

Nucleophilic Substitution of $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$); Isolation of a Ring-slipped Intermediate

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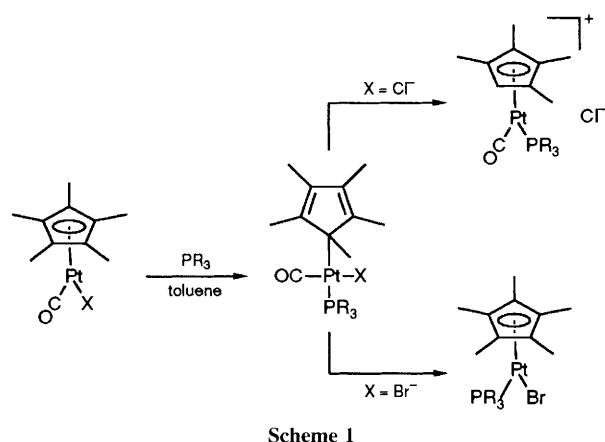
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The toluene mediated reaction of $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) with tertiary phosphines affords the unstable intermediates $[\text{Pt}(\eta^1\text{-C}_5\text{Me}_5)(\text{CO})(\text{PR}_3)\text{X}]$ which decompose with loss of either CO or halide to give $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)\text{Br}]$ or $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)(\text{CO})]^+\text{Cl}^-$.

The ability of the cyclopentadienyl ligand to slip to bonding modes of lower hapticity was first proposed by Schuster-Woldan and Basolo¹ to explain the rapid second order nucleophilic substitution of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ by PPh_3 and has become a generally accepted mechanism for many reactions of complexes containing cyclopentadienyl rings.² Substitution of the cyclopentadienyl ring by a pentamethylcyclopentadienyl ring results in a reduction in the substitution rate owing to an increase in both the electron density at the metal and steric hindrance³ and the latter is sufficiently severe

that only one example of an $\eta^1\text{-C}_5\text{Me}_5$ ligand on a transition metal has been described.⁴

We have found that the reaction of $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$)⁵ with tertiary phosphines in non-polar solvents affords either $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)\text{Br}]$ or $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)(\text{CO})]^+\text{Cl}^-$ (Scheme 1). However, if the reaction is undertaken in toluene, benzene or tetrahydrofuran (thf) an intermediate may be isolated which has been characterised as containing a ring-slipped η^1 -pentamethylcyclopentadienyl group, $[\text{Pt}(\eta^1\text{-C}_5\text{Me}_5)(\text{CO})(\text{PR}_3)\text{X}]$.



For example, equimolar addition of $\text{PPh}_2(2\text{-MeOC}_6\text{H}_4)$ to a toluene solution of $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Cl}]$ at room temperature results in the rapid, quantitative formation of $[\text{Pt}(\eta^1\text{-C}_5\text{Me}_5)(\text{CO})\{\text{PPh}_2(2\text{-MeOC}_6\text{H}_4)\}\text{Cl}]$ **1** which was isolated as a yellow solid by rapid cooling to -78°C .[†] Solution infrared spectroscopy confirms the retention of the carbonyl ligand [$\nu(\text{CO})$ 2061 cm^{-1}] and the magnitude of $^1J_{\text{Pt,P}}$ (1403 Hz) suggests that the phosphine is *trans* to a σ -bound alkyl group.⁶ Confirmation of the presence of the $\eta^1\text{-C}_5\text{Me}_5$ group came from a variable temperature $^{13}\text{C}\{^1\text{H}\}$ study of a sample of **1** in which the pentamethylcyclopentadienyl ring carbons had been 10% ^{13}C enriched.

At -86°C , non-equivalence of the resonances attributable to the ring methyl carbons was detected in the expected 1 : 2 : 2 ratio for an η^1 -pentamethylcyclopentadienyl group (Fig. 1). Three other resonances which may be assigned to the ring carbons were also observed. The first at δ 64.8 exhibits a large phosphorus coupling (76 Hz) indicative of the presence of a phosphine *trans* to the C_5Me_5 group. The magnitude of this coupling and the coupling to ^{195}Pt (385 Hz) is conclusive proof for the formulation of **1** as a σ -bound C_5Me_5 complex.⁷ The other resonances at δ 144.3 and 128.0 are attributable to the two pairs of uncoordinated alkenic ring carbons.

On warming, all the resonances attributable to the pentamethylcyclopentadienyl ring broadened and collapsed. By 24°C , the spectrum exhibited two new averaged resonances, a sharp singlet at δ 13.0 assignable to the methyl carbons and a very broad single resonance at δ 122 due to the five ring carbons. This behaviour is consistent with 1,2-intramolecular migration of the pentamethylcyclopentadienyl ligand. After several days, the cation $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)\{\text{PPh}_2(2\text{-MeOC}_6\text{H}_4)\}(\text{CO})]^+\text{Cl}^-$ **2** precipitated quantitatively.[†]

Although the intermediacy of ring-slipped species is well established in substitution reactions of d^8 transition metal

