Stereochemistry of the Formation and Cleavage of Silicon–Platinum Bonds

By **Colin Eaborn,* David J. Tune,** and **David R. M. Walton,** School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ

The complex (+)-*trans*-[PtCl(*SiR$_3$)(PMe$_2$Ph)$_2$], $[\alpha]_D^{25}$ + 72° (I), is formed with a high degree of retention of configuration at silicon from (+)-R$_3$Si*H [R$_3$Si* = Me(1-C$_{10}$H$_7$)PhSi] and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] in the presence of triethylamine. The (+)-R$_3$Si*H is regenerated with 93% overall retention of configuration when (I) is treated with lithium aluminium hydride, and with rather smaller degrees of retention when (I) is treated with benzenethiol or triethylsilane. Bromine liberates (−)-R$_3$Si*Cl with much racemisation, while iodine gives the racemic chloride. Complex (I) is converted into (+)-*trans*-[PtBr(*SiR$_3$)(PMe$_2$Ph)$_2$], $[\alpha]_D^{25}$ + 70·0°, and (+)-*trans*-[PtI(*SiR$_3$)(PMe$_2$Ph)$_2$], $[\alpha]_D^{25}$ + 54·6°, on treatment with lithium bromide or sodium iodide in acetone.

The complex (−)-*cis*-[PtH(*SiR$_3$)(PPh$_3$)$_2$], $[\alpha]_D^{25}$ − 18·5° (II), is formed from (+)-R$_3$Si*H and [Pt(PPh$_3$)$_2$C$_2$H$_4$], with little loss of optical activity, and probably with retention of configuration at silicon; the (+)-R$_3$Si*H is regenerated with 97% overall retention on treatment with lithium aluminium hydride, and with a slightly smaller degree of overall retention on treatment with phenylacetylene, benzenethiol, or benzoyl chloride. It is suggested that the cleavages of the Si–Pt bonds in (I) and (II), and especially those involving reaction or formation of R$_3$Si*H, may occur *via* oxidative-addition–reductive-elimination sequences, with complete or almost complete retention of configuration at silicon, with the observed losses of activity arising from secondary racemisation; it was shown that (+)-R$_3$Si*H and (more readily) (−)-R$_3$Si*Cl do undergo racemisation in the presence of platinum complexes.

Triphenylsilane and *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] have been found to react to give *trans*-[PtH(Cl)(PMe$_2$Ph)$_2$], which then reacts with additional triphenylsilane to give *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$].

(+)-Et(1-C$_{10}$H$_7$)PhGeH (denoted R'$_3$Ge*H), $[\alpha]_D^{25}$ + 15·0°, reacts with *trans*-[PtH(Cl)(PMe$_2$Ph)$_2$] to give a complex believed to be (+)-*trans*-[PtCl*(GeR'$_3$)(PMe$_2$Ph)$_2$], $[\alpha]_D^{25}$ +12·9°, and with [Pt(PPh$_3$)$_2$C$_2$H$_4$] to give a complex believed to be (−)-*cis*-[PtH(*GeR$_3$')(PPh$_3$)$_2$], $[\alpha]_D^{25}$ −6·0°, neither optically pure. Both products are thought to be formed with predominant retention of configuration at germanium.

We previously described the preparation of the first silicon–platinum compound containing an optically active silicon centre, *viz.*, the complex (+)-*trans*-[PtCl(*SiR$_3$)(PMe$_2$Ph)$_2$] (I), which was made with a specific rotation of +68·8° by treatment of the hydride (+)-R$_3$Si*H [where R$_3$Si* = MePh(1-C$_{10}$H$_7$)Si] with *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] in toluene in the presence of triethylamine.[1] We now report an improved preparation of (I) in a slightly higher state of optical purity, and describe a study of the stereochemistry at silicon of the formation of this complex and of the cleavages of the silicon–platinum bond by several reagents. We also describe the preparation and a similar study of the reactions of a new optically active silicon–platinum complex, the

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[1] C. Eaborn, P. N. Kapoor, D. J. Tune, C. L. Turpin, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **34**, 153.

probable formation of a third such complex in impure form, and the preparation in optically impure state of two optically active germanium–platinum complexes. A *preliminary* account has appeared.[2]

Preparations of the Optically Active Silylplatinum Complexes.—Treatment of *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] with (+)-R$_3$Si*H in benzene in the presence of triethylamine gave complex (I), according to equation (1). The use of toluene as solvent with a reflux time of 65 h gave up to 65% of compound (I), but the yield was unpredictable, and the platinum hydridochloride *trans*-[PtH(Cl)(PMe$_2$Ph)$_2$] was sometimes formed, in yields varying between 40 and 100%. Later studies (see below) showed that use of a longer reaction time in refluxing benzene gave the best results, complex (I) then being consistently isolated in over 50% yield. Recovery of (+)-R$_3$Si*H with $[\alpha]_D^{25}$ +29·1° on treatment of (I) with lithium aluminium hydride shows that (I) must have been at least 93% optically pure; the purity was probably somewhat greater, since it is likely that at least part of the loss of activity occurs in the cleavage rather than in the synthesis.

$$\textit{cis}\text{-}[PtCl_2(PMe_2Ph)_2] + \underset{[\alpha]_D^{25} + 33\cdot6^\circ}{(+)\text{-}R_3Si^*H} + Et_3N \longrightarrow \underset{(I),\ [\alpha]_D^{25} + 72\cdot0^\circ}{(+)\text{-}\textit{trans}\text{-}[PtCl(^*SiR_3)(PMe_2Ph)_2]} + Et_3N,HCl \tag{1}$$

Complex (I) was converted into (+)-*trans*-[PtBr(*SiR$_3$)(PMe$_2$Ph)$_2$], $[\alpha]_D^{25}$ +70·0°, and (+)-*trans*-PtI(*SiR$_3$)(PMe$_2$Ph)$_2$], $[\alpha]_D^{25}$ +54·6°, by treatment with lithium bromide or sodium iodide in acetone.

A new optically active complex (II) was made by use of the recently reported reaction between the Pt^0 complex [Pt(PPh$_3$)$_2$C$_2$H$_4$] and a silicon hydride,[3,4] as indicated in equation (2). Because it dissociates in solution, as described below, the product could not be recrystallised to give a wholly satisfactory elemental analysis, but there is very little doubt about its identity, and since (+)-R$_3$Si*H can be recovered from it with only 3% overall racemisation, complex (II) must be substantially pure optically. The existence of two ν(Pt–H) bands, at 2150 and 2070 cm^{-1}, in the i.r. spectrum of (II) in a Nujol mull was initially worrying, but this probably arises from a solid-state effect, possibly associated with the presence of two crystalline modifications, since only one ν(Pt–H) band, at 2070 cm^{-1}, appears in benzene solution. {The occurrence of two ν(Pt–H) bands in the spectrum of solid *trans*-[PtH(CN)(PMePh$_2$)$_2$] has been attributed to the presence of two crystal forms.[5]} The possibility that the product is a mixture of *cis*- and *trans*-isomers can be ruled out, since even the lower of the two ν(Pt–H) values is much too high for a compound in which the hydrogen atom is *trans* to silicon.[4] The instability of compound (II) in solution prevented a study of its ^{31}P n.m.r. spectrum.

$$[Pt(PPh_3)_2C_2H_4] + \underset{[\alpha]_D^{25} +32\cdot9^\circ}{(+)\text{-}R_3Si^*H} \longrightarrow \underset{(II),\ [\alpha]_D^{25} -18\cdot5^\circ}{(-)\text{-}\textit{cis}\text{-}[PtH(^*SiR_3)(PPh_3)_2]} + C_2H_4 \tag{2}$$

