,5-$Me_2C_6H_3$, R = neopentyl; R^2 = Ph: δ = +401.3; R^2 = *t*Bu: δ = +405.5).[4c] The "phosphanyl moiety" (P_E and P_C) displays a similarly large value for its ^1J(P–P) coupling constant ($^1J_{CE}$ = ±444 Hz), but the resonance of its terminal P atom (P_E) is shifted to the typical high-field region observed for Ta phosphanides (δ_E = –127.7).[15] All in all, the ^{31}P parameters confirm that the solid-state structure of **2** is retained in solution.

Besides the ABCDEX spin system of **2** a minor amount of *cyclo*-(P_4Ph_4)[23] (ca. 4%) is observed in the $^{31}P\{^1H\}$

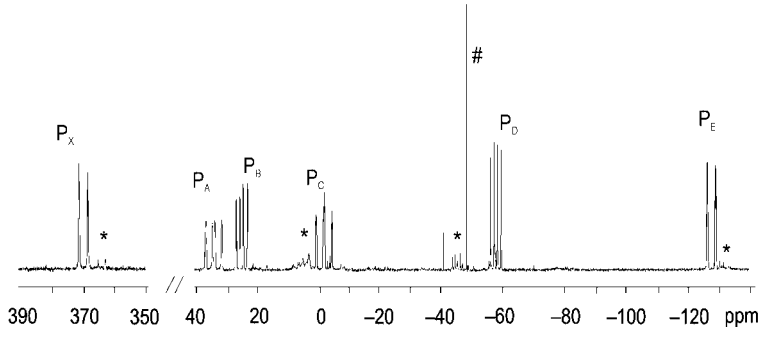


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of **2** (C_6D_6, 161.97 MHz). The singlet of *cyclo*-(P_4Ph_4)[23] is designated by #; * indicates signals of a further diastereomer of **2**. For the assignment of the individual multiplets, see Scheme 1.

NMR spectrum. Furthermore, a number of less intense multiplets are reproducibly observed, with rather similar chemical shifts to **2** (Figure 2). For example, a broad low-field doublet is detected at +364.3 ppm ($^1J_{PP}$ = ca. ±387 Hz). The unequivocal assignment of all signals was impaired by their low intensity (partly owing to the low solubility of **2** once isolated). Most likely, they can be attributed to the presence of a second diastereomer of **2** in solution, which may be formed by inversion of either of the uncoordinated P atoms (P_B or P_D). It is well-known that catenated oligophosphanes have significantly reduced inversion barriers, as was observed, for example, in the heterocycles *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$[24] and [M{*cyclo*-(P_4Cy_4As)}] (M = Li, Na).[25]

While rearrangement of oligophosphanide ligands during transmetalation reactions has been observed in a few instances,[11,26] the mechanism of formation of **2** is obviously rather complex. Presumably, it involves the initial formation of a low-valent Ta intermediate. Subsequently, the phenyl group may be transferred by oxidative addition of the P–C bond to the reduced metal center. ^{31}P NMR spectra of the reaction mixture show the formation of the cyclooligophosphanes *cyclo*-(P_nPh_n) (n = 4–6)[23,27] and the phosphinidene-bridged complex [{Cp*TaCl(μ-PPh)}$_2$][13] (identified by its characteristic low-field singlet at +402.3 ppm) as major products. In addition, numerous low-intensity multiplets are observed but could not be assigned. This seems to indicate the presence of a number of P–P bonded byproducts in the reaction mixture. No further tantalum-containing products could be isolated from the reaction. Attempts to obtain further insights by variation of the stoichiometry, the reaction conditions, and the starting materials have remained futile. Thus, the yield of **2** could not be increased by warming the reaction mixture to +80 °C. Furthermore, **2** could not be obtained from the reaction of 2 equiv. $K_2(P_3Ph_3)$ with [Cp*TaCl$_4$], from the reaction of [{Cp*TaCl(μ-PPh)}$_2$][13] with *cyclo*-(P_5Ph_5) (warming to +100 °C for 2 h), or from the reaction of **1** with [{Cp*TaCl$_2$}$_2$][28] (2:1). Only the cyclophosphanes *cyclo*-(P_nMes_n) (n = 3, 4)[29] were isolated from the reaction of [Cp*TaCl$_4$] with 2 equiv. $[Na_2(THF)_4(P_4Mes_4)]$.[8a] Clearly, a more detailed understanding of the reaction mechanism will only be gained from future studies.

