



## Formation of niobium and tantalum ylide complexes

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### ABSTRACT

The reactions of tri(bis(ethyl)amino)phosphorus ylide  $(Et_2N)_3P=CH_2$  with cyclopentadienyl (Cp) metal (V) tetrachloride  $CpMCl_4$  ( $M = Nb$  **1**;  $Ta$  **3**) and pentamethylcyclopentadienyl ( $Cp^*$ ) metal (V) tetrachloride  $Cp^*MCl_4$  ( $M = Nb$  **2**;  $Ta$  **4**) were investigated. The hexa-coordinate ylide adduct complexes **5** ( $CpNbCl_4(H_2C=P(NEt_2)_3)$ ), **6** ( $Cp^*NbCl_4(H_2C=P(NEt_2)_3)$ ) and **8** ( $Cp^*TaCl_4(H_2C=P(NEt_2)_3)$ ) with pseudo-octahedral geometry were structurally analyzed with X-ray diffraction. Compound **4** ( $Cp^*TaCl_4$ ) reacted with three molar equivalent of phosphorus ylide to form one ionic complex **9** ( $[H_3C-P(NEt_2)_3][Cp^*TaCl_5]$ ) which was also structurally analyzed with X-ray diffraction. The possible formation mechanism of compound **9** has been discussed.

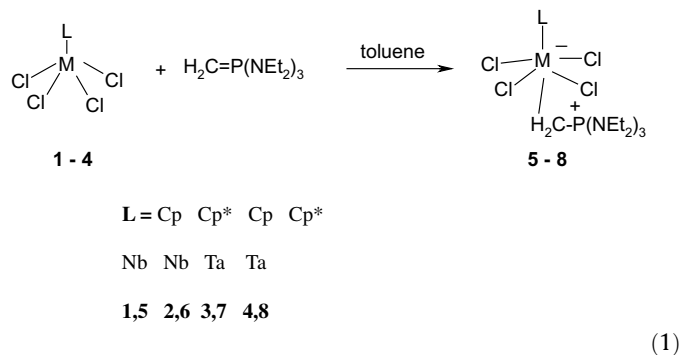
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### 1. Introduction

The synthesis and chemistry of transition-metal phosphonium ylide complexes have been extensively investigated [1]. Interest in this class of organometallic complexes arises principally because these complexes may be important intermediates in catalytic reactions and are considered potential catalysts for new processes. However, ylide complexes are beginning to be exploited in stoichiometric organometallic chemistry as versatile substrates for further synthetic manipulation [2]: essentially, the same reason phosphonium ylides are used so extensively in organic synthesis, and ylide complexes can be as a precursor for the formation of phosphonio methylidyne complexes of transition metal with  $d^0$  electron configurations [3]. The majority of transition-metal phosphonium ylide complexes have been prepared by halide metathesis using preformed phosphorus ylides (Wittig reagents) [4]. In this paper, we employed  $(Et_2N)_3P=CH_2$  ylide and studied its reaction with cyclopentadienyl (Cp) metal (V) tetrachloride and pentamethylcyclopentadienyl ( $Cp^*$ ) metal (V) tetrachloride **1–4**, and finally four ylide adduct complexes **5–8** and an ionic complex **9** were obtained. The formation mechanism of complex **9** was discussed.

### 2. Results and discussion

The reaction of complex **1–4** with one molar of  $(Et_2N)_3P=CH_2$  in toluene gave rise to four ylide adduct complexes **5–8** (Eq. (1))



