## Ti( $\mu$ : $\eta^1$ , $\eta^1$ -OCMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>Rh has a cylindrically symmetric triple bond

## LeGrande M. Slaughter and Peter T. Wolczanski\*

Cornell University, Baker Laboratory, Department of Chemistry, Ithaca, New York, USA 14853

The cylindrical symmetry of Ti( $\mu: \eta^1, \eta^1$ -OCMe<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>)<sub>3</sub>Rh permits maximum Rh(d<sub> $\pi$ </sub>)  $\rightarrow$  Ti(d/p<sub> $\pi$ </sub>) overlap, resulting in a 2.2142(11) Å metal–metal triple bond.

Aspects of heterogeneous materials exhibiting the strong metalsupport 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  $Cp*Zr(\mu:\eta^1,\eta^1-OCH_2PPh_2)_2RhMe_2$  ( $Cp* = \eta^5-C_5Me_5$ ) 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, Cp(HO)<sub>2</sub>ZrRh(PH<sub>3</sub>)<sub>2</sub>Me<sub>2</sub>.<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 Rh(d<sub> $\pi$ </sub>)  $\rightarrow$  Zr(d<sub> $\pi$ </sub>) 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.5,7,8

Treatment of  $TiCl_4(thf)_2$  with 3 equiv. of LiOC-Me<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub><sup>4</sup> in benzene at 25 °C for 3 h afforded (Ph2PCH2CMe2O)3TiCl 1<sup>†</sup> as a viscous, clear yellow oil in 80% yield. Although 1 was typically contaminated with ca. 5% HOCMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, this was of sufficient purity to continue. Upon stirring a benzene solution of tris(alkoxyphosphine)titanium chloride 1 and 0.5 equiv. of [RhCl(cod)]29 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  ${}^{31}P{}^{1}H{}$  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  $ClTi(\mu:\eta^1,\eta^1-OC-$ Me<sub>2</sub>CH<sub>2</sub>Ph<sub>2</sub>P)<sub>3</sub>RhCl (2, Scheme 1),† but suggest that dimeriza- $[ClTi(OCMe_2CH_2Ph_2P)(\mu:\eta^1,\eta^1-OCMe_2CH_2$ tion to  $Ph_2P)_2Rh]_2(\mu\text{-}Cl)_2$  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.  $[TiCl(\mu:\eta^1,\eta^1-OCMe_2CH_2Ph_2P)_2ClRh(\mu:\eta^1,\eta^1-PPh_2CH_2 CMe_2O)]_n$ .

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  $Ti(\mu : \eta^1, \eta^1-OCMe_2CH_2Ph_2P)_3Rh$  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,  $Ti(\mu:\eta^1,\eta^1-OCMe_2CH_2Ph_2P)_3RhCO$  **4**<sup>†</sup> was noted [ $\nu$ (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 crystallograpic investigation of  $Ti(\mu : \eta^1, \eta^1-OC Me_2CH_2Ph_2P)_3Rh\cdot 0.5C_7H_8$ ,  $3\cdot 0.5C_7H_8$ , revealed a  $C_3$  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 phenylphenyl 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>  $108.9(5)^{\circ}$  and the titanium-oxygen [ $d(Ti-O)_{av} 1.830(3)$  Å] and rhodium-phosphine bond lengths [d(Rh-P)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 Ti=Rh bond comprised of one Ti(d/p<sub> $\sigma$ </sub>)-Rh(d/p<sub> $\sigma$ </sub>) and two Rh(d<sub> $\pi$ </sub>)  $\rightarrow$  Ti(dTp<sub> $\pi$ </sub>) interactions. This appraisal is in accord with our EHMO investivations of Cp\*Zr( $\mu$ : $\eta$ <sup>1</sup>, $\eta$ <sup>1</sup>-OCH<sub>2</sub>PPh<sub>2</sub>)RhMe<sub>2</sub>,<sup>5</sup> and more recent Fenske-Hall calculations



Chem. Commun., 1997 2109



**Fig. 1** Side (*a*) and Ti–Rh parallel (*b*) views of Ti( $\mu$ : $\eta^1$ , $\eta^1$ -OC-Me<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>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  $\{MeC(CH_2NSiMe_3)_3\}MFe(CO)_2Cp (M = Ti, Sn)$  by Gade and coworkers.<sup>7</sup> While it is difficult to assess the influence of the alkoxyalkylphosphine bridges on *d*(Ti–Rh), none of the bond angles and distances are characteristically strained while imparting the desired cylindrical symmetry.

We thank the National Science Foundation and Cornell University for support of this research, and Emil B. Lobkovsky for experimental assistance in the X-ray crystallographic study.