A third type of optically active complex was probably produced when *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] was treated with (+)-R$_3$Si*H in benzene, in a reaction which, on the basis of experience with other silicon hydrides,[6] can be assumed to proceed according to equation (3); the (Si–H) band at 2120 cm^{-1} disappeared, and was replaced by a ν(Pt–H) band at 2040 cm^{-1}. Unfortunately the tacky product could not be recrystallised, and no analytical data were obtained.

$$\textit{cis}\text{-}[PtMe_2(PMe_2Ph)_2] + \underset{[\alpha]_D^{25} +32\cdot9^\circ}{3R_3Si^*H} \longrightarrow [PtH(^*SiR_3)(PMe_2Ph)_2] + \underset{[\alpha]_D^{25} +18^\circ}{2R_3Si^*Me} \tag{3}$$

TABLE 1

Specific rotation of *cis*-[PtH(*SiR$_3$)(PPh$_3$)$_2$] in benzene (*c*, 0·865 g/100 ml) at room temperature

Time/min	0	5	10	15
$[\alpha]_D^{25}$/°	−18·5	−15·4	−13·9	−12·4
Time/min	20	25	30	35
$[\alpha]_D^{25}$/°	−12·6	−13·3	−13·0	−13·0

The Dissociation of Complex (II) *in Solution.*—Complex (II) could not be recrystallised from benzene–hexane, and the initially colourless solution became deep red. Examination of the i.r. spectrum of the benzene solution at room temperature showed that a band at 2120 cm^{-1} attributed to ν(Si–H) appeared initially as a weak shoulder, but became strong after 15 min and showed little further change during another 20 min, while the intensity of the ν(Pt–H) band at 2070 cm^{-1} decreased somewhat during the first 15 min and then also remained fairly constant. The optical rotation of the solution also fell during the first 15 min, then remained substantially constant during the next 20 min, as Table 1 shows.

The probable explanation of these results is that dissociation takes place according to equation (4). If complete dissociation to (+)-R$_3$Si*H occurred, the specific rotation of the solution would be +8·45°, and so if the equilibrium value of +13·0° for the specific rotation is due to a mixture of (II) and (+)-R$_3$Si*H then there must be *ca.* 20% of dissociation to free (+)-R$_3$Si*H; this must be regarded only as a very rough figure, how-

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[2] C. Eaborn, D. J. Tune, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1972, 1223.

[3] C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1972, **43**, C5.

[4] C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1973, in the press.

[5] H. C. Clark and H. Kurosawa, *J. Organometallic Chem.*, 1972, **36**, 399.

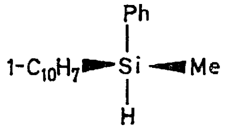
[6] C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1973, in the press.

ever, since on more prolonged standing extensive decomposition occurs, and none of the original complex seems to be present in the blood-red solution after 1 day at room temperature. Dissociation such as that depicted in equation (4) has been observed with *cis*-$[PtH(SiMe_2CH_2{\cdot}CH{=}CH_2)(PPh_3)_2]$;[4] possibly steric interactions between the aryl groups of the R_3Si^* system and those of the PPh_3 group *cis* to it render (II) relatively unstable.

$$\underset{[\alpha]_D^{25}\ -18{\cdot}5^\circ}{(-)\text{-}cis\text{-}[PtH(^*SiR_3)(PPh_3)_2]} + C_6H_6 \rightleftharpoons \underset{[\alpha]_D^{25}\ +32{\cdot}9^\circ}{(+)\text{-}R_3Si^*H} + [Pt(PPh_3)_2C_6H_6] \qquad (4)$$

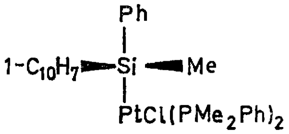
It is noteworthy that when complex (II) decomposes at its m.p. of 106—107 °C naphthalene sublimes out, indicating that an unusual cleavage of the silicon–naphthyl bond has occurred.

The Absolute Configuration of (I), *and the Stereochemistry of the Formation of* (I) *and* (II).—A complete *X*-ray diffraction analysis of compound (I) has shown that the configuration about the silicon atom corresponds with that in R-(+)-R_3Si^*H;[7] the configurations are as represented in the projections (A) and (B). This means that (I) is formed from (+)-R_3Si^*H with retention of configuration at silicon.



(A)

R-(+)-R_3Si^*H



(B) (I)

S-(+)-*trans*-$[PtCl(^*SiR_3)(PMe_2Ph)_2]$

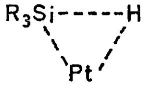
We believe that complex (II) is also formed with retention of configuration at silicon. This is because both (I) and (II) give back (+)-R_3Si^*H of high optical purity on treatment with lithium aluminium hydride. In the case of (I) this means unequivocally that the lithium aluminium hydride reduction occurs with retention of configuration at silicon, and it seems safe to assume that this reaction also involves retention in the case of (II), and thus that the silicon atom in (II) has the same configuration as that in (+)-R_3Si^*H. The o.r.d. results described below support this conclusion.

The formations of (I) and (II) probably involve oxidative additions. With (I) this probably initially gives the six-co-ordinate Pt^{IV} complex $[Pt(Cl)_2H(^*SiR_3)(PMe_2Ph)_2]$, which then loses hydrogen chloride, whereas with (II) the loss of ethylene may be synchronous with the oxidative addition to give the Pt^{II} species. While more complicated multistep routes are conceivable for the oxidative additions, it seems reasonable, in the absence of contrary evidence, to assume that they are simple one-step reactions, in which the Pt atom inserts into the Si–H bond in a three-centre process, as in (C). An analogy between a reacting transition-metal centre and a carbene has been drawn by Halpern,[8] and it is thus of interest that carbenes also undergo insertion into Si–H bonds with retention at silicon, probably in the three-centre process (D).[9]

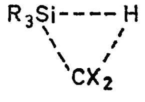
The formation of (−)-$[Co(^*SiR_3)(CO)_4]$ from (−)-R_3Si^*H and cobalt octacarbonyl is also thought, on the basis of indirect evidence (see below), to occur with retention of configuration at silicon.[10]

Optical Rotatory Dispersion Studies.—Some o.r.d. data over a limited wavelength range for the complexes prepared are in Table 2. All four silicon compounds examined give positive plain dispersion curves, which is consistent with their having the same configuration about silicon. The o.r.d. study was especially useful in the case of complex (II), because the difference between (I) and (II) in the sign of rotation at the sodium-D line was initially somewhat worrying in the light of the belief that the configuration at silicon was the same in both cases.

It is noteworthy that association of the positive signs of the plain curves for the four complexes with a configuration at silicon corresponding to that in (+)-R_3Si^*H is consistent with the observations by Sommer and his colleagues that such an association applies to the great majority of (+)-R_3Si^*X species;[11] this must be regarded as partly fortuitous, however, since the platinum system certainly falls well outside the limits on the nature of X laid down by Sommer *et al.* for application of o.r.d. data in configurational assignments.[11]



(C)



(D)

Cleavages of Si–Pt *Bonds in Complexes* (I) *and* (II).—The results of some reactions involving cleavage of the Si–Pt bonds of complexes (I) and (II) are in Table 3. The most useful reaction was the decomposition by lithium aluminium hydride in ether, which in both cases

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[7] C. Eaborn, P. Hitchcock, D. J. Tune, and D. R. M. Walton, *J. Organometallic Chem.*, 1973, **54**, C1.

[8] J. Halpern, *Chem. Eng. News*, 1966, **44**, No. 45, 68.

[9] L. H. Sommer, L. A. Ulland, and G. A. Parker, *J. Amer. Chem. Soc.*, 1972, **94**, 3469.

