A Bis(acetylene)platinum(0) Complex; Crystal and Molecular Structures of $[Pt(PhC_2Ph)_2]$ and $[Pt_2(PMe_3)_2(PhC_2Ph)_2]$

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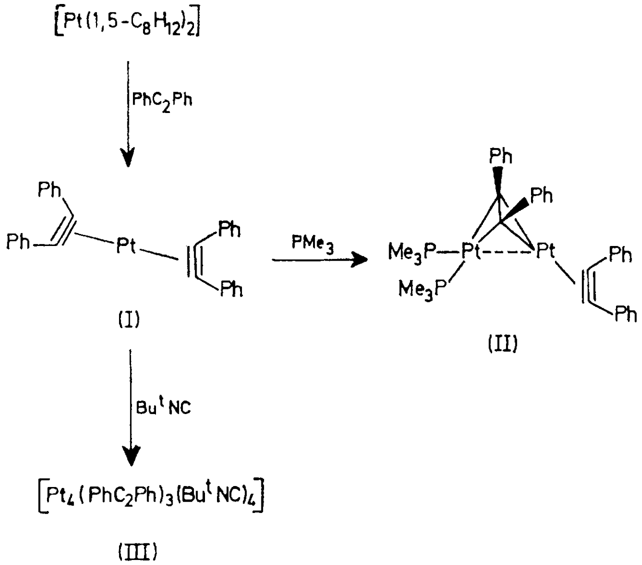
Summary Reaction of $[Pt(1,5\text{-}C_8H_{12})_2]$ with diphenylacetylene affords $[Pt(PhC_2Ph)_2]$, which reacts with trimethylphosphine to give $[Pt_2(PMe_3)_2(PhC_2Ph)_2]$; the structural identity of both new complexes was established by single-crystal *X*-ray diffraction.

The discovery of tris(olefin) complexes of palladium and platinum[1] led to the interesting possibility that related bis(olefin) and bis(acetylene) complexes of these metals could also be prepared, particularly as fourteen-electron two-co-ordinate complexes of the type ML_2 (M = Pd,[2] Pt;[3] L = bulky tertiary phosphine) have been well characterised. As part of a study[4] of the chemistry of bis(cyclo-octa-1,5-diene)-platinum and -palladium, we have characterised bis(diphenylacetylene)platinum, a molecule with apparently significant synthetic potential.

Reaction [room temperature, in light petroleum (b.p. 30—40 °C)] of an excess of diphenylacetylene with $[Pt(1,5\text{-}C_8H_{12})_2]$ afforded (Scheme) complex (I) as pale yellow crystals (from diethyl ether, −40 °C). Elemental analyses and spectroscopy [i.r.: $\nu_{C\equiv C}$ 1 881 cm^{-1}; ^{13}C n.m.r. (measured on a ^{13}C enriched sample in $CDCl_3$ at −25 °C): acetylenic carbon resonance at 124·8 p.p.m., *J*(PtC) 311 Hz] indicated that (I) was possibly a bis(acetylene) metal complex. The structure was established by a single crystal *X*-ray diffraction study.

Crystal data: monoclinic, $P2/n$, $a = 13{\cdot}163(5)$, $b = 6{\cdot}062(2)$, $c = 14{\cdot}354(7)$ Å; $\beta = 115{\cdot}04(3)°$; $Z = 2$. R is currently 0·039 for 3423 independent absorption-corrected ($\mu = 69{\cdot}5\ cm^{-1}$) intensities with $I \geqslant 2{\cdot}0\,\sigma(I)$ collected on a Syntex $P2_1$ four-circle diffractometer at 200 K in the range $2{\cdot}9 \leqslant 2\theta \leqslant 65°$.



Scheme

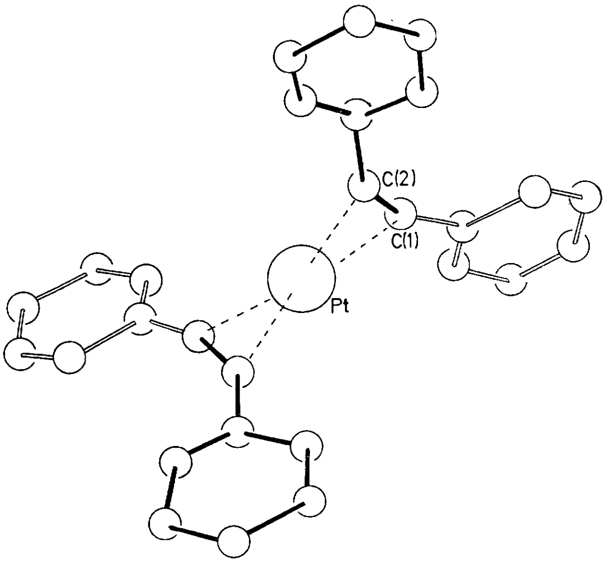


Figure 1. Molecular structure of $[Pt(PhC_2Ph)_2]$.