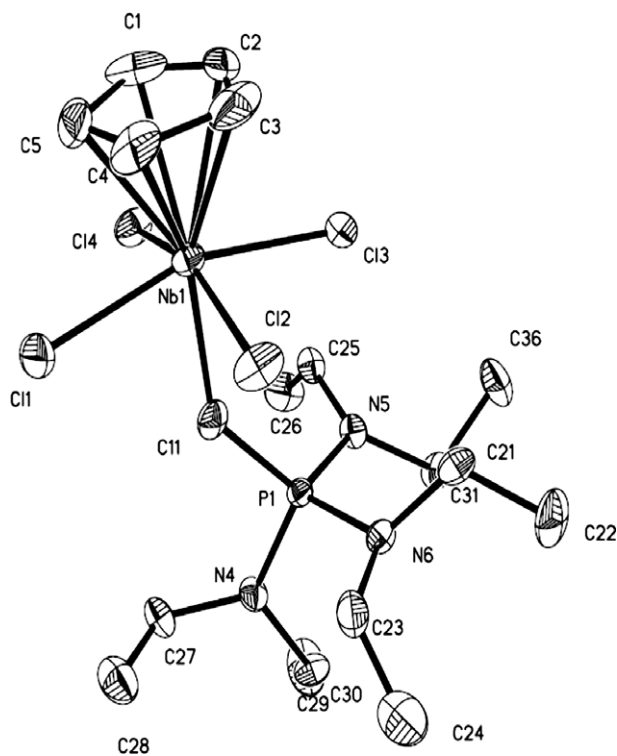
Crystallization at 0 °C in pentane and ether afforded orange–red crystals in 67% **1**; purple–red crystals, 61% **2**; yellow crystals, 56% **3** and orange powder, 71% **4**. The four compounds are stable at room temperature in solid state for at most 1 h seen from their color, and quickly decomposed in solution when exposed to the air.

In the  $^1H$  NMR spectra the signals of the Cp protons are at 6.82 **5** and 6.59 ppm **7**. The signals of the  $Cp^*$  protons are at 2.05 **6** and 2.22 ppm **8**. The methylene (metal- $CH_2$ ) protons show doublets at 3.89 **5**, 3.24 **7**, 2.58 **6**, and 2.45 ppm **8**. In the  $^{31}P$  NMR spectra one singlet was for the phosphorus atom between 68.5 and 72.3 ppm **5–8**. In the  $^{13}C$  NMR spectra, the metal- $CH_2$  carbon shows doublets at 60.3 ppm with the coupling constant is 76 Hz **7**.

In complexes **5**, **6**, and **8** considering the midpoint of  $Cp(Cp^*)$  as a vertex of the octahedron, the metal atom is hexacoordinate with a pseudo-octahedral geometry and surrounded by the ylide ligand, which is *trans* to the C5-ring, and four chloro ligands in the plane (Fig. 1, complex **5**; the molecular structures of complex **6** and **8** in the supplementary materials). Because of the bulky  $Cp(Cp^*)$

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**Fig. 1.** Molecular structure of **5** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Nb1–C11 2.456(4), Nb1–C12 2.420(3), Nb1–C13 2.416(3), Nb1–C14 2.427(3), Nb1–C1 2.474(11), Nb1–C2 2.462(11), Nb1–C3 2.397(13), Nb1–C4 2.457(12), Nb1–C5 2.426(14), Nb1–C11 2.301(10), C11–P1 1.768(10), C11–Nb1–C12 86.44(14), C11–Nb1–C13 158.47(11), C11–Nb1–C14 87.38(14), C12–Nb1–C13 89.54(12), C12–Nb1–C14 157.65(12), C13–Nb1–C14 88.37(11), C11–Nb1–C1 155.8(4), C11–Nb1–C2 155.6(3), C11–Nb1–C3 152.1(4), C11–Nb1–C4 147.9(4), C11–Nb1–C5 149.1(4), C11–Nb1–C1 75.9(3), C11–Nb1–C2 76.7(3), C11–Nb1–C3 82.6(4), C11–Nb1–C4 91.0(5), Nb1–C11–P1 139.1(5).

ligand the metal atom deviates the equatorial plane to the direction of Cp(Cp\*) ligand. The angle Ta–C–P (137.8(3)°) in complex **8** is smaller than those in complex **5** (Nb1–C11–P = 139.1(5)°) and **6** (Nb1–C11–P = 139.4(2)°). This proves the dimension of the metal atom is dominant (Ta > Nb). The P–C bond distances in the three complexes are in the region of those observed for other metal-neutral phosphorus complexes [5].

