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## Methylation of (pentamethylcyclopentadienyl)trichloro- (diphenyldimethylenephosphoranyl-*C,C'*)tantalum(V). Crystal structures of $[\text{TaCp}^*\text{Cl}_3\{(\text{CH}_2)_2\text{PPh}_2\}]$ and $[\text{TaCp}^*\text{Me}_2\{(\text{CH})(\text{CH}_2)\text{PPh}_2\}]$

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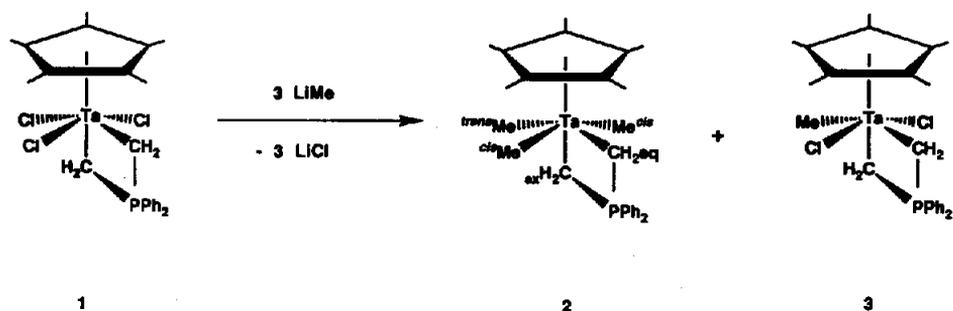
### Abstract

The X-ray diffraction study of  $[\text{TaCp}^*\text{Cl}_3\{(\text{CH}_2)_2\text{PPh}_2\}]$  confirms its monomeric structure, previously proposed on the basis of its NMR behaviour. Alkylation of this compound leads to the isolation of its trimethyl derivative, along with a residue which contains minor amounts of the monomethyl complex. The pyrolysis of the trimethyl complex affords  $[\text{TaCp}^*\text{Me}_2\{(\text{CH})(\text{CH}_2)\text{PPh}_2\}]$  whose crystal structure has been determined by X-ray diffraction methods.

### Results and discussion

We reported previously the isolation of different types of pseudooctahedral cyclopentadienyl tantalum complexes containing neutral and anionic phosphorous ylide ligands.  $[\text{TaCp}^*\text{Cl}_4]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) reacts with  $\text{CH}_2=\text{PRR}'_2$  to give adducts  $[\text{TaCp}^*\text{Cl}_4(\text{CH}_2=\text{PRR}'_2)]$  [1] and with  $\text{Li}(\text{CH}_2)_2\text{PRR}'$  leading to  $[\text{TaCp}^*\text{Cl}_3(\text{CH}_2)_2\text{PRR}']$  [2]. Phosphinomethyl and phosphinothiomethyl complexes  $[\text{TaCp}^*\text{Cl}_3(\text{CH}_2)\text{P}(\text{X})\text{Ph}_2]$  ( $\text{X} = \text{O}$  or  $\text{S}$ ) were also obtained in reactions with the corresponding lithium salts.  $^1\text{H}$  and  $^{31}\text{P}$  NMR characterization of complexes with bidentate anionic ylide ligands showed that derivatives with  $\text{R} = \text{R}' = \text{Me}$  and  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$  exist in benzene solution as an equilibrium mixture of the monomeric complex with chelate ylide and the dimeric species with bridging

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Scheme 1.

bidentate ylide ligand. However, the complex with more sterically demanding substituents  $R = R' = \text{Ph}$  exists only as monomeric species [3].

We report here the chemical behaviour of  $[\text{TaCp}^*\text{Cl}_3\{(\text{CH}_2)_2\text{PPh}_2\}]$  (**1**) and the confirmation of its monomeric nature by an X-ray diffraction study.

