Organometallic Niobium and Tantalum Complexes with Primary Phosphine Ligands: Syntheses and Molecular Structures of [Cp*$MCl_4(PH_2R)$] (M = Nb, Ta; Cp* = C_5Me_5; R = Bu^t, Ad, Cy, Ph, 2,4,6-$Me_3C_6H_2$ (Mes))

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Dedicated to Professor Dieter Fenske on the Occasion of his 60th Birthday.

Abstract. The reaction of [Cp*MCl_4] (M = Nb, Ta; Cp* = C_5Me_5) with PH_2R in toluene at room temperature gives the primary phosphine complexes [Cp*$MCl_4(PH_2R)$] [Cp* = C_5Me_5; M = Nb: R = Bu^t (**1a**), Ad (**2a**), Cy (**3a**), Ph (**4a**), 2,4,6-$Me_3C_6H_2$ (Mes) (**5a**); M = Ta: R = Bu^t (**1b**), Ad (**2b**), Cy (**3b**), Ph (**4b**), Mes (**5b**)] in high yield. **1–5** were characterized spectroscopically (NMR, IR, MS) and by crystal structure determinations. The starting material [Cp*$TaCl_4$] is monomeric in the solid state, as shown by crystal structure determination.

Keywords: Tantalum; Phosphine complexes; Niobium; Phosphines; Hydrogen bonds.

Metallorganische Niob- und Tantal-Komplexe mit primären Phosphanliganden: Synthese und Molekülstrukturen von [Cp*$MCl_4(PH_2R)$] (M = Nb, Ta; Cp* = C_5Me_5; R = Bu^t, Ad, Cy, Ph, 2,4,6-$Me_3C_6H_2$ (Mes))

Inhaltsübersicht. Die Komplexe [Cp*MCl_4] (M = Nb, Ta; Cp* = C_5Me_5) reagieren bei Raumtemperatur in Toluol mit den primären Phosphanen PH_2R unter glatter Bildung der Verbindungen [Cp*$MCl_4(PH_2R)$] [Cp* = C_5Me_5; M = Nb: R = Bu^t (**1a**), Ad (**2a**), Cy (**3a**), Ph (**4a**), 2,4,6-$Me_3C_6H_2$ (Mes) (**5a**); M = Ta: R = Bu^t (**1b**), Ad (**2b**), Cy (**3b**), Ph (**4b**), Mes (**5b**)]. **1–5** wurden spektroskopisch (NMR, IR, MS) und röntgenstrukturanalytisch charakterisiert. Die Ausgangsverbindung [Cp*$TaCl_4$] ist im Festkörper monomer.

Introduction

Organometallic dialkyl- and diarylphosphanido complexes of early transition metals have been studied intensively, while complexes derived from functionalized phosphines which have 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 functionalized 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 reactions yield novel functionalized 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 niobium and tantalum complexes to investigate the influence of the nature of the transition metal on the reactivity towards primary phosphines and alkali metal phosphanides. While the P-Si or P-H bond in zirconium complexes is generally less reactive [2] we expect this bond to be more reactive when the P ligand is coordinated to a group 5 metal. Thus, $[Nb_2Cl_8(PH_2R)_4]$ (R = Cy, Ph) is a suitable molecular precursor for NbP films [4].

To date, only a few phosphanido derivatives of organometallic [5, 6, 7] and inorganic [8, 9] niobium and tantalum compounds, diphosphanediyl complexes [10], one phosphinidene-bridged dimeric Ta^{IV} complex [6] and two stable terminal phosphinidene complexes [9, 11] have been described in the literature, although potential starting materials such as cyclopentadienyl-substituted metal halides, alkyls, hydrides and carbonyls [12] are accessible, as are inorganic metal halides [13].

The Lewis acidity of niobium(V) and tantalum(V) complexes has been extensively studied, and a large number of adducts of $[Cp^RMCl_4]$ with ethers, amines, nitriles, and isonitriles have been reported [14]. Up to now, only a few

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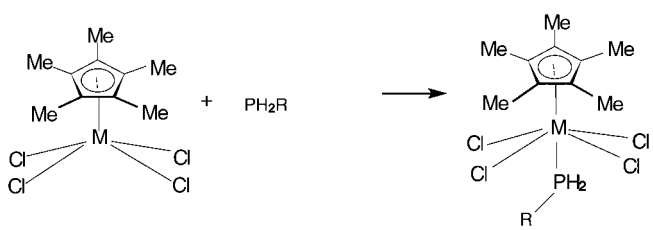
phosphine complexes of cyclopentadienyl tantalum or niobium tetrachloride are known, all but one of which have *tertiary* phosphine ligands [14d, 15, 16, 17]. We recently reported the synthesis of $[Cp'TaCl_4(PH_2Tipp)]$ (Cp' = C_5MeH_4, Tipp = 2,4,6-$Pr^i_3C_6H_2$, which was the first cyclopentadienyl tantalum tetrachloride complex with a primary phosphine [6a]. We now report the synthesis of organometallic niobium and tantalum complexes with a primary phosphine ligand $[Cp^*MCl_4(PH_2R)]$ [Cp* = C_5Me_5; M = Nb: R = Bu^t (**1a**), Ad (**2a**), Cy (**3a**), Ph (**4a**), 2,4,6-$Me_3C_6H_2$ (Mes) (**5a**); M = Ta: R = Bu^t (**1b**), Ad (**2b**), Cy (**3b**), Ph (**4b**), Mes (**5b**)].

Results and Discussion

Synthesis

When an equimolar amount of PH_2R is added to a solution of $[Cp^*MCl_4]$ (M = Nb, Ta) in toluene the phosphine complexes $[Cp^*MCl_4(PH_2R)]$ [M = Nb: R = Bu^t (**1a**), Ad (**2a**), Cy (**3a**), Ph (**4a**), Mes (**5a**); M = Ta: R = Bu^t (**1b**), Ad (**2b**), Cy (**3b**), Ph (**4b**), Mes (**5b**)] can be isolated as yellow or red (**1b** and **3a**) crystals in 85−96% yield (eq. (1)). **1−5** are air- and moisture-sensitive. They are very soluble in toluene, chloroform and dichloromethane, but less soluble in pentane or hexane. In ethers, **1−5** dissolve with liberation of the primary phosphine (^{31}P NMR), which indicates replacement of the phosphine by the coordinating solvent.