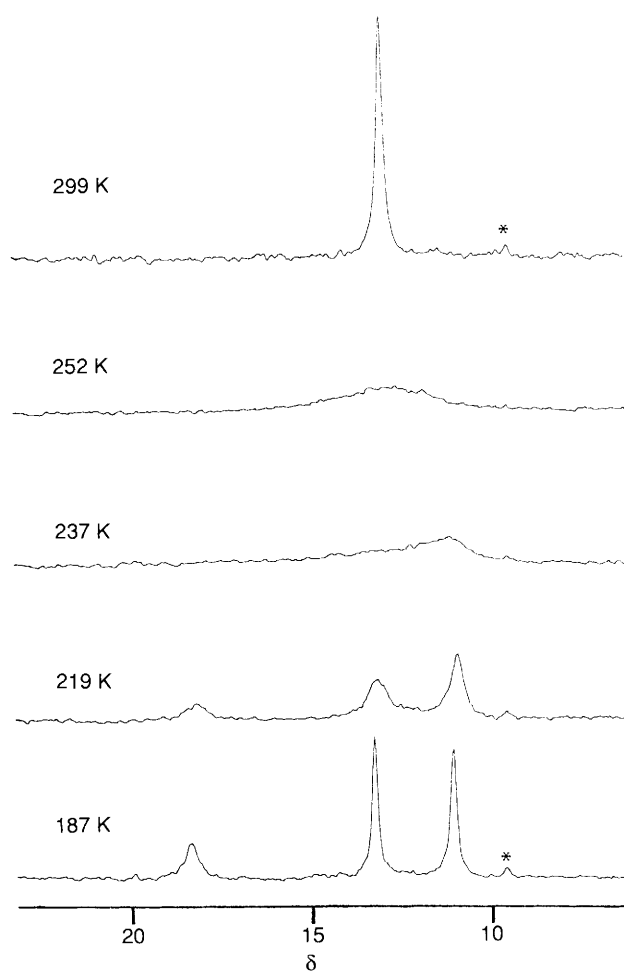


Fig. 1 Variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in the methyl region of $[\text{Pt}(\eta^1\text{-C}_5\text{Me}_5)\{\text{PPh}_2(2\text{-MeOC}_6\text{H}_4)\}(\text{CO})\text{Cl}]$, **1**, in $[\text{D}_8\text{H}_8]\text{thf}$; * indicates $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Cl}]$ impurity

cyclopentadienyl complexes,⁸ the isolation of an η^1 intermediate would suggest that a reaction sequence involving sequential slippage, e.g. $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1 \rightarrow \eta^3 \rightarrow \eta^5$, cannot be ignored. This is particularly true for the heavier transition metals where the square planar configuration required for an η^1 -cyclopentadienyl species is especially favoured.⁹

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[†] Satisfactory C and H analyses were obtained for compounds **1** and **2**. Selected spectroscopic data for **1**: IR (toluene) ν 2061 cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene) δ 12.6 (s, $J_{\text{Pt,P}}$ 1403 Hz); $^{195}\text{Pt}\{^1\text{H}\}$ NMR (toluene, $\Xi = 21.4\text{ MHz}$) δ 543 (d, $J_{\text{Pt,P}}$ 1403 Hz); ^1H NMR (C_6D_6) δ 3.16 (s, 3 H, MeO) and 2.13 (d, 15 H, C_5Me_5 , $J_{\text{P,H}}$ 3.2 and $J_{\text{Pt,H}}$ 15.0 Hz); $^{13}\text{C}\{^1\text{H}\}$ ($[\text{D}_8\text{H}_8]\text{thf}$) 299 K: 165.5 (d, CO, $J_{\text{P,C}}$ 10 Hz), 122 (v br, CMe), 55.6 (s, OMe) and 13.0 (s, Me); 187 K: 165.7 (d, CO, $J_{\text{P,C}}$ 10 and $J_{\text{Pt,C}}$ 2042 Hz), 144.3 (d, CMe, $J_{\text{P,C}}$ 5 and $J_{\text{Pt,C}}$ 25 Hz), 128.0 (d, CMe, $J_{\text{P,C}}$ 5 Hz), 64.8 (d, CMe, $J_{\text{P,C}}$ 76 and $J_{\text{Pt,C}}$ 385 Hz), 55.7 (s, MeO), 18.2 (s, Me), 13.1 (s, Me) and 10.9 (s, Me).

For **2**: IR (CH_2Cl_2) ν 2062 cm^{-1} ; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ -1.9 (s, $J_{\text{Pt,P}}$ 4147 Hz); $^{195}\text{Pt}\{^1\text{H}\}$ NMR (CDCl_3 , $\Xi = 21.4\text{ MHz}$) δ -1306 (d, $J_{\text{Pt,P}}$ 4147 Hz); ^1H NMR (CDCl_3) δ 3.56 (s, 3 H, MeO) and 1.82 (d, 15 H, C_5Me_5 , $J_{\text{P,H}}$ 2.9 and $J_{\text{Pt,H}}$ 13.4 Hz); $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3) 300 K: 161.4 (d, CO, $J_{\text{P,C}}$ 16 and $J_{\text{Pt,C}}$ 2205 Hz), 109.7 (s, $J_{\text{Pt,C}}$ 21 Hz), 55.4 (s, MeO) and 9.17 (s, Me).