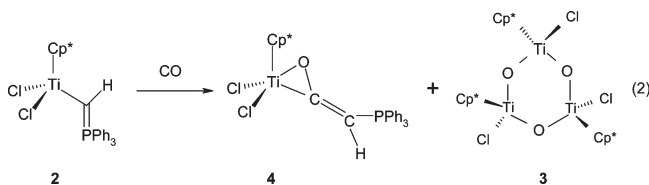


Simple Synthesis of (Triphenylphosphoniomethylidene)(pentamethylcyclopentadienyl) titanium(IV) Dichloride and Its Reaction with Carbon Monoxide [*Organometallics* 2009, 28, 5285. DOI: 10.1021/om9005406]. Nazhen Liu, Aichen Wang, Hongjian Sun, and Xiaoyan Li*

Page 5285. The original title of this note should be replaced by “Simple Synthesis of (Triphenylphosphoniomethylidene)-(pentamethyl cyclopentadienyl)titanium(IV) Dichloride and Its Reaction with Carbon Monoxide”.

Pages 5286–5287. The section “Reduction of $[\text{Cp}^*\text{TiCl}_2(-\text{CH}=\text{PPh}_3)]$ (**2**) with CO” should be completely replaced by the following text.

Reaction of $[\text{Cp}^*\text{TiCl}_2(-\text{CH}=\text{PPh}_3)]$ (2**) with CO.**



The reaction of $[\text{Cp}^*\text{TiCl}_2(-\text{CH}=\text{PPh}_3)]$ (**2**) with carbon monoxide in diethyl ether affords the insertion product, the β -phosphonioacyl complex $[\text{Cp}^*\text{TiCl}_2(\text{OCCH})\text{PPh}_3]$ (**4**), as red crystals. The IR band at 1488 cm^{-1} indicates η^2 coordination of the inserted carbonyl group to the titanium center.¹ The ^1H NMR data shows *E/Z* isomers in CDCl_3 in a ratio of 67:33 with respect to the $\text{C}=\text{C}$ double bond.

The molecular structure (Figure 2) of complex **4** reveals that the titanium center has a tetrahedral coordination geometry with two chlorine atoms, one Cp^* ligand, and one η^2 -coordinated carbonyl group. With respect to the $\text{C}=\text{C}$ double bond, this structure is a *Z* isomer. The $\text{C12}-\text{O1}$ bond length is $1.284(2)\text{ \AA}$, between that of a $\text{C}-\text{O}$ single bond and a $\text{C}=\text{O}$ double bond. The $\text{C12}-\text{C13}$ bond length ($1.353(2)\text{ \AA}$) is situated in the region of $\text{C}=\text{C}$ double-bond distances.

Complex **3** was isolated as a byproduct. This compound is identical with Floriani's oxo complex.² It is thought that the formation of complex **3** was caused by a small amount of water in the reaction mixture.

In conclusion, an α -phosphoniomethylidene complex of titanium, $[\text{Cp}^*\text{TiCl}_2(-\text{CH}=\text{PPh}_3)]$ (**2**), was obtained from transylidation reactions of (pentamethylcyclopentadienyl)-titanium trichloride, $[\text{Cp}^*\text{TiCl}_3]$, with 2 equiv of $\text{Ph}_3\text{P}=\text{CH}_2$. The reaction of complex **2** with CO afforded an insertion product, the β -phosphonioacyl complex $[\text{Cp}^*\text{TiCl}_2(\text{OCCH})\text{PPh}_3]$ (**4**). As a byproduct the trinuclear titanium complex $[\text{Cp}^*\text{Ti}(\mu\text{-O})\text{Cl}]_3$ (**3**) formed through hydrolysis was identified by single-crystal X-ray diffraction.²

Page 5288. Line 9 should read “ ^{31}P NMR (121.5 MHz, C_6D_6 , 300 K): δ 16.0 ppm.”

Page 5288. The section “ $[\text{Cp}^*\text{Ti}(\mu\text{-Cl})\text{Cl}]_3$ (**3**).” should be replaced by the following text.

(1) Weber, K. *Doctoral Thesis*, University of Würzburg, Würzburg, Germany, 1994, pp 123–139.

(2) Carofiglio, T.; Floriani, C.; Sgamellotti, A.; Rosi, M.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* 1992, 1081.