M = Nb: R = Bu^t (**1a**), Ad (**2a**), Cy (**3a**), Ph (**4a**), Mes (**5a**)
M = Ta: R = Bu^t (**1b**), Ad (**2b**), Cy (**3b**), Ph (**4b**), Mes (**5b**)

While $[CpMCl_4(PMe_3)]$ (M = Nb, Ta) [14d, 15] and $[CpNbCl_4(PEt_3)]$ [15] were earlier reported to be unstable, it was shown only recently that stable adducts can be obtained provided no excess of phosphine is 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 [16], as are the phosphine complexes $[CpNbCl_4(L)]$ (L = PMe_3, PMe_2Ph, $PMePh_2$) [17]. With an excess of phosphine, these complexes are readily reduced to niobium(IV) compounds, whereby PMe_3 is the best reducing agent (formation of $PMe_3H^+Cl^-$) [16, 17]. Similarly, $NbCl_5$ reacts with PH_2Cy with formation of $[NbCl_5(PH_2Cy)]$ while an excess of primary phosphine gives $[Nb_2Cl_8(PH_2Cy)_4]$ and $[PH_3Cy]_2[NbCl_6]$ [4]. Here, for **1−5** no reaction was observed with excess phosphine, even in refluxing toluene.

Similarly, $[MCl_5]_2$ (M = Nb, Ta) were reported to be reduced to M(IV) by aliphatic [18] and aromatic [19] amines. Surprisingly, in the reaction of $[Cp^*TaCl_4]$ with aniline the adduct $[Cp^*TaCl_4(NH_2Ph)]$ is formed [20].

Table 1 ^{93}Nb (at 300 K) and $^{31}P\{^{93}Nb\}$ (at 230 K) NMR Spectroscopic Data of $[Cp^*NbCl_4(PH_2R)]$ **1a−5a** and ^{31}P NMR Spectroscopic Data of $[Cp^*TaCl_4(PH_2R)]$ **1b−5b** (at 230 K), in CD_2Cl_2

	1a	**2a**	**3a**	**4a**	**5a**
$\delta(^{93}Nb)$/ppm	−465.2	−459.1	−484.9	−478.7	−452.9
$\delta(^{31}P\{^{93}Nb\})$/ppm	22.4	18.1	9.2	−11.2	−38.7
$^1J_{PH}$/Hz	345	349	351	367	347
	1b	**2b**	**3b**	**4b**	**5b**
$\delta(^{31}P)$/ppm	21.1	17.4	8.9	−11.3	−39.4
$^1J_{PH}$/Hz	345	346	351	366	360
T[a)]/K	285	288	295	275	275

[a)] Temperature at which the triplet structure is first observed.

NMR spectra

At room temperature only broad signals are observed for the PH_2 group in the ^{1}H and ^{31}P NMR spectra of **1−5**, which we attribute primarily to the influence of the quadrupole moments of niobium and tantalum [21].

Dynamic behavior was observed for $[Cp^*TaMe(\eta^2\text{-}C_2H_4)(PPh_2)]$, in which restricted rotation about the Ta-P bond [$\Delta G^{\neq}$ = 48.5 ± 1.3 kJ/mol] occurs [5b], and inversion barriers of terminal phosphanido groups lie in the same range (e.g., 48 to 60 kJ/mol for Nb, Re, Fe, and W complexes) [22].

For **1a−5a**, even on cooling to 230 K, the broad signals do not split into triplets in the proton-coupled ^{31}P NMR spectrum, and we believe this to be due to the quadrupole moment of niobium [21d, 23]. Therefore, we have recorded the ^{93}Nb-decoupled ^{31}P NMR spectra. To effectively decouple the ^{31}P NMR spectra, the ^{93}Nb chemical shifts had to be obtained first (Table 1). On cooling, severe line broadening is observed [23]. Only for **5a** is a doublet observed between 268 and 288 K due to ^{93}Nb-^{31}P coupling ($^1J_{NbP}$ = 236 Hz) which turns into a singlet on ^{31}P decoupling. Below 265 K, extreme line broadening prevents observation of any coupling effects. Comparable V-P coupling constants have been reported [24]. At room temperature, only broad signals are observed in the $^{31}P\{^{93}Nb\}$ NMR spectra; at 230 K the lines sharpen, and the triplet structure due to P-H coupling is observed (Table 1).

For **1b−5b**, on cooling to 230 K, the broad signals split into triplets in the proton-coupled ^{31}P NMR spectrum (shown for **3b** in Fig. 1). Table 1 lists the temperatures at which the triplet structure first occurs for **1b−5b**, as well as chemical shifts and $^1J_{PH}$ coupling constants at 230 K. Attempts to obtain the corresponding ^{181}Ta NMR spectra were thwarted, as the signals are very broad due to the large quadrupole moment of tantalum.

As expected on coordination to a transition metal, the signal of the phosphine ligand is shifted to low field compared to the free phosphine [PH_2R, R = Bu^t (−80.5,

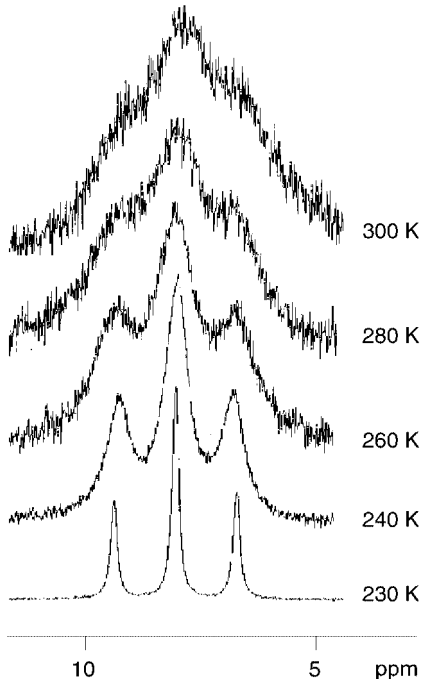


Fig. 1 ^{31}P NMR spectrum of **3b** in the temperature range of 230−300 K.