Early we reported compound **4** (Cp\*TaCl<sub>4</sub>) can only react with 1 equiv. of Ph<sub>3</sub>P=CH<sub>2</sub> to form ylide adduct, which can be deprotonate using appropriate bases such as (Me<sub>3</sub>Si)<sub>2</sub>N<sup>−</sup> and pyridine [3]. We tried to synthesize a carbene complex using compound **4** (Cp\*TaCl<sub>4</sub>) to react with 3 equiv. of tri(bis(ethyl)amino)phosphorus ylide (Et<sub>2</sub>N)<sub>3</sub>P=CH<sub>2</sub>, but finally compound **8** and an unexpected ionic compound **9** ([H<sub>3</sub>C–P(NEt<sub>2</sub>)<sub>3</sub>][Cp\*TaCl<sub>5</sub>]) were isolated (Scheme 1). Crystallization of compound **9** at 0 °C from pentane afforded orange–red crystals in the yield of 45%. The compound **9** is very sensitive to air and water.

In the <sup>1</sup>H NMR spectra signal of the H<sub>3</sub>CP protons in complex **9** was recorded at 2.12 ppm as doublet with the coupling <sup>2</sup>J(HP) =

17 Hz. Cp\* protons were found at 2.07 ppm. In the <sup>31</sup>P NMR spectra the signal shows one singlet for phosphorus atom at 58.6 ppm.

The molecular structure of **9** is composed of two parts: the cation and the tantalum chloride anion (Fig. 2). The former is a phosphonium cation. The later is a hexacoordinate tantalum chloride with a pseudo-octahedral geometry.

The proposed formation mechanism of compound **9** is suggested in Scheme 2. The first step is the formation of ylide adduct compound **8**. Compound **8** reacts with one molar of ylide H<sub>2</sub>C=P(NEt<sub>2</sub>)<sub>3</sub> to form an carbene intermediate **10**, which can be proved by the *in situ* <sup>31</sup>P NMR (52.99 ppm) spectrum of the mother solution, with the generation of phosphonium salt [H<sub>3</sub>C–P(NEt<sub>2</sub>)<sub>3</sub>]Cl. The coordination of the chloride cation in [H<sub>3</sub>C–P(NEt<sub>2</sub>)<sub>3</sub>]Cl to the starting substance **4** affords compound **9**. Different bases such as LiN(SiMe<sub>3</sub>)<sub>2</sub>, NaN(SiMe<sub>3</sub>)<sub>2</sub> and pyridine were used in the reaction to isolate the carbene intermediate **10**, but failed. Because the carbene intermediate **10** is very unstable.

### 3. Experimental

#### 3.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. CpNbCl<sub>4</sub> (**1**), Cp\*NbCl<sub>4</sub> (**2**), CpTaCl<sub>4</sub> (**3**), Cp\*TaCl<sub>4</sub> (**4**) [6] and H<sub>2</sub>C=P(NEt<sub>2</sub>)<sub>3</sub> [7] were synthesized according to the literature procedures. The NMR spectra were recorded using a Bruker Avance 300 MHz spectrometer. <sup>13</sup>C and <sup>31</sup>P NMR resonances were obtained with broad-band proton decoupling.

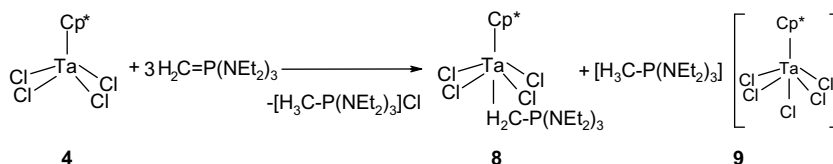
#### 3.2. *trans*-CpNbCl<sub>4</sub>(H<sub>2</sub>C–P(NEt<sub>2</sub>)<sub>3</sub>) (**5**)

