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PREPARATION AND X-RAY CRYSTAL STRUCTURES OF DIMETHYL(DIPHENYLBUT-4-ENYLPHOSPHINE)PLATINUM(II) AND DIMETHYL(DIMETHYLBUT-4-ENYLARSINE)PLATINUM(II)

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Abstract—The compounds [$PtMe_2(Ph_2PCH_2CH_2CH{=}CH_2)$] and [$PtMe_2(Me_2AsCH_2CH_2CH{=}CH_2)$] have been synthesized and their structures have been determined by single-crystal X-ray diffraction. The square-planar complexes have bidentate butenylphosphine or butenylarsine ligands. The bonding is discussed in the light of the observed data.

There have been a number of studies of complexes of tertiary phosphines or arsines which also contain a potentially chelating alkene function.[1-5] Many ligands of this class whose platinum(II) complexes have been described are of the types $RPPh_2$ or $RAsMe_2$, where R is allyl, but-4-enyl, pent-5-enyl, *o*-styryl or *o*-allylphenyl. Many of the complexes studied have been dihalides and a typical example is [$PtCl_2Ph_2PCH_2CH_2CH{=}CH_2$],[2] in which the alkenyl group is coordinated, as shown by its IR stretching frequency of 1501 cm^{-1}, a lowering of some 140 cm^{-1} compared with the uncoordinated ligand. However, the alkene in [$PtCl_2(Ph_3P)Ph_2PCH_2CH_2CH{=}CH_2$] is uncoordinated, as shown by $\nu_{(c\ \ c)}$ at 1635 cm^{-1}.[2]

The present work describes the new complexes $PtMe_2L_2$, where L is either $Ph_2PCH_2CH_2CH{=}CH_2$ or $Me_2AsCH_2CH_2CH{=}CH_2$. In such compounds the relative bonding influences of the alkyl, alkene and phosphine (or arsine) ligands, all high in the *trans*-influence series, are of interest, as is the geometry of coordination of the alkene, affected doubtless by the steric requirements of the alkene to phosphorus (or arsenic) linkage. The crystal structures of two similar complexes[4] of the styryl phosphines $PtMe_2L$ and $Pt(CF_3)_2L$, L = *o*-$Ph_2PC_6H_4CH{=}CH_2$, are very relevant for comparative purposes. These and the title compounds appear to be the only examples of organometallic platinum compounds of their type reported.

EXPERIMENTAL

Preparations

But-3-*enyldiphenylphosphine* (**I**). This was prepared from chlorodiphenylphosphine and but-3-enylmagnesiumbromide as described.[2] The fraction of b.pt 122–123°C at 0.05 mm was collected. Found: C, 40.0; H, 4.9. Calc. for $C_{16}H_{17}P$: C, 40.1; H, 5.0%.

But-3-*enyldimethylarsine* (**II**). Operations were carried out under nitrogen. A Grignard reagent

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prepared from 1-bromobut-3-ene (36.0 g) in ether (150 cm^3) and magnesium (7.2 g) in ether (100 cm^3) was stirred vigorously at 0°C and treated dropwise with Me_2AsCl (37.4 g; prepared by reaction of cacodylic acid with HCl and H_3PO_2; b.pt 107–109°C/760 mm Hg) for 45 min. After a further 15 min under reflux, the mixture was cooled to 0°C and hydrolysed with saturated NH_4Cl solution (400 cm^3). The ethereal layer was separated, dried, concentrated and distilled, b.pt 139–144°C, 17 g, 40% [^{1}H NMR spectrum ($CDCl_3$): vinylic H at 5.00, 4.94, 5.82i; *J*(H—H), 19.7, 8.2, 2.2 Hz; CH_3 at 0.90i]. The methiodide was prepared by reflux with CH_3I in $CHCl_3$, filtered off, washed with ethyl acetate and recrystallized from ethanol (m.pt 179–181°C). Found: C, 27.8; H, 5.3. $C_{17}H_{20}AsI$ requires: C, 27.8; H, 5.3%. Compound **II** has also been prepared from Me_2AsI.[6]

