

# Ti( $\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2$ )<sub>3</sub>Rh has a cylindrically symmetric triple bond

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**The cylindrical symmetry of  $\text{Ti}(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{-PPh}_2)_3\text{Rh}$  permits maximum  $\text{Rh}(\text{d}_\pi) \rightarrow \text{Ti}(\text{d}/\text{p}_\pi)$  overlap, resulting in a 2.2142(11) Å metal–metal triple bond.**

Aspects of heterogeneous materials exhibiting the strong metal–support interaction (SMSI)<sup>1</sup> have been modeled by homogeneous systems,<sup>2–6</sup> some containing M–M' bonds of disparate metals.<sup>5,6</sup> Previously, we conducted an X-ray structural study of  $\text{Cp}^*\text{Zr}(\mu : \eta^1, \eta^1\text{-OCH}_2\text{PPh}_2)_2\text{RhMe}_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) that revealed a short 2.444(1) Å ZrRh bond which was evaluated *via* extended Hückel molecular orbital (EHMO) calculations of an appropriately configured model,  $\text{Cp}(\text{HO})_2\text{ZrRh}(\text{PH}_3)_2\text{Me}_2$ .<sup>5</sup> The metal–metal interaction, which is approximately 0.25 Å shorter than the sum of Zr (1.454 Å) and Rh (1.252 Å) covalent radii, was described in terms of a  $\sigma$  bond and a  $\text{Rh}(\text{d}_\pi) \rightarrow \text{Zr}(\text{d}_\pi)$  bond. While the geometry of the alkoxyalkylphosphine bridges and the single critical  $\pi$  interaction resulted in a strong bond, at least by bond length criteria, the low symmetry of the complex prevented a second  $\pi$  interaction from being significant. As a consequence, we turned our attention to the synthesis of a cylindrically symmetric metal–metal bond in order to increase and perhaps maximize the strength of  $\pi$  interactions between group 4 and 9 metal centers.<sup>5,7,8</sup>

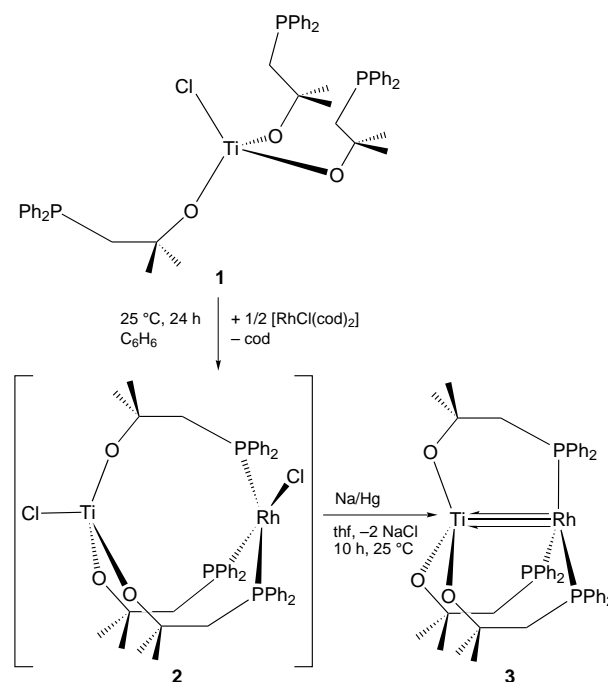
Treatment of  $\text{TiCl}_4(\text{thf})_2$  with 3 equiv. of  $\text{LiOCMe}_2\text{CH}_2\text{PPh}_2$  in benzene at 25 °C for 3 h afforded  $(\text{Ph}_2\text{PCH}_2\text{CMe}_2\text{O})_3\text{TiCl}$  **1**† as a viscous, clear yellow oil in 80% yield. Although **1** was typically contaminated with *ca.* 5%  $\text{HOCMe}_2\text{CH}_2\text{PPh}_2$ , this was of sufficient purity to continue. Upon stirring a benzene solution of tris(alkoxyphosphine)-titanium chloride **1** and 0.5 equiv. of  $[\text{RhCl}(\text{cod})]_2$ <sup>9</sup> for 24 h at 25 °C, a color change from yellow to deep red was noted, and an amorphous red solid was isolated from hexane. The major product displayed broad resonances in its <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra at 23 °C in C<sub>6</sub>D<sub>6</sub>, the latter implying a 2:1 ratio of bound and free phosphines, while the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at –8 °C exhibited broad, complex multiplets at  $\delta$  52.17 and 56.42 in a 2:1 ratio corresponding to bound phosphines. At –80 °C, we postulate the complex as  $\text{ClTi}(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2)_3\text{RhCl}$  (**2**, Scheme 1),† but suggest that dimerization to  $[\text{ClTi}(\text{OCMe}_2\text{CH}_2\text{PPh}_2)(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{-PPh}_2)_2\text{Rh}]_2(\mu\text{-Cl})_2$  is plausible at room temperature. Recrystallization and chromatographic purification efforts failed, and the chemical shifts attributed to impurities (*ca.* 20–25% integrated intensity) were consistent with the formation of various aggregates with bridging alkoxyalkylphosphines [*i.e.*  $[\text{TiCl}(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2)_2\text{ClRh}(\mu : \eta^1, \eta^1\text{-PPh}_2\text{CH}_2\text{-CMe}_2\text{O})]_n$ ].

