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Organometallic tantalum complexes with phosphine, phosphanido and phosphinidene ligands. Syntheses and crystal structures of $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$, $[Cp'Ta(\mu\text{-}PPh_2)(PPh_2)]_2 \cdot C_7H_8$ and $[Cp'TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i_3C_6H_2)\}]_2 \cdot C_7H_8$ ($Cp' = C_5H_4Me$)†

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Abstract—The reaction of $[Cp'TaCl_4]$ ($Cp' = C_5H_4Me$) with $KPPh_2(dioxane)_2$ (1 : 1) in diethyl ether at room temperature gave the phosphanido-bridged tantalum(III) complex $[Cp'Ta(\mu\text{-}PPh_2)(PPh_2)]_2$ (**1**)$\cdot C_7H_8$ as black crystals. $[Cp'TaCl_4]$ reacted with 2,4,6-triisopropylphenylphosphine with formation of the adduct $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**). Attempts to eliminate HCl from **2** with DBU (DBU = 1,8-diazabicyclo-[5,4,0]-undec-7-ene) gave the phosphinidene-bridged tantalum(IV) complex $[Cp'TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i_3C_6H_2)\}]_2$ (**3**)$\cdot C_7H_8$. It was shown independently that DBU acts as a base and as a reducing agent. **1**–**3** were characterized spectroscopically (IR, MS, NMR) as well as by crystal structure determinations. Copyright © 1996 Elsevier Science Ltd

Keywords: methylcyclopentadienyl tantalum complexes; phosphide ligand; phosphanido ligand; phosphinidene ligand.

Organometallic dialkyl- and diarylphosphanido complexes of early transition metals have been studied intensively, while complexes derived from functionalised phosphines which exhibit a reactive phosphorus-ligand bond have been largely neglected [1]. It was recently shown that Zr [2] and Mo [3] complexes react with primary phosphines or alkali metal phosphanides to yield a wide variety of products, whose formation depends on the nature of the organic substituents on phosphorus and the transition metal. The zirconocene derivatives with functionalised phosphorus-based ligands exhibit remarkable reactivity; thus, substitution of the P-based ligand by polar or protic reagents, and insertion of multiply-bonded inorganic or organic systems into the metal–phosphorus bond are observed [2]. The latter yields novel functionalised phosphorus ligands in the coordination sphere of the transition metal that are not available by other routes.

We have now extended our work on zirconocene [2] and molybdenum [3] chemistry to cyclopentadienyl tantalum complexes to investigate the influence of the nature of the transition metal on the reactivity observed in reactions with primary phosphines and alkali metal phosphanides. While the P—Si or P—H bond in zirconium complexes is generally less reactive

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† Dedicated to Professor Hans Georg von Schnering, on the occasion of his 65th birthday.

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[2], we expect this bond to be more reactive when the P ligand is coordinated to a group 5 or 6 metal; thus, modification of the ligand should be possible.

To date, only a few phosphanido derivatives of organometallic [4] and inorganic [5,6] tantalum compounds and two stable terminal phosphinidene complexes [6,7] have been described in the literature, although potential starting materials such as cyclopentadienyl-substituted tantalum halides, alkyls, hydrides or carbonyls [8] are accessible, as are inorganic tantalum halides [9].

We now report the synthesis of a tantalum phosphanido complex $[Cp'Ta(\mu\text{-}PPh_2)(PPh_2)]_2$ (**1**) ($Cp' = C_5H_4Me$), as well as the preparation of the first organometallic tantalum complex with a *primary* phosphine ligand $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**). The latter can be utilised as starting material for the synthesis of the tantalum phosphinidene complex $[Cp'TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i_3C_6H_2)\}]_2$ (**3**).

RESULTS AND DISCUSSION

Synthesis and properties of $[Cp'Ta(\mu\text{-}PPh_2)(PPh_2)]_2$ (1)·C_7H_8

Phosphanido complexes of tantalum are rare. Thus, $[Cp_2TaH_2(PPh_2)]$ was mentioned as an intermediate in the formation of the diphosphene complex $[Cp_2TaH(\eta^2\text{-}P_2Ph_2)]$ in 1989 [4a], but it was only in 1995 that its synthesis and spectroscopic details were reported [4c]. Another monophosphanido complex, $[Cp^*TaMe(\eta^2\text{-}C_2H_4)(PPh_2)]$ ($Cp^* = C_5Me_5$), which is accessible from $[Cp^*TaMe_2(\eta^2\text{-}C_2H_4)]$ and $PHPh_2$, was reported in 1993 [4b]. Hydrogenation of this complex in the presence of $PHPh_2$ gives the trisphosphanido complex $[Cp^*TaH(PPh_2)_3]$. Both complexes exhibit fluxional behaviour at room temperature [4b].

Our attempts to utilise the salt elimination reaction as a synthetic approach to tantalum(V) phosphanido complexes were thwarted due to the high reducing potential of alkali metal phosphanides. Thus, the reaction of $[Cp'TaCl_4]$ with $KPPh_2(dioxane)_2$ (1 : 1) in ether afforded after work up black, rhombic crystals of $[Cp'Ta(\mu\text{-}PPh_2)(PPh_2)]_2$ (**1**)·C_7H_8, which could be handled in air for a short time without decomposition. Similar to the reaction of cyclopentadienyl-substituted molybdenum(V) complexes with $KPPh_2(dioxane)_2$ [10], both reduction of the Ta^V starting material to Ta^{III} (formally $[Cp'TaCl_2]$; comparable Ta^{III} complexes $[Cp^RTaCl_2]$ with $Cp^R = C_5H_5$, C_5Me_5, C_5Me_4Et have been obtained by controlled reduction of $[Cp^RTaCl_4]$) [11] and substitution of the chloro ligands by PPh_2 are observed. Surprisingly, $[Cp^*NbCl_4]$ reacted with $LiPPh_2$ at low temperature to give only the substitution product $[Cp^*NbCl_3(PPh_2)]$, which was characterised by IR and ^1H NMR spectroscopy [12]. However, when a fourfold excess of lithium phosphanide was employed, only reduction products were observed [12].

In the mass spectrum of **1**, a signal for toluene is observed at *ca* 140°C, and at *ca* 290°C the molecular ion peak is observed at $m/z = 1260$, as well as signals for fragments arising from loss of Cp′ ligands and phenyl groups.

No signals due to **1** are observed in the ^1H and ^{31}P NMR spectrum, suggesting the presence of a paramagnetic species.

Synthesis and properties of $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (2) *and* $[Cp'TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i_3C_6H_2)\}]_2$ (3)

When equimolar amounts of $PH_2(2,4,6\text{-}Pr^i_3C_6H_2)$ are added to a toluene solution of $[Cp'TaCl_4]$, a colour change from yellow to orange indicates the formation of the adduct $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**), which can be isolated as yellow crystals.

The Lewis acidity of tantalum(V) and niobium(V) complexes has been extensively studied and a large number of adducts of $[Cp^RMCl_4]$ with ethers, amines, nitriles, and isonitriles has been reported [13]. Up to now, only a few phosphine complexes of cyclopentadienyl tantalum (or niobium) tetrachloride are known, all of which possess *tertiary* phosphine ligands. While $[CpMCl_4(PMe_3)]$ (M = Nb, Ta) [13d, 14] and $[CpNbCl_4(PEt_3)]$ [14] were earlier reported to be unstable, it was shown only recently that stable adducts can be obtained provided there is *no excess* of phosphine present. Thus, the complexes $[Cp^*NbCl_4(L)]$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$), $[Cp^*NbCl_3(Me)(PMe_2Ph)]$ and $[\{Cp^*NbCl_4\}_2(\mu\text{-}dmpe)]$ ($dmpe = Me_2PCH_2CH_2PMe_2$) are accessible in high yield [12], as are the phosphine adducts $[CpNbCl_4(L)]$ ($L = PMe_3$, PMe_2Ph, $PMePh_2$) [15]. With excess phosphine, these complexes are readily reduced to niobium(IV) compounds, with PMe_3 being the best reducing agent (formation of $PMe_3H^+Cl^-$) [12, 15]. With **2**, no reaction is observed with excess phosphine.

