

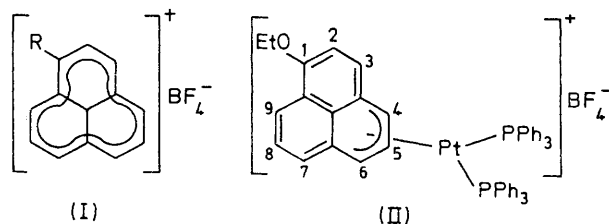
Synthesis and X-Ray Structure of an η^3 -Phenalenyl-Platinum Complex†

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Summary The synthesis and the X-ray structure determination of 4- η^3 -1-ethoxyphenalenyl-bis(triphenylphosphine)platinum tetrafluoroborate are described.

No π -complexes of the phenalenium ring (I; R = H)¹ have yet been described. In connection with our interest in unusual η^3 -bonded complexes of palladium and platinum,^{2,3} we have now carried out the synthesis and the crystal structure determination of the first η^3 -phenalenyl complex (II).



Reaction of (I; R = OEt)⁴ with (η^2 -ethylene)bis(triphenylphosphine)platinum(0) in toluene gave a yellow crystalline solid of stoichiometry expected for (II). The ¹H n.m.r. spectrum (CDCl₃ at 220 MHz) showed resonances due to the ethoxy group at δ 1.57 (t, 3H) and 4.18 (m, 2H, non-equivalent hydrogens) and aromatic resonances at δ 6.8–7.4 as well as 5.45 and 5.60 [br, H(4) and H(6)], 6.34 [t, H(5),

$J\{H(5)-H(6)\} = J\{H(5)-H(4)\} = 8$ Hz], 6.37 [d, H(2), $J(H-H)$ 12 Hz], and 7.96 [d, H(3), $J(H-H)$ 12 Hz]. The high field shifted aromatic resonances at δ 5.45, 5.60, and 6.34 are characteristic of complexes containing η^3 -bonded groups and those at δ 5.45 and 5.60 are similar to those observed for the *ortho*-hydrogens of η^3 -benzylic complexes.^{2,5} Similarly the ¹³C{¹H} n.m.r. spectrum showed high frequency aromatic resonances at δ 81.8 and 87.2 [C(4) and C(6)] and 97.0 [C(5)]. These results are consistent with an η^3 -mode of binding of part of the phenalenyl ring to the metal. The exact positions of attachment could not, however, be deduced from these data and a structure determination was undertaken on a crystal grown from dichloromethane-hexane solution.

Crystal data: C₃₁H₄₃OP₂Pt⁺BF₄⁻·CH₂Cl₂, $M = 1100.7$; monoclinic, $a = 10.560(13)$, $b = 18.83(6)$, $c = 24.36(8)$ Å, $\beta = 102.13(5)^\circ$; space group $P2_1/c$. Three-dimensional X-ray data were collected with the crystal mounted along the a axis using Mo- K_α radiation (graphite monochromator) and a Stoe STADI-2 diffractometer. 3130 independent reflections were collected with $I_{\text{obs}} \geq 3\sigma(I_{\text{obs}})$; the structure was solved using Patterson and Fourier methods, and refinement using block-diagonal least-squares has reduced R to 0.070 at which stage the thermal parameters on the Pt and P atoms are anisotropic and on the other non-hydrogen atoms are isotropic. All the non-hydrogen atoms of the cation are located and refined but those of the anion and the

† No reprints available.