[10] L. H. Sommer, J. E. Lyons, and H. Fujimoto, *J. Amer. Chem. Soc.*, 1969, **91**, 7051; L. H. Sommer and J. E. Lyons, *ibid.*, 1968, **90**, 4197.

[11] L. H. Sommer and J. McLick, *J. Amer. Chem. Soc.*, 1969, **91**, 2001; L. H. Sommer, K. T. Rosborough, and J. McLick, *ibid.*, 1972, **94**, 4217.

regenerated the (+)-R_3Si^*H with little loss of activity, the reaction certainly involving retention at silicon in the case of (I), and slightly less certainly in the case of (II). The smallness of the loss of activity in the cleavage can be associated with (*a*) the rapidity of the reaction at room temperature, which means that there is little opportunity for secondary racemisations, and (*b*) the complete decomposition to platinum metal, which removes from the system any effective catalysts for such racemisations.

TABLE 2

Optical rotatory dispersion data in benzene; all values of α and *M* in degrees of angle

Complex			589 nm	578 nm	546 nm	436 nm	365 nm
trans-$[PtCl(*SiR_3)(PMe_2Ph)_2]$	1·53	$[\alpha]_D^{25}$	+72	+78	+95	+220	+340
		$10^{-2}[M]^{25}$	+5·4	+5·9	+7·2	+16·7	+26
trans-$[PtBr(*SiR_3)(PMe_2Ph)_2]$	1·28	$[\alpha]_D^{25}$	+70	+73	+88	+200	>+500
		$10^{-2}[M]^{25}$	+5·6	+5·8	+7·0	+16	>+40
trans-$[PtI(*SiR_3)(PMe_2Ph)_2]$	0·63	$[\alpha]_D^{25}$	+55	+63	+77	+230	>+1500
		$10^{-2}[M]^{25}$	+4·65	+5·3	+6·5	+19·5	>+125
cis-$[PtH(*SiR_3)(PPh_3)_2]$ [a]	1·1	$[\alpha]_D^{25}$	+18·0	+20·2	+25	+136	>+140
		$10^{-2}[M]^{25}$	+1·3	+1·45	+1·8	+9·8	>+10
cis-$[PtH(*SiR_3)(PPh_3)_2]$ [b]	1·7	$[\alpha]_D^{25}$	−13·2	−12·3	−9·8	+199	>+410
		$10^{-2}[M]^{25}$	−1·28	−1·19	−0·95	+19·3	>+40
trans-$[PtCl(*GeR'_3)(PMe_2Ph)_2]$	1·15	$[\alpha]_D^{25}$	+13·5	+15	+19·5	+45	+145
		$10^{-2}[M]^{25}$	+1·1	+1·22	+1·59	+3·66	+11·8
cis-$[PtH(*GeR'_3)(PPh_3)_2]$ [a]	1·7	$[\alpha]_D^{25}$	−6·0	−5·4	−3·7	+220	>+440
		$10^{-2}[M]^{25}$	−0·61	−0·55	0·38	+22·5	>+41

[a] Freshly prepared solutions. [b] Solution at equilibrium, involving *ca.* 20% dissociation (see text).

TABLE 3

Cleavages of (+)-*trans*-$[PtCl(*SiR_3)(PMe_2Ph)_2]$ (I) and (−)-*cis*-$[PtH(*SiR_3)(PPh_2)_2]$ (II)

Complex	Reagent	Conditions	Products	Predominant stereochemistry
(I)				
$[\alpha]_D^{25}$ +72·0°	$LiAlH_4$	Ether; 0 °C	Pt; (+)-R_3Si^*H (85%), $[\alpha]_D^{25}$ +29·1°	93·0% Retn.
	PhSH	Benzene; reflux; 1 h	*cis*-$[PtCl_2(PMe_2Ph)_2]$ (*ca.* 45%); *trans*-$[Pt(SPh)_2(PMe_2Ph)_2]$ (50%); (+)-R_3Si^*H (17%), $[\alpha]_D^{25}$ +16·9°	75% Retn.
	Et_3SiH	Benzene; reflux; 48 h	(I) (48%); *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ (31%); (+)-R_3Si^*H (6%), $[\alpha]_D^{25}$ +9·1°	63·5% Retn.
	Br_2	Benzene; 20 °C; 1 h	*cis*-$[PtBr_2(PMe_2Ph)_2]$ (88%); (−)-R_3Si^*H (50%) [a] $[\alpha]_D^{25}$ −1·0°	97% Racm.
	I_2	Benzene; 40 °C 20 h	*cis*-$[PtI_2(PMe_2Ph)_2]$ (100%); (±)-R_3Si^*H (100%),[a] $[\alpha]_D^{25}$ 0·0°	100% Racm.
(II)				
$[\alpha]_D^{25}$ −18·5°	$LiAlH_4$	Ether; 20 °C	Pt; (+)-R_3Si^*H (96%), $[\alpha]_D^{25}$ +31·0°	97·0% Retn.
	PhCOCl	0·5 h; 20 °C	*trans*-$[PtCl(COPh)(PPh_3)_2]$ (75%); (+)-R_3Si^*H (60%), $[\alpha]_D^{25}$ +24·7°	87·5% Retn.
	PhC≡CH	0·5 h; 20 °C	$[Pt(PPh_3)_2PhC{\equiv}CH]$ (93%); (+)-R_3Si^*H (62%), $[\alpha]_D^{25}$ +28·0°	92·5% Retn.
	PhSH	0·5 h; 20 °C	*trans*-$[PtH(SPh)(PPh_3)_2]$ (100%) (+)-R_3Si^*H (78%), $[\alpha]_D^{25}$ +27·8°	92% Retn.

[a] After reduction with $LiAlH_4$.

TABLE 4

Racemisation of (+)-R_3Si^*H and (−)-R_3Si^*Cl in benzene in the presence of platinum complexes

Silane	Complex	Mol. ratio	*t*/°C	Time/h	$[\alpha]_D^{25}$ Initial	$[\alpha]_D^{25}$ Final
(−)-R_3Si^*Cl	$[PtH(Cl)(PMe_2Ph)_2]$	1 : 1	*ca.* 20	12	−6·3°	*ca.* −2°
(+)-R_3Si^*H	$[PtH(Cl)(PMe_2Ph)_2]$	2 : 1	70	24	+32·9°	+27·8°
(+)-R_3Si^*H	$[PtCl(COPh)(PPh_3)_2]$	1 : 1	*ca.* 20	48	+32·9°	+28·1°

An attempt to regenerate the R_3Si^*H by hydrogenolysis of the Si–Pt bond (see ref. 12) was unsuccessful, no detectable reaction occurring. When air and moisture were not rigorously excluded during the attempted hydrogenolysis, decomposition to the disiloxane $(R_3Si^*)_2O$ occurred; we did not study this reaction in sufficient detail to establish whether either oxygen or moisture separately would bring about this conversion.

Treatment of (I) with triethylsilane liberated (+)-R_3Si^*H, but only in poor yield. After 48 h at 75 °C in benzene, 48% of (I) was recovered, along with 31% of the hydridochloride *trans*-$[Pt(Cl)H(PMe_2Ph)_2]$, and only 6% of (+)-R_3Si^*H, with a rotation corresponding with 63·5% overall retention of configuration. The substantial loss of activity in this case may be associated with secondary racemisation of the (+)-R_3Si^*H, possibly

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[12] J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 1343.

via or in addition to racemisation of transiently produced R_3Si^*Cl (see below). Table 4 shows that some racemisation of the hydride can, indeed, occur under such conditions.

