Rational Synthesis of Dinuclear Complexes of Platinum(I) and Platinum(II) containing Bridging *Ortho*-metallated Triphenylphosphine Ligands from the Monomeric Bis(chelate) Platinum(II) Complex Pt(o-$C_6H_4PPh_2$)$_2$

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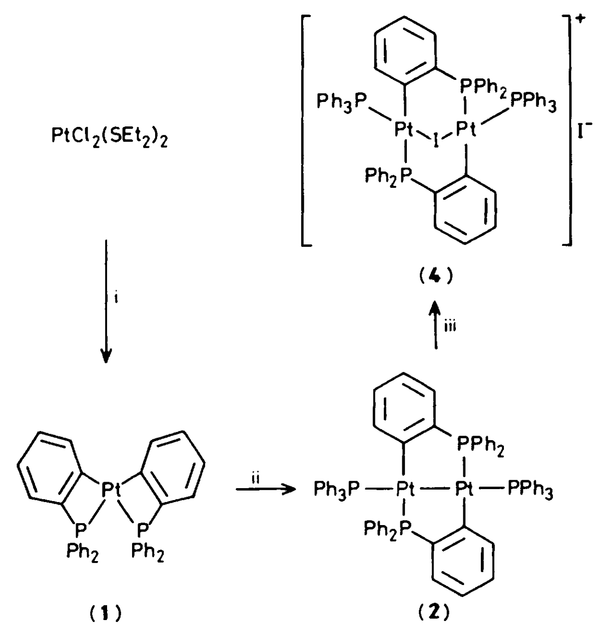
Comproportionation of $Pt(PPh_3)_3$ and the bis(chelate) complex $Pt(o\text{-}C_6H_4PPh_2)_2$ gives a dinuclear complex $Pt_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2(PPh_3)_2$ which is shown by *X*-ray crystallography to contain two *ortho*-metallated triphenylphosphine ligands bridging a Pt^I–Pt^I bond [Pt–Pt 2.630(1) Å]; addition of iodine gives a salt $[Pt_2(\mu\text{-}I)(\mu\text{-}o\text{-}C_6H_4PPh_2)_2(PPh_3)_2]I$, the cation of which has an A-frame structure [Pt–Pt 2.931(2) Å].

Co-ordinated triphenylphosphine can undergo *ortho*-metallation to give either complexes containing a four-membered ring, M–o-$C_6H_4PPh_2$,[1] or dinuclear complexes in which the fragment o-$C_6H_4PPh_2$ bridges two metal atoms, *e.g.* $Rh_2(\mu\text{-}OAc)_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2L_2$ (L = AcOH, py)[2] and $Os_2Cl_2(\mu\text{-}O_2CR)_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2$.[3] Tertiary t-butylarylphosphines readily form cycloplatinated derivatives of the first type,[4] but there is only one well-established example of cycloplatination of triphenylphosphine, *viz.* the isomerisation of $Pt(PPh_3)_2(\eta^2\text{-}MeO_2CC_2CO_2Me)$ to $Pt(o\text{-}C_6H_4PPh_2)\{\sigma\text{-}E\text{-}C(CO_2Me)\text{=}CH(CO_2Me)\}(PPh_3)$ on heating in toluene.[5] Thermolysis of various platinum(II)- or platinum(0)-triphenylphosphine complexes has been claimed to give cycloplatinated products,[6–8] but detailed structural information is lacking. A potentially more general route to cyclometallated derivatives of PPh_3 is the reaction of (o-lithiophenyl)diphenylphosphine, o-$LiC_6H_4PPh_2$, with metal halides. This procedure has already provided the first dinuclear complexes of gold(I) and gold(II) containing μ-o-$C_6H_4PPh_2$[9] and we show here that it gives monomeric and dimeric *ortho*-metallated platinum complexes



Scheme 1. *Reagents*: i, o-$LiC_6H_4PPh_2$ in diethyl ether; ii, $Pt(PPh_3)_3$ in refluxing toluene; iii, I_2 in CH_2Cl_2.