Since **2** or any oligomeric variant could be a useful precursor to the desired heterobinuclear metal–metal bonded species, the red powder was reduced with 2 equiv. of Na/Hg in thf for 10 h at 25 °C. After separation from the salt and Hg, the resulting red–orange solid was dissolved in thf and chromatographed on basic alumina (activity I). The solid generated upon removal of thf was dissolved in toluene (60 °C) and crystallized at –78 °C to afford deep red  $\text{Ti}(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2)_3\text{Rh}$  **3**† as a C<sub>7</sub>H<sub>8</sub> solvate in 24% overall yield. Reactivity studies implicated a robust titanium–rhodium bond: (i) no reaction with H<sub>2</sub> (10 equiv.) was observed upon heating in C<sub>6</sub>D<sub>6</sub> at 140 °C for 2

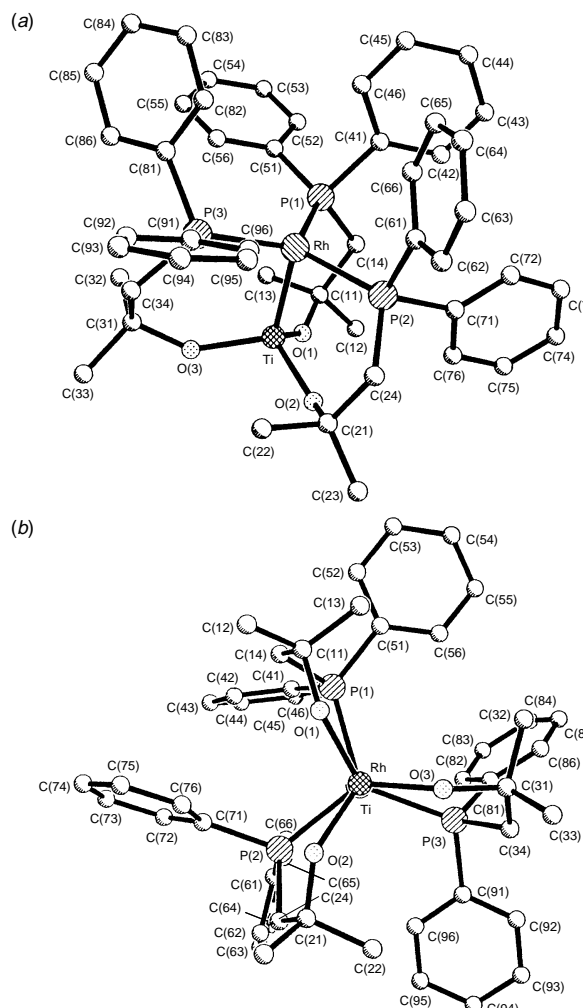
weeks (sealed tube); (ii) reversible formation of a CO adduct,  $\text{Ti}(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2)_3\text{RhCO}$  **4**† was noted [ $\nu(\text{CO})$  1956 cm<sup>–1</sup>] and (iii) within 12 h, 2 equiv. of HCl converted **3** to precursor **2**, generating H<sub>2</sub> and a significant amount of impurities (*ca.* 50%) in the process.