Benzenethiol, which is known to cleave Si–Pt bonds,[12] gave (+)-R_3Si^*H with a rotation corresponding to 75% overall retention of configuration. The complex finally isolated was *trans*-$[Pt(SPh)_2(PMe_2Ph)_2]$, obtained in 50% yield, though a much higher yield of a mixture of this with *cis*-$[PtCl_2(PMe_2Ph)_2]$ was initially formed, presumably by disproportionation of $[PtCl(SPh)(PMe_2Ph)_2]$ (*cf.* ref. 12). Since a reaction temperature of 75 °C was used, the loss of activity may again have occurred in a secondary process, even though the reaction time, 1 h, was relatively short.

Treatment of (I) with bromine gave *cis*-$[PtBr_2(PMe_2Ph)_2]$ in 85% yield, indicating that the chloride R_3Si^*Cl had been displaced. The latter was not isolated, but reduced with lithium aluminium hydride to give (—)-R_3Si^*H of very low rotation, in 50% yield. Since the reduction of the chloride to the hydride involves inversion, formation of the (—)-R_3Si^*H indicates that the R_3Si^*Cl had been formed with slightly dominant retention of configuration.

Cleavage by iodine required a markedly longer reaction time. The complex *cis*-$[PtI_2(PMe_2Ph)_2]$ was formed in quantitative yield, along with inactive chloride R_3Si^*Cl, which was reduced to give the inactive hydride in 100% yield.

Phenylacetylene, which has been found to displace R_3Si^*H readily from various *cis*-$[PtH(SiR_3)(PMe_2Ph)_2]$ complexes,[3,4] reacted with (II) in less than 30 min at room temperature in the absence of a solvent to give $[Pt(PhC{\equiv}CH)(PMe_2Ph)_2]$ in 93% yield and (+)-R_3Si^*H in 62% yield, with an activity indicating 92·5% overall retention of configuration.

The initial product formed from (II) and benzenethiol, *viz.*, *trans*-$[PtH(SPh)(PPh_3)_2]$, is stable in this case, and was isolated in 100% yield, along with (+)-R_3Si^*H in 78% yield, with an activity corresponding with 92% overall retention, a much higher stereospecificity than was observed in the corresponding reaction of complex (I).

Benzoyl chloride, which is a useful reagent for liberating R_3SiH species from *cis*-$[PtH(SiR_3)(PPh_3)_2]$ complexes,[4] readily reacted with compound (II) to give *trans*-$[PtCl(COPh)(PPh_3)_2]$ in 75% yield, and (+)-R_3Si^*H, in 60% yield, the latter having an activity corresponding with 87·5% of overall retention of configuration.

The generally higher stereospecificity of the cleavages with compound (II) than (I) can mainly be associated with the greater solubility and reactivity of (II), which makes it possible to effect complete reaction in fairly short periods at room temperature, thus reducing the opportunity for secondary racemisations. It seems to us most likely that all those cleavages examined with both (I) and (II) which involve separation of R_3Si^*H proceed with complete or greatly predominant retention of configuration at silicon, and that the low optical activity of the silicon hydride isolated in some cases comes from subsequent racemisation. Table 4 shows that significant racemisation can occur even with the hydride (+)-R_3Si^*H in benzene in the presence of platinum complexes of the types produced in the reaction mixtures. In the case of (—)-R_3Si^*Cl there is quite rapid loss of activity even at room temperature in the presence of $[PtH(Cl)(PMe_2Ph)_2]$; † the low rotation of the products from cleavage of (I) with halogens is thus readily explicable in terms of secondary racemisation, since the initial product in each case is the chloride, but it is also possible that some racemisation occurs in the cleavages themselves.

It may be significant that for the cleavages in which the (+)-R_3Si^*H is the initial product, the degree of racemisation is greater when chloride ligands are present, and it could be that at least part of the racemisation actually takes place in R_3Si^*Cl, transiently produced either by direct reductive elimination from the intermediate Pt^{IV} species or from (+)-R_3Si^*H by an interaction of the type represented by equation (5) (see below); this interaction probably itself involves Pt^{IV} intermediates.

$$\equiv PtCl + R_3Si^*H \rightleftharpoons \equiv PtH + R_3SiCl \quad (5)$$

We assume that the cleavages involve oxidative addition–reductive elimination sequences, with the possible exception of the complex reaction which takes place with lithium aluminium hydride. If, as we believe, R_3Si^*H adds to $[PtCl_2(PMe_2Ph)_2]$ with retention at silicon to give a Pt^{IV} species, probably in the three-centre process (A), then it is reasonable to expect that elimination of R_3Si^*H from such a species will also involve retention. Such reasoning cannot be applied directly to the formation and decomposition of complex (II), since the initial addition is to a Pt^0 species to give a Pt^{II} species, whereas the cleavages probably involve interconversions of Pt^{II} and Pt^{IV} species, but there seems no reason to doubt that the R_3Si^*H will again leave the Pt^{IV} intermediate with retention. It does not follow that oxidative addition and reductive elimination of R_3Si^*Cl would necessarily also involve retention and indeed the racemisation of (—)-R_3Si^*Cl in the presence of *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ indicates that inversion processes of some kind are possible.

It is noteworthy that addition of (+)-R_3Si^*H to hex-1-ene in the presence of chloroplatinic acid, $[PtCl_2C_2H_4]$, or platinum on carbon involves a high degree of retention at silicon;[13] since the initial oxidative addition of the (+)-R_3Si^*H to the relevant platinum species can now safely be assumed to involve retention, then the reductive elimination of $R_3Si^*C_6H_{13}$-n must also do so, as suggested by Sommer *et al.*[13]

The complex (—)-$[Co(^*SiR_3)(CO)_4]$ is also thought to be formed from (+)-R_3Si^*H and dicobalt octacarbonyl with retention of configuration at silicon, and the

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† This racemisation itself merits a mechanistic study, which we hope to carry out.

[13] L. H. Sommer, K. W. Michael, and H. Fujimoto, *J. Amer. Chem. Soc.*, 1967, **89**, 1519.

subsequent release of (+)-R_3Si^*H on treatment with triethylsilane is likewise thought to proceed with retention.[10] By contrast, the cleavage of the Si–Co bond in this complex by methanol was assumed to involve inversion,[10] which would be consistent with Sommer's leaving-group rules[14] since the species $HCo(CO)_4$ is fairly acidic and $Co(CO)_4$ would constitute a good leaving group. The retentions we have observed in the cleavages of the Si–Pt bonds are also, on the simplest view, consistent with the rules, since the species $[PtH(X)(PR_3)_2]$ and $[PtH(X)(Y)(Z)(PR_3)_2]$ are very weak acids, the hydrogens being hydridic rather than protonic, and the $Pt(X)(PR_3)_2$ or $Pt(X)(Y)(Z)(PR_3)_2$ group should be a very poor leaving group, and leave silicon with retention at the latter. However, the situation is actually more complex than this, because the leaving group is not really, *e.g.*, $Pt(X)(Y)(Z)(PR_3)_2$, since in our suggested mechanism one of the ligands, say X, is being lost at the same time as the R_3Si^* group, and it is doubtful whether the leaving-group rules can be generally applied to cleavages of silicon–transition metal bonds in the present state of knowledge.

The Interaction of $[PtCl_2L_2]$ *and* R_3Si^*H.—As mentioned above, in some attempts to make complex (I) from *cis*-$[PtCl_2(PMe_2Ph)]_2$ and (+)-R_3Si^*H, fairly high yields of the hydridochloride *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ were obtained. In order to throw light on the best conditions for the preparation of (I) we investigated briefly this conversion of the platinum dichloride into the hydridochloride.

