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### Preliminary communication

## The metallophosphine $\text{Ph}_2\text{PW}(\text{CO})_3\text{Cp}$ as precursor of the “ $\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}$ ” fragment; its ethylene-like displacement from its complexes with platinum(0)

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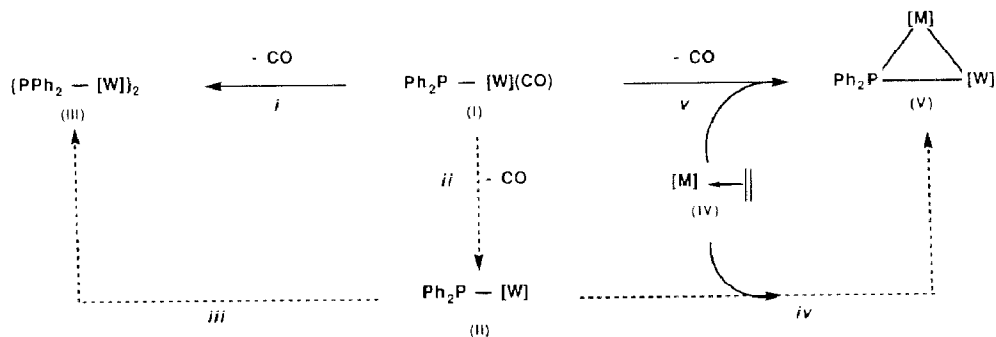
### Abstract

The metallophosphine  $\text{Ph}_2\text{PW}(\text{CO})_3\text{Cp}$  displaces ethylene from the platinum(0) complexes  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ , allowing the synthesis of the new heterometallic complexes  $[\text{Pt}\{\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}\}_2(\text{CO})]$  (*2W-Pt*) (**3**) and  $[\text{Pt}\{\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}\}(\text{PPh}_3)_2]$  (*W-Pt*) (**4a**). One of the  $\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}$  groups of **3** can be replaced by a phosphine ligand to afford **4** and  $[\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}]_2$ .

The current interest in the chemistry of heterometallic compounds containing phosphido bridges as assembling ligands [1] has stimulated the development of general methods for the rational synthesis of such compounds. Metallophosphines of the type  $\text{Ph}_2\text{P}-[\text{M}]$  ( $[\text{M}] = \text{W}(\text{CO})_3\text{Cp}$ ,  $\text{Mo}(\text{CO})_3\text{Cp}$  [2],  $\text{Ru}(\text{CO})_2\text{Cp}$  [3a],  $\text{Fe}(\text{CO})_2\text{Cp}$  [3],  $\text{Co}(\text{CO})_4$  [4]) have sometimes been employed for their synthesis [5]. We present here preliminary results on the use of the metallophosphine  $[\text{Ph}_2\text{PW}(\text{CO})_3\text{Cp}]$  for the stepwise synthesis of phosphido-bridged heterometallic complexes of platinum.

The metallophosphine I (see Scheme 1) is easily prepared [2] by the reaction between  $\text{Na}[\text{CpW}(\text{CO})_3]$  and  $\text{Ph}_2\text{PCl}$  or that between  $[\text{CpW}(\text{CO})_3\text{Cl}]$  and  $\text{Li}[\text{PPh}_2]$ . It decomposes readily with CO evolution (see Scheme 1, *i*) to produce the dinuclear species III [2]. This process may be formally considered to involve the intermediate formation of the hypothetical terminal phosphido species II (see Scheme 1, *ii*), which would dimerize to form III (see Scheme 1, *iii*). On the other hand, a heterometallic complex of type V can be viewed as containing a fragment II coordinated to a metal centre [M] in a manner reminiscent of ethylene coordination in IV. In fact, the isolobal analogy between fragment II and ethylene is well established [6,7].

Our purpose was to know whether the metallophosphine I could be used as a precursor for this fragment and displace the labile ethylene ligand of IV to form V