*Dichloro(but-*3*-enyldiphenylphosphine)platinum* (II) (**III**). This compound was prepared by boiling *cis*-$PtCl_2(PhCN)_2$ with the phosphine in benzene, followed by concentration, cooling, filtration and washing (yield 81%; decomposition 225–235°C). The previously reported[2] method of preparation, from $PtCl_2$ and **I** in $CHCl_3$, gave material of the decomposition range 218–220°C. The $PtCl_2$ required for the preparation of *cis*-$PtCl_2(PhCN)_2$ was prepared from K_2PtCl_4 by the action of acidic cation-exchange resin followed by evaporation to dryness, heating to 140°C/0.01 mm Hg, washing with water, and drying. This gave a product which would react with PhCN, unlike commercially obtained material.

*Dichloro(but-*3*-enyldimethylarsine)platinum*(II) (**IV**). The arsine (1.34 g, 2.01 mol) was added dropwise, under nitrogen, for 5 min to a stirred suspension of platinum dichloride (2.14 g, 8.0 mmol) in degassed chloroform (150 cm^3). After reflux (1 h) and stirring (overnight), the pale yellow solution was evaporated to *ca* 50 cm^3 and the product, a greyish precipitate, collected by filtration. The dichloride was dissolved in acetone (in which it was sparingly soluble), decolourized with charcoal, filtered and recrystallized (yield 1.82 g, 52%). It decomposes above 240°C. Found: C, 17.0; H, 3.1. $C_{12}H_{13}AsCl_2Pt$ requires: C, 16.9; H, 3.0%.

*Dimethyl(but-*3*-enyldiphenylphosphine)platinum* (II) (**V**). Methyllithium (1.15 cm^3, 2 M) in ether was added dropwise to a stirred solution of **III** (0.50 g, 0.99 mmol) in dry benzene (30 cm^3) and ether (5 cm^3) at -78°C. The mixture was allowed to warm to room temperature and then cooled again to -78°C. Water (10 cm^3) was added, and after warming again, the organic layer was separated and the solvents removed. The yellow glassy material was sublimed at 95–115°C/0.001 mm Hg and recrystallized from ethanol. The crystalline product (yield 0.20 g, 43%) had m.pt 121.5–123.5°C. Found: C, 46.5; H, 5.0. $C_{18}H_{23}PPt$ requires: C, 46.4; H, 5.0%.

*Dimethyl(but-*3*-enyldimethylarsine)platinum*(II) (**VI**). This was prepared in a similar manner to **V**. The dark product was sublimed at 40–60°C/0.001 mm Hg and then recrystallized from a little *n*-pentane giving colourless crystals with m.pt 58–60°C (yield 0.21 g, 52%). Found: C, 25.0; H, 5.3. $C_8H_{19}AsPt$ requires: C, 24.9; H, 5.0%.

X-ray crystallography

Crystals of compounds **V** and **VI**, which were air-stable, were mounted on glass fibres for X-ray study. Preliminary cell dimensions were obtained photographically and accurate values by least-squares refinement of diffractometer setting angles (25 reflections in the range $12 < \theta < 14°$ in each case). Intensity data were recorded at 293 K using a CAD-4 diffractometer and monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), as previously described.[7] The structures were solved by the heavy-atom method and refined on *F* by full-matrix least-squares (Pt, P and As anisotropic, C isotropic, hydrogens ignored). The crystal data, intensity measurement parameters, and refinement details for both compounds are given in Table 1. In the case of **VI**, of the two possible configurations in the non-centrosymmetric space group $P2_12_12_1$, that giving the lower *R*-values was taken as the correct absolute structure. The atomic coordinates, thermal parameters and interatomic distances and angles have been deposited as supplementary material. Details of computers, programs, and scattering factor data are given in ref. 7.