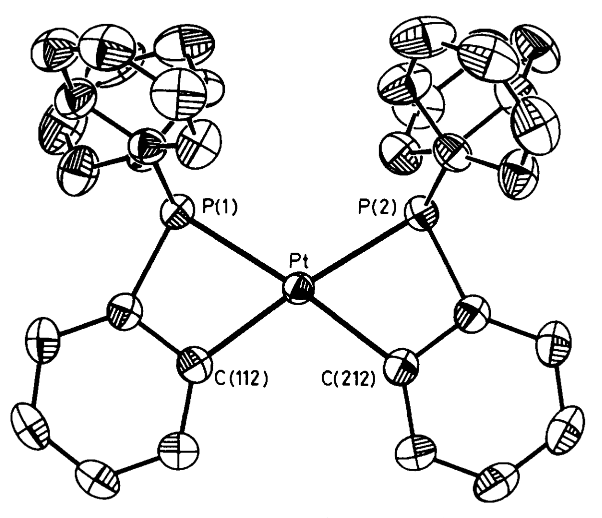


Figure 1. Molecular structure of $Pt(o$-$C_6H_4PPh_2)_2$ (**1**) (50% ellipsoids). Selected dimensions: Pt–P 2.297(1), Pt–C 2.063(2) Å; P–Pt–P 116.25(3), P–Pt–C 68.73(7), C–Pt–C 106.3(1)°.

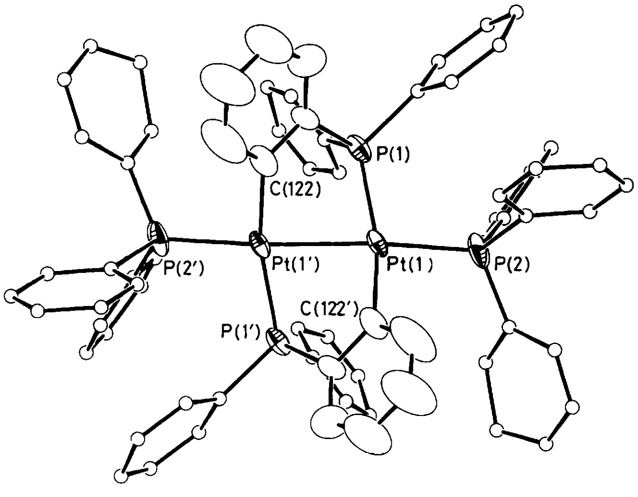


Figure 2. Molecular structure of $Pt_2(\mu$-o-$C_6H_4PPh_2)_2(PPh_3)_2$ (**2a**) viewed down the crystallographically imposed two-fold rotation axis (50% ellipsoids; ring atoms as 0.1 Å radius spheres for clarity). Selected dimensions: Pt–Pt 2.630(1), Pt–P(*trans*-Pt) 2.300(4), Pt–P(*trans*-C) 2.282(4), Pt–C 2.07(2) Å.

that are not readily obtainable from triphenylphosphine itself. The reactions are outlined in Scheme 1.

The lithium derivative, o-$LiC_6H_4PPh_2$, which is formed as a diethyl ether solvate from o-$BrC_6H_4PPh_2$ and Bu^nLi,[10] reacts with either *cis*- or *trans*-$PtCl_2(SEt_2)_2$ (2 : 1 mol ratio) in diethyl ether at −30 °C to give $Pt(o$-$C_6H_4PPh_2)_2$ (**1**) as a colourless, crystalline, air-stable solid in 70% yield. Compound (**1**) is monomeric in CH_2Cl_2 (osmometry) and its i.r. spectrum shows characteristic *ortho*-metallation bands at 1560(w) and 724(s) cm^{-1}.[11] The 24.3 MHz $^{31}P\{^1H\}$ n.m.r. spectrum in $C_6D_5CD_3$ shows a singlet with ^{195}Pt satellites at δ −52.3 [J(PtP) 1352 Hz], the shielding of which suggests the presence of four-membered chelate rings.[12] Single crystal *X*-ray analysis† confirms the bis(chelate) monomeric structure, the metal atom and the ligand donor atoms being almost coplanar and the phosphorus atoms being mutually *cis* (Figure 1). The five-membered ring analogue of (**1**), $Pt(o$-$CH_2C_6H_4PPh_2)_2$, exists as a *cis*-isomer in diethyl ether, but in benzene a mixture of *cis*- and *trans*-isomers is present.[13]