In the NMR spectra, $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**) exhibits dynamic behaviour which we attribute to rotation about the Ta—P bond. Thus, at room temperature only broad signals are observed for the PH_2 group in the ^1H and ^{31}P NMR spectra. Below 290 K a triplet is observed in the proton-coupled ^{31}P NMR spectrum [$\Delta G^\ddagger$ (288 K) $= 67 \pm 2$ kJ mol^{-1} [16]. Similarly, the dynamic behaviour of $[Cp^*TaMe(\eta^2\text{-}C_2H_4)(PPh_2)]$ was attributed to restricted rotation about the Ta—P bond [$\Delta G^\ddagger = 48 \pm 1.3$ kJ mol^{-1}] [4b]. Inversion barriers of terminal phosphanido groups lie in the same range (e.g., 48–60 kJ mol^{-1} for Nb, Re, Fe, and W complexes [17].

As expected on coordination to a transition metal, the signal of the phosphine ligand is shifted to low field compared to the free phosphine (−158.2 ppm, *J*(PH) 203 Hz) [18b, 18c] by 122.5 ppm, and the P—H coupling constant increases by 158 Hz. Accordingly, a low-field shift of the P—H signal by 2.80 ppm is observed in the proton NMR spectrum. Similarly, low-field shifts are observed for the resonances of the *ortho*-Pr^i groups of the aromatic ligand (free phosphine: 1.19 CH*Me*$_2$, 3.41 C*H*Me$_2$ [18], coordinated: 1.29 and 3.90, respectively), while the differences in the chemical shifts of the *para*-Pr^i ligand and the *meta*-H atoms of the phenyl ligand are less pronounced. Comparable effects are observed in the ^{31}P NMR spectra of LiPH(2,4,6-Pr$^i_3$C$_6$H$_2$) (−165 ppm, *J*(PH) 166 Hz) [19] and the corresponding phosphanido complex [Cp$'_2$Zr(Cl){PH(2,4,6-Pr$^i_3$C$_6$H$_2$)}] (−4.6 ppm, *J*(PH) 230 Hz) [19]. For most tantalum and niobium complexes with tertiary phosphine ligands, no ^{31}P NMR data have been reported. However, for those complexes for which data are available, e.g. [Cp*NbCl$_3$(X)(PMe$_2$Ph)] (X = Cl: 2 ppm, X = Me: −1.9 ppm) [12], [CpNbCl$_4$(L)] (L = PMe$_3$: 5 ppm, L = PMe$_2$Ph: 12 ppm, L = PMePh$_2$: 17 ppm) [15] and the cationic complex [Cp$_2$TaH$_2$(PHPh$_2$)]$^+$ (0.2 ppm, *J*(PH) 389 Hz) [4c], broad signals and a low-field shift compared to the free phosphines (PMe$_3$: −62 ppm, PMe$_2$Ph: −46 ppm, PMePh$_2$: −26 ppm, PHPh$_2$: −41.1 ppm, ^{1}*J*(PH) 214.3 Hz) [20] are also observed; however, here the difference is less pronounced.

In the ^{1}H NMR spectrum of **2** and **3**, the signals of the Cp′ ligand are shifted to high field by up to 1 ppm compared to [Cp′TaCl$_4$] [21]. In **2**, the *ipso*-C atom of the triisopropylphenyl ligand (152.2 ppm, *J*(PC) 28 Hz) exhibits the expected chemical shift [18c], however, the PC coupling constant is smaller than in the free phosphine (*J*(PC) 57.2 Hz) [18c] and in [Cp*TaMe(η^2-C$_2$H$_4$)(PPh$_2$)] (145.9 ppm, *J*(PC) 41 Hz) [4b].

No molecular ion peak is observed in the mass spectrum of **2**. Only signals for [Cp′TaCl$_4$] and PH$_2$(2,4,6-Pr$^i_3$C$_6$H$_2$) as well as fragmentation products thereof are observed.

The phosphinidene-bridged tantalum(IV) complex [Cp′TaCl{μ-P(2,4,6-Pr$^i_3$C$_6$H$_2$)}]$_2$ (**3**) is obtained on reacting **2** with DBU (1 : 2 or 1 : 3) in *ca* 55% yield. Also, when [Cp′TaCl$_4$] is reacted *in situ* with PH$_2$(2,4,6-Pr$^i_3$C$_6$H$_2$) and DBU (1 : 1 : 1), only **3** can be isolated, in low yield (*ca* 10–15%). The formation of an intermediate phosphanido complex was not observed. While no reaction of **2** was observed with excess phosphine, we were able to show that [Cp′TaCl$_4$] is reduced by equimolar amounts of DBU to give a paramagnetic Ta^{IV} species (Experimental Section). Thus, in the reaction between [Cp′TaCl$_4$], PH$_2$(2,4,6-Pr$^i_3$C$_6$H$_2$) and DBU, the amine is the reducing agent even in the absence of primary phosphine. Similarly, [MCl$_5$] (M = Nb, Ta) have been reported to be reduced to M^{IV} by aliphatic [22] and aromatic [23] amines. Surprisingly, in the reaction of [Cp*TaCl$_4$] with aniline the adduct [Cp*TaCl$_4$(NH$_2$Ph)] is formed [24]. This adduct also reacts with base (LiNEt$_2$) undergoing elimination of HCl (without reduction) and formation of the Ta^V imido complex [Cp*TaCl$_2$(NPh)] [24].

Stable terminal phosphinidene complexes of inorganic tantalum derivatives, [(SiMe$_3$NCH$_2$CH$_2$)$_3$NTa=PR] (R = Ph, Cy, Bu^t) [7] (yellow) and [(Bu$^t_3$SiO)$_3$Ta=PPh] [6] (red), have been reported, in addition to those known for Mo [25], W [26] and Zr [27]. [(SiMe$_3$NCH$_2$CH$_2$)$_3$NTa=PR] [175.1 (R = Cy) and 227.3 ppm (R = Bu^t)] [7] and [(Bu$^t_3$SiO)$_3$Ta=PPh] [6] (334.6 ppm) have ^{31}P chemical shifts which indicate the presence of a linear MPR unit (bent MPR unit: 660 to 800 ppm [25]), for **3**, a ^{31}P chemical shift of 391.5 ppm is observed. Also, the deshielding effect on coordination to a transition metal is even more pronounced in **3**. Thus, all resonances of the triisopropylphenyl ligand are shifted to low field by 0.1 to 0.5 ppm in the ^{1}H NMR spectrum.

In the mass spectrum, the molecular ion peak of **3** (*m*/*z* 1060) as well as a signal for the monomeric compound (*m*/*z* 530) and fragmentation products of the Cp′TaCl and P(2,4,6-Pr$^i_3$C$_6$H$_2$) fragment are observed.

