Stereochemistry of Cleavage of Silicon–Platinum Bonds in Optically Active Silicon–Platinum Compounds

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Summary The cleavage of the Si–Pt bond in *trans*-(+)-[PtCl(*SiR$_3$)(PPhMe$_2$)$_2$] [R$_3$Si* = MePh(1-naphthyl)Si] by LiAlH$_4$, PhSH, or Et$_3$SiH, and of that in (−)-[PtH(*SiR$_3$)(PPh$_3$)$_2$] by LiAlH$_4$, PhCOCl, PhC≡CH, or PhSH occurs with predominant retention of configuration at silicon.

WE recently described the preparation of the first silicon–platinum complex containing an optically-active silicon centre, *trans*-(+)-[PtCl (*SiR$_3$)(PPhMe$_2$)$_2$] (I) R$_3$*Si = MePh(1-naphthyl)Si.[1] The configuration around the silicon atom in complex (I) has been shown by *X*-ray diffraction studies to correspond with that in the starting hydride (*R*)-(+)-R$_3$Si*H,[2] which means that (I) is formed with retention of configuration. We have now studied the stereochemistry of some cleavages of the Si–Pt bond in (I), with the results shown in the Table.

It will be seen that cleavage by lithium aluminium hydride occurs with retention at silicon with very little loss of optical activity. The cleavages by thiophenol and triethylsilane also occur with predominant retention. accompanied by some racemization. The cleavages by bromine and iodine give initially the silicon chloride, R$_3$Si*Cl; the hydride, R$_3$Si*H, obtained from this by treatment with lithium aluminium hydride is completely or almost completely racemic; since such reduction of the chloride is known to occur cleanly with inversion,[3] the loss of optical activity must have occurred either during the halogen cleavage of (I) itself, or, as we think rather more likely (see below), subsequently in the chloride in the reaction medium.

TABLE

Complex	Reagent	Products[a]	Predomin. stereochem. (%)[b]
(I)[c] $[\alpha]_D$, +72°	LiAlH$_4$ (Et$_2$O)	(+)-R$_3$Si*H, $[\alpha]_D$ +29·1°; Pt; PPh$_2$Me.	Ret. (93)
	PhSH(C$_6$H$_6$)	(+)-R$_3$Si*H, $[\alpha]_D$ +16·9°; *trans*-[Pt(SPh)$_2$L$_2$]; *cis*-[PtCl$_2$L$_2$].	Ret. (74)
	Et$_3$SiH (C$_6$H$_6$)	(+)-R$_3$Si*H, $[\alpha]_D$ +9·1°; *trans*-[PtH(Cl)L$_2$].	Ret. (63·5)
	Br$_2$(C$_6$H$_6$)	(−)-R$_3$Si*Cl{→(−)-R$_3$Si*H, $[\alpha]_D$ −1°}; *cis*-[PtBr$_2$L$_2$].	Racm. (97)
	I$_2$(C$_6$H$_6$)	(±)-R$_3$Si*Cl{→(±)-R$_3$Si*H, $[\alpha]_D$ 0°}; *cis*-[PtI$_2$L$_2$].	Racm. (100)
(II)[d] $[\alpha]_D$ −18·5°	LiAlH$_4$ (Et$_2$O)	(+)-R$_3$Si*H, $[\alpha]_D$ +31·0°; Pt; PPh$_3$.	Ret. (97)
	PhCOCl (no solvent)	(+)-R$_3$Si*H, $[\alpha]_D$ +24·7°; *trans*-[PtCl(COPh)L'$_2$].	Ret. (87·5)
	PhC≡CH (no solvent)	(+)-R$_3$Si*H, $[\alpha]_D$ +28°; [Pt(PhC≡CH)L'$_2$].[e]	Ret. (92·5)
	PhSH (no solvent)	(+)-R$_3$Si*H, $[\alpha]_D$ +27·8°; *trans*-[PtH(SPh)L'$_2$].	Ret. (92)

[a] The rotations are measured at 25° in cyclohexane. [b] The percentages represent the overall results of the Walden cycle (+)-R$_3$Si*H back to R$_3$Si*H. [c] From (+)-R$_3$SiH having $[\alpha]_D$ +33·6°. [d] From (+)-R$_3$SiH having $[\alpha]_D$ + 32·9°. [e] PhC≡CH π-bonded.

