The Phosphinoethylsilyl Group as a Bifunctional Chelate. Asymmetric Induction at Platinum(II)

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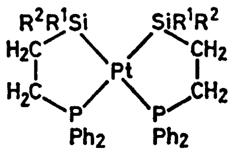
Summary The synthesis of *cis*-[Pt($PPh_2CH_2CH_2SiR^1R^2$)$_2$] is reported, and its geometry, inferred from ^{31}P n.m.r. data, is confirmed by *X*-ray crystallography for $R^1 = R^2 = Me$; when $R^1 \neq R^2$ racemic and *meso*-diastereomers are formed in varying ratio consistent with asymmetric induction during stepwise chelation to give the *rac*-complex as the preferred isomer, and this is proven where $R^1 = Me$, $R^2 = Ph$ by diastereomer separation followed by Pt–Si bond-cleavage with (+)-EtCH(Me)-CH_2I.

The chemistry of diorganophosphinoethylsilanes $R_2PCH_2CH_2SiR^1_3$ remains neglected although representative examples were first isolated some time ago.[1] Unidentate ligation through phosphorus to transition-metal centres has been cursorily investigated in the context of solubility enhancement and as a means for binding complexes to polymer supports through siloxy-linkages.[2,3] A more interesting alternative function for such compounds in co-ordination chemistry is their potential as precursors of bidentate phosphinoethylsilyl complexes $\overline{MPR_2CH_2CH_2SiR^1_2}$; but this has received even less attention,[4] which is surprising in view of the rarity of simple systems which chelate as odd-electron ligands. We have adopted a systematic approach to developing this area through synthesis of analogues of $R_2PCH_2CH_2SiR^1_3$ functionalized at silicon by incorporation of SiH bonds.† Oxidative addition (hydrosilylation) has provided access to a family of new metal complexes, for which pertinent structural comparisons include (i) the relationship of the $\overline{MPR_2CH_2CH_2SiR^1_2}$ configuration to familiar chelates like diphos ($PPh_2CH_2CH_2PPh_2$) and to simple silyl–metal compounds, and (ii) diastereoisomerism resulting from introduction of asymmetric silicon. These considerations are here examined by reference to some novel derivatives of square-planar platinum(II).

$Ph_2PCH_2CH_2SiHR^1R^2$

(1)a–c



(2)

a; $R^1 = R^2 = Me$
b; $R^1 = R^2 = Ph$
c; $R^1 = Me$, $R^2 = Ph$
d; $R^1 = H$, $R^2 = Me$
e; $R^1 = H$, $R^2 = Ph$

The reaction of (**1a**—**c**) with [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) (Et_2O, 25 °C, 10 min) affords the colourless crystalline products (**2a**—**c**), respectively, in *ca.* 90% yield.‡ Lower yields (*ca.* 25%) of the same compounds can be isolated on addition of 1 mol. equiv. of NEt_3 to mixtures of (**1a**—**c**) with [Pt(cod)Cl_2] (benzene, 25 °C, 2 h) and they can also be detected (^1H and ^{31}P n.m.r. spectroscopy) in solution after treatment of [Pt(PPh_3)$_4$] with (**1a**—**c**) (25 °C, 3 h). Similar reactions using $Ph_2PCH_2CH_2SiRH_2$ (R = Me or Ph) give analogous complexes (**2d**, **e**), characterized in solution also by ^1H and ^{31}P n.m.r. spectroscopy, although attempted crystallization resulted in the formation of insoluble materials, probably owing to oligomerization involving further addition of the SiH bonds.

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† To date we have synthesised 26 such compounds; 6 have been reported previously and a further 6 are deuteriated analogues. Complete results will be reported subsequently.

‡ Characterized by microanalysis as well as by the spectroscopic data.