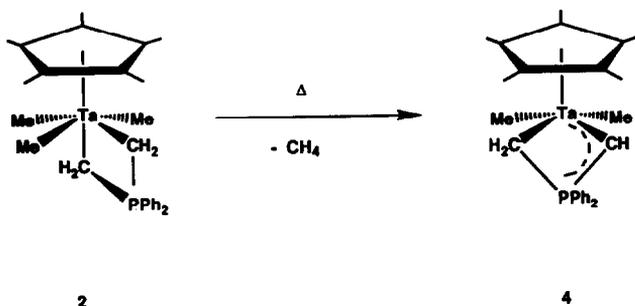
As expected, complex **1** does not react with CO or RNC ( $R = ^1\text{Bu}$  or 2,5- $\text{Me}_2\text{C}_6\text{H}_3$ ) because the central metal atom has no vacant coordination site to accommodate the ligand. Neither is there a deprotonation reaction with bases such as  $\text{CH}_2=\text{PMe}_2\text{Ph}$  or  $\text{NaNH}_2$ . The anionic ylide ligand is transformed into the phosphonium salt by protonation with  $\text{HBF}_4$ . It does not isomerize on heating in benzene- $d_6$  up to  $200^\circ\text{C}$ , and decomposition to unidentified products takes place at higher temperature.

Alkylation of **1** with LiMe in the molar ratio 1:3 leads to a mixture of the methyl derivatives  $[\text{TaCp}^*\text{Cl}_{3-x}\text{Me}_x\{(\text{CH}_2)_2\text{PPh}_2\}]$  [ $x = 3$  (**2**), 1 (**3**)] from which the main component, the trimethyl complex **2** (75%), can be separated by extraction with cold n-hexane from a residue which is essentially the monomethyl complex **3**.

The air-sensitive complex **2**, a microcrystalline yellow-green solid, was analytically and spectroscopically characterized. Its  $^1\text{H}$  spectrum shows one singlet ( $\delta$  1.79) due to the ring methyl protons, two doublets ( $\delta$  1.90,  $^2J(\text{P-H}) = 7.8$  Hz and  $\delta$  -0.91,  $^2J(\text{P-H}) = 11.2$  Hz), respectively, due to the equatorial and axial methylene protons of the ylide ligand, one singlet ( $\delta$  -0.17) for the two methyl groups mutually *trans* and one doublet ( $\delta$  0.07,  $^4J(\text{P-H}) = 2.69$  Hz) for the methyl group *trans* to the equatorial  $\text{CH}_2$  ylide substituent. Two multiplets ( $\delta$  7.78 and  $\delta$  6.99) are also observed for the phenyl groups of the ylide ligand.

The same structure can be deduced from the  $^{13}\text{C}$  NMR spectrum which shows the following pattern. Doublets are observed for the phenyl carbon atoms with an average  $\delta$  C 132.9 and  $J(\text{P-C})$  decreasing in the order  $\text{C}^1 > \text{C}^{2,6} \approx \text{C}^{3,5} > \text{C}^4$ . Two singlets are observed for the ring carbon atoms at  $\delta$  117.5 and for the methyl ring at  $\delta$  11.2. Two doublets are observed for the equatorial ( $\delta$  11.8,  $^1J(\text{P-C}) = 42.4$  Hz) and the axial ( $\delta$  -11.04,  $^1J(\text{P-C}) = 42.4$  Hz) methylene ylide groups. The resonance due to the methyl-Ta carbon *trans* to the ylide ligand appears as a doublet at  $\delta$  59.2 ( $^3J(\text{P-C}) = 20.5$  Hz) whereas the *cis* methyl group gives one singlet at  $\delta$  44.3.

The methyl complex **3** could not be isolated but its presence in solution can be inferred from the  $^1\text{H}$  NMR spectrum which shows two signals, one doublet at  $\delta$



Scheme 2.

0.15 ( ${}^4J(\text{P-H}) = 2.93$  Hz) being due to the methyl-Ta group and the other at  $\delta$  1.83 corresponding to the methyl ring protons.

