

# An Unusual Migratory Insertion of CO into a Pentamethylcyclopentadienyl–Platinum Bond

Lyudmila Leontyeva,<sup>†</sup> Russell P. Hughes,<sup>\*,†</sup> and Arnold L. Rheingold<sup>‡</sup>

Departments of Chemistry, 6128 Burke Laboratory, Dartmouth College, Hanover, New Hampshire 03755, and University of California, San Diego, California 92093-0358

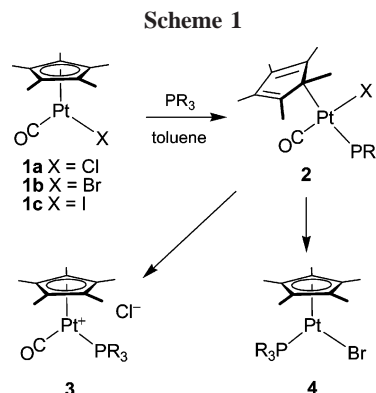
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**Summary:** Instead of undergoing the expected ligand substitution reaction when treated with  $\text{PMe}_3$ , the pentamethylcyclopentadienyl–platinum complex  $\text{Cp}^*\text{Pt}(\text{CO})\text{I}$  (**1c**) adds 2 equiv of phosphine to give the first example of a CO insertion reaction into a transition-metal– $\text{Cp}^*$  bond. The acyl product, *trans*-Pt( $\text{COC}_3\text{Me}_5$ )(I)( $\text{PMe}_3$ )<sub>2</sub> (**5**), has been characterized by single-crystal X-ray diffraction study and appears to be the first reported example of this (cyclopentadienyl)acyl structural motif.

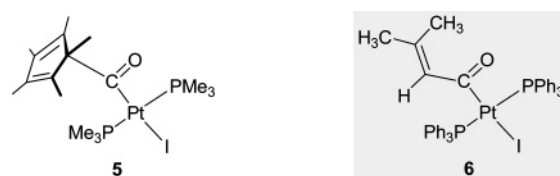
$\eta^5$ -Cyclopentadienyl (Cp) complexes of the transition metals are ubiquitous, and the pentamethylcyclopentadienyl ( $\text{Cp}^*$ ) analogue has also become widely used. For the most part the cyclopentadienyl ligand is a spectator, although ring slippage to  $\eta^3$  and  $\eta^1$  and even complete displacement to give an “ $\eta^0$  ligand” have been observed.<sup>1</sup> However, other than the “tuck-in” complexes resulting from intramolecular C–H bond activation,<sup>2,3</sup> and unusual products arising from dehydrofluorinative coupling with other ligands,<sup>4,5</sup> it is rare that the  $\text{Cp}^*$  ligand engages in chemistry within the coordination sphere. Here we report an unusual migratory insertion reaction of a  $\text{Cp}^*$  ligand to give what appears to be the only crystallographically characterized example of a cyclopentadienyl(carbonyl) structural motif.

Pentamethylcyclopentadienyl compounds of platinum(II) are quite rare. The dimeric carbonyl complex  $[\text{PtCp}^*(\text{CO})]_2$ , reported by Boag in 1988,<sup>6</sup> proved to be a useful source of the mononuclear halo(carbonyl) complexes **1a–c**.<sup>6–8</sup> The reaction of **1a,b** with tertiary phosphines was reported to proceed in toluene solution to give an observable  $\eta^1$ -pentamethylcyclopentadienyl intermediate, **2** [ $\text{PR}_3 = \text{PPh}_2(2\text{-MeOPh})$ ], as shown in Scheme 1, which underwent subsequent halide or CO substitution to give the product **3** or **4**.<sup>7</sup>

Desirous of preparing a  $\text{PMe}_3$  analogue of **4** by carbonyl substitution, we treated the iodide precursor **1c** with  $\text{PMe}_3$  in toluene and discovered that the product was not the expected one. Instead, complex **5** was isolated, arising from incorporation



of two  $\text{PMe}_3$  ligands and a migratory insertion of CO into the  $\text{Cp}^*$ –platinum bond. Attempts to form a monophosphine adduct failed; addition of 1 equiv led only to a mixture of **5** and starting material.