To the solution of CpNbCl<sub>4</sub> (**1**) (0.82 g, 2.65 mmol) in 50 mL of toluene was added H<sub>2</sub>C=P(NEt<sub>2</sub>)<sub>3</sub> (0.69 g, 2.64 mmol) in 20 mL of toluene with stirring at 0 °C. The reaction mixture gradually changed from light-red to brown-red and the product precipitated as red solid. After 12 h at room temperature the reaction solution was filtered. The solid residue was dried and extracted with pentane and diethyl ether, respectively. Complex **5** as a orange–red crystal was obtained from pentane. Yield: 0.99 g (67%). Anal. Calc. for C<sub>18</sub>H<sub>37</sub>Cl<sub>4</sub>N<sub>3</sub>PNb (561.2 g/mol) **5**: C, 38.52; H, 6.65. Found: C, 38.33; H, 6.77%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.05 (t, <sup>3</sup>J(HH) = 7.0 Hz, 18H, CH<sub>3</sub>), 3.12 (m, 12H, CH<sub>2</sub>CH<sub>3</sub>), 3.89 (d, <sup>2</sup>J(HP) = 17.7 Hz, 2H, NbCH<sub>2</sub>P), 6.82 (s, 5H, C<sub>5</sub>H<sub>5</sub>); <sup>13</sup>C NMR (75.5 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): 15.2 (d, <sup>3</sup>J(CP) = 3.0 Hz, CH<sub>3</sub>), 42.2 (d, <sup>2</sup>J(CP) = 4.5 Hz, CH<sub>2</sub>CH<sub>3</sub>), 64.8 (d, <sup>1</sup>J(CP) = 75.5 Hz, TaCH<sub>2</sub>P), 110.7 (s, C<sub>5</sub>H<sub>5</sub>); <sup>31</sup>P NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 68.5.

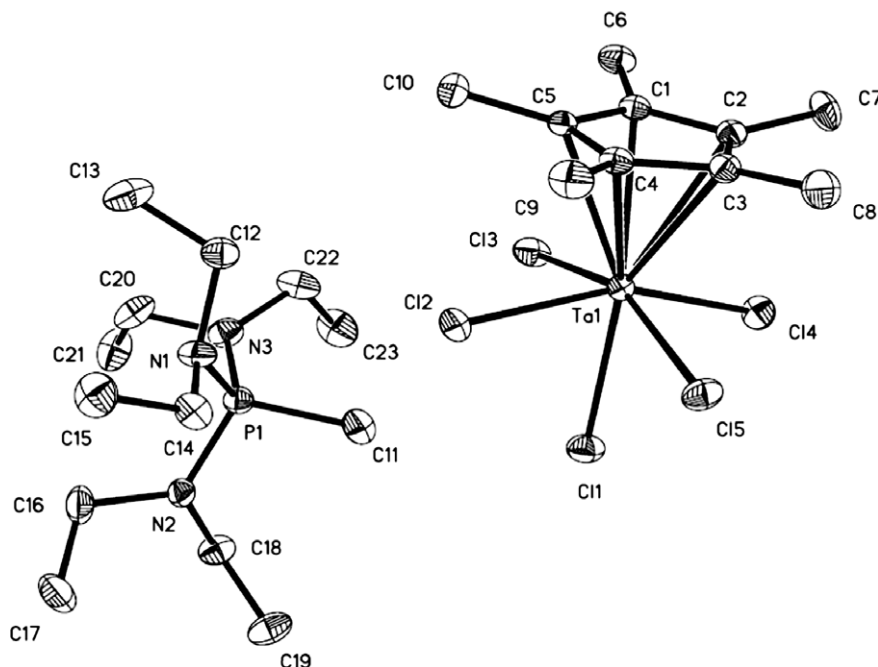
The same synthetic method for **5** was used to obtain complex **6–8**.

#### 3.3. *trans*-Cp\*NbCl<sub>4</sub>(H<sub>2</sub>C–P(NEt<sub>2</sub>)<sub>3</sub>) (**6**)

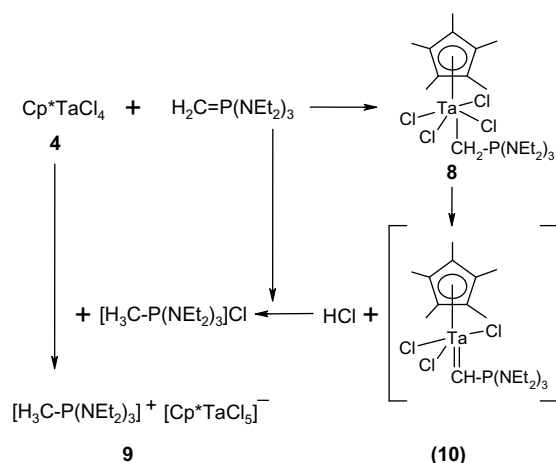
Purple-red crystals from pentane, yield: (61%). Anal. Calc. for C<sub>23</sub>H<sub>47</sub>Cl<sub>4</sub>N<sub>3</sub>PNb (631.3 g/mol) **6**: C, 43.76; H, 7.50. Found: C, 43.61; H, 7.75%. <sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.20 (t, <sup>3</sup>J(HH) = 7.0 Hz, 18H, CH<sub>2</sub>CH<sub>3</sub>), 2.05 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 2.58 (d,