The pyrolysis of complex **2** in toluene at 70–80°C takes place with evolution of methane and leads to the formation of **4** according to Scheme 2.

Complex **4** was characterized by IR,  ${}^1\text{H}$ ,  ${}^{13}\text{C}$  and  ${}^{31}\text{P}$  spectroscopy and its crystal structure was determined by X-ray diffraction methods. The methylidyne proton of the phosphoranyl methyl group shows an IR absorption at  $3733\text{ cm}^{-1}$  and a low field doublet at  $\delta$  7.27 ( ${}^2J(\text{P-H}) = 5.61$  Hz) in the  ${}^1\text{H}$  NMR spectrum. The methylidyne carbon gives a doublet at  $\delta$  168.03 ( ${}^1J(\text{P-C}) = 33.14$  Hz).

*Description of the crystal structures of  $[\text{TaCp}^*\text{Cl}_3\{(\text{CH}_2)_2\text{PPh}_2\}]$  (**1**) and  $[\text{TaCp}^*\text{Me}_2\{(\text{CH})(\text{CH}_2)\text{PPh}_2\}]$  (**4**)*

A view of the complex  $[\text{TaCp}^*\text{Cl}_3\{(\text{CH}_2)_2\text{PPh}_2\}]$  (**1**) is shown in Fig. 1 together with the atom numbering scheme. Selected bond distances and angles are given in Table 1. The pentamethylcyclopentadienyl ring is bound to the Ta atom in a nearly symmetrical  $\eta^5$ -fashion (with Ta–C distances ranging from 2.465(15) to 2.508(14) Å), with the distance between the metal and the centroid of the ring, Ta–CE, of 2.185(13) Å. The  $(\text{CH}_2)_2\text{PPh}_2$  phosphoylide anion acts as a chelating ligand through C(11) [Ta–C(11) = 2.278(14) Å] and C(12) [Ta–C(12) = 2.347(12) Å] forming an almost planar tetraatomic ring with a C(11)–P–C(12) angle of  $100.6(6)^\circ$ . The coordination around the Ta atom is completed by three Cl atoms [Ta–Cl(1) = 2.408(4), Ta–Cl(2) = 2.431(4) and Ta–Cl(3) = 2.416(5) Å]. The complex is pseudooctahedral if the centroid of the cyclopentadienyl ring is considered as occupying a coordination site, even if the Ta atom is displaced by 0.558(1) Å from the mean equatorial plane passing through the three Cl atoms and the C(11) atom.

A comparison of the structure of **1** with that of  $[\text{TaCp}^*\text{Cl}_4(\text{CH}_2=\text{PMePh}_2)]$ , in which the neutral  $(\text{CH}_2=\text{PMePh}_2)$  ylide acts as a monodentate ligand in *trans* position with respect to the Cp\* centroid, shows that the Ta–C distances from the Cp\* ring are slightly longer, average value 2.557 Å, as well as the Ta–CE distance, 2.252 Å and the Ta–Cl bonds, average value 2.446 Å for three Ta–Cl bonds [1]. The Ta–C(ylide) bond length, 2.35(3) Å, is comparable to that found in **1** involving the C(12) atom in *trans* position to the Cp\* centroid, whereas the Ta–C(11)–P and Ta–C(12)–P angles in **1**,  $94.3(6)$  and  $92.9(5)^\circ$ , are much narrower because of the chelation than in  $[\text{TaCp}^*\text{Cl}_4(\text{CH}_2=\text{PMePh}_2)]$ , where the Ta–C(ylide)–P angle was of  $125(2)^\circ$ . The P–C bond lengths in **1** involving the ylide ligand, 1.754(14) and