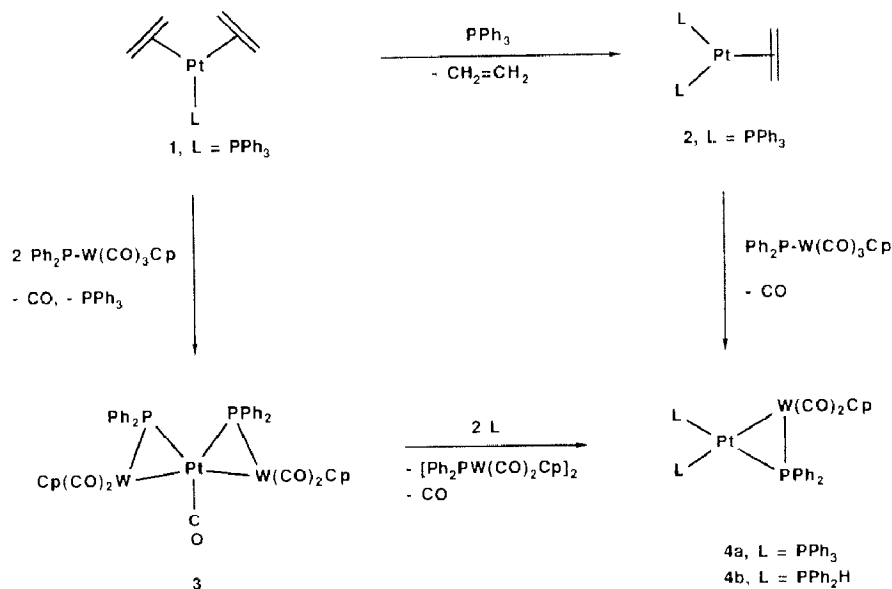


[W] = W(CO)<sub>2</sub>Cp

Scheme 1

(Scheme 1, *iv*, *v*). We have found that the well known ethylene-platinum complexes **1** [8] and **2** [9] do indeed react with Ph<sub>2</sub>PW(CO)<sub>3</sub>Cp in THF, to produce new, orange-red trinuclear (**3**) and the orange dinuclear (**4a**) heterometallic complexes, respectively (Scheme 2). It should be noted that the CO ligand liberated in going from I to II competes with the PPh<sub>3</sub> present, and this accounts for the formation of **3**. Complexes with core structures similar to **3** [7] or **4** [1d] have been recently fully characterized, but the methods of their synthesis were not general and afforded only medium to low yields.

It is well known that controlled addition of PPh<sub>3</sub> to **1** produces **2** by replacement of one molecule of ethylene. Interestingly, we have also found that a fragment (II) and a CO ligand of **3** may be displaced by PPh<sub>3</sub> to produce **4a** and dimer III. This substitution process is very slow but with PPh<sub>2</sub>H in place of PPh<sub>3</sub> it is rapid and selective.



Scheme 2

Complex **4** shows in its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum two resonances for the terminal phosphine ligands and one downfield signal for the bridging phosphido ligand. The P nucleus of the latter ligand shows a large (ca. 200 Hz) and a small (ca. 20 Hz) coupling constant with the *trans*- and *cis*-phosphine ligands, respectively. The coupling between the two *cis*-phosphines was not resolved ( $^2J(\text{PP}) < 10$  Hz).

The expected electron-rich character of the metal–metal bond of complexes **3** and **4** [1d] is being investigated through their reactions with electrophiles. We also have indications that metallophosphines derived from carbonylmetallates of the groups 6, 7 and 8 behave like  $\text{Ph}_2\text{PW}(\text{CO})_3\text{Cp}$ .

### Experimental

Methods and instruments were as described in ref. 1d.

*Preparation of*  $[\text{Pt}\{\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}\}_2(\text{CO})] \cdot \text{C}_7\text{H}_8$  (**3**). To a solution of 0.500 g (0.932 mmol) of  $\text{Na}[\text{W}(\text{CO})_3\text{Cp}] \cdot 2\text{DME}$  [10] in 20 ml of THF at  $-78^\circ\text{C}$  were added 0.932 mmol of  $\text{PPh}_2\text{Cl}$  in 50 ml THF and 0.239 g (0.66 mmol) of  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$  [8]. The mixture was allowed to warm to room temperature (1 h) and the resulting red solution was evaporated to dryness. The residue was extracted with  $2 \times 15$  ml of toluene. After concentration of the solution to 2–3 ml and addition of 40 ml of hexane, 0.470 g (78%) of an orange-red solid separated. This was dried in vacuo and characterized as **3** solvated by one molecule of toluene.

Anal. Found: C, 43.00; H, 3.04.  $\text{C}_{39}\text{H}_{30}\text{O}_5\text{P}_2\text{PtW}_2 \cdot \text{C}_7\text{H}_8$  calc.: C, 42.63; H, 2.96%. IR (KBr)  $\nu(\text{CO})$ : 1976(m), 1922(s), 1908(s), 1849(s), 1830(s)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ : 1989(m), 1920(s), 1844(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, ref. TMS int.):  $\delta$  4.72 (s, 5H, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , ppm, ref.  $\text{H}_3\text{PO}_4$  ext.):  $\delta$  144.8 (s with satellites of Pt and W,  $^1J(\text{P-Pt})$  2124 Hz,  $^1J(\text{P-W})$  325 Hz).

