

## Supplementary Information for B211289M

---

### A quasi-covalent metal-metal bond in an early-late heterobimetallic Ti-Pt complex stabilized by bridging and chelating phosphinoenolate ligands.

---

**Pierre Braunstein,<sup>\*a</sup> Xavier Morise,<sup>a</sup> Marc Bénard,<sup>b</sup> Marie-Madeleine Rohmer,<sup>b</sup> and Richard Welter<sup>c</sup>**

<sup>a</sup> *Laboratoire de Chimie de Coordination, UMR CNRS 7513, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France. E-mail : braunst@chimie.u-strasbg.fr*

<sup>b</sup> *Laboratoire de Chimie Quantique, UMR CNRS 7551, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France.*

<sup>c</sup> *Laboratoire DECMET, UMR CNRS 7513, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France.*

---

#### Synthesis.

All reactions were carried out under an inert atmosphere of nitrogen, using Schlenk line techniques.

**Complex 2.** In the <sup>1</sup>H NMR spectrum, the Cp protons give rise to a singlet at  $\delta$  6.36 ppm and a doublet was observed for the enolate protons at  $\delta$  5.69 ppm (<sup>2</sup>J<sub>PH</sub> = 5 Hz). Its IR spectrum (CH<sub>2</sub>Cl<sub>2</sub>) contains a strong absorption at 1534 cm<sup>-1</sup>, assigned to the  $\nu_{\text{C}=\text{O}}$  +  $\nu_{\text{C}=\text{C}}$  vibration.

**Complex 3.** Reaction of **2** (0.280 g, 0.36 mmol) with [Mo(CO)<sub>4</sub>(NBD)] (0.110 g, 0.36 mmol) in Et<sub>2</sub>O (20 mL) for 36 h, afforded complex **3** as an orange precipitate, which was filtered, washed with pentane (15 mL) and dried in vacuo (0.170 g, 49% yield). IR (Nujol, cm<sup>-1</sup>): 1545m,  $\nu_{\text{C}=\text{C}}$  +  $\nu_{\text{C}=\text{O}}$ , 1858m, 1898s, 1925s, 2022s ( $\nu_{\text{CO}}$ ); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  13.2; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  5.62 (s, 10H, Cp), 5.49 (d, 2H, OCH, <sup>2</sup>J<sub>PH</sub> 0.7 Hz). Anal. Calcd for C<sub>54</sub>H<sub>42</sub>MoO<sub>6</sub>P<sub>2</sub>Ti: C, 65.34; H, 4.26. Found: C, 64.96; H, 4.61.

Complex **5**. Freshly distilled  $\text{CH}_2\text{Cl}_2$  (15 mL) was added at room temperature to solid **2** (1.250 g, 1.59 mmol) and  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  (1.190 g, 1.59 mmol). The reaction mixture was stirred for 3 h, after which the colour turned khaki. After removal of the volatiles under reduced pressure, the residue was washed with  $\text{Et}_2\text{O}$  (2 x 15 mL) (to eliminate side-products amongst which **4b** was identified) and hexane (2 x 20 mL), to afford **5** as an air- and moisture-sensitive, apple green, solid (1.21 g, 77% yield). X-ray quality crystals of **5** were grown by slow diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution at  $-20\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  7.85-6.72 (m, 30H, aromatics), 6.41 (s, 10H, Cp), 5.31 (d,  $^2J_{\text{PH}} = 15.7$  Hz, CH in chelate), 5.16 (d,  $^2J_{\text{PH}} = 0.9$  Hz, CH in bridge).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  56.1 (s,  $^1J_{\text{PtP}} = 1053$  Hz), -5.1 (s,  $^1J_{\text{PtP}} = 4805$  Hz). MS ( $m/z$ ): 980 ( $\text{M}^{++}\text{H}$ , 25), 915 ( $\text{M}^{++}\text{H-Cp}$ , 6), 804 (100), 676 ( $\text{M}^+\text{-Cp-Ph}_2\text{PCHC(Ph)O}$ , 30). Anal. Calcd for  $\text{C}_{50}\text{H}_{42}\text{O}_2\text{P}_2\text{PtTi}$ : C, 61.29; H, 4.32. Found: C, 61.35; H, 4.28.

#### Crystal data of **5**.

Nonius Kappa-CCD area detector diffractometer ( $\text{MoK}\alpha$ ,  $\lambda = 0.71073\text{ \AA}$ ). Yellow crystal, dimensions:  $0.15 \times 0.12 \times 0.10\text{ mm}^3$ ;  $\text{C}_{50}\text{H}_{42}\text{O}_2\text{P}_2\text{PtTi} \cdot 2\text{CH}_2\text{Cl}_2$ ;  $M = 1145.59\text{ g}\cdot\text{mol}^{-1}$ ; triclinic, space group  $P-1$ ;  $a = 11.963(2)\text{ \AA}$ ;  $b = 15.433(3)\text{ \AA}$ ;  $c = 16.420(4)\text{ \AA}$ ;  $\alpha = 65.10(1)^\circ$ ;  $\beta = 81.43(1)^\circ$ ;  $\gamma = 86.04(1)^\circ$ ;  $Z = 2$ ;  $D_c = 1.379\text{ g}\cdot\text{cm}^{-3}$ ;  $\mu(\text{MoK}\alpha) = 3.007\text{ mm}^{-1}$ ; a total of 12350 reflections (Denzo software);  $3.05^\circ < \theta < 27.39^\circ$ , 12253 independent reflections with 7873 having  $I > 2\sigma(I)$ ; 577 parameters; final results:  $R(F) = 0.0696$ ;  $R_w(F) = 0.01844$ ,  $\text{GOF} = 1.030$ , maximum residual electronic density =  $1.499\text{ e}\cdot\text{\AA}^{-3}$ . The cell parameters were determined from reflections taken from one set of ten frames ( $1.0^\circ$  steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against  $F^2$  using the SHELXL97 software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. Disorder was observed at C(51) and C(53) atoms ( $\text{CH}_2\text{Cl}_2$  molecules) where multiple positions of Cl atoms have been considered. The C-Cl distances have been fixed at  $1.77\text{ \AA}$ . Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n $^\circ$  CCDC 197745. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). See

<http://www.rsc.org/suppdata/cc/b2/b211289m> for crystallographic data in CIF or other electronic format.

*Structural comments.* The Cp ligands make an angle of 19.3(2) and 22.1(2)° with the Pt, Ti, O(1) plane. The Pt-Ti and Ti-O(1) bonds make an angle of *ca.* 58 and 41° with the plane passing through the Cp centroids and Ti. The dihedral angle between the mean planes containing Ti, Pt, P(1) and the O(2), Pt, P(2) atoms is 4.40°.

**Table S1:** Atomic parameters used for the extended Hückel calculations

Atom	s shell		p shell		d shell			
	$H_{ii}$ (eV)	Exponent $\zeta$	$H_{ii}$ (eV)	Exponent $\zeta$	$H_{ii}$ (eV) $\zeta_1$	Exponents <sup>a</sup> $\zeta_2$		
H	-13.4	1.3						
C	-21.4	1.625	-11.4	1.625				
O	-32.3	2.275	-14.8	2.275				
P	-18.6	1.6	-14.0	1.6				
Ti	-8.97	1.075	-5.44	0.675	-10.81	4.55 (0.4206)	1.4 (0.7839)	
Pt	-9.077	2.554	-5.475	2.554	-12.59	6.013 (0.6334)	2.696 (0.5513)	

<sup>a</sup> Two Slater orbitals are listed for valence d functions. Each is followed in parenthesis by the coefficients in the double zeta expansion.