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Terminal Alkylphosphanylidene Organotantalum(V) Complexes

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The first terminal organometallic alkylphosphanylidenetantalum(V) complexes $[\mathrm{Cp^{\star}Ta\{1,2\text{-}(NSiMe_3)_2C_6H_4\}(PR)}]$ were obtained with cyclohexyl (**2**) and isopropyl groups (**3**) at phosphorus, whereas adamantyl and *tert*-butyl substituents resulted in the formation of the paramagnetic tantalum(IV) complex $[\mathrm{Cp^{\star}Ta\{1,2\text{-}(NSiMe_3)_2C_6H_4\}Cl}]$ (**4**). DFT studies showed that the terminal cyclohexyl and isopropyl phosphanylidene complexes are stable towards dimerization and dissociation.

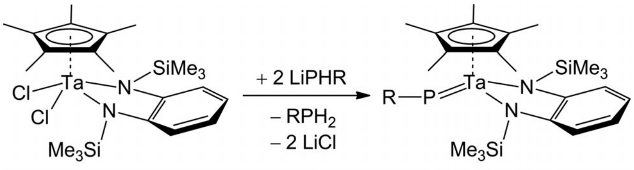
Introduction

Terminal transition-metal phosphanylidene complexes $[\mathrm{L}_n\mathrm{M{=}PR}]$[1] are phosphorus analogues of the well-known carbene complexes, which have many applications in metathesis reactions and natural product synthesis.[2] As is the case for carbene complexes, phosphanylidene complexes can be regarded as electrophilic[1e,3a–3c] or nucleophilic,[1e,3d–3f] depending on the reactivity of the phosphorus atom.[3g] Reactions with alkynes, ketones, and protic reagents[1e,3a–3f] have been reported. Remarkably, phosphaalkenes can be obtained in a phospha-Wittig reaction of nucleophilic phosphanylidene complexes.[3e,3f]

Since the first report of a stable organomolybdenum complex with a terminal phosphanylidene ligand, namely, $[\mathrm{Cp_2Mo(PMes)}]$ (Cp = cyclopentadienyl, Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$),[4] organometallic terminal phosphanylidene complexes have been reported for most d block elements.[5] Organotantalum complexes with bridging phosphanylidene ligands[6b,6d,6e] and one phosphanylphosphanylidene complex[6f] are known, but there is only one report on a terminal organometallic tantalum arylphosphanylidene complex, in which the reactive terminal metal–phosphorus bond is stabilized by sterically demanding ligands at tantalum and phosphorus.[6c] The first terminal phosphanylidene complexes of tantalum, $[\mathrm{Ta(PR)\{N(CH_2CH_2NSiMe_3)_3\}}]$ [R = Ph, cyclohexyl (Cy), *t*Bu][3e] and $[\mathrm{Ta(PPh)\{OSi(}t\mathrm{Bu)_3\}_3}]$,[6a] were reported in 1993 and 1994, respectively. Subsequent reactions include phospha-Wittig reactions[3e] and insertion of acetone.[6c]

Results and Discussion

We herein report the synthesis of the first organometallic, nucleophilic, terminal alkylphosphanylidenetantalum(V) complexes. Upon treatment of $[\mathrm{Cp^*TaCl_4}]$[7] ($\mathrm{Cp^* = C_5Me_5}$) with two equivalents of LiPHR[8] in toluene (to maintain a low concentration of LiPHR in solution) at low temperature (to reduce side reactions), the deep-red phosphanylidene-bridged tantalum(IV) complexes *trans*-$[\{\mathrm{Cp^*TaCl(\mu\text{-}PR)}\}_2]$ (R = Cy, *t*Bu, Ph, Mes) were obtained in high yields.[6d,6e] Reduction could be avoided by employing the bisamido complex $[\mathrm{Cp^*Ta\{1,2\text{-}(NSiMe_3)_2C_6H_4\}Cl_2}]$[9] (**1**) as the starting material. Thus, complexes $[\mathrm{Cp^*Ta\{1,2\text{-}(NSiMe_3)_2C_6H_4\}(PR)}]$ [R = Cy (**2**), *i*Pr (**3**)] are readily available from **1** and two equivalents of lithium phosphanide (LiPHCy, LiPH*i*Pr)[8a] in toluene at –80 °C (Scheme 1).



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R = Cy (**2**), *i*Pr (**3**)

Scheme 1. Synthesis of terminal alkylphosphanylidenetantalum(V) complexes **2** and **3**.