**Scheme 1.**



**Fig. 2.** Molecular structure of **9** (all the hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (°): Ta1–Cl1 2.5118(9), Ta1–Cl2 2.4307(9), Ta1–Cl3 2.4365(9), Ta1–Cl4 2.3960(8), Ta1–Cl5 2.4218(9), Ta1–C1 2.542(3), Ta1–C2 2.571(4), Ta1–C3 2.521(3), Ta1–C4 2.469(3), Ta1–C5 2.472(3), C11–P1 1.775(5), P1–N1 1.646(3), P1–N2 1.629(3), P1–N3 1.622(3), C11–Ta1–Cl2 77.75(3), C11–Ta1–Cl3 79.12(3), C11–Ta1–Cl4 78.83(3), C11–Ta1–Cl5 77.75(3), C12–Ta1–Cl3 86.52(4), C12–Ta1–Cl4 156.50(3), C12–Ta1–Cl5 87.55(4), C13–Ta1–Cl4 87.28(4), C13–Ta1–Cl5 156.85, C14–Ta1–Cl5 89.33(3), C11–P1–N1 113.0(2), C11–P1–N2 106.5(2), C11–P1–N3 115.2(2), N1–P1–N2 110.5(2), N1–P1–N3 105.8(2), N2–P1–N3 105.6(2).



**Scheme 2.** Formation mechanism of complex **9**.

$^2J(\text{HP}) = 17.2$  Hz, 2H,  $\text{NbCH}_2\text{P}$ , 3.34 (m, 12H,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  10.2 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 14.4 (d,  $^3J(\text{CP}) = 3.0$  Hz,  $\text{CH}_3$ ), 44.4 (d,  $^2J(\text{CP}) = 4.5$  Hz,  $\text{CH}_2\text{CH}_3$ ), 65.9 (d,  $^1J(\text{CP}) = 75.5$  Hz,  $\text{TaCH}_2\text{P}$ ), 109.1 (s,  $\text{C}_5(\text{CH}_3)_5$ );  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  69.5.

### 3.4. *trans*- $\text{Cp}^*\text{TaCl}_4(\text{H}_2\text{C}-\text{P}(\text{NEt}_2)_3)$ (**7**)

Yellow powder from pentane, yield: (56%). Anal. Calc. for  $\text{C}_{18}\text{H}_{37}\text{Cl}_4\text{N}_3\text{PTa}$  (649.2 g/mol) **7**: C, 33.30; H, 5.74. Found: C, 33.14; H, 5.91%.  $^1\text{H}$  NMR (300.1 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  0.97 (t,  $^3J(\text{HH}) = 7.1$  Hz, 18H,  $\text{CH}_3$ ), 3.10 (m, 12H,  $\text{CH}_2\text{CH}_3$ ), 3.24 (d,  $^2J(\text{HP}) = 17.7$  Hz, 2H,  $\text{TaCH}_2\text{P}$ ), 6.59 (s, 5H,  $\text{C}_5\text{H}_5$ );  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  13.7 (d,  $^3J(\text{CP}) = 3.0$  Hz,  $\text{CH}_3$ ), 40.4 (d,  $^2J(\text{CP}) = 4.5$  Hz,  $\text{CH}_2\text{CH}_3$ ), 60.3 (d,  $^1J(\text{CP}) = 75.5$  Hz,  $\text{TaCH}_2\text{P}$ ), 116.1 (s,  $\text{C}_5\text{H}_5$ );  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  70.4.