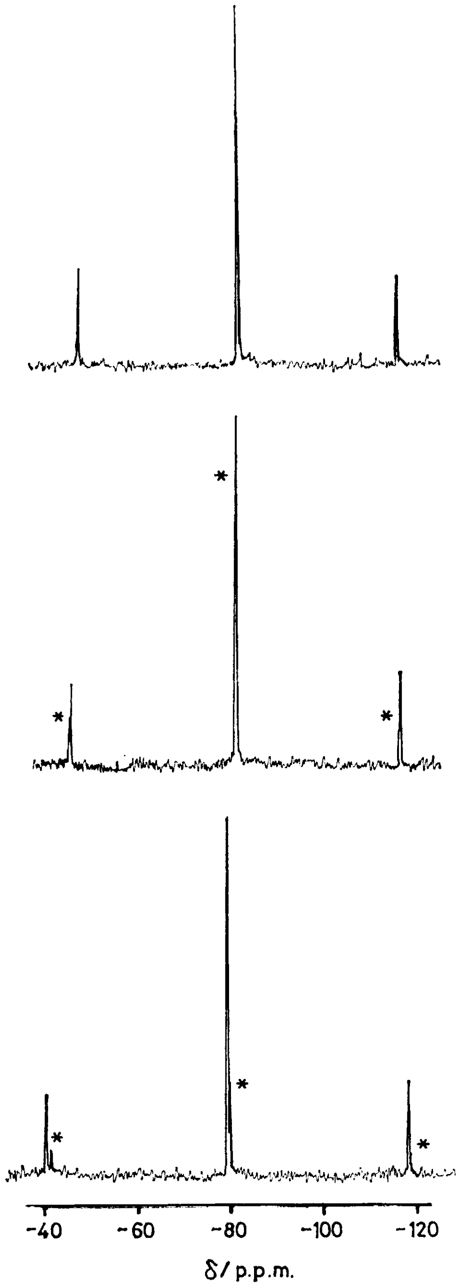

FIGURE 1. Proton-decoupled Fourier-transform ^{31}P n.m.r. spectra (24·3 MHz; δ in p.p.m. rel. to trimethylphosphite) for (**2a**), (**2c**), and (**2e**). For (**2c**) and (**2e**), in each case * indicates the positions of the signal maxima for the less abundant diastereomer.

A *cis*-arrangement for the phosphinoethylsilyl ligands in a typical square-planar Pt^{II} environment is indicated by ^1J(Pt–P) values in the range 1613—1838 Hz for compounds (**2a**—**e**) (Figure 1).[5] This conclusion was substantiated for complex (**2a**) by a single-crystal X-ray study.

Crystal data: $PtSi_2P_2C_{32}H_{40}$, monoclinic, space group $P2_1$, a = 12·313(2), b = 12·588(2), c = 10·560(5) Å, β = 102·69(1)°, D_c = 1·535 g cm^{-3}, Mo-$K_{\alpha 1}$ radiation (λ = 0·71069 Å), μ = 43·9 cm^{-1}, four-circle diffractometry, 2352 independent observable reflections, 1900 with $I > 1\sigma(I)$. The structure was refined to a conventional R = 0·05 and is shown with selected interatomic distances and bond angles in Figure 2. The mean Pt–P bond length of 2·346(4) Å is somewhat longer than that in a cationic (diphos)–Pt^{II} complex[6] or those in Pt^{II} compounds having two unidentate phosphine ligands *trans* to one another; likewise the mean Pt–Si distance, at 2·355(6) Å is long, approaching that *trans* to H in *trans*-[Pt(H)(SiH$_3$)-{P(C$_6$H$_{11}$)}$_2$].[7] Both these effects can be ascribed to the large *trans*-influence of the Si centre which also accounts for the low value of ^1J(Pt–P).[7] The pronounced difference between P–Pt–P and Si–Pt–Si angles in the (distorted) square plane about Pt reflects the unsymmetrical spatial requirements of the chelate.§

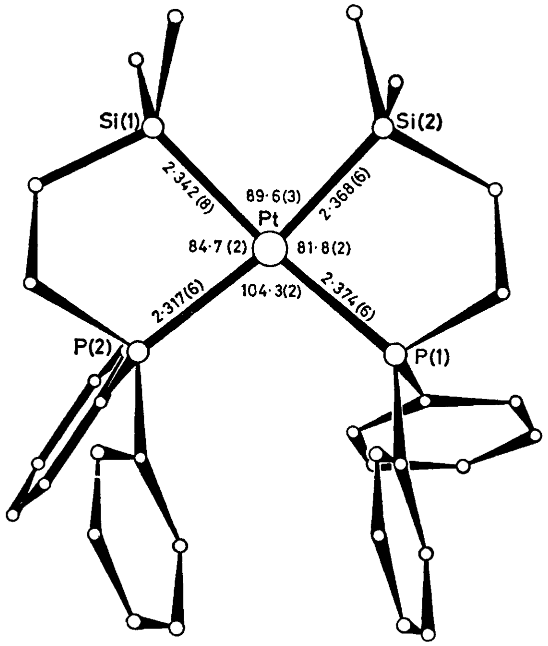

FIGURE 2. Molecular structure showing selected bond lengths and angles for (**2a**).

Compounds (**2c**—**e**) are diastereoisomeric, each containing chiral Si atoms internally related by C_2 (racemic) or σ (*meso*) symmetry operations. The existence of two isomers in each case gives rise to overlapping patterns in ^{31}P n.m.r. spectra (Figure 1), ratio 60:40 (**2c**), 80:20 (**2d**) or 75:25 (**2e**). These ratios imply asymmetric induction during stepwise chelation at the metal centre, which can be intramolecular in formation of (**2d**) or (**2e**) (since either H can be eliminated at Si) but must involve an intermolecular transition-state for formation of (**2c**) in which the Si configuration becomes immutable as the ligand attaches to Pt. Steric considerations suggest that the

§ 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.

predominant diastereomer will be the racemic (enantiomeric) form and this has been confirmed for (**2c**) for which we have succeeded in separating the two diastereomers. We have observed cleavage of the Pt–Si bonds in (**2a**) by MeI to give *trans*-$[PtI_2(PPh_2CH_2CH_2SiMe_3)_2]$ [^1J(Pt–P) 2409 Hz]. An analogous reaction with the more abundant (**2c**) isomer using (+)-2-methylbutyl iodide (R*I) results in formation of two *trans*-products (^{31}P n.m.r. spectroscopy) *i.e.* $[PtI_2(PPh_2CH_2CH_2Si^RMePhR^*)_2]$ and $[PtI_2(PPh_2CH_2CH_2Si^SMePhR^*)_2]$ by a stereoselective pathway from the racemic mixture.

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