## **Footnotes and References**

## \* E-mail: ptwz@cornell.edu

 $\dagger$  Selected analytical data: 1 (C<sub>6</sub>D<sub>6</sub>),  $\delta_{\rm H}$  1.46 (6 H, s, CH<sub>3</sub>), 2.63 (2 H, d,  $J_{\rm PH}$ 3.2 Hz, PCH<sub>2</sub>), 7.01–7.09 (6 H, m, Ph), 7.50 (4 H, td, J 7.5, 1.8 Hz, Ph);  $\delta_{\rm C}$ 32.08 (d, J<sub>PH</sub> 7.6 Hz, CH<sub>3</sub>), 45.70 (d, J<sub>PH</sub> 16.8 Hz, PCH<sub>2</sub>), 88.44 (d, J<sub>PH</sub> 18.3 Hz, OC), 129.04 (d, J 2.2 Hz, m-Ph), 129.12 (s, p-Ph), 133.75 (d, J<sub>PH</sub> 19.1 Hz, o-Ph), 140.44 (d, J<sub>PH</sub> 12.3 Hz, *ipso*-Ph); δ<sub>P</sub> -24.19 (s). 2 (major, C<sub>6</sub>D<sub>6</sub>),  $\delta_{\rm H}$  1.64 (12 H, br s, CH<sub>3</sub>), 1.71 (6 H, br s, CH<sub>3</sub>), 2.77 (4 H, br d,  $J_{\rm PH}$  10 Hz, PCH<sub>2</sub>), 3.07 (2 H, br d,  $J_{\rm PH}$  2 Hz, PCH<sub>2</sub>), 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);  $\delta_{\rm P}$ 17.3 (1 P, br s, v<sub>1/2</sub> 450 Hz, free Ph<sub>2</sub>P), 48 (2 P, br s, v<sub>1/2</sub> 1300 Hz, bound Ph<sub>2</sub>P); (-80 °C, C<sub>7</sub>D<sub>8</sub>); δ<sub>P</sub> 52.17 (2 P, br m, J<sub>RhP</sub> 200 Hz, bound Ph<sub>2</sub>P), 56.42 (1 P, br m, J<sub>RhP</sub> 180 Hz, bound Ph<sub>2</sub>P). **3** (C<sub>6</sub>D<sub>6</sub>), δ1.40 (18 H, s, CH<sub>3</sub>), 3.07 (6 H, br s, PCH<sub>2</sub>), 6.94–6.97 (18 H, m, Ph), 7.26 (12 H, m, Ph);  $\delta_{\rm C}$ 34.83 (s, CH<sub>3</sub>), 45.22 (dd, J 16.5, 8.8 Hz, PCH<sub>2</sub>), 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);  $\delta_{\rm P}$  24.13 (d,  $J_{\rm RhP}$  208 Hz); UV–VIS (thf), 310 nm ( $\varepsilon$  12,100 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>); Anal. Calc. for C<sub>48</sub>H<sub>54</sub>O<sub>3</sub>P<sub>3</sub>-TiRh·0.5C<sub>7</sub>H<sub>8</sub>. C, 63.85; H, 6.03. Found: C, 63.45; H, 5.98%. 4 (C<sub>6</sub>D<sub>6</sub>)  $\delta_{\rm H}$ 1.31 (18 H, s, CH<sub>3</sub>), 3.53 (6 H, br s, PCH<sub>2</sub>), 6.92-7.11 (18 H, m, Ph), 7.48–7.68 (12 H, m, Ph);  $\delta_{\rm P}$  17.6 (d,  $J_{\rm RhP}$  177 Hz).

<sup>‡</sup> Crystallograpic data: **3**0.5C<sub>7</sub>H<sub>8</sub>: monoclinic, space group  $P_{2_1/c}$ , 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,  $\mu = 0.648$  mm<sup>-1</sup>, 6308 independent reflections,  $R_1 = 0.0783$ ,  $wR_2 = 0.1297$ . CCDC 182/612.

- Strong Metal–Support Interactions, ed. R. T. K. Baker, S. J. Tauster and J. A. Dumesic, ACS Symp. Ser. 298, American Chemical Society, Washington, DC, 1986; S. J. Tauster, Acc. Chem. Res., 1987, 20, 389.
- 2 G. S. Ferguson and P. T. Wolczanski, Organometallics, 1985, 4, 1601.
- 3 S. M. Baxter, G. S. Ferguson and P. T. Wolczanski, J. Am. Chem. Soc., 1988, 110, 4231.
- 4 S. M. Baxter and P. T. Wolczanski, Organometallics, 1990, 9, 2498.
- 5 G. S. Ferguson, P. T. Wolczanski, L. Párkányi and M. C. Zonnevylle, Organometallics, 1988, 7, 1967.
- W. J. Sartain and J. P. Selegue, Organometallics, 1989, 8, 2153;
  W. J. Sartain and J. P. Selegue, Organometallics, 1989, 6, 1812;
  W. J. Sartain and J. P. Selegue, J. Am. Chem. Soc., 1985, 107, 5818.
- S. Friedrich, H. Memmler, L. H. Gade, W.-S. Li, I. J. Scowen, M. McPartlin and C. E. Housecroft, *Inorg. Chem.*, 1996, **35**, 2433;
   S. Friedrich, L. H. Gade, I. J. Scowen and M. McPartlin, *Organometallics*, 1995, **14**, 5344;
   S. Friedrich, L. H. Gade, I. J. Scowen and M. McPartlin, *Agnew. Chem., Int. Ed. Engl.*, 1996, **35**, 1338.
- 8 D. Selent, R. Beckhaus and J. Pickardt, *Organometallics*, 1993, 12, 2857; G. Schmid, B. Stutte and R. Boese, *Chem. Ber.*, 1978, 111, 1239.
- 9 G. Giordano and R. H. Crabtree, Inorg. Synth., 1990, 28, 88.
- 10 C. A. Hunter, *Chem. Soc. Rev.*, 1994, **23**, 101; C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525.
- 11 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, New York, 2nd edn., 1993; L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.

Received in Bloomington, IN, USA, 9th July 1997; 7/04890D

2110 Chem. Commun., 1997