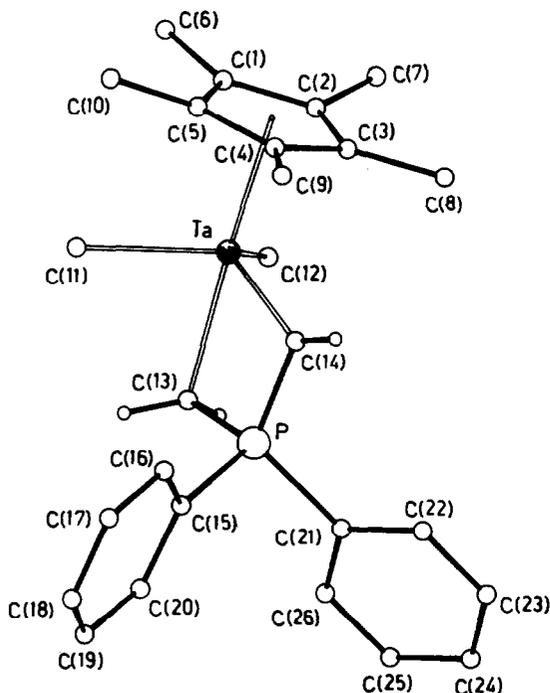


Fig. 2. Perspective view of the molecular structure of the complex  $[\text{TaCp}^*\text{Me}_2\{(\text{CH})(\text{CH}_2)\text{PPh}_2\}]$  (4) with the atomic numbering scheme.

1.788(13) Å, are only slightly shorter than those involving the phenyl groups, 1.805(12) and 1.815(12) Å.

A view of the complex  $[\text{TaCp}^*\text{Me}_2\{(\text{CH})(\text{CH}_2)\text{PPh}_2\}]$  (4) is shown in Fig. 2, together with the atom numbering scheme. Selected bond distances and angles are given in Table 2. The pentamethylcyclopentadienyl ring is bound to the Ta atom in a nearly symmetrical  $\eta^5$ -fashion (with Ta–C distances ranging from 2.448(12) to 2.495(15) Å), with the distance between the metal and the centroid of the ring, Ta–CE, of 2.165(14) Å, only slightly shorter than the corresponding distances found in 1. The  $(\text{CH})(\text{CH}_2)\text{PPh}_2$  dianionic phosphoylide acts as a chelating ligand through the C(13) [Ta–C(13) = 2.310(15) Å] and C(14) [Ta–C(14) = 1.979(15) Å] forming an almost planar tetraatomic ring with a bite C(13)–P–C(14) angle of 96.1(7)°. In the structure of  $[(\text{Cp})_2\text{U}\{(\text{CH})(\text{CH}_2)\text{PPh}_2\}_2\text{U}(\text{Cp})_2]$  the dianionic phosphoylide is different, as it is bonded to both U atoms, acting as chelating and bridging ligand [4]. The coordination around the Ta atom is completed by two C atoms from methyl groups [Ta–C(11) = 2.230(16), Ta–C(12) = 2.198(17) Å]. The complex is pseudotrigonal bipyramidal if the centroid of the cyclopentadienyl ring is considered as occupying a coordination site, even if the Ta atom is displaced by 0.534(1) Å from the equatorial plane passing through the three C(11), C(12) and C(14) atoms. If the axial Ta–C(13) bond is longer than the equatorial Ta–C(11) and Ta–C(12) bonds, the Ta–C(14) bond is much shorter than all other Ta–C bonds. The Ta–C(14) bond length is in the range of those found in complexes with tantalum–alkylidene double bonds, for example, in  $[\text{Ta}(\text{CHCM}_3)(\text{PMe}_3)\text{Cl}_3]_2$ ,

Table 2

Selected bond distances (Å) and angles (°) with esd's in parentheses for complex 4