DISCUSSION OF THE STRUCTURES

The molecular structures of **V** and **VI** are shown in Figs 1 and 2, respectively. Both structures show, as expected, a square-planar arrangement of ligands where the *cis*-methyl groups and the chelate phosphino or arsinobutens are all bonded to the central Pt^{II} ion. The coordinated $PCH_2CH_2CH{=}CH_2$ and $AsCH_2CH_2CH{=}CH_2$ entities are chiral; molecules of each hand alternate in the crystal structure of **V**, whilst those of only one hand are present in **VI**.

The crystal structure of the phosphine complex **V** contains two crystallographically independent molecules, but these differ only very slightly in bond lengths and angles. In many cases, but not all, these differences are comparable with or less than the uncertainties of the determinations. Even the conformation of the phenyl groups is virtually identical in each case.

Table 1. Crystal data and details of data collection and structure refinement for compounds **V** and **VI**

Compound	**V**	**VI**
Molecular formula	$C_{18}H_{23}PPt$	$C_8H_{19}AsPt$
M.wt	465.43	385.24
Crystal system	Triclinic	Orthorhombic
a (Å)	13.273(2)	7.319(1)
b (Å)	11.367(2)	10.745(2)
c (Å)	11.285(1)	14.241(3)
α (°)	84.94(1)	90
β (°)	93.40(1)	90
γ (°)	95.09(1)	90
U (Å^3)	1686.98	1119.95
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
Z	4	4
D_c (g cm^{-3})	1.832	2.284
F(000)	896	712
μ(Mo-K_α) (cm^{-1})	84.9	155.3
$\theta_{min}/\theta_{max}$	1.5, 26.0	1.5, 28.0
Total data	6662	1497
Total unique data	6530	1429
Observed data	5576	1274
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
No. of parameters	181	51
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o)+g(F_o)^2]$	0.0005	0.0024
Final $R(= \Sigma\Delta F/\Sigma F_o)$	0.051	0.053
$wR\{ = [\Sigma(w\Delta F^2)/\Sigma(wF_o^2)]^{1/2}\}$	0.064	0.065

The structure of **V** closely resembles that of $PtMe_2(o\text{-}Ph_2PC_6H_4CH{=}CH_2)$,[4] (**VII**), where the chelate ligand differs from $Ph_2PCH_2CH_2CH{=}CH_2$ sterically to a small extent and electronically in the conjugation of the vinyl and aromatic groups. The interatomic distances for Pt—C and Pt—P in **V**, **VI** and **VII** are shown in Table 2.

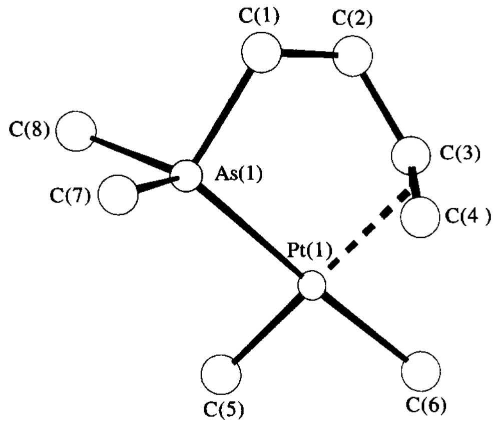

Fig. 2. Molecular structure of $[PtMe_2(Me_2AsCH_2CH_2CH{=}CH_2)]$ (**VI**) showing the labelling of atoms.

Compared with **VII**, **V** has a slightly less strongly bound vinyl group. This may be related to the greater angle between the C=C vectors and the normal to the C(methyl)—Pt—C(methyl) plane for **V** (16.6 and 19.4°) than for **VII** (6.0°). In unconstrained complexes the angle is very small, as in $K[PtCl_3(C_2H_4)]\cdot H_2O$.[8] If closeness to the ideal angle of 0° is taken as a measure of suitable stereochemistry for bidentate coordination to platinum (II), it seems that the butenylphosphino group, despite the greater flexibility of its longer, aliphatic, chain compared with the styrylphosphino grouping, is less favoured than is the latter group. Indeed, Dreiding models indicate that a truly ideal coordination geometry would impose some strain. The $CH{=}CH_2$ group in **VII** was rotated out of the P-phenyl plane, presumably thus achieving a stronger bond with platinum, but losing enthalpy of con-