*Preparation of*  $[\text{Pt}\{\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}\}(\text{PPh}_3)_2]$  (**4**). To a solution of 0.169 g (0.315 mmol) of  $\text{Na}[\text{W}(\text{CO})_3\text{Cp}] \cdot 2\text{DME}$  in 10 ml of THF at  $-78^\circ\text{C}$  were added, 0.315 mmol of  $\text{PPh}_2\text{Cl}$  in 50 ml THF and 0.235 g (0.315 mmol) of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  [9]. The solution was stirred overnight, evaporated to dryness and the residue was extracted with toluene. The solvent was evaporated and the solid residue was washed with methanol (10 ml) and hexane (10 ml) and then dried in vacuo, to give an orange solid (0.230 g, 60%).

Anal. Found: C, 54.73; H, 3.88.  $\text{C}_{55}\text{H}_{45}\text{O}_2\text{P}_3\text{PtW}$  calc.: C, 54.60; H, 3.75%. IR (KBr)  $\nu(\text{CO})$ : 1885(s), 1799(s)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ : 1888(s), 1796(s)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ : 1888(s), 1796(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, ref. TMS int.):  $\delta$  4.56 (s, 5H, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , ppm, ref.  $\text{H}_3\text{PO}_4$  ext.):  $\delta$  149.8 (dd with Pt and W satellites, 1P,  $\text{PPh}_2$ ,  $^2J(\text{P-P}(\text{cis}))$  18 Hz,  $^2J(\text{P-P}(\text{trans}))$  220 Hz,  $^1J(\text{P-Pt})$  2403 Hz,  $^1J(\text{P-W})$  340 Hz), 26.8 (d with Pt satellites, 1P,  $\text{PPh}_3$  *trans* to  $\text{PPh}_2$ ,  $^1J(\text{P-Pt})$  3271 Hz), 16.7 (d with Pt satellites, 1P,  $\text{PPh}_3$  *cis* to  $\text{PPh}_2$ ,  $^1J(\text{P-Pt})$  3290 Hz).

*Preparation of*  $[\text{Pt}\{\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}\}(\text{PPh}_2\text{H})_2]$  (**4b**). To a solution of 0.100 g (0.077 mmol) of **3** in 10 ml of THF was added 0.086 mmol of  $\text{PPh}_2\text{H}$  in 50 ml THF. The solution was stirred for 1 h. The complete transformation to **4b** and  $\{\text{Ph}_2\text{PW}(\text{CO})_2\text{Cp}\}_2$  ( $\delta$   $-63.2$  (s) ppm) was monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The mixture was evaporated to dryness and the residue was extracted with ether. Solid **4b** was obtained from the ether solution, washed with methanol (1 ml) and dried in vacuo.

Anal. Found: C, 48.61; H, 3.67.  $\text{C}_{43}\text{H}_{37}\text{O}_2\text{P}_3\text{PtW}$  calc.: C, 48.83; H, 3.53%. IR

(KBr)  $\nu(\text{CO})$ : 1880(s), 1799(s)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$ : 1874(s), 1797(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm, ref. TMS int.):  $\delta$  4.69 (s, 5H, Cp).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , ppm, ref.  $\text{H}_3\text{PO}_4$  ext.):  $\delta$  145.0 (dd with Pt and W satellites, 1P,  $\text{PPh}_2$ ,  $^2J(\text{P}-\text{P}(\text{cis}))$  18 Hz,  $^2J(\text{P}-\text{P}(\text{trans}))$  208 Hz,  $^1J(\text{P}-\text{Pt})$  2345 Hz,  $^1J(\text{P}-\text{W})$  368 Hz), 3.3 (d with Pt satellites, 1P,  $\text{PPh}_2\text{H trans}$  to  $\text{PPh}_2$ ,  $^1J(\text{P}-\text{Pt})$  3012 Hz), -6.8 (d with Pt satellites, 1P,  $\text{PPh}_2\text{H cis}$  to  $\text{PPh}_2$ ,  $^1J(\text{P}-\text{Pt})$  3213 Hz). From  $^{31}\text{P}$  NMR:  $^1J(\text{PH})$  367 Hz ( $\text{PPh}_2\text{H trans}$ ), 337 Hz ( $\text{PPh}_2\text{H cis}$ ).

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