<i>Distances</i>			
Ta-CE <sup>a</sup>	2.165(14)	C(2)-C(3)	1.37(2)
Ta-C(11)	2.230(16)	C(3)-C(4)	1.43(2)
Ta-C(12)	2.198(17)	C(4)-C(5)	1.41(2)
Ta-C(13)	2.310(15)	C(1)-C(5)	1.38(2)
Ta-C(14)	1.979(15)	C(1)-C(6)	1.51(3)
P-C(13)	1.734(17)	C(2)-C(7)	1.54(2)
P-C(14)	1.666(14)	C(3)-C(8)	1.53(2)
P-C(15)	1.795(13)	C(4)-C(9)	1.51(2)
P-C(21)	1.826(15)	C(5)-C(10)	1.52(2)
C(1)-C(2)	1.40(2)		
<i>Angles</i>			
CE-Ta-C(11)	103.5(6)	C(12)-Ta-C(13)	76.4(6)
CE-Ta-C(12)	106.7(5)	C(12)-Ta-C(14)	114.8(7)
CE-Ta-C(13)	175.3(6)	C(13)-Ta-C(14)	71.8(6)
CE-Ta-C(14)	103.5(5)	Ta-C(13)-P	88.8(6)
C(11)-Ta-C(12)	110.5(7)	Ta-C(14)-P	103.0(8)
C(11)-Ta-C(13)	78.5(6)	C(13)-P-C(14)	96.1(7)
C(11)-Ta-C(14)	116.5(6)		

<sup>a</sup> CE is the centroid of the Cp\* ring.

determined by a low-temperature neutron diffraction study, the Ta-C bond length is 1.898(2) Å [5]. Considering that the P-C(14) bond, 1.666(14), is shorter than the P-C(13), 1.734(17) Å, delocalization of the double bond can be envisaged with the Ta-C(14)-P system.

## Experimental

All reactions and manipulations of air- and moisture-sensitive materials were performed under an argon atmosphere employing standard Schlenk techniques or in a Vacuum Atmospheres glovebox equipped with a HE-63-P Dri Train. Solvents were dried, freshly distilled and degassed prior to use. [TaCp\*Cl<sub>3</sub>{(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}] was prepared and isolated as described [2] and LiMe (Fluka) used without further purification.

Infrared spectra were recorded as Nujol mulls (4000–200 cm<sup>-1</sup>) between polyethylene films on a Perkin-Elmer 583 spectrophotometer. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were measured on a Varian FT-80A and Varian Unix 300 MHz instruments. Chemical shifts are reported in δ units (positive chemical shifts to a higher frequency) relative to tetramethylsilane (TMS) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). C and H analyses were carried out on a Perkin-Elmer 240B microanalyzer.

### Preparation of [TaCp\*Cl<sub>3-x</sub>Me<sub>x</sub>{(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}] (x = 3 (2), 1 (3))

LiMe (1.2 M solution) in ether (4.73 ml, 7.55 mmol) was slowly added to 1 (1.50 g, 2.36 mmol) in toluene (75 ml) at -78°C. The resultant suspension was allowed to warm up to ambient and stirred for ca. 1 h. Then, it was filtered, concentrated to dryness to give a yellow-green solid mixture of 2 and 3 in ca. 5:1 molar ratio,

respectively. **2** can be separated by extraction with cold *n*-hexane (4 × 15 ml). The clear yellow-green solution obtained was concentrated to *ca.* 20 ml, cooled to -40°C overnight to give yellow-green crystals of **2**. Yield 75% (1.01 g).