The ^{31}P NMR spectra of compounds **2** and **3** exhibit a broad singlet at δ = 443.0 and 454.7 ppm, respectively, which is indicative of a bent MPR group, as was observed in $[\mathrm{Ta(PPh)\{OSi(}t\mathrm{Bu)_3\}_3}]$[6a] ($\delta$ = 334.6 ppm). Complexes

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with linear MPR groups are observed at higher field, for example, $[Ta(PR)\{N(CH_2CH_2NSiMe_3)_3\}]$[3e] [209.8 (R = Cy) and 227.3 ppm (R = *t*Bu)]. A low-field shift of the *ipso*-carbon atoms [^{13}C NMR: C4, 46.0 ppm (for **2**); C13, 35.3 ppm (for **3**); Figures 1 and 2] and their protons [^{1}H NMR: 4.67 ppm (for **2**); 4.78 ppm (for **3**)] is caused by the electron deficiency of these organometallic complexes.

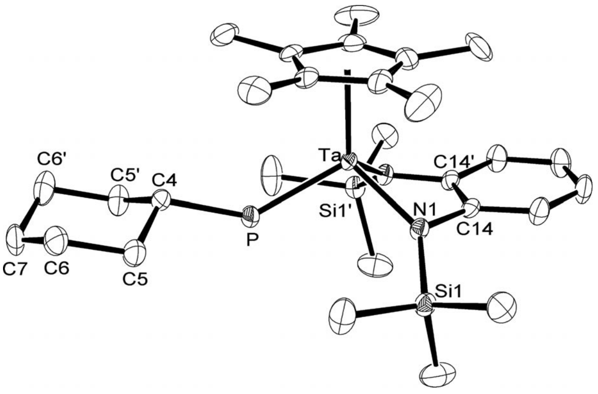


Figure 1. ORTEP diagram of **2** (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: Ta–P 227.20(8), Ta–N1 202.9(2), P–C4 186.6(3), N1–C14 141.7(2), Ta–P–C4 136.46(9), P–Ta–N1 105.87(4), N1–Ta–N1′ 85.26(6).

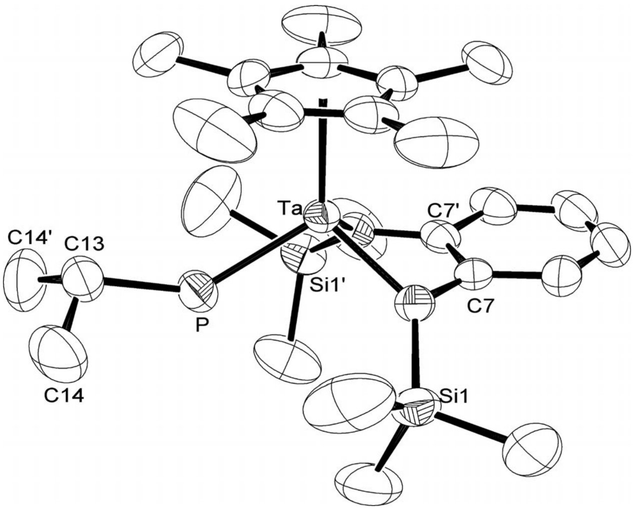


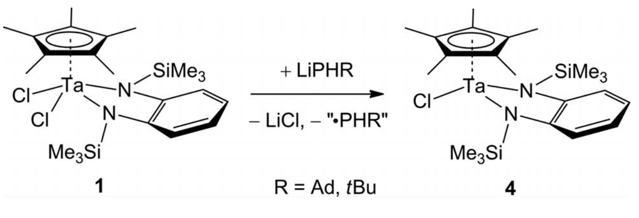
Figure 2. ORTEP diagram of **3** (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: Ta–P 226.5(1), Ta–N1 201.9(2), P–C13 186.7(5), N1–C7 141.2(4), Ta–P–C13 138.2(2), P–Ta–N1 104.12(8), N1–Ta–N1′ 85.5(1).