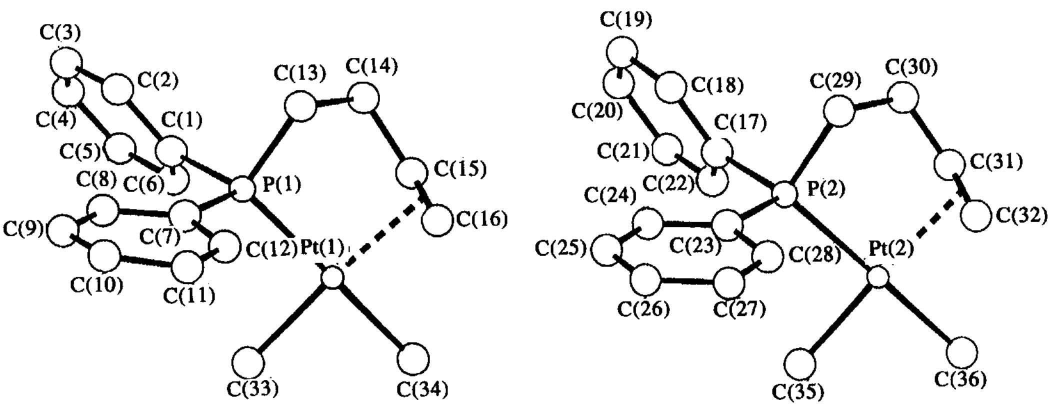

Fig. 1. Structures of the two independent molecules of $[PtMe_2(Ph_2PCH_2CH_2CH{=}CH_2)]$ (**V**) showing the labelling of atoms.

Table 2. Bond lengths (Å) between Pt and C, P or As

Compound	V[a]	VI[a]	VII[b]
Pt—P or As	2.273(2), 2.282(2)	2.405(2)	2.276
Pt—CH_3 (*trans* to P or As)	2.10(1), 2.11(1)	2.08(3)	2.17
Pt—CH_3 (*cis* to P or As)	2.06(1), 2.06(1)	1.98(3)	2.05
Pt—CH	2.24(1), 2.29(1)	2.22(2)	2.22
Pt—CH_2	2.25(1), 2.26(1)	2.28(2)	2.20

[a] This work.
[b] = ref. 4.

jugation. It may be that the π-acceptor properties of the vinyl group are enhanced by the resulting increased localization of the π-density.

The mean Pt—P distance of 2.278 Å is indistinguishable from the Pt—P distance (2.276 Å) in **VII**. These Pt—P distances may be compared with 2.326 and 2.321 Å in *cis*-$PtMe_2(PPh_2Me)_2$[9] and 2.245 to 2.250 Å in the two crystal forms of *cis*-$PtCl_2(PPh_2Me)_2$.[10] The distance is greater than in the dichloride owing, in effect, to the greater competition of the methyl groups for the Pt σ-bonding orbitals. The more weakly σ-bonding but effectively σ-bonding alkene, however, slightly assists the Pt—P bond in the phosphino-alkene complex compared with the bis-phosphine complex. The Pt—As distance in **VI** is 2.405 Å, which may be compared with that of only 2.317 Å in the dichloride $PtCl_2$(*o*-$Ph_2AsC_6H_4CH{=}CH_2$),[5] doubtless for reasons similar to the phosphorus case.

The change from Ph_2P to Me_2As on passing from **V** to **VI** is accompanied by decreases in the Pt—CH_3 distances (Table 2). It is notable that the decrease is greater for the *cis*-methyl group. The decrease would be consistent with As being a weaker σ-donor than P, perhaps because of orbital incompatibility. The CH_3—Pt σ-bond would then be favoured by a reduction in electronic charge on Pt. The possibly greater π-acceptor character of P does not appear to be significant in this instance. The Pt—(C=C) distance is little affected by the PPh_2 to $AsMe_2$ change in the *cis* position.

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