Molecular structures of [Cp′Ta(μ-PPh$_2$)(PPh$_2$)]$_2$(**1**)·C$_7$H$_8$, [Cp′TaCl$_4${PH$_2$(2,4,6-Pr$^i_3$C$_6$H$_2$)}] (**2**) *and* [Cp′TaCl{μ-P(2,4,6-Pr$^i_3$C$_6$H$_2$)}]$_2$ (**3**)·C$_7$H$_8$

Single crystals of **1** were obtained by covering a saturated toluene solution with a layer of n-heptane. The compound crystallises in the triclinic space group $P\bar{1}$ and has one formula unit per unit cell (Table 1, Table 4). The unit cell also contains a disordered toluene molecule without bonding interactions. Single crystals of **2** are obtained as yellow needles on cooling a saturated pentane solution to 5°C. **2** crystallises in the triclinic space group $P\bar{1}$ and has two formula units per unit cell (Table 2, Table 4). **3** is obtained as dark red cubes on cooling a saturated toluene/pentane solution to −20°C. The compound crystallises in the monoclinic space group $P2_1/n$ with two formula units per unit cell (Table 3, Table 4). The unit cell also contains two disordered toluene molecules without bonding interactions.

The pronounced tendency of low-valent Ta^{III} and Ta^{IV} complexes to form binuclear complexes is also exhibited in the molecular structures of **1** and **3**. Both consist of centrosymmetric dimeric molecules in which Ta atoms are bound by two bridging phosphanido (PPh$_2$, **1**) or phosphinidene [P(2,4,6-Pr$^i_3$C$_6$H$_2$), **3**] groups. In **1** each Ta atom also bears a terminal PPh$_2$ ligand (Fig. 1), in **3** there are terminal chloro ligands (Fig. 2). In both complexes, a Cp′ group completes the coordination of the Ta atom. The centrum of the Ta$_2$P$_2$ rings in **1** and **3** coincides with a crystallographic inversion centre [**1**: 0, 1/2, 0 (c), **3**: 0, 0, 1/2 (b)].

The four-membered metallacycles Ta(1)—P(2)—Ta(1)′—P(2)′ (**1**) and Ta—P—Ta′—P′ (**3**) are planar. The bond lengths and angles of the central Ta$_2$P$_2$ ring in **1** [Ta(1)—P(2)$_{br}$ 2.458(2), 2.486(2) Å;

Table 1. Selected bond lengths [Å] and bond angles [°] for **1**·C_7H_8

Ta(1)—P(1)	2.390(2)	Ta(1)—P(2)	2.486(2)
Ta(1)—P(2)′	2.458(2)	Ta(1)—Ta(1)′	3.024(2)
P(1)—C101	1.822(5)	P(1)—C(201)	1.821(6)
P(2)—C(301)	1.851(5)	P(2)—C(401)	1.849(5)
C(101)—C(102)	1.372(9)	C(101)—C(106)	1.412(8)
C(102)—C(103)	1.401(10)	C(103)—C(104)	1.40(2)
C(104)—C(105)	1.38(2)	C(105)—C(106)	1.394(11)
C(201)—C(206)	1.386(9)	C(210)—C(202)	1.398(9)
C(202)—C(203)	1.393(10)	C(203)—C(204)	1.36(2)
C(204)—C(205)	1.39(2)	C(205)—C(206)	1.389(10)
C(301)—C(306)	1.397(8)	C(301)—C(302)	1.382(9)
C(302)—C(303)	1.395(10)	C(303)—C(304)	1.391(14)
C(304)—C(305)	1.363(13)	C(305)—C(306)	1.402(8)
C(401)—C(406)	1.387(8)	C(401)—C(402)	1.392(8)
C(402)—C(403)	1.381(11)	C(403)—C(404)	1.36(2)
C(404)—C(405)	1.372(13)	C(405)—C(406)	1.389(8)
C(1)—C(5)	1.426(8)	C(1)—C(2)	1.432(8)
C(1)—C(6)	1.492(8)	C(2)—C(3)	1.433(9)
C(3)—C(4)	1.408(8)	C(4)—C(5)	1.408(8)
Ta—C(Cp) 2.379(5) to 2.471(5)			
Ta(1)—P(2)—Ta(1)′	75.43(5)	P(2)—Ta(1)—P(2)′	104.58(5)
P(1)—Ta(1)—P(2)	104.15(6)	P(1)—Ta(1)—P(2)′	99.97(6)
C(201)—P(1)—C(101)	100.3(3)	C(201)—P(1)—Ta(1)	126.4(2)
C(101)—P(1)—Ta(1)	133.1(2)	C(102)—C(101)—C(106)	118.2(6)
C(102)—C(101)—P(1)	120.4(4)	C(106)—C(101)—P(1)	121.4(5)
C(101)—C(102)—C(103)	122.4(7)	C(104)—C(103)—C(102)	118.4(9)
C(105)—C(104)—C(103)	120.3(7)	C(104)—C(105)—C(106)	120.3(9)
C(105)—C(106)—C(101)	120.3(8)	C(202)—C(201)—C(206)	118.6(6)
C(202)—C(201)—P(1)	119.6(5)	C(206)—C(201)—P(1)	121.6(5)
C(201)—C(202)—C(203)	119.4(8)	C(204)—C(203)—C(202)	121.7(8)
C(205)—C(204)—C(203)	119.4(7)	C(204)—C(205)—C(206)	119.9(8)
C(205)—C(206)—C(201)	120.9(8)	C(401)—P(2)—C(301)	98.1(2)
C(401)—P(2)—Ta(1)′	117.6(2)	C(301)—P(2)—Ta(1)′	121.0(2)
C(401)—P(2)—Ta(1)	122.4(2)	C(301)—P(2)—Ta(1)	123.7(2)
Ta(1)′—P(2)—Ta(1)	75.43(5)	C(302)—C(301)—C(306)	118.3(5)
C(302)—C(301)—P(2)	120.1(5)	C(306)—C(301)—P(2)	121.6(4)
C(301)—C(302)—C(303)	121.3(7)	C(304)—C(303)—C(302)	119.8(8)
C(305)—C(304)—C(303)	119.7(6)	C(304)—C(305)—C(306)	120.7(7)
C(305)—C(306)—C(301)	120.3(6)	C(402)—C(401)—C(406)	117.7(5)
C(402)—C(401)—P(2)	121.3(5)	C(406)—C(401)—P(2)	120.7(4)
C(401)—C(402)—C(403)	120.4(7)	C(404)—C(403)—C(402)	120.5(8)
C(405)—C(404)—C(403)	121.2(8)	C(404)—C(405)—C(406)	118.5(7)
C(405)—C(406)—C(401)	121.8(6)	C(5)—C(1)—C(2)	107.0(5)
C(5)—C(1)—C(6)	126.7(5)	C(2)—C(1)—C(6)	126.1(6)
C(3)—C(2)—C(1)	107.3(5)	C(4)—C(3)—C(2)	108.6(5)
C(3)—C(4)—C(5)	107.8(5)	C(4)—C(5)—C(1)	109.1(5)

Ta(1)—P(2)—Ta(1)′ 75.43(5)°; P(2)—Ta(1)—P(2)′ 104.58(5)°] are comparable to those of the central Ta_2Cl_2 rings in inorganic binuclear complexes of type $[TaCl_2L_2(\mu\text{-}Cl)]_2$ (L = SMe_2 [28], PMe_3 [29], $Me_2PCH_2CH_2PMe_2$ [30]), while the central Ta_2P_2 ring in **3** is nearly square [Ta—P 2.317(6), Ta—P′ 2.338(2) Å, P—Ta—P′ 96.49(8), Ta—P—Ta′ 83.51(8)°] indicating substantial p_π-d_π back bonding of the phosphorus lone pair.