In conclusion, we have shown that the unprecedented $(P_6Ph_5)^{3-}$ ligand containing six catenated phosphorus atoms is stabilized in the Ta phosphinidene complex [Cp*Ta(Ph)(P_6Ph_5)] (**2**). This adds to the growing evidence that, although not always straightforward,[9,11] the transmetalation reaction of alkali metal oligophosphanediides with transition metal halides represents a viable route to phosphorus-rich metal complexes with unusual structures and reactivities.

Experimental Section

All experiments were performed under an inert atmosphere. The NMR spectra were recorded with a Bruker AVANCE-DRX-400 spectrometer. ^{1}H NMR (400.13 MHz): internal standard solvent, external standard TMS. ^{31}P NMR (161.9 MHz): external standard 85% H_3PO_4. ^{13}C NMR (100.16 MHz): internal standard solvent, external standard TMS. For the assignment of the phosphorus signals, see Scheme 1. The mass spectrum was recorded with a MASPEC II spectrometer (FAB-MS, matrix: 3-nitrobenzyl alcohol). The IR spectra were recorded with an FTIR spectrometer Perkin–Elmer System 2000 (KBr) in the range 350–4000 cm^{-1}. All solvents were purified by distillation, dried, saturated with argon, and stored over a potassium mirror. $[Na_2(THF)_4(P_4Ph_4)]$ (**1**)[8a] and [Cp*TaCl$_4$][30] were synthesized according to the literature procedures.

2: A solution of **1** (6.18 g, 8.1 mmol) in toluene (40 mL) was added dropwise to a suspension of [Cp*TaCl$_4$] (1.85 g, 4.0 mmol) in toluene (30 mL) at –80 °C. The mixture turned dark-brown immediately on addition. The dark suspension was slowly warmed to room temperature and stirred overnight. The solvent was reduced to ca. 30 mL and the mixture was filtered. The dark-brown residue was washed three times with 20 mL of toluene. Then the combined filtrates were reduced to ca. 20 mL and the clear, dark brown solution was layered with *n*-hexane (35 mL). Dark red crystals of **2** formed on storage at room temperature for several weeks. Yield: 0.61 g (16% ref. to [Cp*TaCl$_4$]); m.p. 180–181 °C (red oil). ^{1}H NMR (C_6D_6): δ = 1.81 (s, 15 H, Cp*), 6.28–8.18 (m, 30 H, Ph) ppm. ^{13}C{^{1}H,^{31}P} NMR (C_6D_6): δ = 12.10 (s, C_5Me_5), 113.49–147.63 (s, Ph, C_5Me_5), 182.70 (s, *ipso*-C of Ta–Ph) ppm. ^{31}P{^{1}H} NMR (C_6D_6): ABCDEX spin system, δ_X = +370.3 (br. d, 1 P), δ_A = +34.0 (br. ddd, 1 P), δ_B = +24.9 (m, 1 P), δ_C = –1.8 (br. m, 1 P), δ_D = –57.6 (ddd, 1 P), δ_E = –127.7 (br. d, 1 P), $^1J_{AX}$ = ±471 Hz, $^1J_{BD}$ = ±204 Hz, $^1J_{BC}$ = ±391 Hz, $^1J_{AD}$ = ±355 Hz, $^1J_{CE}$ = ±444 Hz. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3135 (w), 3050 (m), 2986 (m), 2957 (m), 2898 (m), 2723 (w), 1953 (w), 1882 (w), 1807 (w), 1753 (w), 1649 (w), 1579 (m), 1567 (m), 1551 (m), 1476 (m), 1433 (s), 1374 (m), 1333 (w), 1303 (m), 1262 (m), 1237 (w), 1184 (w), 1152 (w), 1082 (m), 1068 (m), 1054 (m), 1023 (s), 998 (m), 909 (m), 842 (m), 803 (m), 733 (s), 689 (s), 617 (vw), 563 (m), 520 (w), 479 (m), 467 (m), 405 (m). MS (FAB): m/z = 964.94 [M + H]$^+$; $C_{46}H_{45}P_6Ta$ (964.59): calcd. C 57.27, H 4.70; found C 57.36, H 4.59.

On one occasion, the product still contained some *cyclo*-(P_5Ph_5) and a green, insoluble material as byproducts. In this case, the compound was purified by dissolving in toluene, filtration, and layering the clear filtrate with *n*-hexane.