$^{1}J_{PH}$ = 174), Ad (−81.9, $^{1}J_{PH}$ = 187), Cy (−111.3, $^{1}J_{Ph}$ = 187), Ph (−122.1, $^{1}J_{PH}$ = 197), Mes (−153.8, $^{1}J_{PH}$ = 203)], by ca. 100−120 ppm, and the P-H coupling constant increases by 160−170 Hz.

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_2Ph)] (X = Cl: 2 ppm, X = Me: −1.9 ppm) [16], [$CpNbCl_4$(L)] (L = PMe_3: 5 ppm, L = PMe_2Ph: 12 ppm, L = $PMePh_2$: 17 ppm) [17] and the cationic complex [$Cp_2TaH_2(PHPh_2)]^+$ (0.2 ppm, J_{PH} = 389 Hz) [5c], broad signals and a low-field shift relative to the free phosphines (PMe_3: −62 ppm, PMe_2Ph: −46 ppm, $PMePh_2$: −26 pp, $PHPh_2$: −41 ppm, $^{1}J_{PH}$ = 214 Hz) [25] are also observed; however, here the difference is less pronounced.

In the ^{1}H NMR spectrum of **1−5** in $CDCl_3$, the signals of the Cp* ligand are shifted to high field by ca. 0.25 ppm compared to [Cp*MCl_4] [2.56 ppm (M = Nb), 2.73 ppm (M = Ta)] [26]. However, a low-field shift by ca. 1−4 ppm is observed for the carbon atoms of the Cp* ligand in the ^{13}C NMR spectra of **1−5** compared to [Cp*MCl_4] [135.7 ppm (M = Nb), 132.9 ppm (M = Ta)] [27].

Mass spectra

No molecular ion peaks were observed in the mass spectra of **1−5**. For all complexes, only signals for [Cp*$MCl_3]^+$, [Cp*$MCl_2]^+$, [Cp*$MCl]^+$, [Cp*$]^+$ and [$PH_2R]^+$, as well as fragmentation products thereof [28], were observed.

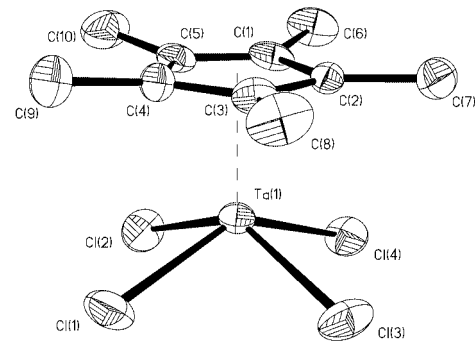


Fig. 2 Molecular structure of [Cp*$TaCl_4$] showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [48]. Hydrogen atoms are omitted for clarity.

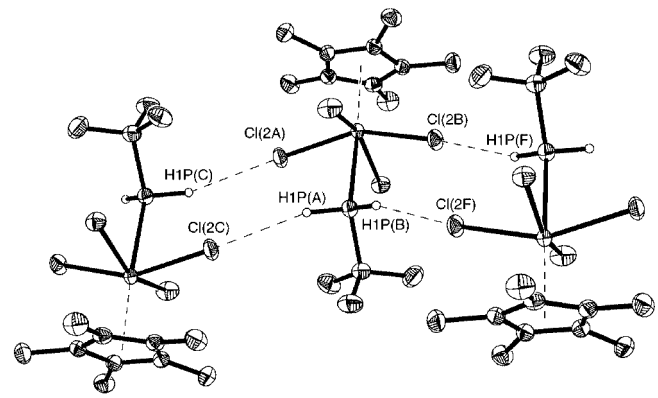


Fig. 3 Molecular structure of and hydrogen bonding in [Cp*$MCl_4(PH_2Bu^t)$] [M = Nb (**1a**), Ta (**1b**)] (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [48]. Hydrogen atoms other than PH are omitted for clarity.

IR spectra

In the IR spectra of the phosphine complexes, absorptions for the asymmetric and symmetric P-H vibrations are observed between 2375 and 2411 cm^{-1}. Unexpectedly, for **5** the corresponding bands were not observed, even though the presence of the primary phosphine was established beyond doubt by NMR spectroscopy and crystal structure determination. Possibly, the presence of hydrogen bonding is the reason for this.

Molecular structures of [Cp$TaCl_4$] and* **1−5**

Single crystals of [Cp*$TaCl_4$] (Fig. 2) can be obtained from a concentrated solution in dichloromethane, and **1−5** can be obtained from a concentrated solution in *n*-pentane or *n*-hexane. The corresponding niobium and tantalum complexes are isotypic and isostructural.

Besides [Cp'$TaCl_4(PH_2Tipp)$] [6a] complexes **1−5** (Figures 3−7), are the first primary phosphine complexes of [Cp*MCl_4] to be crystallographically characterized.

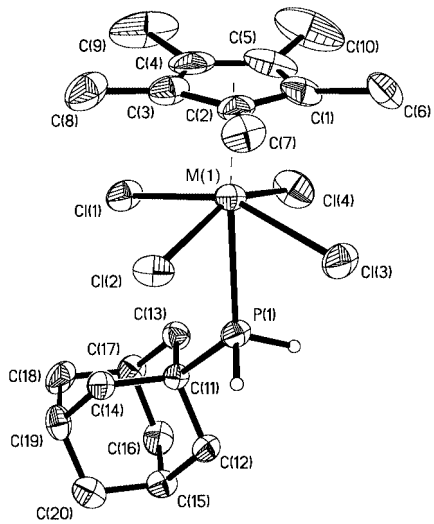


Fig. 4 Molecular structure of [Cp*$MCl_4(PH_2Ad)$] [M = Nb (**2a**), Ta (**2b**)] showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS, XP) [48]. Hydrogen atoms other than PH are omitted for clarity. Only one of the two independent molecules is shown.

