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Preliminary communication

The absolute configuration of the optically-active silylplatinum complex (+)-*trans*-[PtCl{SiMe(1-$C_{10}H_7$)Ph}($PMe_2Ph)_2$]

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SUMMARY

Crystallographic data are presented which reveal that the complex (+)-[PtCl{SiMe(1-$C_{10}H_7$)Ph}($PMe_2Ph)_2$] has the absolute configuration (*S*) which corresponds with that of the (*R*) (+)-Me(1-$C_{10}H_7$)PhSiH from which it is made.

We recently prepared the complex (+)-*trans*-[PtCl{SiMe(1-$C_{10}H_7$)Ph}($PMe_2Ph)_2$], (I), the first complex containing an optically-active silicon centre bound to platinum, by treating the silane (*R*)(+)-Me(1-$C_{10}H_7$)PhSiH, (II), with *cis*-[$PtCl_2(PMe_2Ph)_2$]. The value of the optical rotation of (II) regenerated by treating (I) with lithium aluminium hydride demonstrated that little loss of activity had occurred during the cycle[1], and it seemed likely that the formation of (I) from (II), and the reformation of (II), both proceeded with retention of configuration at silicon. We have now carried out an X-ray crystallographic study which shows (I) to have the configuration corresponding with that[2] of the hydride, (II), from which it was made. (The absolute configuration of (I) has thus to be designated (*S*).)

Crystals of (I) are monoclinic (space group $P2_1$) with a=12.80, b=12.49, c=10.19 Å, β=104.5°, Z=2. X-ray diffraction data were collected on a Hilger and Watts four-circle diffractometer using monochromated Mo-K_α radiation. On the basis of a data set of 2680 unique reflections with $F_0^2/\sigma(F_0^2)>2.5$, the atomic positional and vibrational parameters were refined by least-squares methods to a present unweighted discrepancy index of 0.042. At this point comparison of observed and calculated values for structure factor magnitudes of Friedel pairs of reflections showing significant differences allowed the assignment of absolute configuration shown in Fig. 1. The coordination around platinum is square planar with a slight tetrahedral distortion; the deviation from the mean plane of the five heavy atoms is approx-

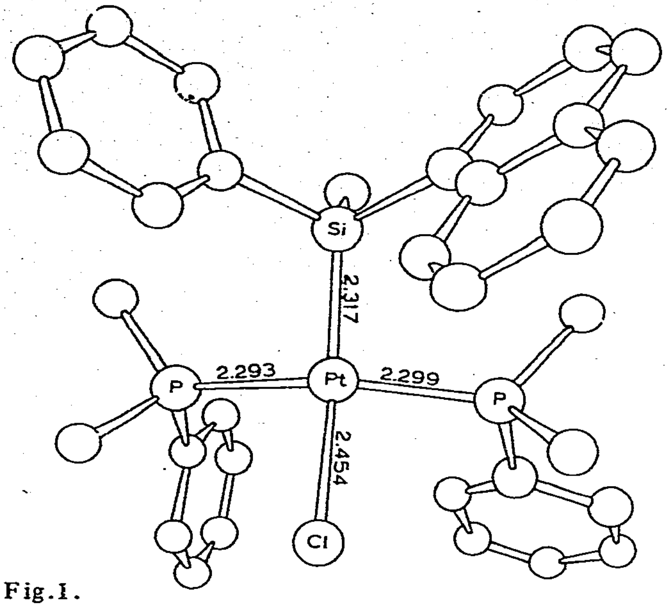

Fig.1.

imately 0.3 Å for each of the coordinated atoms. The standard deviations of the bond lengths shown are approximately 0.004 Å.

The results have important implications in the interpretation of the stereochemistry of reactions at the Si–Pt bond[3]. An additional noteworthy feature is the Pt–Cl bond length, which is identical within the limits of error to that (*viz.* 2.45 Å) observed for the Pt–Cl bond in the complex *trans*-[PtCl(SiMePh$_2$)(PMe$_2$Ph)$_2$][4]; these unusually long bonds reflect the large *trans*-influence of organosilyl ligands attached to platinum[5].

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