Acknowledgments

Financial support from the Studienstiftung des Deutschen Volkes (PhD grant for R. W.) and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank H. C. Starck GmbH & Co. KG for a generous donation of $TaCl_5$.

[1] a) A. H. Cowley, A. R. Barron, *Acc. Chem. Res.* **1988**, *21*, 81; b) A. H. Cowley, *Acc. Chem. Res.* **1997**, *30*, 445; c) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley & Sons, New York, chapter 3, **1998**; d) F. Mathey, N. H. T. Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938; e) K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127; f) K. Lammertsma, *Phosphinidenes*, in: *Topics in Current Chemistry: New Aspects in Phosphorus Chemistry III* (Ed.: J.-P. Majoral), Springer, Berlin, Heidelberg, **2003**.

[2] Terminal phosphinidene complexes of Ta: a) C. C. Cummins, R. R. Schrock, W. M. Davis, *Angew. Chem.* **1993**, *105*, 758; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 756; b) J. B. Bonanno, P. T. Wolczanski, E. B. Lobkovsky, *J. Am. Chem. Soc.* **1994**, *116*, 11159.

[3] Review: J. Olkowska-Oetzel, J. Pikies, *Appl. Organomet. Chem.* **2003**, *17*, 28.

[4] Complexes with an η^2-bound phosphanyl phosphinidene moiety (PPR_2): a) H. Krautscheid, E. Matern, I. Kovacs, G. Fritz, J. Pikies, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1917; b) E. Matern, J. Pikies, G. Fritz, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2136; c) J. S. Figueroa, C. C. Cummins, *Angew. Chem.* **2004**, *116*, 1002; *Angew. Chem. Int. Ed.* **2004**, *43*, 984.
[5] A complex with an η^1-bound phosphanyl phosphinidene moiety (PPR_2): J. Pikies, E. Baum, E. Matern, J. Chojnacki, R. Grubba, A. Robaszkiewicz, *Chem. Commun.* **2004**, 2478.
[6] a) K. Issleib, K. Krech, *Chem. Ber.* **1965**, *98*, 2545; b) K. Issleib, E. Fluck, *Z. Anorg. Allg. Chem.* **1965**, *339*, 274; c) K. Issleib, K. Krech, *Chem. Ber.* **1966**, *99*, 1310; d) K. Issleib, M. Hoffmann, *Chem. Ber.* **1966**, *99*, 1320; e) K. Issleib, Ch. Rockstroh, I. Duchek, E. Fluck, *Z. Anorg. Allg. Chem.* **1968**, *360*, 77; f) K. Issleib, K. Krech, *J. Prakt. Chem.* **1969**, *311*, 463.
[7] a) J. Geier, H. Rüegger, M. Wörle, H. Grützmacher, *Angew. Chem.* **2003**, *115* 4081; *Angew. Chem. Int. Ed.* **2003**, *42*, 3951; b) J. Geier, J. Harmer, H. Grützmacher, *Angew. Chem.* **2004**, *116*, 4185; *Angew. Chem. Int. Ed.* **2004**, *43*, 4093.
[8] a) R. Wolf, A. Schisler, P. Lönnecke, C. Jones, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2004**, 3277; b) R. Wolf, E. Hey-Hawkins, *Z. Anorg. Allg. Chem*., in press; DOI: 10.1002/zaac.200500384.
[9] R. Wolf, PhD Thesis, University of Leipzig, **2005**.
[10] R. Wolf, E. Hey-Hawkins, *Angew. Chem.* **2005**, *117*, 6398; *Angew. Chem. Int. Ed.* **2005**, *44*, 6241.
[11] For other examples of transmetalation reactions of $M_2(P_nR_n)$ with transition-metal halides see: a) H. Köpf, R. Voigtländer, *Chem. Ber.* **1981**, *114*, 2731; b) R. A. Jones, M. H. Seeberger, B. R. Whittlesey, *J. Am. Chem. Soc.* **1985**, *107*, 6424.