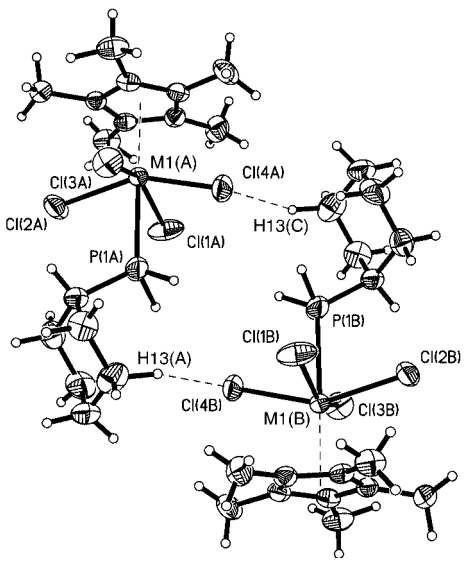


Fig. 5 Molecular structure of and hydrogen bonding in [Cp*$MCl_4(PH_2Cy)$] [M = Nb (**3a**), Ta (**3b**)] (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [48]. Hydrogen atoms other than PH are omitted for clarity.

In **1**, the atoms M(1), P(1), Cl(1), Cl(3), C(3), C(6), C(7), C(8) are located on a crystallographic mirror plane (in *x*, $^1/_4$, *z*). In **2**, there are two independent molecules in the asymmetric unit (space group $P\bar{1}$). In **4**, the phenyl ring is disordered over two positions, as shown in Fig. 6. The niobium complex [$CpNbCl_4(PMePh_2)$] [17], the amine complex [Cp*$TaCl_4(NH_2Ph)$] (29) and the isocyanide complex [Cp*$TaCl_4$(CN-2,6-$Me_2C_6H_3$)] [29] are structurally related.

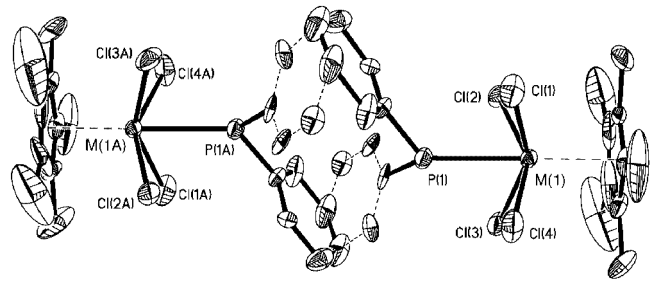


Fig. 6 Molecular structure and disorder of the phenyl rings in [Cp*$MCl_4(PH_2Ph)$] (M = Nb (**4a**), Ta (**4b**)] (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [48]. Hydrogen atoms other than PH are omitted for clarity.

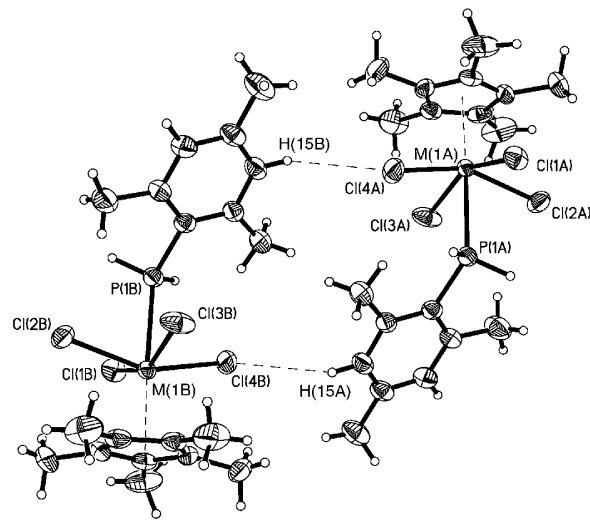


Fig. 7 Molecular structure of and hydrogen bonding in [Cp*$MCl_4(PH_2Mes)$] [M = Nb (**5a**), Ta (**5b**)] (ORTEP plot, 50% probability, SHELXTL PLUS; XP) [48]. Hydrogen atoms other than PH are omitted for clarity.

In **1**−**5**, the metal 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 (Table 2). In **1**−**5**, the metal atom is shifted towards the Cp* ligands and lies ca. 0.6 Å (compared to ca. 0.8 Å in [Cp*$TaCl_4$], Fig. 2) above the plane defined by the four chlorine ligands, which is parallel to the plane defined by the Cp* ring.

The M-Cl bond lengths of **1**−**5** [2.377(1)−2.450(1) Å] are about 0.05 Å longer than those observed in [Cp*$TaCl_4$], and 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) [30], 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] [30]. For **1** and **5**, the range of M-Cl bond lengths is larger due to the presence of hydrogen bonding. In the Bu^t derivatives **1**, intermolecular Cl-H(P) interactions (H···Cl 2.90 Å) lead to formation of a polymeric ladder (Fig. 3), while in the Cy

Table 2 Selected Structural Parameters of $[Cp^*NbCl_4(PH_2R)]$ **1a−5a**, $[Cp^*TaCl_4]$ and $[Cp^*TaCl_4(PH_2R)]$ **1b−5b**

	distance M to Cl_4 plane (Å)	M−Cl (Å)	M−P (Å)	M−P−C (deg)
Bu^t (**1a**)	0.576(1)	2.3989(7)−2.4497(7)	2.6639(7)	130.6(1)
Ad (**2a**)[a]	0.584(2), 0.589(2)	2.403(2)−2.430(2)	2.662(2), 2.667(2)	129.5(3), 130.3(2)
Cy (**3a**)	0.600(1)	2.4192(7)−2.4215(8)	2.6423(8)	121.8(1)
Ph (**4a**)	0.603(1)	2.396(3)−2.430(2)	2.642(2)	125.7(5)
Mes (**5a**)	0.586(1)	2.384(1)−2.446(1)	2.691(1)	126.8(1)
$[Cp^*TaCl_4]$	0.806(2)	2.346(3)−2.367(3)	−	−
Bu^t (**1b**)	0.580(1)	2.390(1)−2.438(1)	2.675(1)	131.0(2)
Ad (**2b**)[a]	0.588(1), 0.594(1)	2.392(2)−2.417(2)	2.674(2), 2.681(2)	129.5(2), 129.8(2)
Cy (**3b**)	0.601(1)	2.404(1)−2.411(1)	2.652(1)	121.8(2)
Ph (**4b**)	0.602(2)	2.393(4)−2.418(4)	2.651(3)	125.7(7)
Mes (**5b**)	0.591(1)	2.377(1)−2.429(1)	2.704(1)	126.8(2)

[a] There are two independent molecules in the asymmetric unit.

