Organometallics **2007,** *26,* 1411−1413

Phosphorus Ylide as a Precursor for the Formation of New High-Valent Tantalum Phosphonio Methylidyne Complexes

Xiaoyan Li,*,† Aichen Wang,† Liang Wang,† Hongjian Sun,† Klaus Harms,‡ and Jörg Sundermeyer‡

School of Chemistry and Chemical Engineering, Shandong University,
Shanda Nanlu 27, 250100 Jinan, People's Republic of China, and
Department of Chemistry, University of Marburg, Hans-Meerwein-Strasse, 35032 Marburg, Germany

Received November 21, 2006

Two new high-valent tantalum(V) phosphonio methylidyne complexes, [CpTa(C−PPh_3)(CH−PPh_3)-Cl] (**4**) and [CpTa(C−PPh_3)(CH−PPh_3)$_2$] (**5**), have been obtained respectively via transylidation reactions of $CpTaCl_4$ with 5 and 7 equiv of the phosphorus ylide $Ph_3P{=}CH_2$. Complex **4** was structurally analyzed with X-ray diffraction. The possible formation mechanism has been discussed. To our knowledge this presentation is the first example of a stable tantalum complex with a terminal [M≡C−PPh_3] function.

The topic of high-valent methylidene and methylidyne complexes with d^0 electron configurations is an important and interesting one, because they can be highly reactive catalysts for the alkene and alkyne metathesis reactions, respectively.[1−6] Recently, we have successfully used a phosphorus ylide as a precursor for the formation of phosphonio methylidyne complexes of tungsten,[7] rhenium,[8] and niobium[9] with d^0 electron configurations. The rhenium phosphonio methylidyne complex, by reacting with diphenylketene through a Wittig reaction, gives rise to an allenylidene complex,[10] which is a novel class of compounds in organometallic chemistry[11,12] and can be used as precursors of new carbene complexes,[13] as metal-containing polymers,[14,15] and as intermediates for organic synthesis.[16] In order to increase the yield and the stability of the phosphonio methylidyne complex, we have introduced amino and cyclopentadienyl (C_5H_5, Cp) groups.

Owing to the isolobal relationship between $CpTaCl_4$ and $W(NR)Cl_4$ (Scheme 1), these two complexes should have similar reactivities toward (triphenylmethylene)phosphorane. The transylidation reaction of $CpTaCl_4$ (**1**) with 7 equiv of (triphenylmethylene)phosphorane gave the complex [CpTa(C−PPh_3)(CH−PPh_3)$_2$] (**5**) (Scheme 2). Complex **5** is also isolobal with [W(NMes)(C−PPh_3)(CH−PPh_3)$_2$] and [W(NDip)(CH−PPh_3)$_2$(C−PPh_3)].[7] To our knowledge this presentation is the first example of a stable tantalum complex with a terminal [M≡C−PR_3] function.

By careful investigation of the stoichiometry of this transformation and by characterization of some intermediates and byproducts, a reaction mechanism is proposed in Scheme 3: the first intermediate is the hexacoordinate ylide adduct **2**, which can be isolated in good yield when the parent compound **1** is treated with 1 equiv of $Ph_3P{=}CH_2$ in toluene. Compound **2** is stable as a solid, but in solution it is deprotonated by 6 equiv of $Ph_3P{=}CH_2$ to provide complex **5** and phosphonium chloride. As an intermediate the phosphonio methylidyne complex **4** can be isolated when the parent compound **1** is treated with 5 equiv of $Ph_3P{=}CH_2$ in toluene. The phosphonio methylidyne complex **3** cannot be isolated as an intermediate when **2** is treated with 2 equiv of $Ph_3P{=}CH_2$ in toluene. There is some collateral evidence for intermediate **3**, as transylidation reactions of [$CpNbCl_4$] with (triphenylmethylene)phosphorane afforded phosphonio methylidyne complexes (Scheme 4).[9]

Complexes **4** and **5** have been fully characterized by NMR and elemental analysis. The ^1H NMR spectra show one singlet at 5.92 ppm (**4**) and 5.61 ppm (**5**) for the cyclopentadienyl ligand, respectively. The ^{31}P NMR spectra of **4** show two

---

* To whom correspondence should be addressed. Fax: 0086-531-8564464. E-mail: xli63@sdu.edu.cn (X.L.).

† Shandong University.