[12] Structural data of **2**: $C_{46}H_{45}P_6Ta$, M = 964.59, monoclinic, space group $P2_1/n$, a = 9.701(5) Å, b = 21.309(5) Å, c = 20.476(5) Å, α = 90.0°, β = 97.826(5)°, γ = 90.0°, V = 4193(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.528 Mg·m^{-3}, μ = 2.882 mm^{-1}, $\theta_{max.}$ = 27.00°, R = 0.0587, Rw = 0.1178. The data were collected with a Siemens SMART CCD diffractometer [$\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å, T = 213(2) K], 9123 independent reflections, 538 parameters, 0 restraints, max. residual electron density 1.209 e·Å^{-3}. An empirical absorption correction was carried out with SADABS (G. M. Sheldrick, SADABS – a Program for Empirical Absorption Correction, Göttingen, **1998**), and the structure solution with Patterson methods (G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, **1997**). Ta, P and C atoms were refined anisotropically (SHELXL-97: G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, **1997**). CCDC-293167 contains 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.
[13] S. Blaurock, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2002**, 2975.
[14] G. A. A. Hadi, K. Fromm, S. Blaurock, S. Jelonek, E. Hey-Hawkins, *Polyhedron* **1997**, *16*, 721.
[15] a) P. J. Domaille, B. M. Foxman, T. J. McNeese, S. S. Wreford, *J. Am. Chem. Soc.* **1980**, *102*, 4114; b) G. I. Nikonov, L. G. Kuzmina, P. Mountford, D. A. Lemenovskii, *Organometallics* **1995**, *14*, 3588.
[16] A search in the CSD (November **2003**) for tantalum complexes of tertiary phosphanes give 188 compounds (503 Ta–P distances) with a range of d(Ta–P) = 2.363–2.854 Å (av. 2.601 Å).
[17] S. Blaurock, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2515.
[18] a) K. E. Stockman, K. L. Houseknecht, E. A. Boring, M. A. Sabat, M. G. Finn, R. N. Grimes, *Organometallics* **1995**, *14*, 3014; b) K. Mashima, Y. Tanaka, A. Nakamura, *Organometallics* **1995**, *14*, 5642; c) E. Boring, M. Sabat, M. G. Finn, G. N. Grimes, *Organometallics* **1997**, *16*, 3993.
[19] R. Blom, A. Haaland, *J. Mol. Struct.* **1985**, *128*, 21.
[20] L. Weber, *Chem. Rev.* **1992**, *92*, 1839.
[21] Recent calculations on the model compound [Nb($PPMe_2$)(NH_2)$_3$] indicate that the multiply bonded character of the Nb–P bond is relatively small; cf. C. C. Cummins, *Angew. Chem.* **2006**, *118*, 876; *Angew. Chem. Int. Ed.* **2006**, *45*, 862.
[22] a) A. Castro, M. V. Galakhov, M. Gómez, P. Gómez-Sal, A. Martín, P. Royo, *J. Organomet. Chem.* **1998**, *554*, 185; b) P. Royo, J. Sánchez-Nieves, *J. Organomet. Chem.* **2000**, *597*, 61.
[23] M. Baudler, B. Carlsohn, W. Böhm, D. Reuschenbach, *Z. Naturforsch., Teil B* **1976**, *31*, 558.
[24] R. Wolf, M. Finger, C. Limburg, A. C. Willis, S. B. Wild, E. Hey-Hawkins, *Dalton Trans.* **2006**, 831.
[25] A. Bashall, F. Garcia, A. D. Hopkins, J. A. Wood, M. McPartlin, A. D. Woods, D. S. Wright, *Dalton Trans.* **2003**, 1143.
[26] a) A. Schisler, P. Lönnecke, T. Gelbrich, E. Hey-Hawkins, *Dalton Trans.* **2004**, 2895; b) A. Schisler, PhD Thesis, Universität Leipzig, **2003**.
[27] a) L. R. Smith, J. L. Mills, *J. Chem. Soc., Chem. Commun.* **1974**, 808; b) L. R. Smith, J. L. Mills, *J. Am. Chem. Soc.* **1976**, *98*, 3852; c) P. R. Hoffman, K. G. Caulton, *Inorg. Chem.* **1975**, *14*, 1997.
[28] C. Ting, N. C. Baenzinger, L. Messerle, *J. Chem. Soc., Chem. Commun.* **1988**, 1133.
[29] C. Frenzel, E. Hey-Hawkins, *Phosphorus Sulfur Silicon* **1998**, *143*, 1.
[30] R. D. Sanner, S. T. Carter, W. J. Bruton Jr, *J. Organomet. Chem.* **1982**, *240*, 157.

Received: January 25, 2006
Published Online: February 22, 2006