X-ray structure analysis of **2** and **3**[10] confirmed the bent geometry of the MPR unit [Ta–P–C4/C13 136.46(9)/138.2(2)°] and short Ta–P bonds [Ta–P 227.20(8) pm in **2**, 226.5(1) pm in **3**]. The dependence of the Ta–P bond length on the substituents and geometrical arrangement at phosphorus is also demonstrated in the complexes $[Ta(PCy)\{N(CH_2CH_2NSiMe_3)_3\}]$[3e] [214.5(7) pm, TaPC is linear] and $[Ta(PPh)\{OSi(t\mathrm{Bu})_3\}_3]$[6a] [231.7(4) pm, Ta–P–C 110.2(4)°, bent TaPC]. These Ta–P bonds are shorter than the sum of the covalent radii of Ta and P (277 pm).[11]

Furthermore, the tantalum-bisamido group forms a five-membered ring with an envelope conformation (Figures 1 and 2) and fold angles TaN_2/N_2C_2 of 137.0(1) (for **2**) and 135.6(2)° (for **3**). The fold angle in the starting material **1** [129.6(1)°, see Supporting Information] is about 7° smaller than in **2** and **3** but 8° larger than that in the bis(triisopropylsilyl) derivative $[Cp^*Ta\{1,2\text{-}(NSi\mathit{i}Pr_3)_2C_6H_4\}Cl_2]$ (121.3°).[12] This difference is caused by the lower steric demand of the phosphanylidene unit and the higher steric demand of the isopropyl substituents. The nitrogen atoms are in a trigonal-planar environment [sum of bond angles: 358.0(5)° (for **2**), 359.5(3)° (for **3**)]. The N–C bond lengths of 141.7(2) pm (for **2**) and 141.2(4) pm (for **3**) are in the range of single bonds; the corresponding bond lengths of diimine complexes are about 128 pm.[13]

Density functional theory (DFT) calculations have shown that only the highest occupied molecular orbitals (HOMOs) of **2** and **3** are accessible, and their lowest unoccupied molecular orbitals (LUMOs) are shielded by the bulky substituents on the nitrogen atom (see the Supporting Information for details). Thus, dimerization of these complexes involving transfer of electron density from the HOMO of one monomer to the LUMO of another cannot occur. Furthermore, homolytic cleavage of the Ta–P double bond with formation of a tantalum(III) species and cyclic oligophosphanes can also be excluded (Supporting Information). However, owing to the availability of the HOMOs, **2** and **3** should readily react with suitable small molecules.

Attempts to extend the synthetic approach shown in Scheme 1 to the corresponding adamantyl and *tert*-butyl phosphanylidene derivatives resulted in a redox reaction and the formation of the corresponding tantalum(IV) complex $[Cp^*Ta\{1,2\text{-}(NSiMe_3)_2C_6H_4\}Cl]$ (**4**, Scheme 2). The EPR spectrum of **4** shows an eight-line pattern (g = 1.794, A = 44 mT) caused by the spin I = 7/2 of ^{181}Ta (N = 99.98%).[14] The formation of oligophosphanes, such as cyclotetraphosphanes and cyclotriphosphanes, as oxidation products could be verified by ^{31}P NMR spectroscopy. The calculated thermodynamic properties alone do not explain why reactions of **1** with Ad- and *t*Bu-substituted lithium phosphanides give tantalum(IV) species **4**, whereas reactions of **1** with the Cy- and *i*Pr-substituted lithium phosphanides result in formation of 18 valence-electron terminal phosphanylidene complexes **2** and **3** (PR as 4e$^-$ donor, bisamido ligand as 8e$^-$ donor; see the Supporting Information).



Scheme 2. Redox reaction with formation of $[Cp^*Ta\{1,2\text{-}(NSiMe_3)_2\text{-}C_6H_4\}Cl]$ (**4**).

Compound **4** crystallized from *n*-pentane and was structurally characterized.[10] The molecule has a piano-stool geometry with a four-coordinate tantalum atom (Figure 3).

The five-membered TaN_2C_2 ring has only a slightly folded envelope conformation [fold angle TaN_2/N_2C_2 160.7(1)° compared to 129.6(1)° in **1**, see the Supporting Information], as removal of one chloro ligand in the coordination sphere of tantalum leads to less steric interaction and therefore to greater planarity of the chelate ring.

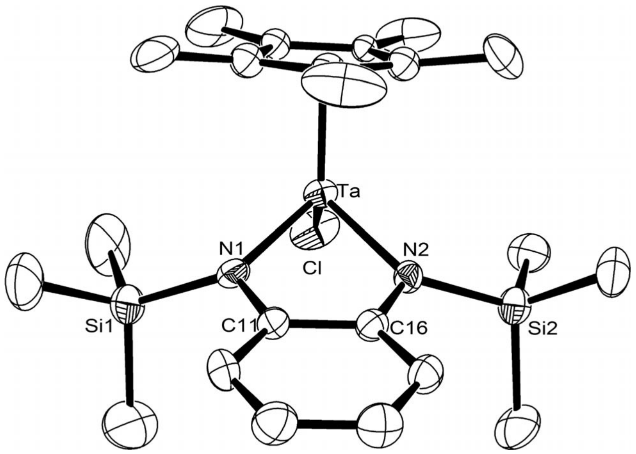


Figure 3. ORTEP diagram of **4** (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: Ta–Cl 234.22(8), Ta–N1 204.7(2), Ta–N2 203.3(2), N1–C11 140.7(3), N2–C16 141.7(3), N1–Ta–N2 78.98(9), N1–Ta–Cl 109.41(8), N2–Ta–Cl 109.31(7).