(**3**) and Mes derivatives (**5**), interaction between a chlorine ligand and a CH group of the cyclohexyl ring or a *meta*-H of the mesityl ring of a second molecule leads to formation of dimers (Figs. 5 and 7). Owing to this interaction the phosphorus atom in **3** occupies an axial position of the cyclohexyl ring, although the larger substituent usually prefers an equatorial position [31].

While the M-P bond lengths of niobium and tantalum phosphine complexes are in the range of 2.59 to 2.67 Å [14, 15, 30, 32, 33, 34, 35, 36], **1−5** exhibit rather long M-P bonds [Ta(1)-P(1) bonds of 2.651(3)−2.704(1) Å; Nb(1)-P(1) bonds of 2.642(2)−2.691(1) Å] which is possibly due to the steric influence of the chlorine ligands or the *trans* effect of the Cp* ligand. These distances are longer than the sum of the covalent radii of Ta or Nb and P [37]. In the structurally related complexes $[CpNbCl_4(PMePh_2)]$ [Nb-P = 2.7844(9) Å] [17], $[CpNbCl_3(PPh_2CH_2CH_2PPh_2)]$ [Nb-P = 2.787(1) Å] [38] and $[Cp^*TaCl_2(CO)_2(PMe_3)]$ [Ta-P = 2.707(2) Å] [30], in which the phosphine ligand is in a position *trans* to the cyclopentadienyl ligand, lengthening of the M-P bond was also observed.

The M-P-C bond angles are large (ca. 122−131°, Table 2) due to the greater steric demand of the R group compared to two hydrogen atoms at phosphorus.

Reactivity of **1−5**

We expected the complexes **1−5** to be suitable precursors for the preparation of phosphanido and phosphinidene complexes. However, when $[Cp^*TaCl_4(PH_2R)]$ (R = Bu^t, Cy, Ad, Ph, Mes) were treated with DBU an internal redox reaction occurred with formation of $[(DBU)H][Cp^*TaCl_4]$ (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) and the corresponding diphosphane ($P_2H_2R_2$) or decomposition products thereof [39]. For the aryl-substituted phosphine complexes, there was also indication in the ^{31}P NMR spectra for formation of tantalum phosphinidene complexes, which could, however, not be isolated. These phosphinidene-bridged tantalum(IV) complexes, *trans*-$[\{Cp^*TaCl(\mu\text{-}PR)\}_2]$ (R = Cy, Bu^t, Ph, Mes), were however obtained from $[Cp^*TaCl_4]$ and two equivalents of LiPHR in toluene at low temperature [40]. **1b−5b** react with BuLi with formation of the known complex $[Cp^*TaCl_2(\eta^4\text{-}C_4H_6)]$ [41].

Experimental Section

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded at 25°C (unless otherwise indicated) in $CDCl_3$ with an AVANCE DRX 400 spectrometer (Bruker), ^1H NMR (400 MHz): internal standard solvent (chloroform), external standard TMS; ^{13}C NMR (100.61 MHz): external standard TMS, internal standard solvent; ^{31}P NMR (161.97 MHz): external standard 85% H_3PO_4; ^{93}Nb NMR (97.89 MHz): external standard $[PPh_4][NbCl_6]$. The IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer in the range 350−4000 cm^{-1}. MS: Varian MAT 711 (El, 70 eV, source temperature 180°C). The melting points were determined in sealed capillaries under argon and are uncorrected. $[Cp^*MCl_4]$ (M = Nb, Ta) [42] and PH_2R (R = Bu^t [43], Ad [44], Cy [43], Ph [45], Mes [46]) were prepared according to literature procedures.

General procedure for the synthesis of $[Cp^*MCl_4(PH_2R)]$ [M = Nb; R = Bu^t (1a), Ad (2a), Cy (3a), Ph (4a), Mes (5a); M = Ta: R = Bu^t (1b), Ad (2b), Cy (3b), Ph (4b), Mes (5b)]

$[Cp^*MCl_4]$ was suspended in toluene and PH_2R was added by syringe with stirring. The reaction mixture was stirred at room temperature until a clear solution was obtained. Then the solvent was removed to dryness, and the residue extracted with *n*-pentane or *n*-hexane. Cooling to 5°C afforded crystals. The products are air- and moisture-sensitive. The complexes are soluble in CH_2Cl_2 and $CHCl_3$ without decomposition.

1a: 0.5 g (1.4 mmol) $[Cp^*NbCl_4]$ (in 20 mL toluene), 0.15 g (1.7 mmol) PH_2Bu^t (in 5 mL toluene), red crystals from *n*-hexane, yield: 0.6 g (94%). Mp: ca. 222°C (decomp.).

Anal. Calcd for $C_{14}H_{26}Cl_4PNb$ (460.03): C, 36.6; H, 5.7; P, 6.7. Found: C, 36.8; H, 5.9; P, 6.5%.

^1H NMR: δ 1.51 (d, 9H, CMe_3, $^3J_{PH}$ = 13.0 Hz), 2.30 (s, 15H, C_5Me_5), ca. 5.1 (d, 2H, PH_2, $^1J_{PH}$ ≈350 Hz). ^{13}C NMR: δ 14.9 (s, C_5Me_5), 31.1 (s, CMe_3), 35.5 (s, CMe_3), 139.6 (s, C_5Me_5). ^{31}P NMR: δ ca. 20 (br).