Triphenylsilane and *cis*-$[PtCl_2(PMe_2Ph)_2]$ in 2 : 1 mol ratio were heated at reflux in benzene and the reaction was monitored by means of the i.r. spectrum. This showed that *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ was first formed, but the ν(Pt–H) band at 2190 cm^{-1} and the ν(Si–H) band at 2120 cm^{-1} both then decreased slowly in intensity. After three days *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$ was isolated in 60% yield, along with chlorotriphenylsilane in an amount corresponding to slightly more than 1 mol for each mol of *cis*-$[PtCl_2(PMe_2Ph)_2]$ taken. It thus seems that the sequence of reactions (6) and (7) is

$$cis\text{-}[PtCl_2(PMe_2Ph)_2] + Ph_3SiH \longrightarrow cis\text{-}[PtH(Cl)(PMe_2Ph)_2] + Ph_3SiCl \quad (6)$$

$$cis\text{-}[PtH(Cl)(PMe_2Ph)_2] + Ph_3SiH \longrightarrow trans\text{-}[PtCl(SiPh_3)(PMe_2Ph)_2] + H_2 \quad (7)$$

occurring. Reaction (6) is of a type observed by Chalk and Harrod,[15] while reaction (7) is of a type used in the making of silicon–platinum complexes.[12]

When (+)-R_3Si^*H and *cis*-$[PtCl_2(PMe_2Ph)_2]$ in 2 : 1 mol ratio were heated together at 110 °C for 15 h in the absence of a solvent, the hydridochloride *cis*-$[PtH(Cl)(PMe_2Ph)_2]$ was obtained in virtually quantitative yield. In a similar reaction, but in benzene under reflux, the original complex took 4 days to dissolve, and during this time the ν(Pt–H) band of *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ appeared at 2190 cm^{-1}. At this stage the ν(Si–H) band at 2120 cm^{-1} was also strong, but during an additional 2 days this band disappeared, leaving the ν(Pt–H) band. It thus seems that while a reaction of type (6) occurs with (+)-R_3Si^*H, as with triphenylsilane, the hydrogen evolution of type (7) does not take place. There is some steric strain in complex (I); this is probably substantially increased in an intermediate of the type $[PtH(Cl)_2(^*SiR_3)(PMe_2Ph)_2]$, and the loss of the bulky R_3Si^*Cl to give $[PtHCl(PMe_2Ph)_2]$ will be favoured over loss of hydrogen chloride to give (I), which can occur in the presence of triethylamine.

The interaction of (+)-R_3Si^*H with *cis*-$[PtCl_2(PMe_2Ph)_2]$ to give the hydridochloride appears to be very slow at temperatures well below the reflux points in benzene or toluene, and use of a longer reaction time at a lower temperature coupled with an increase in the proportion of triethylamine seemed to favour the formation of complex (I).

Optically Active Germyl–Platinum Complexes.—We have described the preparation of the complex (+)-*trans*-$[PtCl(^*GeR'_3)(PMe_2Ph)_2]$ (III) in a low state of optical purity [$R'_3 = Et(1\text{-}C_{10}H_7)Ph$ here and elsewhere].[1] We have now made it in a somewhat higher, but still low, state of optical purity, and also the complex *cis*-$[PtH(^*GeR'_3)(PPh_3)_2]$ (IV), also probably optically impure.

Complex (III) was prepared by interaction of (+)-R'_3Ge^*H[$R'_3Ge^* = Et(1\text{-}C_{10}H_7)PhGe$][16] and *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ at 70 °C for 8 h, according to equation (8). The *trans*-configuration is assigned by analogy with the closely related silicon compound (I) described above. The (+)-R'_3Ge^*H we used had a rotation of only +15°, compared with the highest known rotation of +23·6°, and we could expect to obtain complex (III) with a rotation of *ca.* +20° by starting with an optically pure sample of (+)-R'_3Ge^*H. By comparison of rotations of various R'_3Ge^*X and R_3Si^*X compounds, we estimate very roughly that an optically pure sample of complex (III) would have an $[\alpha]_D^{25}$ value in the region of 50°. The loss of activity at the germanium centre is not surprising in view of the ease of thermal racemisation of (+)-R'_3Ge^*H.

$$\underset{[\alpha]_D^{25}+15{\cdot}0^\circ}{(+)\text{-}R'_3Ge^*H} + trans\text{-}[PtH(Cl)(PMePh)_2] \longrightarrow \underset{(III),\ [\alpha]_D^{25}\ +12{\cdot}9^\circ}{(+)\text{-}trans\text{-}[PtCl(^*GeR'_3)(PMe_2Ph)_2]} + H_2 \quad (8)$$

No reaction took place when (+)-R'_3Ge^*H was heated with *cis*-$[PtCl_2(PMe_2Ph)_2]$ in benzene in the presence of triethylamine, although (+)-R_3Si^*H under these conditions gives complex (I). In contrast, while (+)-

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[14] L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, 1964, **86**, 3276; L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, p. 3280; L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, 1967, **89**, 857; L. H. Sommer, 'Stereochemistry, Mechanism and Silicon,' McGraw-Hill, New York, 1965, ch. 8.

[15] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

[16] C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organometallic Chem.*, 1972, **37**, 251.

R'_3Ge*H reacts with *trans*-[PtH(Cl)($PMe_2Ph)_2$] as described above, (+)-R_3Si*H does not.

Treatment of (+)-R'_3Ge*H with [Pt($PPh_3)_2C_2H_4$] in hexane gave a complex thought to be (−)-*cis*-[PtH(*GeR'_3)($PPh_3)_2$] (IV) according to equation (9). The structure of the product is again assigned by analogy with the complex (−)-*cis*-[PtH(*SiR_3)($PPh_3)_2$] which was obtained from (+)-R_3Si*H in the corresponding reaction, since both complexes exhibit a ν(Pt–H) band at 2070 cm^{-1}. Complex (IV) resembles the silicon complex in undergoing dissociation in benzene, and so could not be recrystallised to give a satisfactory elemental analysis.

$$\underset{[\alpha]_D^{25}\ +15{\cdot}0^\circ}{(+)\text{-}R_3'Ge^*H} + Pt(PPh_3)_2C_2H_4 \longrightarrow \underset{(IV),\ [\alpha]_D^{25}\ -6{\cdot}0^\circ}{(-)\text{-}cis\text{-}[PtH(^*GeR_3)(PPh_3)_2]} + C_2H_4 \qquad (9)$$

Like the related silicon compounds, complexes (III) and (IV) both show plain positive dispersion curves, as the o.r.d. data in Table 2 illustrate. While o.r.d. curves are not as reliable a guide to configuration with germanium as they are with silicon compounds,[16] the results are consistent with the assumption that the germanium complexes (III) and (IV) resemble their silicon analogues in being formed from the parent hydride with retention of configuration.

EXPERIMENTAL

General.—All reactions involving platinum complexes were carried out under dry nitrogen. Solvents were carefully dried, and when possible were distilled from the drying agent directly on to the reactant under dry nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 257 Grating Spectrophotometer and optical rotations on a Perkin-Elmer 141 Polarimeter.