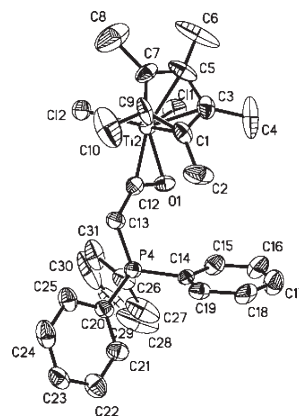


Figure 2. Molecular structure of **4**. Selected bond distances (\AA) and angles (deg): $\text{O1}-\text{C12} = 1.284(16)$, $\text{Ti2}-\text{O1} = 1.995(10)$, $\text{Ti2}-\text{C12} = 2.029(16)$, $\text{Ti2}-\text{C11} = 2.356(5)$, $\text{Ti2}-\text{C12} = 2.290(5)$, $\text{P4}-\text{C13} = 1.762(16)$, $\text{C13}-\text{C12} = 1.353(19)$; $\text{O1}-\text{Ti2}-\text{C12} = 37.2(5)$, $\text{O1}-\text{Ti2}-\text{C11} = 116.5(3)$, $\text{C12}-\text{Ti2}-\text{C12} = 94.5(4)$, $\text{O1}-\text{Ti2}-\text{C11} = 88.5(3)$, $\text{C12}-\text{Ti2}-\text{C11} = 122.1(5)$, $\text{C12}-\text{Ti2}-\text{C11} = 96.61(19)$, $\text{C12}-\text{O1}-\text{Ti2} = 72.8(9)$, $\text{O1}-\text{C12}-\text{C13} = 127.1(15)$, $\text{C13}-\text{C12}-\text{Ti2} = 162.5(13)$, $\text{O1}-\text{C12}-\text{Ti2} = 70.0(8)$.

$[\text{Cp}^*\text{TiCl}_2(\text{OCCH})\text{PPh}_3]$ (**4**). Complex **2** (0.20 g, 3.78 mmol) was dissolved in diethyl ether (20 mL) and kept under CO (1 atm) at $0\text{ }^\circ\text{C}$. After it was warmed to room temperature, the mixture was stirred for another 12 h and then filtered. Complex **4** as red crystals was obtained from a diethyl ether solution. Yield: 0.12 g (56.0%). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{Cl}_2\text{OPTi}$ (**4**; 557.3 g/mol): C, 64.66; H, 5.61. Found: C, 64.91; H, 6.02. ^1H NMR (300.1 MHz, C_6D_6 , 300 K): δ 2.10 (s, 15H, CH_3), 4.47 (d, $^2J(\text{HP}) = 29.1\text{ Hz}$, 0.6H, $\text{C}=\text{CHP}$), 3.70 (d, $^2J(\text{HP}) = 25.5\text{ Hz}$, 0.4H, $\text{C}=\text{CHP}$), 6.86–7.10, 7.32–7.43 and 7.60–7.68 (m, 15H, $\text{P}(\text{C}_6\text{H}_5)_3$). ^{31}P NMR (121.5 MHz, C_6D_6 , 300 K): δ 10.2 (s, 0.6P), 15.5 (s, 0.4P) ppm.

Complex **3** was obtained as brilliant yellow crystals (trace) and structurally characterized and confirmed.²

Page 5288. The paragraph “Crystallographic Data for **3**.” should be replaced by the following text.

Crystallographic Data for **4:** $\text{C}_{30}\text{H}_{31}\text{Cl}_2\text{OPTi}$, $M_r = 557.29$, triclinic, space group $P\bar{1}$, $a = 14.517(11)\text{ \AA}$, $b = 15.480(11)\text{ \AA}$, $c = 17.133(13)\text{ \AA}$, $\alpha = 88.518(15)^\circ$, $\beta = 73.931(14)^\circ$, $\gamma = 63.486(14)^\circ$, $V = 3289(4)\text{ \AA}^3$, $Z = 4$, $D_c = 1.125\text{ g cm}^{-3}$, 14 273 collected reflections, 9600 unique reflections ($R_{\text{int}} = 0.0893$), $\theta_{\text{max}} = 23.45^\circ$, semiempirical absorption correction $R1 = 0.1243$ (for 9600 reflections with $I > 2\sigma(I)$), $wR2 = 0.4114$ (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.

Page 5288. “CCDC-715899 (**3**)” should be replaced by “CCDC-763344 (**4**)”.

Supporting Information Available: A CIF file giving crystallographic data for complex **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

DOI: 10.1021/om1001588

Published on Web 03/11/2010