2a: 0.4 g (1.1 mmol) $[Cp^*NbCl_4]$ (in 20 mL toluene), 0.25 g (1.5 mmol) PH_2Ad (in 5 mL toluene), yellow crystals from *n*-pentane, yield: 0.5 g (85%). Mp: ca. 212°C (decomp.).

Anal. Calcd for $C_{20}H_{32}Cl_4PNb$ (538.14): C, 44.6; H, 6.0; P, 5.7. Found: C, 45.0; H, 5.5; P, 5.9%.

Table 3 Crystal Data and Structure Refinement for [Cp*$TaCl_4$], [Cp*$NbCl_4(PH_2R)$] (**1a**−**5a**) and [Cp*$TaCl_4(PH_2R)$] (**1b**−**5b**)

	[Cp*$TaCl_4$]	**1a**	**1b**	**2a**
formula	$C_{10}H_{15}Cl_4Ta$	$C_{14}H_{26}Cl_4NbP$	$C_{14}H_{26}Cl_4PTa$	$C_{20}H_{32}Cl_4NbP$
M_r	457.97	460.03	548.07	538.14
temperature	220	220	220	220
crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1/n$	Pnma	Pnma	P $\bar{1}$
a/Å	6.4966(4)	9.4109(1)	9.4240(2)	13.2670(9)
b/Å	28.032(2)	11.6304(2)	11.6673(2)	13.5027(9)
c/Å	8.2269(6)	17.3789(3)	17.4409(3)	15.1653(9)
α/deg				66.391(1)
β/deg	113.164(1)			81.817(1)
γ/deg				70.871(1)
V/Å^3	1377.5(2)	1902.16(5)	1917.67(6)	2351.7(3)
Z	4	4	4	4
ρ_{calcd}/(Mg m^{-3})	2.208	1.606	1.898	1.520
F(000)	864	936	1064	1104
crystal size/mm	0.30 x 0.30 x 0.20	0.50 x 0.30 x 0.30	0.40 x 0.30 x 0.20	0.30 x 0.20 x 0.20
abs. coeff./mm^{-1}	8.722	1.268	6.362	1.038
$2\Theta_{max}$/deg	1.45−28.30	2.11−27.14	2.10−27.11	1.47−28.58
no of rflns collected	8450	9537	9526	14477
no of indep rflns	3136	2076	2086	10414
R_{int}	0.0319	0.0260	0.0405	0.0339
no of params	194	157	157	584
R1 [$I > 2\sigma(I)$]	0.0545	0.0227	0.0241	0.0762
wR2 (all data)	0.1072	0.0571	0.0586	0.1822
$(\Delta/\rho)_{min}$/(e Å^{-3})	1.802	0.274	1.055	1.204
$(\Delta/\rho)_{mac}$/(e Å^{-3})	−2.704	−0.601	−1.454	−0.968

	2b	**3a**	**3b**	**4a**
formula	$C_{20}H_{32}Cl_4PTa$	$C_{16}H_{28}Cl_4NbP$	$C_{16}H_{28}Cl_4PTa$	$C_{16}H_{22}Cl_4NbP$
M_r	626.18	486.06	574.10	480.02
temperature	220	220	220	220
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	P $\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	13.2878(1)	11.6118(7)	11.6575(8)	8.5856(1)
b/Å	13.5127(1)	15.0851(9)	15.113(1)	29.9927(4)
c/Å	15.1832(2)	11.3684(7)	11.3935(8)	8.5864(2)
α/deg	66.301(1)			
β/deg	81.800(1)	92.625(1)	92.569(1)	115.087(1)
γ/deg	70.840(1)			
V/Å^3	2357.83(4)	1989.3(2)	2005.3(2)	2002.46(6)
Z	4	4	4	4
ρ_{calcd}/(Mg m^{-3})	1.764	1.623	1.902	1.592
F(000)	1232	992	1120	968
crystal size/mm	0.50 x 0.40 x 0.40	0.40 x 0.30 x 0.20	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
abs. coeff./mm^{-1}	5.186	1.217	6.089	1.208
$2\Theta_{max}$/deg	1.46−28.00	1.75−26.32	1.75−23.33	1.36−27.53
no of rflns. collected	13682	8635	7727	10702
no of indep. rflns.	9811	3562	2882	4150
R_{int}	0.0565	0.0246	0.0207	0.1448
no of parameters	471	311	311	214
R1 [$I > 2\sigma(I)$]	0.0423	0.0284	0.0214	0.0665
wR2 (all data)	0.1160	0.0719	0.0581	0.1826
$(\Delta/\rho)_{min}$/(e Å^{-3})	1.604	0.335	0.357	1.228
$(\Delta/\rho)_{mac}$/(e Å^{-3})	−2.169	−0.490	−0.990	−1.504

	4b	**5a**	**5b**
formula	$C_{16}H_{22}Cl_4PTa$	$C_{19}H_{28}Cl_4NbP$	$C_{19}H_{48}Cl_4PTa$
M_r	568.06	522.09	610.13
temperature	220	220	220
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	8.5472(1)	8.3005(4)	8.3033(3)
b/Å	30.1372(1)	34.521(2)	34.562(1)
c/Å	8.6366(2)	8.6633(4)	8.6772(3)
β/deg	115.522(1)	116.415(1)	116.541(1)
V/Å^3	2007.60(3)	2223.2(2)	2227.8(1)
Z	4	4	4
ρ_{calcd}/Mg m^{-3}	1.879	1.560	1.819
F(000)	1096	1064	1192
crystal size/mm	0.40 x 0.30 x 0.20	0.30 x 0.30 x 0.20	0.40 x 0.30 x 0.20
abs. coeff./mm^{-1}	6.081	1.095	5.487
$2\Theta_{max}$/deg	1.35−27.56	2.36−28.30	1.18−28.26
no of rflns. collected	10983	13616	13107
no of indep. rflns.	4177	5212	5003
R_{int}	0.1069	0.0497	0.0303
no of parameters	213	338	234
R1 [$I > 2\sigma(I)$]	0.0638	0.0467	0.0297
wR2 (all data)	0.1713	0.0887	0.0667
$(\Delta/\rho)_{min}$/e Å^{-3}	2.817	0.713	1.040
$(\Delta/\rho)_{mac}$/e Å^{-3}	−3.051	−0.626	−0.924