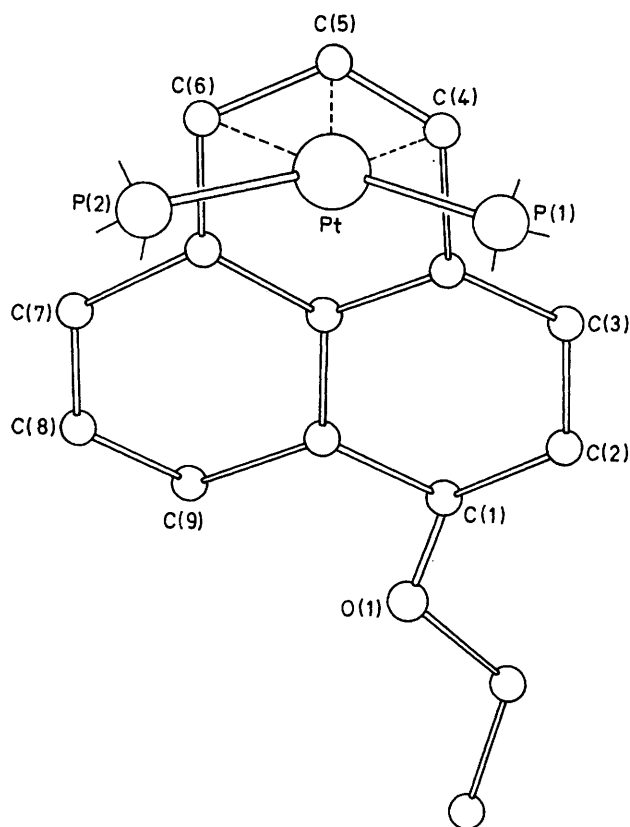


FIGURE. The molecular structure of the cation of complex (II); phenyl groups on phosphorus atoms are omitted for clarity. Bond lengths: Pt-P(1), 2.290(6); Pt-P(2), 2.287(6); Pt-C(4), 2.32(3); Pt-C(5), 2.17(3); Pt-C(6), 2.21(3) Å.

† The atomic co-ordinates for this structure 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.

§ With reference to H_3PO_4 as external standard.

¹ For reviews, see D. H. Reid, *Quart. Rev.*, 1965, **19**, 274; S. Hünig and E. Wolff, *Chimia (Switz.)*, 1968, **22**, 33; I. Murata, *Topics Non-benzenoid Aromatic Chem.*, 1973, **1**, 159.

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³ A. Keasey, P. M. Bailey, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1977, 178.

⁴ H. Prinzbach and V. Freudenberger, *Angew. Chem. Internat. Edn.*, 1965, **4**, 243; S. Hünig and E. Wolff, *Annalen*, 1970, **732**, 7.

⁵ A. Keasey, B. E. Mann, and P. M. Maitlis, unpublished results.

solvent of crystallisation (dichloromethane) show high thermal vibration and disorder which is only partially accounted for at this stage.

The structure found (Figure) confirms that the platinum is η^3 -bonded and shows that the C(4), C(5), and C(6) atoms are bound to the metal.† The phenalenyl ligand is not planar, but the plane defined by atoms C(4)-C(5)-C(6) is at an angle of 149° to that containing the remaining (naphthalenyl) carbon atoms of the phenalenyl ligand. The ethoxy group is approximately coplanar with the naphthalenyl carbon atoms and it is possible that the co-ordination to C(4)-C(5)-C(6) is adopted because this minimises non-bonded interactions between the ethoxy group and the $Pt(PPh_3)_2$ unit. The dihedral angle between the plane of the allylic species [C(4)C(5)C(6)] and the co-ordination plane of the metal [PtP(1)P(2)] is 108° .

The ^{31}P n.m.r. spectrum shows two main multiplets at δ 16.8§ [$J(P-P)$ 15, $J(P-Pt)$ 4282 Hz] and 16.4§ [$J(P-P)$ 15, $J(P-Pt)$ 4178 Hz], as well as two smaller ones, of ca. 10% of the intensity of the main ones, at δ 12.5§ [$J(P-P)$ 17, $J(P-Pt)$ 4112 Hz] and 18.7§ [$J(P-P)$ 17, $J(P-Pt)$ 4376 Hz]. We assign the two smaller multiplets to an isomer (III) of (II) in which the $Pt(PPh_3)_2$ is bonded to C(7)-C(8)-C(9). The presence of the ethoxy group on C(1) will be expected to make the bonding more asymmetric than in (II) and this is consistent with the greater difference in chemical shift and $J(P-Pt)$ exhibited by the phosphorus atoms of the PPh_3 groups in complex (III). There was no evidence for the occurrence of a dynamic process which interchanged (II) and (III) though the 1H n.m.r. spectrum showed broadening at higher temperature; this may be due to a reversible dissociation of the $Pt(PPh_3)_2$ group.

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