Conclusions

In summary, the formation of alkylphosphanylidenetantalum(V) complexes depends on the steric demand of the substituent on the phosphorus atom. Thus, the first terminal organometallic alkylphosphanylidenetantalum(V) complexes were obtained with cyclohexyl and isopropyl groups at phosphorus, whereas adamantyl and *tert*-butyl substituents resulted in the formation of paramagnetic tantalum(IV) complex **4**. The stability of **2** and **3** with respect to dimerization was clarified by DFT calculations. Future studies will focus on investigating the reactivity of these compounds.

Experimental Section

2: At 0 °C, *n*BuLi (1.44 M in *n*-hexane, 11 mL, 16 mmol) was added dropwise to a solution of $CyPH_2$ (1.90 g, 16 mmol) in *n*-hexane (15 mL). After 2 h of stirring at room temperature, the reaction mixture was filtered. At –80 °C, a suspension of the white precipitate in toluene (20 mL) was added dropwise to a solution of **1** (4.79 g, 8 mmol) in toluene (40 mL). The reaction mixture was stirred for 15 h at room temperature. After removal of the volatile material, the remaining solid was extracted with *n*-pentane. Red crystals of **2** were obtained at –20 °C, yield 2.24 g (41%). ^1H NMR (400 MHz, C_6D_6): δ = 0.49 [s, 18 H, $Si(CH_3)_3$], 1.10–1.58 (m, 6 H, Cy), 1.70 [s with sh., 17 H, $C_5(CH_3)_5$ and Cy], 2.10 (d, $^3J_{HP}$ = 11 Hz, 2 H, Cy), 4.67 (m, 1 H, Cy), 7.04 (m, 2 H, *o*-CH), 7.22 ppm (m, 2 H, *m*-CH). $^{13}C\{^1H\}$ APT NMR (100 MHz, C_6D_6): δ = 3.5 [s, $Si(CH_3)_3$], 10.7 [s, $C_5(CH_3)_5$], 26.2 [s, CH_2, Cy(6,6′)] (numbering scheme in Figure 1), 27.5 [s, CH_2, Cy(7)], 36.0 [s, CH_2, Cy(5,5′)], 46.0 [d, $^1J_{CP}$ = 39 Hz, CH, P-C(4)], 115.3 [s, $C_5(CH_3)_5$], 123.0 (s, *m*-CH), 124.5 (s, *o*-CH), 133.6 ppm (s, N–C). ^{31}P NMR (160 MHz, C_6D_6): δ = 443.0 ppm (s). ESI-MS (*n*-pentane/CH_3CN, 1:2): *m*/*z* = 681.27 $[M + H]^+$.

3: At –80 °C, *n*BuLi (1.57 M in *n*-hexane, 7 mL, 11 mmol) was added dropwise to a solution of *i*PrPH_2 (0.85 g, 11 mmol) in *n*-pentane (20 mL). The reaction mixture was stirred and slowly warmed to room temperature over 3 h and then filtered. A suspension of the slightly green precipitate in toluene (20 mL) was added dropwise to a solution of **1** (2.20 g, 3 mmol) in toluene (30 mL) at –80 °C. The reaction mixture was stirred for 15 h at room temperature. The volatile material was removed, and the remaining solid was extracted with *n*-pentane. Red crystals of **3** were obtained at 7 °C, yield 0.81 g (36%). ^1H NMR (400 MHz, C_6D_6): δ = 0.48 [s, 18 H, $Si(CH_3)_3$], 1.34 [m, 6 H, $CH(CH_3)_2$], 1.75 [s, 15 H, $C_5(CH_3)_5$], 4.78 [m, 1 H, $CH(CH_3)_2$], 7.05 (m, 2 H, *o*-CH), 7.21 ppm (m, 2 H, *m*-CH). $^{13}C\{^1H\}$ APT NMR (100 MHz, C_6D_6): δ = 3.5 [s, $Si(CH_3)_3$], 10.7 [s, $C_5(CH_3)_5$], 26.0 [s, $CH(CH_3)_2$], 35.3 [d, $^1J_{CP}$ = 41 Hz, $PCH(CH_3)_2$], 115.4 [s, $C_5(CH_3)_5$], 123.0 (s, *m*-CH), 124.5 (s, *o*-CH), 133.4 ppm (s, N–C). ^{31}P NMR (160 MHz, C_6D_6): δ = 454.7 ppm (s). ESI-MS (*n*-pentane): *m*/*z* = 641.2 $[M + H]^+$.