Even though the 18-electron rule predicts the presence of a Ta═Ta double bond in **1** and a Ta—Ta single bond in **3**, the Ta—Ta distance of 3.024(2) Å in **1** is longer than the Ta═Ta double bond lengths reported in the literature (2.55–2.85 Å in inorganic octahedral ditantalum(III) complexes) [31]. Although the Ta—Ta bond length is strongly dependent on the number and type of ligands (e.g., hydrido-bridged complexes generally have shorter Ta—Ta bonds than comparable halogen-bridged complexes) [31], and in the Ta^{IV} complex $[TaCl_2(PMe_3)_2(\mu\text{-}Cl)_2]_2$ [32] a value of 2.83 Å is given for a Ta—Ta single bond, the long Ta—Ta distance in **1** and the paramagnetic behaviour indicate the absence of a Ta═Ta double bond. The lengthening of the Ta—Ta bond in **1** can also be

Table 2. Selected bond lengths [Å] and bond angles [°] for **2**

Ta(1)—Cl(1)	2.402(2)	Ta(1)—Cl(2)	2.417(2)
Ta(1)—Cl(3)	2.416(2)	Ta(1)—Cl(4)	2.386(2)
Ta(1)—C(Cp′)	2.423(8) to 2.496(8)		
Ta—Cp(Centre)	2.145		
P(1)—H(1A)	1.42	P(1)—H(1B)	1.42
Ta(1)—P(1)	2.710(2)	P(1)—C(7)	1.841(8)
C(1)—C(5)	1.413(13)	C(1)—C(2)	1.426(13)
C(1)—C(6)	1.506(13)	C(2)—C(3)	1.392(13)
C(3)—C(4)	1.401(14)	C(4)—C(5)	1.40(2)
C(7)—C(8)	1.407(12)	C(7)—C(12)	1.404(12)
C(8)—C(9)	1.385(12)	C(8)—C(13)	1.535(12)
C(9)—C(10)	1.405(13)	C(10)—C(11)	1.391(13)
C(10)—C(16)	1.521(12)	C(11)—C(12)	1.395(13)
C(12)—C(19)	1.524(12)	C(13)—C(14)	1.50(2)
C(13)—C(15)	1.537(14)	C(16)—C(18)	1.50(2)
C(16)—C(17)	1.53(2)	C(19)—C(21)	1.50(2)
C(19)—C(20)	1.531(14)		
Cl(4)—Ta(1)—Cl(1)	88.07(10)	Cl(4)—Ta(1)—Cl(3)	86.50(8)
Cl(1)—Ta(1)—Cl(3)	153.37(7)	Cl(4)—Ta(1)—Cl(2)	150.88(7)
Cl(1)—Ta(1)—Cl(2)	86.07(9)	Cl(3)—Ta(1)—Cl(2)	86.10(7)
Cl(4)—Ta(1)—P(1)	78.56(8)	Cl(1)—Ta(1)—P(1)	77.12(7)
Cl(3)—Ta(1)—P(1)	76.25(7)	Cl(2)—Ta(1)—P(1)	72.33(7)
C(7)—P(1)—H(1A)	105.9(3)	Ta(1)—P(1)—H(1A)	105.9(5)
C(7)—P(1)—H(1B)	105.9(3)	Ta(1)—P(1)—H(1B)	105.91(5)
H(1A)—P(1)—H(1B)	106.2	Cl(1)—Ta(1)—Cp(Centre)	103.8
Cl(2)—Ta(1)—Cp(Centre)	104.0	Cl(3)—Ta(1)—Cp(Centre)	102.8
Cl(4)—Ta(1)—Cp(Centre)	105.1	P(1)—Ta(1)—Cp(Centre)	176.3
C(7)—P(1)—Ta(1)	125.7(3)	C(5)—C(1)—C(2)	105.7(8)
C(5)—C(1)—C(6)	127.7(9)	C(2)—C(1)—C(6)	126.5(8)
C(3)—C(2)—C(1)	109.5(8)	C(2)—C(3)—C(4)	107.4(8)
C(5)—C(4)—C(3)	108.6(8)	C(4)—C(5)—C(1)	108.8(9)
C(8)—C(7)—C(12)	120.4(8)	C(8)—C(7)—P(1)	119.7(6)
C(12)—C(7)—P(1)	119.9(6)	C(9)—C(8)—C(7)	118.6(8)
C(9)—C(8)—C(13)	117.5(7)	C(7)—C(8)—C(13)	123.9(8)
C(8)—C(9)—C(10)	122.8(8)	C(11)—C(10)—C(9)	117.0(8)
C(11)—C(10)—C(16)	122.7(8)	C(9)—C(10)—C(16)	120.3(7)
C(10)—C(11)—C(12)	122.6(8)	C(11)—C(12)—C(7)	118.7(8)
C(11)—C(12)—C(19)	116.4(8)	C(7)—C(12)—C(19)	124.8(8)
C(14)—C(13)—C(8)	112.0(8)	C(14)—C(13)—C(15)	111.6(9)
C(8)—C(13)—C(15)	109.8(8)	C(18)—C(16)—C(10)	112.6(8)
C(18)—C(16)—C(17)	110.2(9)	C(10)—C(16)—C(17)	110.2(8)
C(21)—C(19)—C(12)	112.2(8)	C(21)—C(19)—C(20)	111.3(9)
C(12)—C(19)—C(20)	110.1(8)		

attributed to the high steric demand of the bridging PPh_2 ligands. In **3**, The Ta—Ta bond length of 3.100(3) Å is comparable to that observed in **1**. As **3** exhibits diamagnetic behaviour, the presence of a Ta—Ta single bond must be assumed. A comparable value of 3.165 Å is observed for a Ta—Ta bond in $[TaCl_3(SMe_2)(\mu\text{-}SPh)]_2$ [33].

The Ta(1)—P(1) bond length of the terminal phosphanido ligand in **1** of 2.390(2) Å is only slightly shorter than that in $[TaH(PPh_2)_2(dmpe)]$ [Ta—P 2.430(6) and 2.404(6) Å] [5]. In both compounds, the P atom of the terminal phosphanido group is trigonal-planar (sum of bond angles *ca* 360°), indicating that the PPh_2 group is acting as a three-electron donor. In contrast, an increase in the Ta—P bond length and a pyramidal geometry of the P atom are observed when the phosphanido ligand acts as a one-electron donor (e.g., $[Cp_2TaH_2(PPh_2)]$, Ta—P 2.595(3) Å) [4c].

In **3**, the Ta—P bond lengths of the bridging phosphinidene ligand are comparable to that observed for the terminal phosphanido group in **1**. The dependence of the Ta—P bond length on the substituents and geometrical arrangement at phosphorus is demonstrated in the following complexes: Thus, the Ta—P double bond in $[(SiMe_3NCH_2CH_2)_3NTa{=}PCy]$ [7] of 2.145(7) Å (TaPC is linear) is much shorter than that observed for $[(Bu^t_3SiO)_3Ta{=}PPh]$ [6] (2.317(4) Å, Ta—P—C 110.2(4)°, bent TaPC). However, all these distances are shorter than the sum of the covalent radii of Ta and P (2.44 Å) [34].