‡ University of Marburg.

(1) (a) Schrock, R. R. *Chem. Commun.* **2005**, 2773−2777. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145−179.

(2) (a) Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 1954. (b) Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350.

(3) List, A. K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2010.

(4) Holmes, J. S.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476.

(5) Schmidbaur, H.; Müller, G.; Pichl, R. *Angew. Chem.* **1986**, *98*, 572; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 574.

(6) (a) Hughes, K. A.; Dopico, P. G.; Sabat, M.; Finn, M. G. *Angew. Chem.* **1993**, *32*, 603; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 554. (b) Reynolds, K. A.; Dopico, P. G.; Sundermann, M. J.; Hughes, K. A.; Finn, M. G. *J. Org. Chem.* **1993**, *58*, 1298. (c) Reynolds, K. A.; Dopico, P. G.; Brody, M. S.; Finn, M. G. *J. Org. Chem.* **1997**, *62*, 2564.

(7) Li, X.; Schopf, M.; Stephan, J.; Harms, K.; Sundermeyer, J. *Organometallics* **2002**, *21*, 2356−2358.

(8) Li, X.; Stephan, J.; Harms, K.; Sundermeyer, J. *Organometallics* **2004**, *23*, 3359−3361.

(9) Li, X.; Sun, H.; Harms, K.; Sundermeyer, J. *Organometallics* **2005**, *24*, 4699−4701.

(10) Li, X.; Schopf, M.; Stephan, J.; Kippe, J.; Harms, K.; Sundermeyer, J. *J. Am. Chem. Soc.* **2004**, *126*, 8660−8861.

(11) (a) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797−2858. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59−128. (c) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257.

(12) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383−406.

(13) Pilette, D.; Ouzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809.

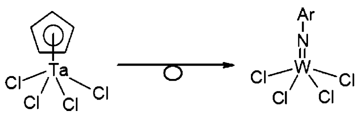
(14) (a) Macomber, D.; Hung, M. H.; Liang, M.; Verma, A. G.; Madhukar, P. *Macromolecules* **1988**, *21*, 1187. (b) Hagihara, N.; Songashira, K.; Takahashi, *Adv. Polym. Sci.* **1981**, *41*, 149. (c) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci.: Polym. Chem. Ed. Engl.* **1980**, *18*, 349−361.

(15) (a) Schrock, R. R.; Luo, S.; Lee, J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883−3895. (b) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 12131−12132. (c) Mizumoto, T.; Masuda, T.; Higashimura, T. *Macromol. Chem. Phys.* **1995**, *196*, 1769−1771.

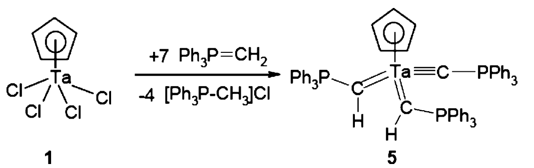
(16) Schubert, U., Ed. *Advances in Metal Carbene Chemistry*; Kluwer Academic: Dordrecht, The Netherlands, 1989.