4: R = *t*Bu: *n*BuLi (2.22 M in *n*-hexane, 8 mL, 19 mmol) was added dropwise to a solution of *t*BuPH_2 (1.69 g, 19 mmol) in *n*-hexane (20 mL). The reaction mixture was stirred for 20 min and then filtered. A suspension of the white precipitate in toluene (20 mL) was added dropwise to a solution of **2** (4.73 g, 7 mmol) in toluene (30 mL) at –80 °C. After stirring for 15 h, the solvent was removed, and the residue was extracted with *n*-pentane. Red crystals of **4** were obtained at –60 °C, yield 1.61 g (36%).

4: R = Ad: *n*BuLi (2.22 M in *n*-hexane, 6 mL, 14 mmol) was added dropwise to a solution of AdPH_2 (2.46 g, 15 mmol) in *n*-hexane (20 mL). The reaction mixture was stirred for 2 h and then filtered. A suspension of the yellow precipitate in toluene (30 mL) was added dropwise to a solution of **2** (4.40 g, 7 mmol) in toluene (30 mL) at –80 °C. After stirring for 15 h, the solvent was removed, and the residue was extracted with *n*-pentane. Red crystals of **4** were obtained at –60 °C, yield 1.28 g (16%). EPR: *g* = 1.794, *A* = 44 mT. ESI-MS (*n*-pentane/CH_3CN, 1:2): *m*/*z* = 601.17 $[M]^+$.

Supporting Information (see footnote on the first page of this article): DFT calculations and further experimental details.

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[10] Data for **2**: $C_{28}H_{48}N_2PSi_2Ta$, $M = 680.78$, monoclinic, space group $P2_1/m$, $a = 814.64(1)$ pm, $b = 1675.27(2)$ pm, $c = 1160.18(2)$ pm, $\beta = 98.094(2)°$, $V = 1.56757(4)$ nm^3, $Z = 2$, $\rho_{calc} = 1.442$ Mg m^{-3}, $\mu = 3.652$ mm^{-1}, $\theta_{max} = 26.37°$, $R = 0.0182$, $Rw = 0.0325$. $T = 130(2)$ K, 3318 independent reflections, 264 parameters, max. residual electron density 0.774 e Å^{-3}. Data for **3**: $C_{25}H_{44}N_2PSi_2Ta$, $M = 640.72$, orthorhombic, space group $Pbcm$, $a = 1233.19(4)$ pm, $b = 1419.03(5)$ pm, $c = 1707.38(6)$ pm, $V = 2.9878(2)$ nm^3, $Z = 4$, $\rho_{calc} = 1.424$ Mg m^{-3}, $\mu = 3.827$ mm^{-1}, $\theta_{max} = 30.51°$, $R = 0.0556$, $Rw = 0.0584$. $T = 200(2)$ K, 4708 independent reflections, 166 parameters, max. residual electron density 1.084 e Å^{-3}. Data for **4**: $C_{22}H_{37}ClN_2Si_2Ta$, $M = 602.12$, orthorhombic, space group $P2_12_12_1$, $a = 1530.74(2)$ pm, $b = 1553.55(2)$ pm, $c = 2157.70(3)$ pm, $V = 5.1312(1)$ nm^3, $Z = 8$, $\rho_{calc} = 1.559$ Mg m^{-3}, $\mu = 4.492$ mm^{-1}, $\theta_{max} = 30.51°$, $R = 0.0375$, $Rw = 0.0367$. $T = 130(2)$ K, 15636 independent reflections, 587 parameters, 50 restraints, max. residual electron density 1.195 e Å^{-3}. The data were collected with an Oxford Diffraction CCD Xcalibur-S diffractometer (CrysAlis Pro: data collection and data reduction software package, Agilent Technologies, including the program SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics). The structures were solved by direct methods with SHELXS-97, and the refinement of all non-hydrogen atoms was performed with SHELXL-97.[15] Structure figures were generated with ORTEP.[16] CCDC-923046 (for **2**), -923047 (for **3**), and -923048 (for **4**) 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.

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