Heating (**1**) with $Pt(PPh_3)_3$ in toluene for 12 h causes comproportionation and opening of the four-membered rings to form the diplatinum(I) complex $Pt_2(\mu$-o-$C_6H_4PPh_2)_2(PPh_3)_2$ (**2**), which shows the expected molecular weight in CH_2Cl_2 (osmometry) and *ortho*-metallation bands at 1560(w) and 725(s) cm^{-1}. The $^{31}P\{^1H\}$ n.m.r. spectrum of (**2**) consists of an AA′BB′ pattern with complex satellites arising from isotopomers containing one and two ^{195}Pt nuclei; the derived P–P and Pt–P coupling constants‡ are similar to those

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† $C_{36}H_{28}P_2Pt$, (**1**) M = 717.65, triclinic, $P\bar{1}$, a = 9.328(1), b = 11.311(1), c = 14.574(2) Å, α = 79.44(1), β = 86.16(1), γ = 74.75(1)°, Z = 2; Philips PW1100 diffractometer, $\bar{\lambda}$ = 0.7107 Å; R = 0.020, R_w = 0.022 for 5713 unique reflections [$3 < 2\theta < 55°$, $I \geqslant 3\sigma(I)$], 352 parameters, H atoms by calculation.

$C_{72}H_{58}P_4Pt_2 \cdot 2H_2O \cdot CH_2Cl_2$, (**2a**) M = 1643.24, monoclinic, $C2/c$ or Cc, a = 25.937(4), b = 12.085(2), c = 22.752(1) Å, β = 109.336(7)°, Z = 4; Philips PW1100 diffractometer, $\bar{\lambda}$ = 0.7107 Å; refined in $C2/c$, site symmetry 2, R = 0.079, R_w = 0.107 for 5199 unique reflections [$4 < 2\theta < 55°$, $I \geqslant 3\sigma(I)$], 383 parameters, H atoms by calculation, solvent H not included, CH_2Cl_2 occupancy factor = 0.5 specified. Structure possibly affected by disorder or pseudosymmetry (Cc pseudo $C2/c$), ring atom thermal parameters unexpectedly high (U^2_{max} *ca.* 0.4 Å^2) with patterns suggesting large librational modes, attempted refinement in Cc unsuccessful.

$C_{72}H_{58}I_2P_4Pt_2 \cdot CH_2Cl_2$, (**4**), M = 1776.07, monoclinic, $P2_1/c$, a = 12.365(1), b = 29.988(3), c = 18.113(2) Å, β = 98.65(1)°, Z = 4; Philips PW1100 diffractometer, $\bar{\lambda}$ = 0.7107 Å; R = 0.067, R_w = 0.070 for 4118 unique reflections [$4 < 2\theta < 45°$, $I \geqslant 3\sigma(I)$], 381 parameters, H atoms by calculation, solvent H not included, solvent rotationally disordered, 1 × 0.5 and 1 × 0.25 occupancy factor fragments included.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ $^{31}P\{^1H\}$ N.m.r. data at 80.98 MHz for (**2**) (in CH_2Cl_2, chemical shift to high frequency of external 85% H_3PO_4): δ_A −2.6, δ_B 25.4 p.p.m., J(AA′) ±55, J(AB) 10, J(AB′) 10, J(BB′) ±226, J(AX) −140, J(BX) 1149, J(AX′) 1937, J(BX′) 1866 Hz, where P_A, $P_{A'}$ are the phosphorus atoms in the cyclometallated ring, P_B, $P_{B'}$, are the phosphorus atoms of the PPh_3 ligands, and the arrangement of $Pt_{X,X'}$ is B(A)X′–X(A′)B′.

(**4**) (CH_2Cl_2): δ_A 5.6, δ_B 15.5 p.p.m., J(AA′) 29, J(AB) 20, J(AB′) 0, J(BB′) 0, J(AX) 0, J(BX) 123, J(AX′) 1677, J(BX′) 5065 Hz.