An ORTEP of the molecular structure of **5** is shown in Figure 1, and details of the crystallographic determination are provided in Table 1. Selected bond lengths and angles are presented in Table 2. There are significant deviations from planarity around Pt, and even though the individual angles between adjacent ligands C(1)–Pt(1)–P(1) 92.92(8)°, C(1)–Pt(1)–P(2) 90.46(8)°, P(1)–Pt(1)–I(1) 89.51(2)°, and P(2)–Pt(1)–I(1) 90.26(2)° do not differ dramatically from 90°, the angles between mutually trans-ligand pairs do differ significantly from 180°, with the P(1)–Pt(1)–P(2) angle of 165.48(3)° and the C(1)–Pt(1)–I(1) angle of 167.41(8)°. While a search of the Cambridge Crystallographic Database<sup>9</sup> revealed several platinum complexes with a combination of trans-phosphines, acyl, and chloro ligands, none contained  $\text{PMe}_3$  ligands; compound **6**, containing an iodo ligand, was the closest structure available for comparison with **5**.<sup>10</sup> It also shows similar deviations from linearity between trans-ligands, with a P–Pt–P angle of 171.2° and a C–Pt–I angle of 167.5°. The carbon–carbon distances within the pentamethylcyclopentadienyl ring are consistent with the expected alternation of single and double bonds.

\* Corresponding author. E-mail: rph@dartmouth.edu.

<sup>†</sup> Dartmouth College.

<sup>‡</sup> University of California, San Diego.

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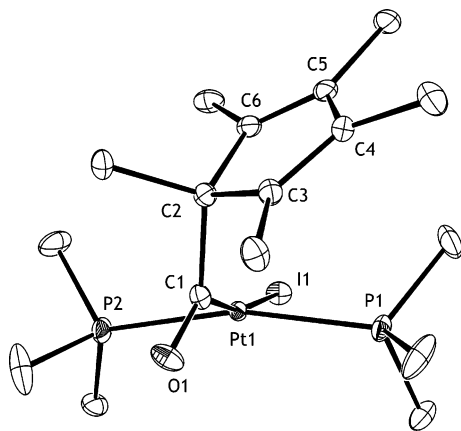
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**Figure 1.** ORTEP diagram for **5** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are excluded for clarity.

**Table 1. Crystallographic Summary for 5**

formula	C <sub>17</sub> H <sub>33</sub> IOP <sub>2</sub> Pt
fw	637.36
space group	P2(1)/c
<i>a</i> , Å	13.9899(14)
<i>b</i> , Å	10.9587(11)
<i>c</i> , Å	16.0610(16)
$\alpha$ , deg	90
$\beta$ , deg	115.8150(10)
$\gamma$ , deg	90
<i>V</i> , Å <sup>3</sup>	2216.6(4)
<i>Z</i>	4
cryst color, habit	yellow, block
<i>D</i> (calcd), g/cm <sup>3</sup>	1.910
$\mu$ (Mo K $\alpha$ ( $\lambda$ = 0.71073)), mm <sup>-1</sup>	7.868
temp, K	100(2)
diffractometer	Bruker Smart Apex
no. of reflns indep	5157 [ <i>R</i> <sub>int</sub> = 0.0288]
<i>R</i> ( <i>F</i> ) [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )], % <sup>a</sup>	1.82
<i>R</i> ( <i>wF</i> <sup>2</sup> ) [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )], % <sup>a</sup>	4.26

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R(wF^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

**Table 2. Selected Bond Lengths and Angles for 5**

bond lengths (Å)		bond angles (deg)	
Pt(1)–C(1)	1.994(3)	C(1)–Pt(1)–P(1)	92.92(8)
Pt(1)–P(1)	2.2973(7)	C(1)–Pt(1)–P(2)	90.46(8)
Pt(1)–P(2)	2.3030(7)	P(1)–Pt(1)–P(2)	165.48(3)
Pt(1)–I(1)	2.7306(3)	C(1)–Pt(1)–I(1)	167.41(8)
O(1)–C(1)	1.206(3)	P(1)–Pt(1)–I(1)	89.51(2)
C(1)–C(2)	1.587(4)	P(2)–Pt(1)–I(1)	90.26(2)
C(2)–C(6)	1.518(3)	O(1)–C(1)–C(2)	117.1(2)
C(2)–C(3)	1.523(4)	O(1)–C(1)–Pt(1)	125.6(2)
C(3)–C(4)	1.349(4)	C(2)–C(1)–Pt(1)	117.25(17)
C(4)–C(5)	1.467(4)		
C(5)–C(6)	1.342(4)		