Characterization data of complex **2**: Anal. Found: C, 56.37; H, 5.78. C<sub>27</sub>H<sub>38</sub>PTa calc.: C, 56.45; H, 5.39%. IR (Nujol mull):  $\nu$  2325(w), 1305(m), 1150(m), 1108(m), 1023(s), 967(m), 875(m), 809(m), 740(s), 693(s), 521(s), 483(m), 456(m) and 349(m) cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\delta$  ppm, in C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.78(m, 4H), 6.99(m, 6H), C<sub>6</sub>H<sub>5</sub>;  $\delta$  1.90(d, 2H, <sup>2</sup>J(P-H) = 7.8 Hz), Ta-CH<sub>2</sub>(ec.);  $\delta$  1.79(s, 15H), C<sub>5</sub>Me<sub>5</sub>;  $\delta$  0.072(d, 3H, <sup>4</sup>J(P-H) = 2.69 Hz), Ta-Me(trans);  $\delta$  -0.17(s, 6H), Ta-Me(cis);  $\delta$  -0.91(d, 2H, <sup>2</sup>J(P-H) = 11.23 Hz), Ta-CH<sub>2</sub>(ax.) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$  ppm, in C<sub>6</sub>D<sub>6</sub>): C<sup>1</sup>,  $\delta$  140.76(d, <sup>1</sup>J(P-C) = 50.53 Hz), C<sup>2,6</sup>,  $\delta$  129.65(d, <sup>2</sup>J(P-C) = 10.25 Hz), C<sup>3,5</sup>,  $\delta$  130.90(d, <sup>3</sup>J(P-C) = 10.25 Hz), C<sup>4</sup>,  $\delta$  130.34(d, <sup>4</sup>J(P-C) = 2.19 Hz), C<sub>6</sub>H<sub>5</sub>;  $\delta$  117.48s, C<sub>5</sub>Me<sub>5</sub>;  $\delta$  59.18(d, <sup>3</sup>J(P-C) = 20.5 Hz), Ta-Me(trans);  $\delta$  44.37s, Ta-Me(cis);  $\delta$  11.80(d, <sup>1</sup>J(P-C) = 42.47 Hz), Ta-CH<sub>2</sub>(ec.);  $\delta$  11.17s, C<sub>5</sub>Me<sub>5</sub>;  $\delta$  -11.04(d, <sup>1</sup>J(P-C) = 42.47 Hz), Ta-CH<sub>2</sub>(ax.) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR ( $\delta$  ppm, in C<sub>6</sub>D<sub>6</sub>):  $\delta$  31.63s, (CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> ppm.

#### Preparation of [TaCp\*Me<sub>2</sub>{(CH)(CH<sub>2</sub>)PPh<sub>2</sub>}] (**4**)

A solution of **2** (1 g, 1.74 mmol) in toluene (40 ml) was heated at 70–80°C during 2 days. The solution was evaporated to dryness and the residue extracted with *n*-hexane (3 × 15 ml). The resulting solution was concentrated to *ca.* 20 ml and cooled at -40° for 12 h to give yellow crystals of **4**. Yield 75% (0.73 g). Anal. Found: C, 55.72; H, 6.09. C<sub>26</sub>H<sub>34</sub>PTa calc.: C, 55.91; H, 6.14%. IR (Nujol mull):  $\nu$  3782(w), 3733(vs), 1303(w), 1154(w), 1102(m), 1024(m), 998(s), 935(vs), 834(m), 743(s), 697(vs), 605(m), 514(m), 484(m), 460(m), 425(w) and 347(w) cm<sup>-1</sup>. <sup>1</sup>H NMR ( $\delta$  ppm, in C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.63(m, 4H), 6.54(m, 6H), C<sub>6</sub>H<sub>5</sub>;  $\delta$  7.27(d, 1H, <sup>2</sup>J(P-H) = 5.61 Hz), Ta-CH;  $\delta$ , 2.22(d, 2H, <sup>2</sup>J(P-H) = 14.65 Hz), Ta-CH<sub>2</sub>;  $\delta$  1.83(s, 15H), C<sub>5</sub>Me<sub>5</sub>;  $\delta$  0.16(d, 6H, <sup>4</sup>J(P-H) = 2.44 Hz), Ta-Me ppm. <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$  ppm, in C<sub>6</sub>D<sub>6</sub>):  $\delta$  168.03(d, <sup>1</sup>J(P-C) = 33.14 Hz), Ta-CH; C<sup>1</sup>,  $\delta$  137.51(d, <sup>1</sup>J(P-C) = 55.85 Hz), C<sup>3,5</sup>  $\delta$  130.88(d, <sup>3</sup>J(P-C) = 10.35 Hz), C<sup>4</sup>,  $\delta$  129.79(d, <sup>4</sup>J(P-C) = 2.76 Hz), C<sub>6</sub>H<sub>5</sub>;  $\delta$  113.45s, C<sub>5</sub>Me<sub>5</sub>;  $\delta$  51.23(d, <sup>3</sup>J(P-C) = 2.76 Hz) Ta-Me;  $\delta$  30.98(d, <sup>1</sup>J(P-C) = 28.3 Hz) Ta-CH<sub>2</sub>;  $\delta$  11.22s, C<sub>5</sub>Me<sub>5</sub> ppm. <sup>31</sup>P{<sup>1</sup>H} NMR ( $\delta$  ppm, in C<sub>6</sub>D<sub>6</sub>):  $\delta$  -6.89s, (CH)(CH<sub>2</sub>)PPh<sub>2</sub> ppm.