We have also prepared the new optically active complex (II) (probaly *cis*), m.p. 106—107° (decomp.), ν(Pt–H) 2150 and 2070 cm^{-1} by means of the reaction represented in equation (1) (*cf.* ref. 4). Cleavage by lithium aluminium hydride

$$\underset{[\alpha]^{25}_{D}\ +\ 32\cdot9^\circ}{(+)\text{-}R_3Si^*H} + [Pt(PPh_3)_2C_2H_4] \rightarrow \underset{[\alpha]^{25}_{D}\ -\ 18\cdot5^\circ\ (c,\ 0\cdot86\ \text{in}\ C_6H_6)}{\underset{\text{(II)}}{(-)\text{-}[PtH(^*SiR_3)(PPh_3)_2]}} + C_2H_4 \qquad (1)$$

gives back the original hydride with 97% overall retention of configuration (see Table). Since we can safely assume that the reactions of (I) and (II) with lithium aluminium hydride involve the same stereochemistry at silicon, this means that the configuration about silicon in complex (II) is, in spite of the negative rotation, the same as that in the complex (I) and thus as that in (*R*)-(+)-R_3Si^*H. [In agreement with this view, (I) and (II) were found to give plain o.r.d. curves of the same (positive) sign; the molecular rotation of (II) is positive below 520 nm, and is greater than that of (I) below 440 nm]. It follows that the formation of (II), as well as its reaction with lithium aluminium hydride, occurs with highly specific retention at silicon. Cleavages by benzoyl chloride, phenylacetylene, and thiophenol also occur with predominant retention of configuration.

The substantial racemization observed in the halogen cleavages, and the smaller amount of racemization found in the (+)-R_3Si^*H samples obtained from the other cleavages, probably occur after the initial cleavages. The $[\alpha]^{25}_{D}$ value of a sample of (−)-R_3Si^*Cl fell from −6·3° to *ca.* −2° in 12 h in the presence of *trans*-$[PtHCl(PMe_2Ph)_2]$ in benzene at room temperature, and the $[\alpha]^{25}_{D}$ values of (+) R_3Si^*H samples in benzene fell from +32·9° to *ca.* +28·0° in the presence of a 0·5 molar proportion of *trans*-$[PtHCl(PMe_2Ph)_2]$ (24 h at 70°) or a 1·0 molar proportion of *trans*-$[PtCl(COPh)(PPh_3)_2]$ (48 h at room temperature). There is less chance of such racemization in the lithium aluminium hydride reactions since the complex is decomposed to platinum metal.

It is likely that all the observed Si–Pt bond cleavages proceed through Pt^{IV} intermediates, in oxidative-addition reductive-elimination sequences, and it is noteworthy that the silicon hydride rather than the chloride separates from the intermediate $[PtH(Cl)(^*SiR_3)(COPh)(PPh_3)_2]$, and the silicon chloride, rather than the iodide or bromide from the species $[PtX_2Cl(^*SiR_3)(PPhMe_2)_2]$ (X = Br or I).

As would be expected, complex (I) gives optically active species, *viz.* *trans*-(+)-$[PtBr(^*SiR_3)(PPhMe_2)_2]$, m.p. 164·5—166°, $[\alpha]^{25}_{D}$ + 70° (*c*, 1·28 in C_6H_6), and *trans*-(+)-$[PtI(^*SiR_3)(PPhMe_2)_2]$, m.p. 183—184°, $[\alpha]^{25}_{D}$ + 55° (*c*, 1·63 in C_6H_6), on treatment with lithium bromide or sodium iodide in acetone.

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