The Ta—Cl bond length in **3** [2.350(2) Å] is shorter

Table 3. Selected bond lengths [Å] and bond angles [°] for **3**·C_7H_8

Ta—P	2.317(6)	Ta—P′	2.338(2)
Ta—Cl(1)	2.350(2)	Ta—Ta′	3.100(3)
P—C(7)	1.824(8)	P—Ta′	2.338(2)
Ta—Cp(Centre)	2.071	Ta—C(Cp)	2.349(10) to 2.451(9)
C(1)—C(5)	1.40(2)	C(1)—C(2)	1.43(2)
C(2)—C(3)	1.41(2)	C(3)—C(4)	1.39(2)
C(4)—C(5)	1.416(14)	C(5)—C(6)	1.50(2)
C(7)—C(12)	1.385(11)	C(7)—C(8)	1.419(11)
C(8)—C(9)	1.388(11)	C(8)—C(13)	1.508(12)
C(9)—C(10)	1.376(12)	C(10)—C(11)	1.384(11)
C(10)—C(16)	1.517(11)	C(11)—C(12)	1.406(11)
C(12)—C(19)	1.513(11)	C(13)—C(15)	1.52(2)
C(13)—C(14)	1.53(2)	C(16)—C(17)	1.500(14)
C(16)—C(18)	1.527(13)	C(19)—C(21)	1.52(2)
C(19)—C(20)	1.54(2)		
P—Ta—P′	96.49(8)	P—Ta—Cl(1)	105.02(12)
P′—Ta—Cl(1)	105.57(8)	P—Ta—Ta′	48.54(8)
P′—Ta—Ta′	47.95(11)	Cl(1)—Ta—Ta′	113.34(8)
C(7)—P—Ta	139.9(3)	C(7)—P—Ta′	136.6(3)
Ta—P—Ta′	83.51(8)	Cl(1)—Ta—Cp(Centre)	112.8
P—Ta—Cp(Centre)	118.3	P′—Ta—Cp(Centre)	116.7
C(5)—C(1)—C(2)	108.3(10)	C(3)—C(2)—C(1)	106.4(10)
C(4)—C(3)—C(2)	109.6(10)	C(1)—C(5)—C(4)	108.2(10)
C(3)—C(4)—C(5)	107.5(10)	C(4)—C(5)—C(6)	124.9(12)
C(1)—C(5)—C(6)	126.9(12)	C(12)—C(7)—P	119.9(6)
C(8)—C(7)—P	119.2(6)	C(9)—C(8)—C(7)	117.3(8)
C(12)—C(7)—C(8)	120.8(7)	C(7)—C(8)—C(13)	122.8(7)
C(9)—C(8)—C(13)	119.9(7)	C(9)—C(10)—C(11)	118.2(8)
C(10)—C(9)—C(8)	123.4(8)	C(11)—C(10)—C(16)	118.7(8)
C(9)—C(10)—C(16)	123.1(7)	C(7)—C(12)—C(11)	118.9(7)
C(10)—C(11)—C(12)	121.4(8)	C(11)—C(12)—C(19)	117.4(7)
C(7)—C(12)—C(19)	123.6(7)	C(8)—C(13)—C(14)	113.2(9)
C(8)—C(13)—C(15)	110.7(9)	C(17)—C(16)—C(10)	109.9(8)
C(15)—C(13)—C(14)	112.4(11)	C(10)—C(16)—C(18)	113.1(7)
C(17)—C(16)—C(18)	112.7(9)	C(12)—C(19)—C(20)	109.7(8)
C(12)—C(19)—C(21)	113.1(8)	C(21)—C(19)—C(20)	111.9(11)

than those in octahedral Ta derivatives (e.g., $[TaCl_2(\mu\text{-}Cl)(\mu\text{-dmpm})]_2$, dmpm = $Me_2PCH_2PMe_2$, Ta—Cl (terminal) 2.435(7), 2.457(6) Å [35], *trans*-$[CpTaCl_2(CO)(PMe_2Ph)_2]$, Ta—Cl 2.518(4), 2.539(4) Å [13d], $[Cp^*TaCl_3(PMe_3)]$, Ta—Cl 2.395(3) to 2.416(3) Å [11b], *cis*-$[Cp^*TaCl_2(CO)_2(PMe_3)]$, Ta—Cl 2.504(2), 2.512(2) Å [11b]), indicating a less pronounced *trans* effect of the bridging phosphorus ligand.

$[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**) (Figs 3 and 4) is the first phosphine adduct of $[Cp'TaCl_4]$ to be crystallographically characterised. A niobium complex, $[CpNbCl_4(PMePh_2)]$ [15], an amine complex, $[Cp^*TaCl_4(NH_2Ph)]$ [24], and an isocyanide complex $[Cp^*TaCl_4(CN\text{-}2,6\text{-}Me_2C_6H_3)]$ [24] which are structurally related, have been reported.

In **2**, the Ta atom has a pseudo-octahedral geometry, with the phosphine ligand located *trans* to the Cp′ ligand and the four chlorine ligands bent away from the Cp′ ligand [Cl(4)—Ta(1)—Cl(1) 88.07(10), Cl(4)—Ta(1)—Cl(3) 86.50(8), Cl(1)—Ta(1)—Cl(2) 86.07(9), Cl(3)—Ta(1)—Cl(2) 86.10(7)]. The Ta atom is shifted towards the Cp′ ligands and lies 0.58 Å above the plane defined by the four chlorine ligands, which is parallel to the plane defined by the Cp′ ring.

The Ta—Cl bond lengths [Ta(1)—Cl(1) 2.402(2), Ta(1)—Cl(2) 2.417(2), Ta(1)—Cl(3) 2.416(2), Ta(1)—Cl(4) 2.386(2)] are comparable to those observed in related compounds [e.g. $Cp^*TaCl_3(PMe_3)]$, Ta—Cl 2.395(3) to 2.416(3) Å] [11b], while an increase in bond length is observed due to a strong *trans* effect in *cis*-$[Cp^*TaCl_2(CO)_2(PMe_3)]$ [Ta—Cl 2.504(2), 2.512(2) Å] [11b].

While the Ta—P bond lengths of phosphine adducts are in the range 2.59–2.67 Å [11b,13,14, 35–38], **2** exhibits a rather long Ta(1)—P(1) bond length of 2.710(2) Å, which is possibly due to the steric influence of the chlorine ligands or the *trans* effect of the Cp′ ligand. In the structurally related complexes $[CpNbCl_4(PMePh_2)]$ [Nb—P 2.7844(9) Å] [15] and

Table 4. Crystal data and structure refinement for $[\mathrm{Cp'Ta}(\mu\text{-}\mathrm{PPh_2})(\mathrm{PPh_2})]_2$ (**1**) · C_7H_8, $[\mathrm{Cp'TaCl_4}\{\mathrm{PH_2}(2,4,6\text{-}\mathrm{Pr^i_3C_6H_2})\}]$ (**2**), and $[\mathrm{Cp'TaCl}\{\mu\text{-}\mathrm{P}(2,4,6\text{-}\mathrm{Pr^i_3C_6H_2})\}]_2$ (**3**) · C_7H_8

	1 · C_7H_8	**2**	**3** · C_7H_8
Formula	$C_{67}H_{62}P_4Ta_2$	$C_{21}H_{32}Cl_4PTa$	$C_{49}H_{68}Cl_2P_2Ta_2$
Molecular weight	1353.03	638.19	1151.78
Temperature (K)	213(2)	200(2)	200(2)
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a (Å)	10.083(5)	6.6244(13)	10.5457(12)
b (Å)	11.212(6)	10.159(2)	16.39(5)
c (Å)	13.191(7)	18.944(4)	14.021(2)
α (°)	102.62(4)	86.90(3)	90
β (°)	97.99(4)	81.93(3)	94.957(11)
γ (°)	101.03(4)	76.45(3)	90
V (Å^3)	1403(1)	1226.8(4)	2415(7)
Z	1	2	2
d_{calc} (g cm^{-3})	1.601	1.728	1.584
2Θ range (°)	3–60	4–47	4–50
h (min., max.)	0/14	−6/7	−12/12
k (min., max.)	−15/15	−11/9	0/19
l (min., max.)	−18/18	−21/15	−16/16
Total reflections	8040	4804	4389
Independent reflections	7609 [R(int.) 0.0439]	3441 [R(int.) 0.0904]	4298 [R(int.) 0.0186]
Parameters	345	273	382
Absorption coefficient (μ cm^{-1})	38.73	49.86	47.36
Largest diff. peak/hole (e Å^{-3})	4.3/−3.7[a]	1.7/−2.2	2.0/−1.1
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0520$, $wR2 = 0.1450$	$R1 = 0.0407$, $wR = 0.1110$	$R1 = 0.0355$, $wR = 0.0806$
R indices (all data)	$R1 = 0.0522$, $wR2 = 0.1454$	$R1 = 0.0495$, $wR2 = 0.1147$	$R1 = 0.0840$, $wR = 0.0933$
Goodness-of-fit (F^2)	1.078	1.106	0.997

[a] Located on the Ta—Ta vector.