### 3.5. *trans*- $\text{Cp}^*\text{TaCl}_4(\text{H}_2\text{C}-\text{P}(\text{NEt}_2)_3)$ (**8**)

Orange crystals, yield: (71%). Anal. Calc. for  $\text{C}_{23}\text{H}_{47}\text{Cl}_4\text{N}_3\text{PTa}$  (719.4 g/mol) **8**: C, 38.40; H, 6.59. Found: C, 38.26; H, 6.75%.  $^1\text{H}$  NMR (300.1 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  0.89 (t,  $^3J(\text{HH}) = 7.0$  Hz, 18H,  $\text{CH}_2\text{CH}_3$ ), 2.22 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 2.45 (d,  $^2J(\text{HP}) = 17.2$  Hz, 2H,  $\text{TaCH}_2\text{P}$ ), 3.02 (m, 12H,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  11.8 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 14.4 (d,  $^3J(\text{CP}) = 3.7$  Hz,  $\text{CH}_3$ ), 40.3 (d,  $^2J(\text{CP}) = 4.5$  Hz,  $\text{CH}_2\text{CH}_3$ ), 62.1 (d,  $^1J(\text{CP}) = 75.5$  Hz,  $\text{TaCH}_2\text{P}$ ), 110.7 (s,  $\text{C}_5(\text{CH}_3)_5$ );  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  72.3.

### 3.6. $[\text{H}_3\text{C}-\text{P}(\text{NEt}_2)_3][\text{Cp}^*\text{TaCl}_5]$ (**9**)

To the solution of  $\text{Cp}^*\text{TaCl}_4$  **4** (0.82 g, 1.79 mmol) in 30 mL of toluene was added  $\text{H}_2\text{C}=\text{P}(\text{NEt}_2)_3$  (1.40 g, 5.36 mmol) in 20 mL of toluene with stirring at 0 °C. The reaction mixture gradually changed from orange–yellow to red. After 12 h at room temperature the reaction was filtered. The solid residue was dried and extracted with pentane and diethyl ether, respectively. Complex **8** as an orange crystals and complex **9** as a orange–red crystal were obtained in the yields of 16% (0.21 g) and 45% (0.61 g) from pentane and ether, respectively. Anal. Calc. for  $\text{C}_{23}\text{H}_{48}\text{Cl}_5\text{N}_3\text{PTa}$  (755.8 g/mol) **9**: C, 36.55; H, 6.40. Found: C, 36.34; H 6.55%.  $^1\text{H}$  NMR (300.1 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  0.88 (t,  $^3J(\text{HH}) = 7.0$  Hz, 18H,  $\text{CH}_2\text{CH}_3$ ), 2.07 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 2.12 (d,  $^2J(\text{HP}) = 17.2$  Hz, 3H,  $\text{PCH}_3$ ), 2.74 (m, 12H,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  11.1 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 14.2 (d,  $^3J(\text{CP}) = 2.2$  Hz,  $\text{CH}_3$ ), 38.7 (d,  $^2J(\text{CP}) = 4.5$  Hz,  $\text{CH}_2\text{CH}_3$ ), 65.9 (d,  $^1J(\text{CP}) = 75.5$  Hz,  $\text{TaCH}_2\text{P}$ ), 115.7 (s,  $\text{C}_5(\text{CH}_3)_5$ );  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  58.6.

### 3.7. Crystallographic data for **5**

$\text{C}_{18}\text{H}_{37}\text{Cl}_4\text{N}_3\text{PNb}$ ,  $M_r = 561.19$ , crystal dimensions 0.218 × 0.162 × 0.105 mm, triclinic, space group  $P\bar{1}$ ,  $a = 8.79030(10)$  Å,  $b = 11.60460(10)$  Å,  $c = 13.97950(10)$  Å,  $\alpha = 66.5730(10)^\circ$ ,  $\beta =$

77.7250(10)°,  $\gamma = 74.4470(10)^\circ$ ,  $V = 1251.46(2) \text{ \AA}^3$ ,  $T = 273(2) \text{ K}$ ,  $Z = 2$ ,  $D_{\text{Calc}} = 1.853 \text{ g/cm}^3$ ,  $\mu = 0.981 \text{ mm}^{-1}$ . A total of 19704 reflections were collected, 5719 unique ( $R_{\text{int}} = 0.0442$ ),  $\theta_{\text{max}} = 27.48^\circ$ , semiempirical absorption correction  $R_1 = 0.0269$  (for 5719 reflections with  $I > 2\sigma(I)$ ),  $wR_2 = 0.0910$  (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all  $F^2$  (SHELXL-97) with non-hydrogen atoms anisotropic.