^{1}H NMR: δ 1.75 [br, 6H, CH_2(CH)$_2$], 2.01 [br, 3H, CH(CH$_2$)$_3$], 2.21 [d, 6H, (CH_2)$_3$C, $^4J_{PH}$ = 8 Hz], 2.30 (s, 15H, C$_5Me_5$), ca. 4.9 (d, 2H, PH$_2$, $^1J_{PH}$ ≈340 Hz). ^{13}C NMR: δ 14.3 (s, C$_5Me_5$), 29.3 [s, CH(CH$_2$)$_3$], 29.4 [s, CH$_2$(CH)$_2$], 37.1 [s, (CH$_2$)$_3$C], 41.7 (s, C-PH$_2$), 138.9 (s, C_5Me$_5$). ^{31}P NMR: δ ca. 16 (br).

3a: 0.9 g (2.4 mmol) [Cp*NbCl$_4$] (in 30 mL toluene), 0.35 g (2.9 mmol) PH$_2$Cy, red crystals from *n*-pentane, yield: 1.1 g (95%). Mp: ca. 212°C (decomp.).

Anal. Calcd for $C_{16}H_{28}Cl_4PNb$ (486.06): C, 39.5; H, 5.8; P, 6.4. Found: C, 40.2; H, 5.7; P, 6.2%.

^{1}H NMR: δ 0.86 (m, 2H, H4 in Cy), 1.28 (m, 4H, H3/H5 in Cy), 1.72 (m, 4H, H2/H6 in Cy), 2.22 (m, 1H, H1 in Cy), 2.30 (s, 15H, C$_5Me_5$), ca. 5.1 (d, 2H, PH$_2$, $^1J_{PH}$ ≈350 Hz). ^{13}C NMR: δ 14.2 (s, C$_5Me_5$), 26.5 (s, C4 in Cy), 27.5 (d, C3/C5 in Cy, $^3J_{PC}$ = 8.6 Hz), 32.2 (br, C2/C6 in Cy), 33.8 (br, C1 in Cy), 138.7 (s, C_5Me$_5$). ^{31}P NMR: δ ca. 5 (br).

4a: 0.4 g (1.1 mmol) [Cp*NbCl$_4$] (in 20 mL toluene), 0.12 g (1.3 mmol) PH$_2$Ph, yellow crystals from *n*-hexane, yield: 0.48 g (96%). Mp: ca. 212°C (decomp.).

Anal. Calcd for $C_{16}H_{22}Cl_4PNb$ (480.02): C, 40.1; H, 4.6; P, 6.5. Found: C, 41.6; H, 4.8; P, 6.8%.

^{1}H NMR: δ 2.30 (s, 15H, C$_5Me_5$), ca. 6.1 (d, 2H, PH$_2$, $^1J_{PH}$ ≈370 Hz), 7.44 (br, 3H, *o*-H and *p*-H in Ph), 7.70 (br, 2H, *m*-H in Ph). ^{13}C NMR: δ 14.2 (s, C$_5Me_5$), 127.0 (s, *m*-C in Ph), 129.8 (s, *p*-C in Ph), 131.3 (s, *o*-C in Ph), 134.4 (s, *ipso*-C in Ph), 138.7 (s, C_5Me$_5$). ^{31}P NMR: δ ca. −12 (br).

5a: 0.4 g (1.1 mmol) [Cp*NbCl$_4$] (in 20 mL toluene), 0.16 g (1.2 mmol) PH$_2$Mes, yellow crystals from *n*-hexane, yield: 0.52 g (94%). Mp: ca. 229°C (decomp.).

Anal. Calcd for $C_{19}H_{28}Cl_4PNb$ (522.09): C, 43.7; H, 5.4; P, 5.9. Found: C, 42.6; H, 4.8; P, 6.6%.

^{1}H NMR: δ 2.19 (s, 3H, *p*-Me in Mes), 2.31 (s, 15H, C$_5Me_5$), 2.36 (s, 6H, *o*-Me in Mes), ca. 6.1 (d, 2H, PH$_2$, $^1J_{PH}$ ≈360 Hz), 6.92 (s, 2H, *m*-H in Mes). ^{13}C NMR: δ 14.5 (s, C$_5Me_5$), 22.0 (s, *p*-Me in Mes), 24.7 (s, *o*-Me in Mes), 126.0 (s, *m*-C in Mes), 128.9 (s, *p*-C in Mes), 129.7 (s, *o*-C in Mes), 138.6 (s, C_5Me$_5$), 143.0 (s, *ipso*-C in Mes). ^{31}P NMR: δ ca. −40 (br).

1b: 1.5 g (3.3 mmol) [Cp*TaCl$_4$] (in 30 mL toluene), 0.32 g (3.5 mmol) PH$_2$Bu^t (in 5 mL toluene), yellow crystals from *n*-hexane, yield: 1.74 g (96%). Mp: ca. 245°C (decomp.).

Anal. Calcd for $C_{14}H_{26}Cl_4PTa$ (548.07): C, 30.7; H, 4.8; P, 5.6. Found: C, 30.8; H, 4.9; P, 5.3%.

^{1}H NMR: δ 1.48 (d, 9H, CMe$_3$, $^3J_{PH}$ = 12.7 Hz), 2.50 (s, 15H, C$_5Me_5$), ca. 4.9 (d, 2H, PH$_2$, $^1J_{PH}$ ≈300 Hz). ^{13}C NMR: δ 13.4 (s, C$_5Me_5$), 30.7 (s, CMe_3), 33.2 (s, CMe$_3$), 133.8 (s, C_5Me$_5$). ^{31}P NMR: δ ca. 19 (br).