10.1021/om061068b CCC: $37.00

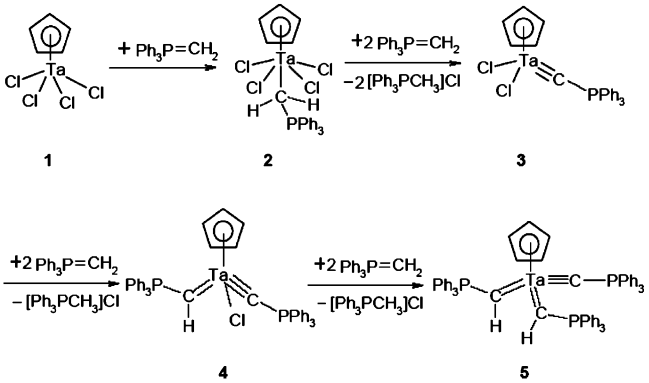
Scheme 1. Isolobal Relationship



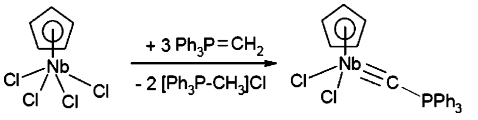
Scheme 2. Synthesis of Complex 5



Scheme 3. Proposed Mechanism for the Formation of Complexes 4 and 5



Scheme 4



doublets for [Ta=CH−PPh$_3$] and [Ta≡C−PPh$_3$] at 23.7 and −21.7 ppm, respectively, with the coupling constant ^4J(PP) = 5.0 Hz. The ^{31}P NMR spectra of **5** reveal a triplet for [Ta≡C−PPh$_3$] at −27.7 ppm and a doublet at 19.7 ppm for the two [Ta=CH−PPh$_3$] functionalities (^4J(PP) = 4.0 Hz). The differences in metal−carbon bond orders are also reflected in the ^{13}C NMR spectra of **4** and **5**, showing resonances at 117.7 ppm (**4**) and 79.2 ppm (**5**) for [Ta=CH−PPh$_3$] and 208.0 ppm (**4**) and 202.1 ppm (**5**) for [Ta≡C−PPh$_3$], which are comparable with those for the related isolobal complexes of tungsten [W(NMes)(C−PPh$_3$)(CH−PPh$_3$)$_2$] and [W(NDip)(CH−PPh$_3$)$_2$(C−PPh$_3$)].[7]

By recrystallization from pentane at 4 °C crystals of **4** as yellow prisms suitable for X-ray diffraction analysis were obtained. The molecular geometry is shown in Figure 1 with selected bond distances and angles. The tantalum atom is found in a slightly distorted pseudo-tetrahedral geometry, reminiscent of a three-legged piano stool. The structure is related to that of [CpNb(N^{t}Bt)(CH−PPh$_3$)Cl][17] by formal replacement of an [N^t-Bt] with an isoelectronic [C−PR$_3$] ligand. The Ta1−C2 distance of 2.040(6) Å in the [Ta=CH−PPh$_3$] moiety is consistent with a tantalum−carbon double bond[1a] and matches the bond length of structurally and electronically related d^0 phosphonium methylidene complexes.[7] (Nb−C6 = 2.043 Å in [CpNb(N^{t}Bt)(CH−PPh$_3$)Cl],[17] W−C32 = 1.994 Å and W−C51 = 2.022 Å in [W(NDip)(CH−PPh$_3$)$_2$(C−PPh$_3$)]).

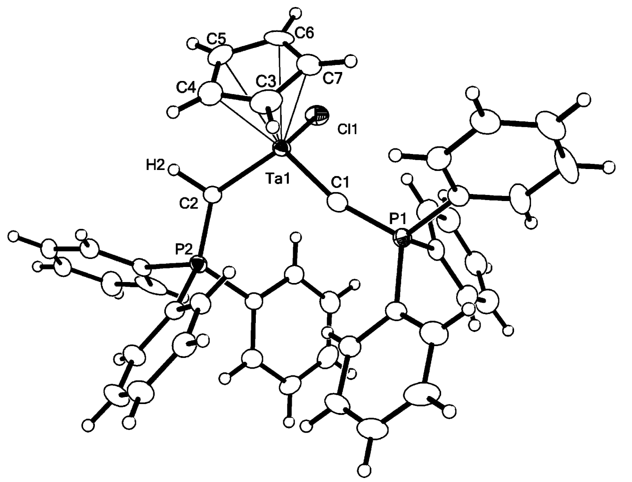


Figure 1. X-ray crystal structure of **4**. Selected bond distances (Å) and angles (deg): Ta1−C1 = 1.853(7), Ta1−C2 = 2.040(6), Ta1−C3 = 2.385(7), Ta1−C4 = 2.470(8), Ta1−C5 = 2.555(6), Ta1−C6 = 2.521(6), Ta1−C7 = 2.431(6), Ta1−Cl1 = 2.4116(17), P1−C1 = 1.700(7), P2−C2 = 1.715(6); P1−C1−Ta1 = 164.9(4), P2−C2−Ta1 = 136.3(4), Cl−Ta−Cl1 = 102.3(2), C2−Ta−Cl1 = 103.9(2), C2−Ta−C1 = 105.8(3).