### 3.8. Crystallographic data for **6**

$\text{C}_{23}\text{H}_{47}\text{Cl}_4\text{N}_3\text{PNb}$ ,  $M_r = 631.32$ , crystal dimensions  $0.260 \times 0.175 \times 0.106 \text{ mm}$ , monoclinic, space group  $P2(1)/c$ ,  $a = 8.7212(3) \text{ \AA}$ ,  $b = 15.7440(7) \text{ \AA}$ ,  $c = 22.3528(11) \text{ \AA}$ ,  $\beta = 100.615(3)^\circ$ ,  $V = 3016.7(2) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{Calc}} = 1.390 \text{ g/cm}^3$ ,  $\mu = 0.823 \text{ mm}^{-1}$ . A total of 23648 reflections were collected, 6899 unique ( $R_{\text{int}} = 0.0356$ ),  $\theta_{\text{max}} = 27.46^\circ$ , semiempirical absorption correction  $R_1 = 0.0556$  (for 6899 reflections with  $I > 2\sigma(I)$ ),  $wR_2 = 0.1797$  (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all  $F^2$  (SHELXL-97) with non-hydrogen atoms anisotropic.

### 3.9. Crystallographic data for **8**

$\text{C}_{23}\text{H}_{47}\text{Cl}_4\text{N}_3\text{PTa}$ ,  $M_r = 719.34$ , crystal dimensions  $0.292 \times 0.188 \times 0.128 \text{ mm}$ , monoclinic, space group  $P2(1)/c$ ,  $a = 8.71480(10) \text{ \AA}$ ,  $b = 15.7278(2) \text{ \AA}$ ,  $c = 22.3510(3) \text{ \AA}$ ,  $\beta = 100.8040(10)^\circ$ ,  $V = 3009.23(7) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{Calc}} = 1.583 \text{ g/cm}^3$ ,  $\mu = 4.077 \text{ mm}^{-1}$ . A total of 28406 reflections were collected, 6919 unique ( $R_{\text{int}} = 0.0265$ ),  $\theta_{\text{max}} = 27.50^\circ$ , semiempirical absorption correction  $R_1 = 0.0360$  (for 6919 reflections with  $I > 2\sigma(I)$ ),  $wR_2 = 0.1037$  (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all  $F^2$  (SHELXL-97) with non-hydrogen atoms anisotropic.

### 3.10. Crystallographic data for **9**

$\text{C}_{23}\text{H}_{48}\text{Cl}_5\text{N}_3\text{PTa}$ ,  $M_r = 755.81$ , crystal dimensions  $0.36 \times 0.36 \times 0.15 \text{ mm}$ , orthorhombic, space group  $Pbca$ ,  $a = 8.9442(5) \text{ \AA}$ ,  $b = 22.8872(14) \text{ \AA}$ ,  $c = 29.7470(19) \text{ \AA}$ ,  $V = 6089.4(6) \text{ \AA}^3$ ,  $T = 193(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{Calc}} = 1.649 \text{ g/cm}^3$ ,  $\mu = 4.119 \text{ mm}^{-1}$ . A total of 45618 reflections were collected, 5979 unique ( $R_{\text{int}} = 0.0545$ ),  $\theta_{\text{max}} = 26.06^\circ$ , semiempirical absorption correction  $R_1 = 0.0241$  (for 5979 reflections with  $I > 2\sigma(I)$ ),  $wR_2 = 0.0544$  (all data). The structure was

solved by direct methods and refined with full-matrix least-squares on all  $F^2$  (SHELXL-97) with non-hydrogen atoms anisotropic.

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### Appendix A. Supplementary material

CCDC 666142, 664095, 664097 and 664096 contain the Supplementary crystallographic data for **5**, **6**, **8** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.05.007](https://doi.org/10.1016/j.jorganchem.2008.05.007).

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