#### Determination of the crystal structures of [TaCp\*Cl<sub>3</sub>{(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}] (**1**) and [TaCp\*Me<sub>2</sub>{(CH)(CH<sub>2</sub>)PPh<sub>2</sub>}] (**4**)

A crystal of approximate dimensions 0.12 × 0.20 × 0.45 (**1**) and 0.20 × 0.25 × 0.30 mm (**4**) was selected for the X-ray analysis.

*Crystal data* (**1**): C<sub>24</sub>H<sub>29</sub>Cl<sub>3</sub>PTa, *M* = 635.77, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 11.831(4), *b* = 12.508(5), *c* = 16.921(8) Å,  $\beta$  = 102.41(2)°, *V* = 2446(2) Å<sup>3</sup> (by least-squares refinement from the  $\theta$  values of 30 accurately measured reflections,  $\bar{\lambda}$  = 1.54184 Å), *Z* = 4, *D*<sub>c</sub> = 1.727 g cm<sup>-3</sup>, *F*(000) = 1248,  $\mu$ (Cu-K $\alpha$ ) = 120.76 cm<sup>-1</sup>.

*Crystal data* (**4**): C<sub>26</sub>H<sub>34</sub>PTa, *M* = 558.48, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 11.876(5), *b* = 12.874(4), *c* = 15.983(9) Å,  $\beta$  = 103.65(2)°, *V* = 2375(2) Å<sup>3</sup> (by least-squares refinement from the  $\theta$  values of 30 accurately measured reflections,  $\bar{\lambda}$  = 0.71073 Å), *Z* = 4, *D*<sub>c</sub> = 1.562 g cm<sup>-3</sup>, *F*(000) = 1112,  $\mu$ (Mo-K $\alpha$ ) = 46.50 cm<sup>-1</sup>.

Data for both compounds were collected at room temperature (22°C) on a Siemens AED diffractometer, using nickel-filtered Cu- $K_{\alpha}$  (1) and niobium-filtered Mo- $K_{\alpha}$  (4) radiation and the  $\theta/2\theta$  scan type. All reflections with  $\theta$  in the range 3–70° (1) and 3–24° (4) were measured; of 4637 (1) and 3754 (4) independent reflections, 2969 (1) and 2163 (4), having  $I \geq 2\sigma(I)$ , were considered observed and used in the analyses. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles were analyzed following Lehmann and Larsen [6]. Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.4547 and 0.7021 (1) and 1.6347 and 0.6300 (4) respectively [7]). Only the observed reflections were used in the structure solution and refinement.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares with anisotropic thermal parameters in the last cycles for all the non hydrogen atoms. The four hydrogen atoms at C(11) and C(12) (1) and the three at C(13) and C(14) (4) were clearly located in the final  $\Delta F$  map and refined isotropically, the remaining ones were placed at their calculated positions

Table 3

Fractional atomic coordinates ( $\times 10^4$ ) with esd's in parentheses for the non-hydrogen atoms of complex 1