The solution NMR data are consistent with the solid-state structure, with three resonances (ratio 2:2:1) observed for the pentamethylcyclopentadiene methyl groups, contrasting with the fluxional ring-whizzing  $\eta^1$ -Cp\* observed in **2**.<sup>7</sup> No <sup>195</sup>Pt coupling is observed to any of the diene methyl groups. The PMe<sub>3</sub> ligands

are trans, as evidenced by the virtually coupled triplet observed in the <sup>1</sup>H NMR spectrum and the single <sup>31</sup>P resonance; the <sup>1</sup>H and <sup>31</sup>P resonances both show the expected coupling to <sup>195</sup>Pt. The C=O stretch is observed in the IR spectrum at 1634 cm<sup>-1</sup>.

The mechanism of formation of **5** quite likely occurs by ring slippage of the Cp\* ligand to form an intermediate analogous to **2**, but perhaps the smaller more nucleophilic PMe<sub>3</sub> [compared to the PPh<sub>2</sub>(2-MeOPh) used in the original work] reacts faster with this to induce migratory insertion of Cp\* to CO, compared to rate of ligand substitution by loss of iodide or CO.<sup>7</sup> It is unusual to observe a new reaction of a ligand as common as Cp\*, but this particular combination of circumstances has produced one.

## Experimental Section

Reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which was deoxygenated over BASF catalyst and dried over Aquasorb. NMR spectra were recorded on a Varian Unity Plus 500 FT spectrometer. <sup>1</sup>H NMR spectra were referenced to the protio impurity in the solvent: C<sub>6</sub>D<sub>6</sub> (7.15 ppm), CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm), *d*<sub>8</sub>-toluene (2.09 ppm, methyl group). <sup>31</sup>P NMR spectra were referenced to external H<sub>3</sub>PO<sub>4</sub> (0.00 ppm). Coupling constants are reported as absolute values in hertz. Elemental analyses were performed by Schwartzkopf (Woodside, NY). Compound **1c** was prepared according to the literature procedure.<sup>8</sup>

**Complex 5.** Cp\*Pt(CO)I (10.0 mg, 0.0206 mmol) was dissolved in toluene (1 mL), and a solution of PMe<sub>3</sub> (0.004 mL; 0.0412 mmol) in toluene (2 mL) was added dropwise at room temperature. The color of the solution changed to yellow. The solvent was removed in vacuo, and the residue was crystallized from ether/heptane to give the product (0.007 g; 53%). Anal. Calc for C<sub>17</sub>H<sub>33</sub>IOP<sub>2</sub>Pt: C, 32.04, H, 5.18. Found: C, 32.22, H, 5.01. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz, 21 °C):  $\delta$  1.12 (s, 3H, CH<sub>3</sub>, Cp\*), 1.27 (t, <sup>2</sup>*J*<sub>PH</sub> = 4.0 Hz, <sup>3</sup>*J*<sub>PH</sub> = 34 Hz, 18H, 2PMe<sub>3</sub>), 1.62 (s, 6H, 2CH<sub>3</sub>, Cp\*), 1.29 (s, 6H, 2CH<sub>3</sub>, Cp\*). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene, 202.3 MHz, 21 °C):  $\delta$  -22.91 (s, <sup>1</sup>*J*<sub>PIP</sub> = 3135 Hz, PMe<sub>3</sub>). IR (KBr): 1634 cm<sup>-1</sup> (C=O).

**Crystallographic Structural Determination.** Crystal, data collection, and refinement parameters are collected in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. DIFABS absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.

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**Supporting Information Available:** Full crystallographic data for **5** in the form of a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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