Preparation of (+)-*Methyl*-(1-*naphthyl*)*phenylsilane*, (+)-R_3Si*H.—An improved route to this compound, developed in these laboratories by Dr. K. T. Rosborough,[17] was used. In this the (±)-methyl-(1-naphthyl)phenylsilyl (−)-menthoxide is made from (±)-chloro(methyl)phenylsilyl (−)-menthoxide and 1-naphthyl-lithium as follows.

n-Butyl-lithium (1 mol) in diethyl ether (500 ml) was added to 1-bromonaphthalene (1 mol) in diethyl ether (300 ml) at 0 °C.[18] The solution was subsequently stirred at 0 °C for 15 min, and (±)-chloro(methyl)phenylsilyl (−)-menthoxide[19] (1 mol) in diethyl ether (200 ml) was added at 0 °C. The mixture was heated under reflux for 3 h, then cooled and added to ice-cold dilute hydrochloric acid (800 ml, 2N). The ether layer was separated, washed, and dried (Na_2SO_4), and the ether was evaporated off. The residual oil was fractionated at reduced pressure to give (±)-methyl-(1-naphthyl)phenylsilyl (−)-menthoxide (296 g, 74%), b.p. 208 °C/0·2 mmHg (lit.,[20] 173—177 °C/0·07 mmHg).

The diastereoisomeric menthoxides were resolved by the method of Sommer *et al.*[20] to give (−)-methyl-(1-naphthyl)-phenylsilyl (−)-menthoxide, m.p. 82—84 °C, $[\alpha]_D^{25}$ −54·9° (*c*, 2·0 g/100 ml in cyclohexane). A solution of this menthoxide (24 g, 0·060 mol) in diethyl ether (100 ml) was added to a suspension of lithium aluminium hydride (4 g, 0·10 mol) in diethyl ether (100 ml) and the mixture was warmed to reflux for 100 h. After cautious addition of acetone to destroy the residual lithium aluminium hydride, the mixture was added to ice-cold dilute hydrochloric acid (400 ml, 2N). The ether extract was washed and dried (Na_2SO_4), and the ether was evaporated off. The bulk of the (−)-menthol was removed by sublimation at 70 °C/0·1 mmHg, and the residual solid was eluted in 1 : 1 benzene–pentane through a silica gel column (60 × 2·5 cm).[17] The product was recrystallised twice from pentane to give (+)-methyl-(1-naphthyl)phenylsilane (12 g, 80%), m.p. 63·5—64 °C (lit.,[20] 63·5—65·4 °C), $[\alpha]_D^{25}$ +34·0° (*c*, 1·77 g/100 ml in cyclohexane); ν(Si–H), 2115 cm^{-1} (Nujol mull).

Preparation of Complex (I), (+)-trans-*Chloro*[*methyl*-(1-*naphthyl*)*phenylsilyl*]*bis*(*dimethylphenylphosphine*)*platinum*-(II).—A mixture of (−)-methyl-(1-naphthyl)phenylsilane, $[\alpha]_D^{25}$ +33·6°, *cis*-[PtCl_2($PMe_2Ph)_2$] (1·5 g, 2·8 mmol), benzene (20 ml), and triethylamine (20 ml) was heated under reflux for 100 h, during which the complex dissolved and a white solid separated. The mixture was cooled and filtered, and the filtrate was concentrated to leave an oil, which was washed with light petroleum (b.p. 60—80 °C, 10 ml) to leave a tacky solid. Recrystallisation from toluene–light petroleum (b.p. 60—80 °C) at −40 °C gave the impure *complex* (1·35 g, 65%), $[\alpha]_D^{25}$ +53·5° (*c*, 1·74 g/100 ml in benzene), and further recrystallisation from benzene–pentane gave pure (+)-***trans***-[PtCl{SiMe(1-$C_{10}H_7$)Ph}($PMe_2Ph)_2$], m.p. 158—160 °C, $[\alpha]_D^{25}$ +72·0° (*c*, 1·53 g/100 ml in benzene) (Found: C, 52·6; H, 5·0. Calc. for $C_{33}H_{37}ClP_2PtSi$: C, 52·6; H, 4·9%).

Preparation of Complex (II), (−)-cis-*Hydrido*[*methyl*-(1-*naphthyl*)*phenylsilyl*]*bis*(*triphenylphosphine*)*platinum*(II).—A suspension of Pt($PPh_3)_2C_2H_4$ (0·80 g, 1·07 mmol) was stirred with a solution of (+)-methyl-(1-naphthyl)phenylsilane (0·40 g, 1·6 mmol), $[\alpha]_D^{25}$ +32·9°, in degassed n-hexane (10 ml) for 40 h at room temperature, during which ethylene was evolved and the colour of the suspended solid gradually lightened to a creamy white. The *solid* was filtered off and washed with n-hexane (5 ml) to give (−)-[PtH{SiMe(1-$C_{10}H_7$)Ph}($PPh_3)_2$] (1·025 g, 99%), m.p. 106—107 °C, $[\alpha]_D^{25}$ −18·5° (*c*, 0·865 g/100 ml in benzene), ν(Pt–H) (Nujol mull), 2150 and 2070 cm^{-1} (Found: C, 64·8; H, 4·9. Calc. for $C_{53}H_{46}P_2PtSi$: C, 65·75; H, 4·8%).

Reaction of Complex (I) *with Hydrogen*.—A sample of (I) (0·43 g, 0·57 mmol), $[\alpha]_D^{25}$ +72°, was dissolved in tetrahydrofuran (20 ml), and hydrogen (deoxygenated by use of an Engelhard ' deoxo ' catalytic purifier) was passed in at atmospheric pressure with shaking for 3 h. The solvent was taken off under reduced pressure and the residual oil extracted with light petroleum (10 ml) to leave unchanged (+)-[PtCl(*SiR_3)($PMe_2Ph)_2$] (0·42 g, 95%). The i.r. spectrum of the extract (liquid film) indicated that it contained some disiloxane, (R_3Si*$)_2$O, and *trans*-[PtH(Cl)($PMe_2Ph)_2$], ν(Pt–H) 2190 cm^{-1}.

Cleavages of Complex (I).—(i) A solution of (I) (0·40 g, 0·53 mol), $[\alpha]_D^{25}$ +72°, in tetrahydrofuran (15 ml) was added

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[17] K. A. Rosborough, personal communication, 1967.

[18] H. Gilman and C. G. Brennan, *J. Amer. Chem. Soc.*, 1951, **73**, 4640.

[19] L. H. Sommer and K. T. Rosborough, *J. Amer. Chem. Soc.*, 1969, **91**, 7067.

[20] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271.

dropwise to a suspension of lithium aluminium hydride (0·10 g, 2·6 mmol) in diethyl ether (5 ml) at 0 °C. The mixture, which quickly turned bright red then black, was stirred for 1 h and then treated with 2N-hydrochloric acid (20 ml). The ether layer was separated, washed, and dried (Na_2SO_4), and the solvents were removed under reduced pressure. The residual oil was eluted in 1 : 1 benzene–light petroleum (b.p. 40—60 °C) through a silica gel column (15 × 1·2 cm) to give (+)-R_3Si^*H (0·11 g, 85%), m.p. 61—62 °C, $[\alpha]_D^{25}$ +29·1° (*c*, 1·56 g/100 ml in cyclohexane), the i.r. spectrum of which was identical with that of an authentic sample; ν(Si–H), 2115 cm^{-1} (Nujol mull).

(ii) Bromine (0·051 g, 0·32 mmol) in benzene (4 ml) was added to (I), $[\alpha]_D^{25}$ +72° (0·25 g, 0·32 mmol), in benzene (5 ml) at room temperature. After 1 h of stirring a white solid had separated and the bromine colour had disappeared. The solid was filtered off and recrystallised from ethanol to give *cis*-$[PtBr_2(PMe_2Ph)_2]$ (0·183 g, 88%), m.p. 201—204 °C (lit.,[21] 201—204 °C). The filtrate was evaporated under reduced pressure to leave an oil, which was extracted with n-pentane (10 ml). The n-pentane solution was filtered and added to a suspension of lithium aluminium hydride (0·1 g, 2·6 mmol) in diethyl ether (10 ml) and the mixture was stirred for 30 min. Hydrochloric acid (20 ml, 2N) was added, and the organic layer was separated, washed, and dried ($CaSO_4$). The solvents were again taken off under reduced pressure, and the residual oil was eluted in 4 : 1 n-pentane–benzene through a silica gel column (15 × 1·2 cm) to give (+)-R_3Si^*H (0·04 g, 50%), $[\alpha]_D^{25}$ −1·0° (*c*, 2·1 g/100 ml in cyclohexane), the i.r. spectrum of which was identical with that of an authentic sample; ν(Si–H), 2120 cm^{-1} (liquid film).