An X-ray crystallographic investigation of  $\text{Ti}(\mu : \eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2)_3\text{Rh} \cdot 0.5\text{C}_7\text{H}_8$ , **3**·0.5C<sub>7</sub>H<sub>8</sub>, revealed a C<sub>3</sub> symmetry for the O<sub>3</sub>TiRhP<sub>3</sub> core of **3** [dihedral angle OTiRhP<sub>av</sub> 15.8(20)°] that is broken when the external framework is included (Fig. 1). The OCCP bridge conformations adjust to maximize the number of favourable edge-to-face phenyl–phenyl interactions, thereby skewing the periphery.<sup>10</sup> A distorted trigonal monopyramidal geometry is evident for Rh, with Ti positioned apically and P–Rh–P angles of 113.22(5), 120.59(5) and 124.18(5)° describing an equatorial plane approximately perpendicular to the TiRh vector [Ti–Rh–P(1–3) 96.29(5), 89.72(5), 97.30(5)°]. The Ti center is roughly tetrahedral [O–Ti–O 107.7(2), 109.8(2), 112.4(2)°; O–Ti–Rh<sub>av</sub> 108.9(5)°] and the titanium–oxygen [ $d(\text{Ti–O})_{\text{av}}$  1.830(3) Å] and rhodium–phosphine bond lengths [ $d(\text{Rh–P})_{\text{av}}$  2.319(3) Å] are normal.

The titanium–rhodium bond distance of 2.2142(11) Å characterizes an extremely short heterobimetallic metal–metal bond. When compared to the sum of Ti (1.324 Å) and Rh covalent radii, the 0.362 Å reduction in bond length represents a large deviation (FSR = 0.860)<sup>11</sup> that supports formulation of a  $\text{Ti} \equiv \text{Rh}$  bond comprised of one  $\text{Ti}(\text{d}/\text{p}_\sigma)\text{--Rh}(\text{d}/\text{p}_\sigma)$  and two  $\text{Rh}(\text{d}_\pi) \rightarrow \text{Ti}(\text{d}/\text{p}_\pi)$  interactions. This appraisal is in accord with our EHMO investigations of  $\text{Cp}^*\text{Zr}(\mu : \eta^1, \eta^1\text{-OCH}_2\text{PPh}_2)_2\text{RhMe}_2$ ,<sup>5</sup> and more recent Fenske–Hall calculations



Scheme 1



**Fig. 1** Side (a) and Ti-Rh parallel (b) views of  $\text{Ti}(\mu:\eta^1, \eta^1\text{-OCMe}_2\text{CH}_2\text{PPh}_2)_3\text{Rh}$  **3**. Selected (see text) interatomic distances (Å) and angles (°): Ti-Rh 2.2142(11), Ti-O(1) 1.833(4), Ti-O(2) 1.831(4), Ti-O(3) 1.827(4), Rh-P(1) 2.318(2), Rh-P(2) 2.316(2), Rh-P(3) 2.322(2); O(1)-Ti-Rh 109.5(1), O(2)-Ti-Rh 108.5(1), O(3)-Ti-Rh 108.9(1), Ti-O(1)-C(11) 143.8(3), Ti-O(2)-C(21) 137.9(4), Ti-O(3)-C(31) 144.1(3), O(1)-C(11)-C<sub>av</sub> 108.3(14), O(2)-C(21)-C<sub>av</sub> 109.0(25), O(3)-C(31)-C<sub>av</sub> 108.4(12), (O)C-C-P<sub>av</sub> 117.3(25), O(1)-Ti-Rh-P(1) 17.5(2), O(2)-Ti-Rh-P(2) 13.7(2), O(3)-Ti-Rh-P(3) 16.2(2).

on models of  $\{\text{MeC}(\text{CH}_2\text{NSiMe}_3)_3\}\text{MFe}(\text{CO})_2\text{Cp}$  (M = Ti, Sn) by Gade and coworkers.<sup>7</sup> While it is difficult to assess the influence of the alkoxyalkylphosphine bridges on  $d(\text{Ti-Rh})$ , none of the bond angles and distances are characteristically strained while imparting the desired cylindrical symmetry.