$[\mathrm{Cp^*TaCl_2(CO)_2(PMe_3)}]$ [Ta—P 2.707(2) Å] [11b], in which the phosphine ligand is in a position *trans* to the cyclopentadienyl ligand, lengthening of the metal–P bond was also observed.

EXPERIMENTAL

All experiments were carried out under purified dry nitrogen (for **1**) or argon (for **2** and **3**). Solvents were dried and freshly distilled under nitrogen or argon. For **1**: the IR spectrum was recorded on a Perkin-Elmer 883 in the range 200–4000 cm^{-1}; MS: Varian MAT 711 (EI, 70 eV, source temperature 180°C). For **2** and **3**, the IR spectra were recorded on a FT spectrometer System 2000 (Perkin-Elmer) in the range 200–4000 cm^{-1}; NMR spectra with an AVANCE DRX 400 spectrometer (Bruker), ^{1}H NMR: internal standard solvent (e.g., benzene, toluene), ^{31}P NMR: external standard 85% H_3PO_4; MS: with a Sektorfeldgerät AMD 402 (AMD Intectra GmbH) (EI, 70 EV). The EPR spectrum was recorded with a Bruker ESP 300E. The melting points were determined in sealed capillaries under nitrogen or argon and are uncorrected. $[\mathrm{Cp'TaCl_4}]$ [13b], $\mathrm{KPPh_2(dioxane)_2}$ [39], and $\mathrm{PH_2}(2,4,6\text{-}\mathrm{Pr^i_3C_6H_2})$ [18] were prepared by literature procedures.

Synthesis of $[\mathrm{Cp'Ta}(\mu\text{-}\mathrm{PPh_2})(\mathrm{PPh_2})]_2$ (**1**) · C_7H_8

$[\mathrm{Cp'TaCl_4}]$ (0.50 g, 1.24 mmol) and $\mathrm{KPPh_2(dioxane)_2}$ (0.49 g, 1.24 mmol) were placed in a Schlenk tube. 20 cm^3 of ether was added at room temperature. A brown solution was obtained. The solvent was removed to dryness and the residue extracted with toluene. After filtering, the solution was covered with a layer of n-heptane. After several days at room temperature black rhombic crystals of **1** were obtained: *ca* 40 mg (20% based on $\mathrm{KPPh_2(dioxane)_2}$), m.p. 167°C. EI-MS (70 eV), *m/z* (%): 1260 (28.4) [$\mathrm{M^+} = [\mathrm{Cp'Ta}(\mu\text{-}\mathrm{PPh_2})(\mathrm{PPh_2})]_2^+$], 1181 (12.0) [$(\mathrm{M\text{-}Cp'})^+$], 1104 (19.4) [$(\mathrm{M\text{-}2Cp'})^+ = [\mathrm{Ta}(\mu\text{-}\mathrm{PPh_2})(\mathrm{PPh_2})]_2^+$], 1026(5.7) [$(\mathrm{M\text{-}Ph\text{-}2Cp'})^+$], 998 (5.8) [$(\mathrm{M\text{-}2Ph\text{-}2Cp'})^+$], 920 (4.3) [$(\mathrm{M\text{-}3Ph\text{-}2Cp'})^+$], 552 (3.9) [$(\mathrm{Ta(PPh_2)_2})^+$], and fragmentation products thereof. IR (KBr, cm^{-1}): $\tilde{\nu} = 3056$ m, 2957 w, 2920 w, 2850 w, 2350 w, 2322 vw, 1954 vw, 1879 vw, 1804 vw, 1750 vw, 1610 vw, 1578 m, 1474 m, 1429 m, 1379 m, 1300 m, 1266 m, 1177 m, 1154 w, 1127 w, 1081 w, 1063 w, 1026 m, 997 w, 890 vw, 865 w, 843 w, 800 m, 737 s, 696 vs, 560 vw, 512 s, 484 m, 452 m, 425 m, 308 w.

Synthesis of $[\mathrm{Cp'TaCl_4}\{\mathrm{PH_2}(2,4,6\text{-}\mathrm{Pr^i_3C_6H_2})\}]$ (**2**)

$[\mathrm{Cp'TaCl_4}]$ (1.95 g, 4.88 mmol) was suspended in 30 cm^3 toluene and with stirring $\mathrm{PH_2}$(2,4,6-