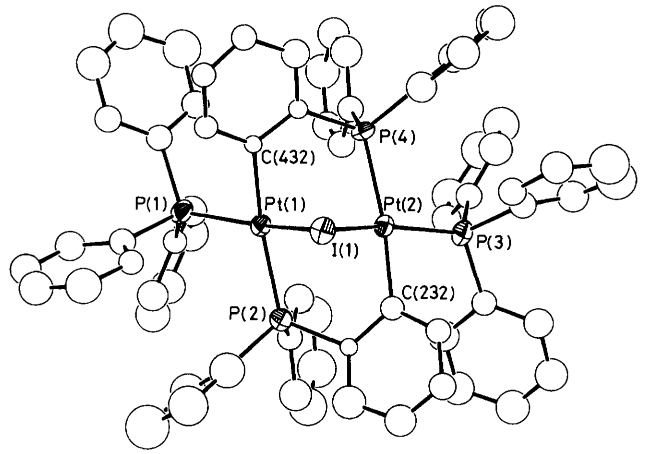

Figure 3. Molecular structure of the cation of $[Pt_2(\mu\text{-}I)(\mu\text{-}o\text{-}C_6H_4PPh_2)_2(PPh_3)_2]I$ (**4**) (50% probability surfaces). Selected dimensions: Pt–Pt 2.931(2), Pt–P(*trans*-I) 2.268(6), Pt–P(*trans*-C) 2.375(6), Pt–I 2.706(2), Pt–C 2.046(3), 2.090(2) Å.

of the complex $Pt_2\{\mu\text{-}o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}_2$ (**3**) obtained by heating $Pt(OH)Me(Ph_2PCH_2CH_2PPh_2)$ in methanol.[14] Slow recrystallisation of (**2**) from dichloromethane in the presence of moist air yields a solvate $Pt_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2(PPh_3)_2\cdot 2H_2O\cdot CH_2Cl_2$ (**2a**). A single crystal *X*-ray study of (**2a**)[†] at −135 °C shows (Figure 2) that the two $o\text{-}C_6H_4PPh_2$ units bridge two planar co-ordinated platinum atoms which are 2.630(1) Å apart, *cf.* 2.628(1) Å in (**3**). As in (**3**), the Pt–P bonds *trans* to platinum (2.300 Å) are longer than those *trans* to carbon (2.282 Å), reflecting the high *trans*-influence of the Pt–Pt bond. Consistent with this interpretation, the axial PPh_3 ligands of (**2**) are readily displaced by other ligands without disruption of the bridging cyclometallated framework to give a range of platinum(I) dimers $Pt_2(\mu\text{-}o\text{-}C_6H_4PPh_2)_2L_2$ ($L = PMe_3, PEt_3, PMe_2Ph, PMePh_2$, and Bu^tNC).

Like (**3**), the new complexes readily undergo oxidative additions, *e.g.* reaction of (**2**) with iodine and recrystallisation of the product from dichloromethane–hexane affords orange-red crystals of the 1:1 adduct $[Pt_2(\mu\text{-}I)(\mu\text{-}o\text{-}C_6H_4PPh_2)_2(PPh_3)_2]I\cdot CH_2Cl_2$ (**4**).[‡] X-Ray analysis shows that the cation is a typical A-frame molecule containing two approximately planar co-ordinated platinum(II) atoms symmetrically bridged by two $o\text{-}C_6H_4PPh_2$ units and by an iodine atom (Figure 3).[†] The presence of the iodine causes the Pt–Pt distance in (**4**) [2.931(2) Å] to be greater than that in (**2**), the Pt–I–Pt angle being only 65.56(5)°. The basic geometry is very similar to that of the μ-methylene complex $Pt_2(\mu\text{-}CH_2)\{\mu\text{-}o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}$, in which the Pt–Pt distance is 2.915(1) Å and the Pt–CH_2–Pt angle [88.9(4)°] is much less than the normal tetrahedral value.[15] A similar arrangement is also found in the cation $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{=}Ph_2PCH_2PPh_2)_2]^+$, where the Rh–Cl–Rh angle is 82.38(5)°,[16] the opening-out presumably being due to the shorter metal–halogen and longer metal–metal distances in the dirhodium cation relative to (**4**).

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