

A Di-platinum(IV) Complex containing Bridging *o*-Xylylene† and Ph₂PCH₂PPh₂ Groups: Synthesis and Structure of [Pt₂Me₄Br₂(μ-CH₂C₆H₄CH₂)(μ-Ph₂PCH₂PPh₂)]

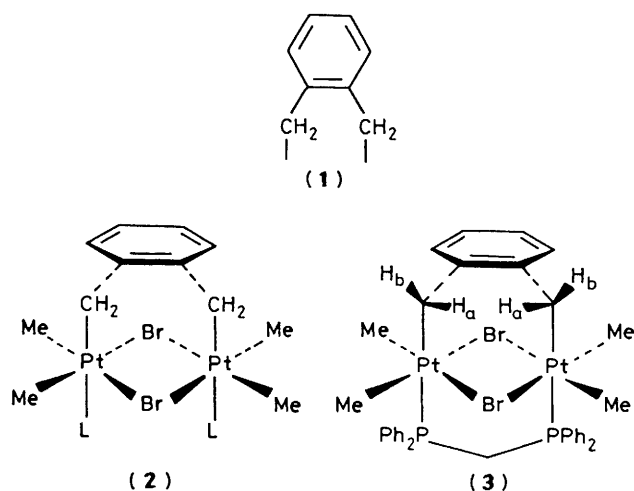
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The title compound is the first example of a platinum(IV) complex containing bridging Ph₂PCH₂PPh₂ (dppm) and the first example of *o*-xylylene bridging two metal atoms that are not directly bonded.

There is much interest in the *o*-xylylene† diradical (I) as a chelate ligand for d- and f-block elements: the diradical can act as a 2e donor or as a π-(η⁴) donor.¹⁻⁶ An example of an *o*-xylylene diradical bridging two cobalt atoms, which are directly bonded, viz. [Co₂(μ-CO)₂(μ-CH₂C₆H₄CH₂)(η⁵-C₅H₅)₂], is also known.⁷

We report here on the title compound, the first example of the ligand (I) bridging two metal atoms that are not directly bonded. The title compound is also the first example of a platinum(IV) complex containing a bridging Ph₂PCH₂PPh₂ (μ-dppm) ligand. It has been shown that although the mononuclear η²-dppm-platinum complex [PtMe₂(η²-dppm)] readily adds methyl iodide to give a platinum(IV) complex, [PtMe₃I-(η²-dppm)], the isomeric μ-dppm complex [Me₂Pt(μ-dppm)₂-PtMe₂] is unreactive, even to neat methyl iodide.⁸

† *o*-Phenylenedimethyl.



We find that *cis*-[PtMe₂L₂], L = AsMe₂Ph or AsMe₂(C₆H₄OMe-2), react smoothly with an equimolar amount of *o*-xylylene dibromide in benzene solution to give platinum(IV) adducts, formulated as [Pt₂Me₄Br₂(μ-CH₂C₆H₄CH₂)L₂] (2) on the basis of elemental analysis, molecular weight determination, and ¹H n.m.r. spectroscopy. The addition with L = AsMe₂(C₆H₄OMe-2) goes faster (20 min, 80 °C) than with L = AsMe₂Ph (2 h) owing to neighbouring group participation by the *ortho*-methoxy group.^{9,10} The displaced arsines are quaternized by the second mole of *o*-xylylene dibromide used. We reasoned that it might be possible to displace the two arsine ligands, L, by dppm and have found this to be the case. Thus treatment of either of the complexes (2) with one equivalent of dppm in benzene at 40 °C for 10 min gives a complex which we formulated as [Pt₂Me₄Br₂(μ-CH₂C₆H₄CH₂)(μ-dppm)] (3) on the basis of elemental analysis and n.m.r. measurements; this has been confirmed by structural determination by X-ray diffraction (*vide infra*). The ³¹P-{¹H} n.m.r. spectrum (in CH₂Cl₂) shows the expected 19-line pattern from which the following data can be derived: δ(P) -16.5 p.p.m., ¹J(PtP) 1155, ³J(PtP) 32, ²J(PtPt) 205, J(PP) 12 Hz. ¹J(PtP) and ³J(PtP) are of the same sign, in contrast with complexes of type [Pt₂X₄(PR₃)₂] (X = halogen), where they are of opposite sign.¹¹ In the ¹H n.m.r. spectrum the xylylene methylene hydrogens [H_a or H_b in (3)] are non-equivalent. One is coupled to both platinum whilst the other is coupled to only one platinum: H_a (or H_b) δ 2.51, ²J(H_aH_b) 9.4, ²J(PtH) 26.8, ³J(PH) 13.5 Hz; H_b (or H_a) δ 5.02, ²J(PtH) 108.0, ⁴J(PtH) 5.4, ³J(PH) 9.0 Hz. The data for the PtCH₃ and PCH₂P hydrogens are in agreement with the structure (3).