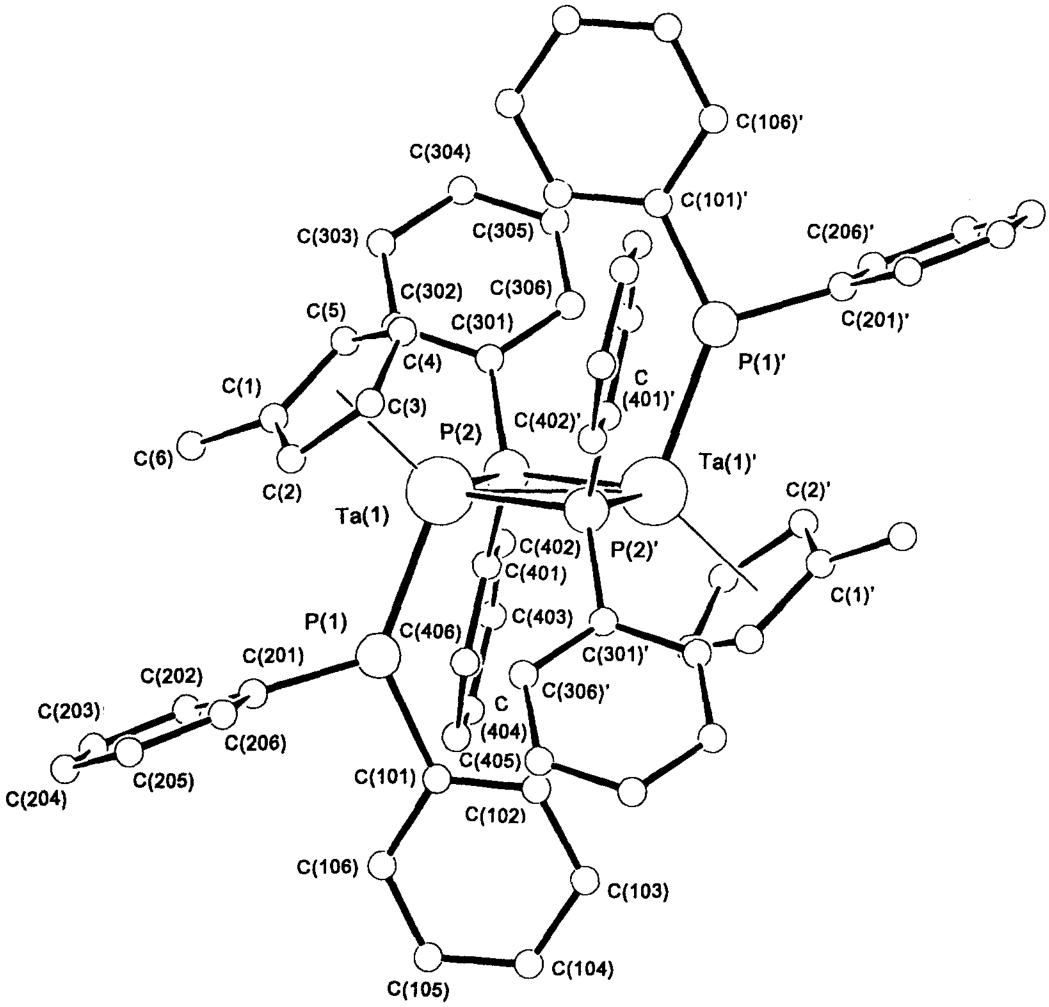

Fig. 1. Molecular structure of $[Cp'Ta(\mu\text{-}PPh_2)(PPh_2)]_2$ (**1**) showing the atom numbering scheme employed (SCHAKAL plot) [43]. Hydrogen atoms are omitted for clarity.

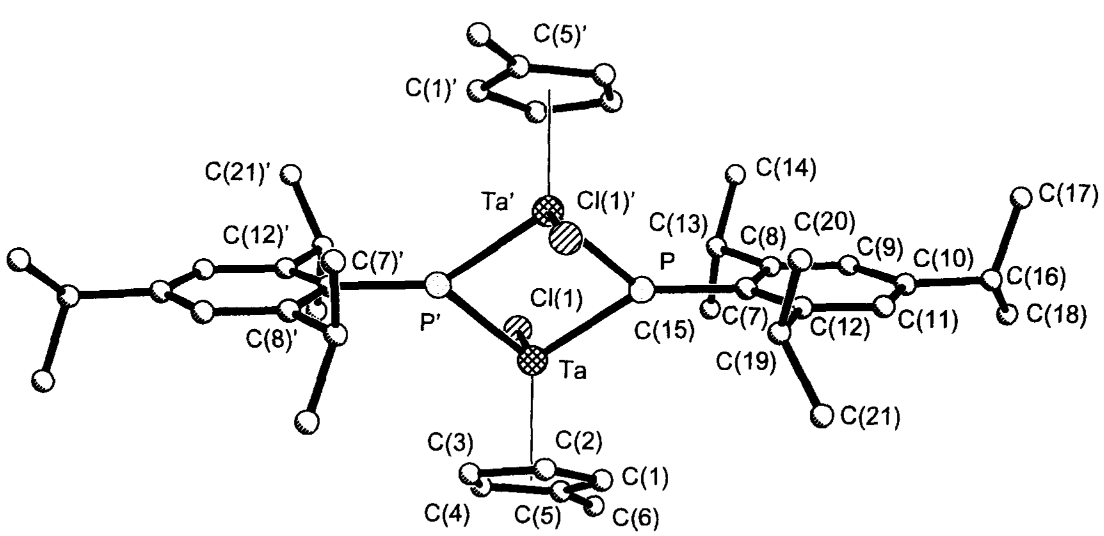

Fig. 2. Molecular structure of $[Cp'TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i_3C_6H_2)\}]_2$ (**3**) showing the atom numbering scheme employed (SHELXTL PLUS; XP) [41]. Hydrogen atoms are omitted for clarity.

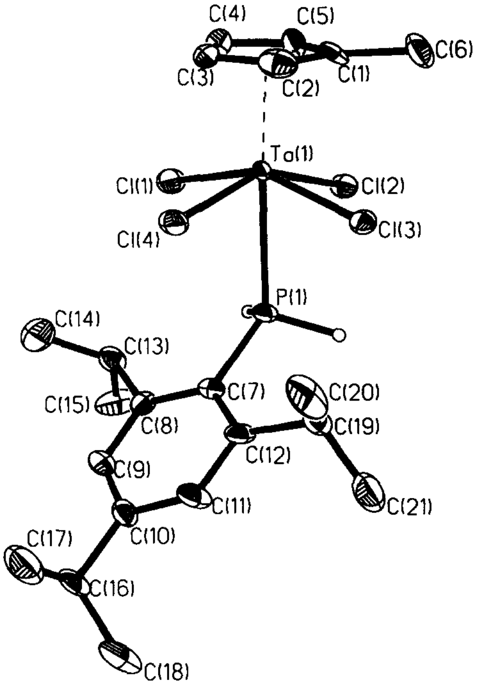

Fig. 3. Molecular structure of $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [41]. Hydrogen atoms (other than P—H) are omitted for clarity.

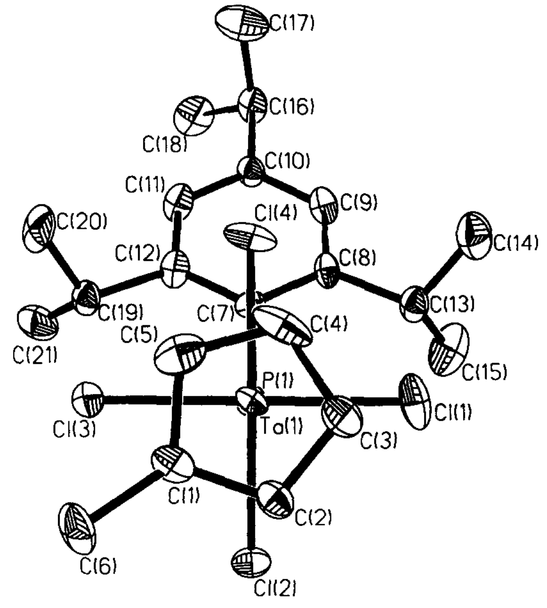

Fig. 4. View along the Ta—P bond axis of $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**) (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [41]. Hydrogen atoms are omitted for clarity.

$Pr^i_3C_6H_2$) (1.15 g, 4.88 mmol) was added with a syringe. The reaction is exothermic and a clear orange solution is obtained. The solution was stirred overnight. Then the solvent was removed to dryness and the residue extracted with pentane. Cooling to 5°C afforded yellow needles of **2**: 2.8 g (90%). The product is only slightly air sensitive but is hydrolysed rapidly. **2** is soluble in CH_2Cl_2 and $CHCl_3$ without decomposition. M.p. 147°C.