The Ta1−C1 distance of 1.853 Å in [Ta≡C−PPh$_3$] lies within the range expected for a metal−carbon triple bond[17−19] (1.850 Å in [Ta(CPh)(η^5-C$_5$Me$_5$)(PMe$_3$)$_2$Cl],[18] 1.851 Å in [Ta(CCMe$_3$)(H)(dmpe)$_2$(ClAlMe$_3$)][19]) and compares perfectly with that of the related d^0 phosphonium methylidyne complexes[7−9] (Re1−C1 = 1.758 Å in [Re(N^{t}Bu)(C−P(NEt$_2$)$_3$)Cl$_3$],[8] W−C = 1.813 Å in [W(NDip)(CH−PPh$_3$)$_2$(C−PPh$_3$)],[7] Nb−C =1.829 Å in [CpNb(C−PPh$_3$)Cl$_2$]).[9]

The ylidic C$_{yl}$−P distances C1−P1 = 1.700(7) and C2−P2 = 1.715(6) Å are substantially shorter than other C$_{ar}$−P distances of the PPh$_3$ group (1.806−1.830 Å), reflecting a considerable contribution of the charged resonance form.[8,9]

The angle of the P1−C1−Ta1 = 164.9(4)° deviates slightly from the expected 180° for an sp hybridized C atom. This can be explained by the significant steric repulsion between the two triphenylphosphine groups in complex **4**. The PPh$_3$ group on the carbyne carbon is pushed toward the C5 ring. As a consequence of the strong trans influence of both phosphonio methylidene and phosphonio methylidyne units, the distances Ta−C5 = 2.555(6) and Ta−C6 = 2.521(6) Å in trans positions are considerably longer than Ta1−C3 = 2.385(7) Å in a cis position, while the other two distances Ta1−C4 = 2.470(8) and Ta1−C7 = 2.431(6) Å are close to the average value of these five distances, 2.47 Å.

Complexes **4** and **5** are formally 18- and 20-electron species, respectively, with a polar tantalum−carbon triple bond. They are very reactive toward CO, CH$_3$NC, and Ph$_2$=C=C=O. Currently we are investigating these reactions. We will report the results in the near future.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. CpTaCl$_4$ and H$_2$C=PPh$_3$ were synthesized according to literature procedures. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujol mulls between KBr disks, were recorded on a Nicolet 5700 instrument. NMR spectra were recorded on a Bruker AV 400

---

(17) Schmidt, S.; Sundermeyer, J.; Moeller, F. *J. Organomet. Chem.* **1994**, *475*, 157.

(18) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171−176.

(19) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710−1716.

MHz spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling.

Synthesis of 2. To 0.84 g (2.16 mmol) of $CpTaCl_4$ (**1**) in 50 mL of toluene was added 0.60 g (2.16 mmol) of $Ph_3P{=}CH_2$ in 10 mL of toluene at 0 °C. After it was stirred for 2 h at ambient temperature, the yellow suspension was filtered, reduced in volume, layered with pentane, and stored at 4 °C. The product precipitated as a yellow powder. Yield: 1.0 g (59%). Anal. Calcd for $C_{24}H_{22}Cl_4PTa$ (**2**; 664.17 g/mol): C, 45.21; H, 3.34. Found: C, 45.25; H, 3.48. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 4.05 (d, ^2J(PH) = 16.2 Hz, 2H, $TaCH_2PPh_3$), 6.35 (s, 5H, C_5H_5), 6.93−7.73 (m, 15H, PC_6H_5). ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ 123.98 (s, C_5H_5), 134.35 (d, ^1J(PC) = 9.6 Hz, $TaCH_2PPh_3$), 128.53 (d, ^3J(PC) = 12.0 Hz, Ph C_{meta}), 132.11 (d, ^4J(PC) = 2.6 Hz, Ph C_{para}), 134.35 (d, ^2J(PC) = 9.6 Hz, Ph C_{ortho}). ^{31}P NMR (162.0 MHz, C_6D_6, 300 K): δ 33.1 (s, $TaCH_2PPh_3$).