(iii) Iodine (0·097 g, 0·38 mmol) in benzene (10 ml) was added to complex (I) (0·3 g, 0·38 mmol), $[\alpha]_D^{25}$ +72°, in benzene (5 ml). The mixture was stirred for 20 h at 40 °C, after which the iodine colour had disappeared. Solvent was removed under reduced pressure, and the residual oil was extracted with n-pentane (20 ml). The residue was recrystallised from ethanol to give the bright yellow *cis*-$[PtI_2(PMe_2Ph)_2]$ (0·306 g, 100%), m.p. 169—171 °C (lit.,[21] 168—171 °C). The pentane extract was added to lithium aluminium hydride (0·1 g, 2·6 mmol) in diethyl ether (30 ml), and the mixture was stirred for 2 h then treated with 2N-hydrochloric acid (40 ml). The organic layer was separated, washed, and dried ($CaSO_4$), and the solvents were removed under reduced pressure to leave, as an oil, (±)R_3Si^*H (0·10 g, 100%), $[\alpha]_D^{25}$ 0° (*c*, 0·91 g/100 ml in cyclohexane).†

(iv) Benzenethiol (1·0 ml) and complex (I) (0·27 g, 0·35 mmol), $[\alpha]_D^{25}$ +72°, were heated under reflux in benzene (10 ml) for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with pentane (20 ml) to leave a pale yellow solid {0·204 g, 93·5% if assumed to be a 1 : 1 mixture of *cis*-$[PtCl_2(PMe_2Ph)_2]$ and *trans*-$[Pt(SPh)_2(PMe_2Ph)_2]$}. This was dissolved in benzene, the solution was filtered, and pentane was added to precipitate the bright yellow *trans*-$[Pt(SPh)_2(PMe_2Ph)_2]$ (0·11 g, 50%), m.p. 185—187 °C (lit.,[12] 181—182 °C) (Found: C, 48·8; H, 5·0. Calc. for $C_{28}H_{32}P_2PtS_2$: C, 48·8; H, 4·7%). The pentane extract was concentrated, and eluted in 1 : 1 benzene–light petroleum (b.p. 40—60 °C) through a silica gel column (15 × 1·2 cm) to give (+)-R_3Si^*H (0·015 g, 17%), $[\alpha]_D^{25}$ +16·9° (*c*, 0·61 g/100 ml in cyclohexane).

(v) Triethylsilane (0·075 g, 0·635 mmol) and complex (I) (0·48 g, 0·635 mmol), $[\alpha]_D^{25}$ +72°, were heated in benzene on a bath at 75 °C for 48 h. The mixture was then cooled, some of the benzene was evaporated off, and pentane was added to precipitate (I) (0·23 g, 48%), m.p. 158—160 °C. On standing, more solid separated, and was identified as *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ (0·09 g, 31%), m.p. 102—104 °C (lit.,[5] 102—104 °C), ν(Pt–H), 2190 cm^{-1} (Nujol mull). Solvents and triethylsilane were removed from the mother-liquor under reduced pressure, and the residual oil was eluted in 4 : 1 pentane–benzene through a silica gel column (15 × 1·2 cm) to give (+)-R_3Si^*H (0·009 g, 6%), $[\alpha]_D^{25}$ +9·1° (*c* 0·88 g/100 ml in cyclohexane).

*Preparation of (+)-*trans*-Bromo- and -Iodo-[methyl-(1-naphthyl)phenylsilyl]bis(dimethylphenylphosphine)platinum-*(II).—(i) Lithium bromide (0·25 g, 3·0 mmol) in acetone (5 ml) was added to (I) (0·17 g, 0·22 mmol), $[\alpha]_D^{25}$ +72°, in acetone (5 ml). The mixture was stirred for 10 min at room temperature and then evaporated to dryness. The residue was extracted with toluene (20 ml), the extract was filtered and concentrated, and pentane was added to give the pale yellow *product* (+)-$[PtBr\{SiMe(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2]$ (0·115 g, 65%), m.p. 164·5—166 °C, $[\alpha]_D^{25}$ +70·0° (*c*, 1·28 g/100 ml in benzene) (Found: C, 49·6; H, 4·7. Calc. for $C_{33}H_{37}BrPtP_2Si$: C, 49·6; H, 4·8%).

(ii) When sodium iodide (0·45 g, 3·0 mmol) in acetone (5 ml) was added to (I) (0·18 g, 0·23 mmol), $[\alpha]_D^{25}$ +72°, in acetone (5 ml) the solution immediately became deep yellow and a white solid separated. After 10 min of stirring at room temperature, the mixture was evaporated to dryness. The residue was extracted with toluene (20 ml), the extract was filtered and concentrated, and pentane was added. The mixture was kept at −40 °C for 12 h, during which yellow *crystals* separated. These were identified as (+)-*trans*-$[PtI\{SiMe(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2]$ (0·14 g, 70%), m.p. 183—184 °C, $[\alpha]_D^{25}$ +54·6° (*c*, 1·63 g/100 ml in benzene) (Found: C, 47·0; H, 4·6. Calc. for $C_{33}H_{37}IP_2PtSi$: C, 46·8; H, 4·4%).

Cleavages of Complex (II).—(i) Complex (II) (0·40 g, 0·41 mmol), $[\alpha]_D^{25}$ −18·5°, was added from a solid-addition tube to a suspension of lithium aluminium hydride (0·1 g, 2·6 mmol) in diethyl ether (20 ml) at room temperature. An immediate reaction occurred, and a green suspension was formed. The mixture was stirred for 1 h, then treated with 2N-hydrochloric acid (50 ml). The ether layer was separated, washed, and dried ($CaSO_4$), and the solvent was removed under reduced pressure. The residual oil was eluted in 4 : 1 pentane–benzene through a silica gel column (15 × 1·2 cm) to give (+)-R_3Si^*H (0·098 g, 96%), m.p. 59—61 °C, $[\alpha]_D^{25}$ +31·0° (*c*, 1·07 g/100 ml in cyclohexane).

(ii) When benzoyl chloride (2 ml) was added to (II) (0·30 g, 0·3 mmol), $[\alpha]_D^{25}$ −18·5°, the complex dissolved completely. The mixture was stirred for 30 min and light petroleum (b.p. 60—80 °C) (10 ml) was added. The pale yellow solid which separated was recrystallised to give *trans*-$[PtCl(COPh)(PPh_3)_2]$ (0·201 g, 75%), m.p. 285—290 °C (decomp.), after decarbonylation at *ca.* 210 °C [lit.,[22] m.p. 285—291 °C (decomp.) after decarbonylation at 210 °C]; ν(C=O) 1614 and 890 cm^{-1} (Nujol mull). Solvent and benzoyl chloride were removed from the filtrate under reduced pressure, and the residual oil was eluted in 4 : 1 pentane–benzene through a silica gel column (15 × 1·2 cm)

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† In this and subsequent experiments, the i.r. spectrum of the R_3Si^*H was identical with that of an authentic sample.