^1H NMR (400 MHz; C_7D_8; 298 K, ppm): 1.12 [d, $^3J(HH)$ 6.8 Hz, 6 H, 4-(Me_2CH)C_6H_2], 1.29 [d, $^3J(HH)$ 6.5 Hz, 12 H, 2,6-(Me_2CH)$_2C_6H_2$], 2.09 (s, br, 3H, C_5H_4Me), 2.68 [sept, $^3J(HH)$ 6.8 Hz, 1 H, 4-(Me_2CH)C_6H_2], 3.90 [broad with fine structure, 2 H, 2,6-(Me_2CH)$_2C_6H_2$], 5.69 (s, br 2 H, C_5H_4Me), *ca* 5.8 [br, 1 H, $PH_2\{[2,4,6\text{-}(Me_2CH)_3C_6H_2\}]$, 6.23 (s, 2H, C_5H_4Me), *ca* 6.7 [br, 1 H, $PH_2\{2,4,6\text{-}(Me_2CH)_3C_6H_2\}]$, 7.12 [s, 2 H, 2,4,6-($Me_2$CH)$_3C_6H_2$]. ^1H NMR (400 MHz; toluene-d_8; 263 K, ppm): all signals broaden apart from the broad signals at *ca* 5.8 and 6.7 ppm; the broad P—H resonances are observed as sharp singlets at 6.10 and 6.99 ppm [J(PH) 357 Hz] at low temperature. ^{31}P NMR (C_7D_8, ppm): (a) 300 K, *ca* −36, broad, $\nu_{1/2}$ *ca* 800 Hz, (b) T < 290 K, −35.7 t [^1J(PH) 360.9 Hz]. ^{13}C NMR (C_7D_8 298 K, ppm): 16.1 (C_5H_4Me); 24.4, 24.9 [2,4,6-(Me_2CH)$_3C_6H_2$]; 34.3, 35.1 [2,4,6-(Me_2CH)$_3C_6H_2$]; 121.1, 122.5, 135.1 (C_5H_4Me); 152.2 (d, J(PC) 28 Hz, C_{ipso}-PH_2), other signals for 2,4,6-(Me_2CH)$_3C_6H_2$ are obscured by those of toluene. EI-MS (70 eV): no molecular ion peak is observed. Only signals for $[Cp'TaCl_4]$ and $PH_2(2,4,6\text{-}Pr^i_3C_6H_2)$ as well as fragmentation products thereof are observed, *m/z* (%): 402 (100) ($[Cp'TaCl_4]^+$), 236 (35) $[PH_2(2,4,6\text{-}Pr^i_3C_6H_2)^+]$, 204 (90) $[(2,4,6\text{-}Pr^i_3C_6H_2)^+]$, 79 (25) $[(Cp')^+]$, 43 (30) $[(Pr^i)^+]$. IR (KBr, cm^{-1}): $\tilde{\nu} = 3113$ s, 2926 m, 2866 m, 1600 m, 1561 sh, 1498 m, 1459 m, 1424 m, 1382 m, 1361 m, 1170 sh, 1105 m, 1080 m, 1048 m, 938 s, 869 m, 746 m, 414 sh. Found: C 39.1; H 5.3; Cl 22.4. Calc. for $C_{21}H_{32}Cl_4PTa$ (638.2): C 39.5; H 5.1; Cl 22.2%.

Synthesis of $[Cp'TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i_3C_6H_2)\}]_2$ (**3**)$\cdot C_7H_8$

With stirring, DBU (0.96 g, 6.29 mmol, 1 cm^3) was added with a syringe to a yellow solution of $[Cp'TaCl_4\{PH_2(2,4,6\text{-}Pr^i_3C_6H_2)\}]$ (**2**) (2.0 g, 3.14 mmol) in 30 cm^3 toluene. A colour change to red-brown was observed. The solution was stirred at r.t. for 2 h. Then the solvent was removed to dryness and the residue dissolved in 20 cm^3 pentane/2 cm^3 toluene giving a red-brown solution. Cooling to −20 C yielded dark red cubic crystals of **3**$\cdot C_7H_8$. **3** is soluble in CH_2Cl_2 and $CHCl_3$ without decomposition. The product is only slightly air sensitive but hydrolysed rapidly. The crystals were ground and the resulting powder dried *in vacuo* to remove the included toluene. Yield: 0.91 g (55%). M.p. 268 C. ^1H NMR (400 MHz, C_6D_6, 298 K, ppm): 1.28 [d, $^3J(HH)$ 5.6 Hz, 24 H, 2,6-(Me_2CH)$_2C_6H_2$], 1.51 [d, $^3J(HH)$ 6.6 Hz, 12 H, 4-(Me_2CH)C_6H_2], 1.96 (s, 6 H, C_5H_4Me), 3.27 [sept, $^3J(HH)$ 6.6 Hz, 2 H, 4-(Me_2CH)C_6H_2], 3.93 [broad with fine structure, 4 H, 2,6-$(Me_2CH)_2C_6H_2$], 5.24 (s, br, 4 H, C_5H_4Me), 5.91 (s, br, 4 H, C_5H_4Me), 7.36 [s, 4 H, 2,4,6-$(Me_2CH)_3C_6H_2$]. ^{31}P NMR (C_6D_6, ppm): 391.5, s. EI-MS (70 eV, *m/z* (%)): 1060 (100) [M^+ = [Cp′TaCl{μ-P(2,4,6-$Pr^i_3C_6H_2$)}]$_2^+$], 530 (1.0) [Cp′TaCl{μ-P(2,4,6-$Pr^i_3C_6H_2$)}$^+$], 204 (60) [(2,4,6-$Pr^i_3C_6H_2)^+$], 79 (20) [$(Cp')^+$], 43 (40) [$(Pr^i)^+$], as well as fragmentation products thereof. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2958 s, 2924 m, 2865 m, 1596 m, 1490 sh, 1459 m, 1419 m, 1379 m, 1359 m, 1313 m, 1262 m, 1099 m, 1031 m, 936 sh, 876 m, 805 s, 753 sh, 506 sh. Found: C, 47.1; H, 5.8. Calc. for $C_{42}H_{60}Cl_2P_2Ta_2$ (1059.7): C, 47.6, H, 5.7%.

Reaction of [Cp′TaCl$_4$] *with DBU*

DBU (0.8 g, 5.0 mmol) was added with a syringe to a stirred yellow suspension of [Cp′TaCl$_4$] (2.0 g, 5.0 mmol) in 30 cm^3 toluene. A colour change to red-brown was observed. The solution was stirred at r.t. for 5 h. Then the solvent was removed to dryness and the residue was washed with 20 cm^3 pentane and dissolved in 30 cm^3 CH_2Cl_2. An EPR spectrum of the CH_2Cl_2 solution showed the 8-line spectrum expected for a paramagnetic tantalum compound (Ta: $I = 7/2$).

Data collection and structure refinement for [Cp′Ta(μ-PPh_2)(PPh_2)]$_2$ (**1**)·C_7H_8, [Cp′TaCl$_4${PH_2(2,4,6-$Pr^i_3C_6H_2$)}] (**2**), *and* [Cp′TaCl{μ-P(2,4,6-$Pr^i_3C_6H_2$)}]$_2$ (**3**)·C_7H_8

Data (Mo-K_α = 0.71069 Å) were collected with a Stoe STADI 4 diffractometer (for **1** and **3**) and with a Siemens CCD (SMART) (for **2**). 25 reflections (2Θ range: 2–25°) (**1**) or 80 reflections (2θ range: 28–40°) (**3**) were used for determination of the unit cell parameters; for **2**, 1930 reflections (2θ range: 12–25°) were used for refinement of the unit cell parameters. Absorption correction: psi-scans. The structures were solved by direct methods (**1**, **3**: SHELXS-86 [40], **2**: SHELXTL PLUS [41]) and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F^2 (**1**, **3**: SHELXL-93 [42], **2**: SHELXTL PLUS [41]). Restrictions for **1**: Ta, P and C atoms anisotropic, H atoms isotropic in calculated positions. One molecule of toluene (disordered, only C atoms located and refined isotropically) per formula unit of **1** is present in the unit cell. Restrictions for **2**: Ta, P, Cl and C atoms anisotropic, H atoms isotropic in calculated positions. Restrictions for **3**: Ta, P, Cl and C atoms anisotropic, H atoms isotropic in calculated positions. One molecule of toluene (disordered, only C atoms located and refined isotropically) per formula unit of **3** is present in the unit cell. A summary of data collection parameters is given in Table 4. Anisotropic atomic parameters and full lists of bond lengths and angles have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.

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