Synthesis of 4. A 1.19 g portion (3.06 mmol) of $CpTaCl_4$ (**1**) was dissolved in 50 mL of toluene, and 4.24 g (15.26 mmol) of $Ph_3P{=}CH_2$ in 50 mL of toluene was added dropwise with stirring at 0 °C. The reaction mixture was warmed to ambient temperature and stirred for 4 days. During this period, the reaction mixture turned orange. After removal of the solvent at reduced pressure, the solid residue was extracted with pentane (80 mL) and diethyl ether (2 × 80 mL), respectively. Repeated recrystallization from pentane at 4 °C yielded yellow single crystals suitable for X-ray diffraction. Yield: 0.85 g (33.9%). Anal. Calcd for $C_{43}H_{36}ClP_2Ta$ (**4**; 831.0 g/mol): C, 62.14; H, 4.37; Cl, 4.26. Found: C, 62.02; H, 4.50; Cl, 4.16. ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 5.28 (d, ^2J(PH) = 3.0 Hz, 1H, $TaCHPPh_3$), 5.92 (s, 5H, C_5H_5), 6.94−7.94 (m, 30 H, PC_6H_5). ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K): δ 105.2 (s, C_5H_5), 117.7 (d, ^1J(PC) = 46.6 Hz, TaCHP), 130.2 (d, ^4J(PC) = 2.2 Hz), 130.3 (d, ^4J(PC) = 2.2 Hz), 133.1 (d, ^3J(PC) = 10.0 Hz), 134.2 (d, ^3J(PC) = 9.0 Hz), 134.9 (d, ^1J(PC) = 84.6 Hz), 135.7 (d, ^1J(PC) = 84.5 Hz), 208.0 (s br, TaCP). ^{31}P NMR (81.0 MHz, C_6D_6, 300 K): δ 23.7 (d, ^4J(PP) = 6.0 Hz, 1P, TaCHP), −21.7 (d, ^4J(PP) = 6.0 Hz, 1P, TaCP).

Synthesis of 5. A 0.90 g portion (2.31 mmol) of $CpTaCl_4$ (**1**) was dissolved in 50 mL of toluene, and 4.49 g (16.16 mmol) of $Ph_3P{=}CH_2$ in 50 mL of toluene was added dropwise with stirring at 0 °C. The reaction mixture was warmed to ambient temperature and stirred for 3 days. During this period, the reaction mixture turned red-brown. The filtrate was concentrated to 50 mL under reduced pressure and layered with pentane (50 mL). At −30 °C the orange product precipitated as a powder. Yield: 0.52 g (21%). Anal. Calcd for $C_{62}H_{52}TaP_3$ (**5**; 1070.8 g/mol): C, 69.54; H, 4.89. Found: C, 69.39; H, 4.50. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 3.46 (dd, ^2J(PH) = 4.0 Hz, ^4J(PH) = 1.2 Hz, 2H, TaCHP), 5.61 (s, 5H, C_5H_5), 7.02−8.07 (m, 45 H, $P(C_6H_5)_3$). ^{13}C NMR (125.8 MHz, C_6D_6, 300 K) δ 79.2 (d, ^1J(PC) = 48.5 Hz, TaCHP), 103.6 (s, C_5H_5), 129.3 (d, ^4J(PC) = 2.7 Hz), 129.7 (d, ^4J(PC) = 2.7 Hz), 132.6 (d, ^3J(PC) = 9.3 Hz), 133.1 (d, ^2J(PC) = 9.7 Hz), 133.9 (d, ^2J(PC) = 8.8 Hz), 136.5 (d, ^1J(PC) = 81.4 Hz), 137.5 (d, ^1J(PC) = 80.4 Hz), 202.1 (s br, TaCP). ^{31}P NMR (81.0 MHz, C_6D_6, 300 K): δ 19.7(d, ^4J(PP) = 4.0 Hz, 2P, TaCHP), −27.7 (t, ^4J(PP) = 4.0 Hz, 1P, TaCP).

Crystallographic Data for 4: $C_{43}H_{36}ClP_2Ta$, M_r = 831.06, crystal dimensions 0.20 × 0.16 × 0.05 mm, monoclinic, space group $C2/c$, a = 40.635(3) Å, b = 10.1305(5) Å, c = 18.5388(15) Å, β = 107.268(6)°, V =7287.6(9) Å^3, T = 193(2) K, Z = 8, D_c = 1.515 g cm^{-3}, μ = 3.207 mm^{-1}, total reflections collected 39 754, 6396 unique reflections (R_{int} = 0.0788), $\theta_{\max}$ = 25.00°, semiempirical absorption correction, R1 = 0.0397 (for 4552 reflections with $I > 2\sigma(I)$), wR2 = 0.0920 (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.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-226534. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the NSFC (Nos. 20572062 and 20372042), by the Doctoral Program of the MOE (Nos. 20050422010 and 20050422011), and by the Deutsche Forschungsgemeinschaft (No. SFB 260).

Supporting Information Available: Tables containing full X-ray crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM061068B