2b: 0.6 g (1.3 mmol) [Cp*TaCl$_4$] (in 20 mL toluene), 0.31 g (1.9 mmol) PH$_2$Ad (in 5 mL toluene), yellow crystals from *n*-pentane, yield: 0.7 g (87%). Mp: ca. 237°C (decomp.).

Anal. Calcd for $C_{20}H_{32}Cl_4PTa$ (626.18): C, 38.4; H, 5.2; P, 4.9. Found: C, 38.8; H, 5.4; P, 4.5%.

^{1}H NMR: δ 1.75 [br, 6H, CH_2(CH)$_2$], 2.02 [br, 3H, CH(CH$_2$)$_3$], 2.20 [br, 6H, (CH_2)$_3$C], 2.50 (s, 15H, C$_5Me_5$), ca. 4.8 (d, 2H, PH$_2$, $^1J_{PH}$ ≈320 Hz). ^{13}C NMR: δ 13.4 (s, C$_5Me_5$), 29.2 [s, CH(CH$_2$)$_3$], 29.3 [s, CH$_2$(CH)$_2$], 37.1 [s, (CH$_2$)$_3$C], 41.9 (s, C-PH$_2$), 133.7 (s, C_5Me$_5$). ^{31}P NMR: δ ca. 15 (br).

3b: 0.7 g (1.5 mmol) [Cp*TaCl$_4$] (in 20 mL toluene), 0.2 g (1.7 mmol) PH$_2$Cy, yellow crystals from *n*-pentane, yield: 0.85 g (95%). Mp: ca. 230°C (decomp.).

Anal. Calcd for $C_{16}H_{28}Cl_4PTa$ (575.10): C, 33.4; H, 4.9; P, 5.4. Found: C, 32.7; H, 4.9; P, 5.8%.

^{1}H NMR: δ 1.26 (m, 2H, H4 in Cy), 1.38 (m, 4H, H3/H5 in Cy), 1.77 (m, 4H, H2/H6 in Cy), 2.20 (m, 1H, H1 in Cy), 2.49 (s, 15H, C$_5Me_5$), ca. 5.0 (d, 2H, PH$_2$, $^1J_{PH}$ ≈360 Hz). ^{13}C NMR: δ 13.3 (s, C$_5Me_5$), 23.3 (s, C4 in Cy), 27.6 (d, C3/C5 in Cy, $^3J_{PC}$ = 8.5 Hz), 31.3 (d, C2/C6 in Cy, $^2J_{PC}$ = 15.4 Hz), 33.8 (d, br, C1 in Cy, $^1J_{PC}$ = 7 Hz), 133.5 (s, C_5Me$_5$). ^{31}P NMR: δ ca. 7 (br).

4b: 0.5 g (1.1 mmol) [Cp*TaCl$_4$] (in 20 mL toluene), 0.14 g (1.5 mmol) PH$_2$Ph (in 5 mL toluene), yellow crystals from *n*-hexane, yield: 0.57 g (95%). Mp: ca. 217°C (decomp.).

Anal. Calcd for $C_{16}H_{22}Cl_4PTa$ (568.06): C, 33.8; H, 3.9; P, 5.5. Found: C, 35.2; H, 4.2; P, 5.5%.

^{1}H NMR: δ 2.50 (s, 15H, C$_5Me_5$), ca. 5.9 (d, 2H, PH$_2$, $^1J_{PH}$ ≈360 Hz), 7.42 (br, 3H, *o*-H and *p*-H in Ph), 7.69 (br, 2H, *m*-H in Ph). ^{13}C NMR: δ 14.1 (s, C$_5Me_5$), 126.7 (s, *m*-C in Ph), 129.8 (s, *p*-C in Ph), 131.9 (s, *o*-C in Ph), 134.3 (s, C_5Me$_5$), 135.3 (s, *ipso*-C in Ph). ^{31}P NMR: δ ca. −12 (br).

5b: 0.6 g (1.3 mmol) [Cp*TaCl$_4$] (in 20 mL toluene), 0.19 g (1.4 mmol) PH$_2$Mes, yellow crystals from *n*-hexane, yield: 0.71 g (92%). Mp: ca. 232°C (decomp.).

Anal. Calcd for $C_{19}H_{28}Cl_4PTa$ (610.13): C, 37.4; H, 4.6; P, 5.1. Found: C, 38.6; H, 4.1; P, 6.0%.

^{1}H NMR: δ 2.29 (s, 3H, *p*-Me in Mes), 2.51 (s, 15H, C$_5Me_5$), 2.58 (s, 6H, *o*-Me in Mes), ca. 6.1 (d, 2H, PH$_2$, $^1J_{PH}$ ≈345 Hz), 6.93 (s, 2H, *m*-H in Mes). ^{13}C NMR: δ 14.2 (s, C$_5Me_5$), 22.5 (s, *p*-Me in Mes), 25.2 (s, *o*-Me in Mes), 123.3 (s, *m*-C in Mes), 130.4 (s, *p*-C in Mes), 134.2 (s, C_5Me$_5$), 141.5 (s, *o*-C in Mes), 143.8 (s, *ipso*-C in Mes). ^{31}P NMR: δ ca. −40 (br).

X-ray Crystal Structure Determination of [Cp*TaCl$_4$] and 1−5: Data [λ(Mo$_{K\alpha}$) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for refinement (SAINT) of the unit cell parameters. Empirical absorption correction with SADABS [47]. The structures were solved by direct methods (SHELXTL PLUS) [48]. Nb, Ta, Cl, P and C atoms were refined anisotropically; H atoms were located by difference maps and refined isotropically for **1**−**3** and **5**. Due to disorder of the phenyl ring in **4**, no H atoms were refined for the phosphine ligand. Table 3 lists crystallographic details. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre ([Cp*TaCl$_4$]: CCDC 185935, **1a**: CCDC 185927, **2a**: CCDC 185937, **3a**: CCDC 185930, **4a**: CCDC 185931, **5a**: CCDC 185934, **1b**: CCDC 185932, **2b**: CCDC 185928, **3b**: CCDC 185929, **4b**: CCDC 185933, **5b**: CCDC 185936). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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