Atom	x	y	z
Ta	187(1)	1516(1)	2270(1)
Cl(1)	2000(3)	593(4)	2705(2)
Cl(2)	-1328(3)	2328(4)	1247(2)
Cl(3)	-860(4)	-154(4)	2052(3)
P	1376(2)	2088(3)	931(2)
C(1)	-455(11)	2982(13)	3044(7)
C(2)	714(11)	2738(10)	3454(7)
C(3)	684(10)	1720(10)	3776(7)
C(4)	-416(11)	1331(11)	3597(7)
C(5)	-1166(10)	2105(14)	3126(6)
C(6)	-862(20)	4098(17)	2755(12)
C(7)	1712(15)	3515(14)	3636(9)
C(8)	1676(12)	1195(16)	4391(7)
C(9)	-887(14)	311(14)	3907(9)
C(10)	-2455(11)	2053(20)	2878(11)
C(11)	1282(11)	2793(11)	1833(7)
C(12)	602(10)	923(11)	1048(6)
C(13)	2848(10)	1896(11)	825(6)
C(14)	3054(12)	1248(14)	202(8)
C(15)	4171(15)	1154(18)	78(11)
C(16)	5066(15)	1719(17)	542(13)
C(17)	4879(13)	2309(18)	1141(13)
C(18)	3778(11)	2456(13)	1303(8)
C(19)	769(10)	2831(11)	17(7)
C(20)	1016(14)	3857(14)	-54(9)
C(21)	622(15)	4408(14)	-790(11)
C(22)	-6(15)	3876(21)	-1430(12)
C(23)	-239(13)	2825(20)	-1356(9)
C(24)	116(11)	2277(14)	-641(7)

Table 4

Fractional atomic coordinates ( $\times 10^4$ ) with esd's in parentheses for the non-hydrogen atoms of complex 4

Atom	x	y	z
Ta	4735(1)	1738(1)	2257(1)
P	5775(3)	2118(3)	845(2)
C(1)	3914(11)	1857(13)	3543(8)
C(2)	5122(10)	1935(11)	3823(8)
C(3)	5488(11)	2842(10)	3523(8)
C(4)	4490(12)	3370(12)	3036(8)
C(5)	3536(11)	2722(12)	3048(8)
C(6)	3215(17)	969(16)	3768(10)
C(7)	5882(16)	1245(13)	4519(9)
C(8)	6710(12)	3300(13)	3770(9)
C(9)	4458(16)	4455(13)	2669(11)
C(10)	2285(13)	3062(16)	2722(10)
C(11)	2925(15)	1498(16)	1492(11)
C(12)	5554(17)	241(13)	2695(9)
C(13)	5047(13)	1000(13)	1014(9)
C(14)	5708(12)	2698(12)	1763(8)
C(15)	5040(12)	2720(12)	-147(8)
C(16)	4488(14)	3674(13)	-137(11)
C(17)	3917(18)	4124(15)	-888(15)
C(18)	3903(18)	3712(20)	-1652(16)
C(19)	4424(17)	2719(20)	-1683(12)
C(20)	5009(14)	2290(16)	-940(10)
C(21)	7241(12)	1942(10)	696(7)
C(22)	8106(14)	2630(12)	1015(9)
C(23)	9203(14)	2480(15)	916(11)
C(24)	9466(13)	1661(15)	471(10)
C(25)	8617(16)	944(14)	149(10)
C(26)	7512(12)	1069(12)	262(9)

(C-H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. A weighting scheme  $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$  was used in the last cycles of refinement with  $K = 0.588$  and  $g = 0.014$  (1) and  $K = 0.687$  and  $g = 0.003$  (4). Final  $R$  and  $R'$  values were 0.0576 and 0.0768 (1) and 0.0415 and 0.0507 (4) respectively. The SHELX-76 and SHELXS-86 computer programs were used [8]. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 9. Final atomic coordinates for the non hydrogen atoms of (1) and (4) are given in Tables 3 and 4 respectively. All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the Gould Povernode 6040 of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Parma. Additional data (H-atom coordinates, thermal parameters) are available from the Cambridge Crystallographic Data Centre or from the authors on request.

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