The X-ray crystal structure[‡] shows the environment of each platinum to be approximately octahedral with the bridging *o*-xylylene and dppm ligands *trans* to each other forming a

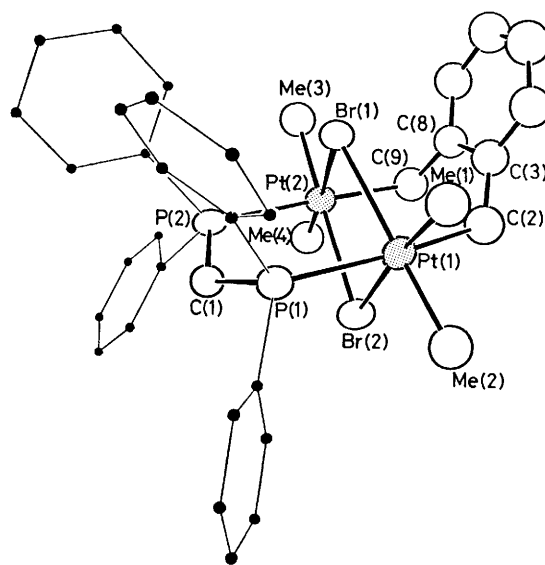


Figure 1. Molecular structure of [Pt₂Me₄Br₂(μ-CH₂C₆H₄CH₂)(μ-Ph₂PCH₂PPh₂)] (3). Bond lengths and angles are normal for Pt^{IV} complexes. Selected parameters: Pt(1)-C(2) 2.06(2), Pt(2)-C(9) 2.12(2), Pt(1) . . . Pt(2) 3.46 Å; Pt(1)-C(2)-C(3) 119(2), Pt(2)-C(9)-C(8) 114(2)°.

9-membered ring in the chair conformation (Figure 1). The CH₂C₆H₄CH₂ ligand spans the two platinum centres as a 2e donor, there being no direct interaction between the platinum and aromatic carbon atoms [Pt(1) . . . C(3) 3.08, Pt(2) . . . C(8) 3.05 Å]. The fold angle, defined as the angle between the *o*-xylylene ligand plane and the Pt₂C₂ plane, is 65°. For mononuclear species a fold angle of this magnitude is indicative of some π-η¹-interaction³ and corresponds to much shorter metal-aromatic carbon distances than in our compound, where the stereochemical situation is quite different.

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‡ Crystal data: C₃₇H₃₂Br₂P₂Pt₂, orthorhombic, space group P2₁2₁2₁, a = 10.481(3), b = 17.694(5), c = 18.842(7) Å, Z = 4. The current R is 0.047 for 2279 independent F₀ having I > 2σ(I). Pt, Br, and P atoms were assigned anisotropic thermal parameters and hydrogen atoms were included in calculated positions. The P-phenyl rings were refined as rigid groups. No absorption corrections were applied [μ(Mo-Kα) = 104.7 cm⁻¹] owing to the irregular shape of the only crystal fragment available for data collection.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.