

## Electronic Supplementary Infomation

### Unprecedented Reversible Coupling of Alkynyl and Phosphide ligands on a Dinuclear Platinum Framework

**Alberto Albinati,<sup>a</sup> Valeria Filippi,<sup>b</sup> Piero Leoni,<sup>\*b</sup> Lorella Marchetti,<sup>b</sup> Marco Pasquali<sup>b</sup> and Vincenzo Passarelli<sup>b</sup>**

<sup>a</sup> Dipartimento di Chimica Strutturale e Stereochemica Inorganica (DCSSI) e Facoltà di Farmacia, Università di Milano, Via Venezian 21, I-20133 Milano, Italy

<sup>b</sup> Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy. Fax: 39 050 2219246; tel: 39 050 2219217; e-mail: leoni@dcci.unipi.it

#### [Pt<sub>2</sub>(μ-P'<sup>t</sup>Bu<sub>2</sub>) {μ,η<sup>1</sup>:η<sup>2</sup>-C(Ph)CH<sub>2</sub>} (C≡C-Ph)(CO)(PH'<sup>t</sup>Bu<sub>2</sub>)(Br)] (3)

Anal. Calcd. for C<sub>33</sub>H<sub>49</sub>BrOP<sub>2</sub>Pt<sub>2</sub>: C, 39.9; H, 5.0. Found: C, 40.1; H, 5.1. δ<sub>H</sub> (C<sub>6</sub>D<sub>6</sub>, 298 K): 8–7 (10H, phenyl), 4.76 (s, 1H, CH), 4.48 (dd, 1H, PH, <sup>1</sup>J<sub>PH</sub> = 345.2 Hz, <sup>3</sup>J<sub>HP</sub> = 4.0 Hz), 4.23 (t, 1H, CH, <sup>3</sup>J<sub>HP</sub> = 11.6 Hz), 1.56 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 15.2 Hz), 1.43 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 14.4 Hz), 1.34 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 14.0 Hz), 0.79 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 14.6 Hz). δ<sub>P</sub> (C<sub>6</sub>D<sub>6</sub>, 298 K): 35.3 (<sup>1</sup>J<sub>P2Pt1</sub> = 1865 Hz, <sup>2</sup>J<sub>P1P2</sub> = 329 Hz, <sup>3</sup>J<sub>P2Pt2</sub> = 35 Hz), -30.5 (<sup>1</sup>J<sub>P1Pt1</sub> = 2347 Hz, <sup>1</sup>J<sub>P1Pt2</sub> = 2107 Hz, <sup>2</sup>J<sub>P1P2</sub> = 329 Hz). δ<sub>Br</sub> (C<sub>6</sub>D<sub>6</sub>, 298 K): -4187.5 (<sup>1</sup>J<sub>Pt2P1</sub> = 2107 Hz, <sup>3</sup>J<sub>Pt2P2</sub> = 35 Hz), -4255.5 (<sup>1</sup>J<sub>P1Pt1</sub> = 2347 Hz, <sup>1</sup>J<sub>P2Pt1</sub> = 1865 Hz). IR (nujol mull): ν<sub>CO</sub> = 2064 cm<sup>-1</sup>.

#### [Pt<sub>2</sub>(μ-κP:η<sup>2</sup>-P'<sup>t</sup>Bu<sub>2</sub>-C≡C-Ph){μ,η<sup>1</sup>:η<sup>2</sup>-C(Ph)CH<sub>2</sub>} (CO)(P'<sup>t</sup>Bu<sub>2</sub>H)][PF<sub>6</sub>] {4[PF<sub>6</sub>]}

Anal. Calcd. for C<sub>33</sub>H<sub>49</sub>F<sub>6</sub>OP<sub>3</sub>Pt<sub>2</sub>: C, 37.4, H, 4.7. Found: C, 37.7; H, 4.7. δ<sub>H</sub> (CDCl<sub>3</sub>, 298 K): 7.1–6.5 (10H, phenyl), 4.22 (d, 1H, PH, <sup>1</sup>J<sub>HP</sub> = 363 Hz), 4.07 (s, 1H, CH), 4.03 (s, 1H, CH), 1.49 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 18.2 Hz), 1.36 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 18.2 Hz), 1.07 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 16 Hz), 0.85 (d, 9H, CH<sub>3</sub>, <sup>3</sup>J<sub>HP</sub> = 16.2 Hz). δ<sub>P</sub> (CDCl<sub>3</sub>, 298 K): 64.2 (d, <sup>3</sup>J<sub>P1P2</sub> = 15 Hz, <sup>1</sup>J<sub>P1Pt2</sub> = 3885 Hz, <sup>2</sup>J<sub>P1Pt1</sub> = 138 Hz), 26.2 (d, <sup>1</sup>J<sub>P2Pt1</sub> = 2916 Hz, <sup>2</sup>J<sub>P2Pt2</sub> = 228 Hz, <sup>3</sup>J<sub>P1P2</sub> = 15 Hz), -137.0 (sp, <sup>1</sup>J<sub>PF</sub> = 707 Hz). δ<sub>Br</sub> (CDCl<sub>3</sub>, 298 K): -5427.4 (dd, <sup>2</sup>J<sub>Pt2P2</sub> = 228 Hz, <sup>1</sup>J<sub>Pt2P1</sub> = 3885 Hz), -5444.1 (dd, <sup>1</sup>J<sub>Pt1P2</sub> = 2916 Hz, <sup>2</sup>J<sub>Pt1Pt1</sub> = 138 Hz). IR (nujol mull): ν<sub>CO</sub> = 2067 cm<sup>-1</sup>.