The molecular structure (Figure 1) shows that the co-ordination at the platinum atom is essentially tetrahedral (D_{2d}),[5] the angle between the two $\overline{\mathrm{Pt{\cdot}C{=}C}}$ planes being 82°.

The platinum atom lies on a crystallographic two-fold axis of rotation, at a mean distance of 2·025(5) Å from the two acetylenic carbon atoms [C(1)–C(2) = 1·280(6) Å], and is effectively coplanar with all carbon atoms of the PhC_2Ph ligand (maximum deviation from the mean PtC_{14} plane is 0·3 Å). Co-ordination of the acetylene to the metal shows the expected bending of the phenyl rings away from the platinum atom [$\angle$PhC$\,\underset{\cdots\cdots}{\overset{\cdots\cdots}{\cdots\cdots}}\,$C (mean) = 153°].

Treatment of K_2PtCl_4 with acetylenic-diols $R^1R^2C(OH)$-$C{\equiv}CC(OH)R^1R^2$ in ethanol was reported[6] to give complexes [Pt(acetylene)$_2$] for which planar hydrogen-bonded ring structures were proposed. From comparison of the $\nu_{C\equiv C}$ stretching frequencies with (I) it seemed likely that these complexes are also *pseudo*-tetrahedral 14-electron two-co-ordinate complexes.†

Complex (I) appears to function as a ready source of polynuclear platinum species on treatment with phosphines or isocyanides. Reaction with 1 mol. equiv. of trimethylphosphine (Et_2O, 0 °C) gave orange-yellow crystals (II) ($\nu_{C\equiv C}$ 1 851 cm^{-1}). Examination of the ^{31}P n.m.r. spectrum [$(CD_3)_2CO$, resonance at 20·4 p.p.m. (rel. to external H_3PO_4), $J(PPt^1)$ 3530 Hz, $J(PPt^2)$ 44 Hz] indicated that the complex was dinuclear. This was confirmed by X-ray crystallography.

Crystal data: monoclinic, $P2_1/c$, a = 12·963(3), b = 16·486(8), c = 17·498(10) Å; β = 116·04(4)°; Z = 4. R is currently 0·066 for a limited data set collected in the range $2\theta \leqslant 50°$ at room temperature. 2158 absorption-corrected (μ = 88·4 cm^{-1}) intensities with $I \geqslant 2{\cdot}0\sigma(I)$ were used to solve and refine the structure shown in Figure 2.

In the binuclear complex (II) one platinum atom carries both PMe_3 ligands, the diphenylacetylene ligands showing different co-ordination modes. Thus, Ph(3)C(3)C(4)Ph(4) lies terminally to, and coplanar with Pt(2), its geometrical features closely resembling those of the PhC_2Ph ligand in complex (I) [C(3)–C(4) = 1·26(5) Å; Pt–C (mean) = 2·01(3) Å, and $\angle$C–C≡C = 153°], whereas Ph(5)C(5)C(6)Ph(6) co-ordinates to both metal atoms in a bridging mode, lying almost perpendicular to the Pt–Pt vector, with C(5) and C(6) approximately equidistant from the two platinum atoms [Pt–C (mean) = 2·10(3) Å]. The phenyl rings [Ph(5) and Ph(6)] are no longer coplanar, but twisted at 60° and 48°, respectively, to the C(5)–C(6) bond (planes are 80° to each other). This fact, and the lengthening of this bond to 1·36(5) Å suggests a more pronounced rehybridization of these central carbon atoms in this bridging mode, than when terminally bonded. The Pt–Pt separation [2·890(2) Å] is larger than that found in most bridged Pt–Pt complexes.

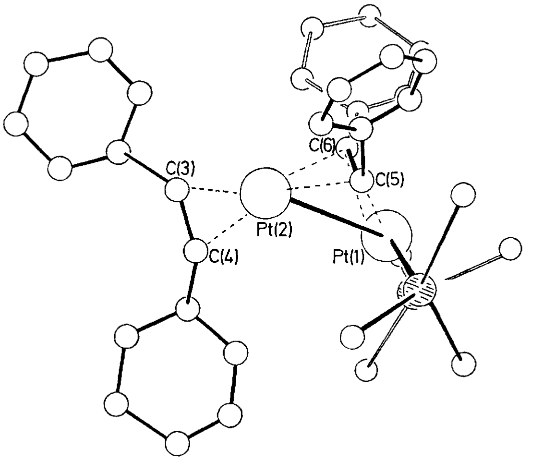


FIGURE 2. Molecular structure of $[Pt_2(PhC_2Ph)_2(Me_3P)_2]$.

With t-butyl isocyanide, (I) affords a tetranuclear cluster $[Pt_4(PhC_2Ph)_3(Bu\ NC)_4]$ (III) which is not isostructural with the recently described Ni_4 clusters $[Ni_4(CF_3C_2CF_3)_3(CO)_4]$[7] and $[Ni_4(PhC_2Ph)_3(Bu\ NC)_4]$.[8]

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† Recently confirmed by X-ray crystallography (R. J. Dubey, *Acta. Cryst.*, 1975, **B13**, 1864).

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