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## Footnotes and References

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† *Selected analytical data*: **1** ( $\text{C}_6\text{D}_6$ ),  $\delta_{\text{H}}$  1.46 (6 H, s,  $\text{CH}_3$ ), 2.63 (2 H, d,  $J_{\text{PH}}$  3.2 Hz,  $\text{PCH}_2$ ), 7.01–7.09 (6 H, m, Ph), 7.50 (4 H, td,  $J$  7.5, 1.8 Hz, Ph);  $\delta_{\text{C}}$  32.08 (d,  $J_{\text{PH}}$  7.6 Hz,  $\text{CH}_3$ ), 45.70 (d,  $J_{\text{PH}}$  16.8 Hz,  $\text{PCH}_2$ ), 88.44 (d,  $J_{\text{PH}}$  18.3 Hz, OC), 129.04 (d,  $J$  2.2 Hz, *m*-Ph), 129.12 (s, *p*-Ph), 133.75 (d,  $J_{\text{PH}}$  19.1 Hz, *o*-Ph), 140.44 (d,  $J_{\text{PH}}$  12.3 Hz, *ipso*-Ph);  $\delta_{\text{P}}$  –24.19 (s). **2** (major,  $\text{C}_6\text{D}_6$ ),  $\delta_{\text{H}}$  1.64 (12 H, br s,  $\text{CH}_3$ ), 1.71 (6 H, br s,  $\text{CH}_3$ ), 2.77 (4 H, br d,  $J_{\text{PH}}$  10 Hz,  $\text{PCH}_2$ ), 3.07 (2 H, br d,  $J_{\text{PH}}$  2 Hz,  $\text{PCH}_2$ ), 6.62–6.93 (12 H, m, Ph), 6.95–7.10 (6 H, m, Ph), 7.34–7.54 (8 H, m, Ph), 7.67–7.80 (4 H, m, Ph);  $\delta_{\text{C}}$  –17.3 (1 P, br s,  $\nu_{1/2}$  450 Hz, free  $\text{Ph}_2\text{P}$ ), 48 (2 P, br s,  $\nu_{1/2}$  1300 Hz, bound  $\text{Ph}_2\text{P}$ ); (–80 °C,  $\text{C}_7\text{D}_8$ );  $\delta_{\text{P}}$  52.17 (2 P, br m,  $J_{\text{RHP}}$  200 Hz, bound  $\text{Ph}_2\text{P}$ ), 56.42 (1 P, br m,  $J_{\text{RHP}}$  180 Hz, bound  $\text{Ph}_2\text{P}$ ). **3** ( $\text{C}_6\text{D}_6$ ),  $\delta_{\text{H}}$  1.40 (18 H, s,  $\text{CH}_3$ ), 3.07 (6 H, br s,  $\text{PCH}_2$ ), 6.94–6.97 (18 H, m, Ph), 7.26 (12 H, m, Ph);  $\delta_{\text{C}}$  34.83 (s,  $\text{CH}_3$ ), 45.22 (dd,  $J$  16.5, 8.8 Hz,  $\text{PCH}_2$ ), 77.96 (dd,  $J$  3.8, 3.0 Hz, OC), 128.32 (s, Ph), 128.51 (s, Ph), 133.17 (dd,  $J$  10.7, 5.3, *o*-Ph), 141.76 (ddd,  $J$  18.3, 11.1, 3.4, *ipso*-Ph);  $\delta_{\text{P}}$  24.13 (d,  $J_{\text{RHP}}$  208 Hz); UV–VIS (thf), 310 nm ( $\epsilon$  12,100  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ); Anal. Calc. for  $\text{C}_{48}\text{H}_{54}\text{O}_3\text{P}_3\text{TiRh}$ : C, 63.85; H, 6.03. Found: C, 63.45; H, 5.98%. **4** ( $\text{C}_6\text{D}_6$ )  $\delta_{\text{H}}$  1.31 (18 H, s,  $\text{CH}_3$ ), 3.53 (6 H, br s,  $\text{PCH}_2$ ), 6.92–7.11 (18 H, m, Ph), 7.48–7.68 (12 H, m, Ph);  $\delta_{\text{P}}$  17.6 (d,  $J_{\text{RHP}}$  177 Hz).

‡ *Crystallographic data*:  $\text{3-0.5C}_7\text{H}_8$ : monoclinic, space group  $P2_1/c$ ,  $a = 13.899(2)$ ,  $b = 14.527(2)$ ,  $c = 24.016(3)$  Å,  $\beta = 96.040(10)^\circ$ ,  $U = 4822.2(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 293(2)$  K,  $\mu = 0.648 \text{ mm}^{-1}$ , 6308 independent reflections,  $R_1 = 0.0783$ ,  $wR_2 = 0.1297$ . CCDC 182/612.

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