[21] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[22] M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 865; S. P. Dent, C. Eaborn, A. Pidcock, and B. Ratcliff, *J. Organometallic Chem.*, 1972, **46**, C68.

to give (+)-R_3Si^*H (0·045 g, 60%), $[\alpha]_D^{25}$ +24·7° (*c*, 0·86 g/100 ml in cyclohexane).

(iii) A sample of complex (II) (0·40 g, 0·41 mmol), $[\alpha]_D^{25}$ −18·5°, dissolved immediately when phenylacetylene (1 ml) was added. The mixture was stirred for 30 min, and pentane was added. The cream solid which separated was filtered off and recrystallised from benzene–methanol to give $[Pt(PPh_3)_2Ph{\cdot}C{\equiv}CH]$ (0·315 g, 93%), m.p. 140—142 °C (decomp.) [lit.,[23] 141—148 °C (decomp.)]; ν(C≡C), 1680 cm^{-1} (Nujol mull). The filtrate was treated as in (ii) to give (+)-R_3Si^*H (0·063 g, 62%), m.p. 57—60 °C, $[\alpha]_D^{25}$ +28·0° (*c*, 1·43 g/100 ml in cyclohexane).

(iv) Complex (II) (0·40 g, 0·41 mmol), $[\alpha]_D^{25}$ −18·5°, dissolved immediately when benzenethiol (1·0 ml) was added. The mixture was stirred for 30 min, and pentane was then added to precipitate, as a pale yellow solid, *trans*-$[PtH(SPh)(PPh_3)_2]$ (0·34 g, 100%), m.p. 134—136 °C (decomp.) [lit.,[24] 132—134 °C (decomp.)], ν(Pt–H), 2120 cm^{-1} (Nujol mull). The residual solution was treated as in (ii) to give (+)-R_3Si^*H (0·08 g, 78%), m.p. 56—58 °C, $[\alpha]_D^{25}$ +27·8° (*c*, 1·68 g/100 ml in cyclohexane).

Probable Preparation of (−)-*Hydrido[methyl-*(1-*naphthyl*)-*phenylsilyl]bis(dimethylphenylphosphine)platinum*(II).—A mixture of *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0·225 g, 0·45 mmol) and (+)-methyl-(1-naphthyl)phenylsilane (0·113 g, 0·45 mmol), $[\alpha]_D^{25}$ +32·9°, in degassed benzene was set aside under nitrogen for 8 days at room temperature, during which the originally colourless solution became pale green. The i.r. spectrum (liquid film) showed that the ν(Si–H) band at 2120 cm^{-1} had disappeared, and a new ν(Pt–H) band had appeared at 2040 cm^{-1}. The benzene was removed under reduced pressure to leave an oil, which was washed with pentane (2 × 5 ml) to give a tacky solid, $[\alpha]_D^{25}$ +18° (*c*, 1·1 g/100 ml in benzene), showing a strong band at 2040 cm^{-1}, which was probably (+)-*cis*-$[PtH\{SiMe(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2]$. When pentane was added to the benzene solution an uncharacterisable red oil separated.

Racemisation Studies.—(i) (−)-Methyl-(1-naphthyl)-phenylsilyl chloride (0·056 g, 0·20 mmol), $[\alpha]_D^{25}$ −6·3°, was stirred with *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ (0·10 g, 0·20 mmol) in benzene (2 ml) at room temperature for 15 h. The rotation of a 1 ml sample was then measured, and corresponded with $[\alpha]_D^{25}$ −2·0° (*c*, 2·6 g/100 ml in benzene).

(ii) A sample of (+)-R_3Si^*H (0·1 g, 0·4 mmol), $[\alpha]_D^{25}$ +32·9°, was stirred with *trans*-$[PtCl(COPh)(PPh_3)_2]$ (0·35 g, 0·4 mmol) in benzene (10 ml) at room temperature for 48 h. The benzene was removed under reduced pressure, and the residue was extracted with pentane. The pentane solution was filtered, a quarter volume of benzene was added, and the solution was eluted through a silica gel column (15 × 1·2 cm) to give (+)-R_3Si^*H, m.p. 59—61 °C, $[\alpha]_D^{25}$ +28·1° (*c*, 1·07 g/100 ml in cyclohexane).

(iii) A sample of (+)-R_3Si^*H (0·1 g, 0·4 mmol), $[\alpha]_D^{25}$ +32·9°, was stirred with *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ (0·1 g, 0·2 mmol) in benzene at 70 °C for 24 h. Work-up as in (ii) gave (+)-R_3Si^*H, m.p. 59—61 °C, $[\alpha]_D^{25}$ +27·8° (*c*, 1·1 g/100 ml in cyclohexane).

The Reaction of cis-*Dichlorobis(dimethylphenylphosphine)-platinum*(II) *with Silicon Hydrides.*—(i) A mixture of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (1·0 g, 1·9 mmol) and triphenylsilane (1·0 g, 3·8 mmol) in benzene (20 ml) was heated under reflux for 3 days. Solvent was removed under reduced pressure, and the residual oil was extracted with pentane (20 ml) at 20 °C and with hot light petroleum (b.p. 60—80 °C) (3 × 40 ml) to leave a white *solid*. This was recrystallised from benzene–pentane to give *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$,$C_6H_6$ (0·88 g, 57%), m.p. 169—171 °C (lit.,[12] 169—171 °C) (Found: C, 56·5; H, 5·3. Calc. for $C_{40}H_{43}ClP_2PtSi$: C, 56·9; H, 5·1%). Evaporation of the solvent from the pentane extract gave chlorotriphenylsilane (0·57 g, 51%), m.p. 89—91 °C (lit.,[25] 94—95 °C), the i.r. spectrum of which was identical with that of an authentic sample.

(ii) A mixture of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0·272 g, 0·50 mmol) and (+)-R_3Si^*H (0·25 g, 1·0 mmol) was stirred on a bath at 110 °C for 15 h. The mixture was cooled and extracted with pentane (10 ml), and the residual solid was recrystallised from benzene–pentane to give *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ (0·25 g, 100%), m.p. 102—104 °C (lit.,[12] 102—104 °C), ν(Pt–H) 2190 cm^{-1} (Nujol mull). When the solvent was removed from the pentane extract, the i.r. spectrum of the residue showed no ν(Si–H) peak at 2120 cm^{-1}.

(iii) A mixture of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0·272 g, 0·50 mmol) and (+)-R_3Si^*H (0·25 g, 1·0 mmol) in benzene (10 ml) was heated under reflux for 4 days, during which the complex dissolved. The i.r. spectrum (liquid film) showed a ν(Pt–H) peak at 2190 cm^{-1}, attributable to *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ and a ν(Si–H) peak at 2120 cm^{-1}. After a further 2 days of heating the ν(Si–H) peak had disappeared but the ν(Pt–H) peak remained. (The benzene used was sodium-dried, but was not redistilled before use. One abortive experiment suggested reaction might not occur with more rigorously dried, redistilled solvent.)

Preparation of (+)-trans-*Chloro[ethyl-*(1-*naphthyl*)*phenylgermyl]bis(dimethylphenylphosphine)platinum*(II).—A mixture of (+)-R'_3Ge^*H (0·36 g, 1·18 mmol), $[\alpha]_D^{25}$ +15·0°,[16] and *trans*-$[PhH(Cl)(PMe_2Ph)_2]$ (0·60 g, 1·18 mmol) were heated at 70 °C for 8 h in an open Schlenk tube in a current of dry nitrogen. The mixture was then cooled, and the resulting yellow oil was washed with light petroleum (b.p. 60—80 °C) (10 ml) to remove unchanged (+)-R'_3Ge^*H, and then dissolved in benzene (5 ml). Addition of pentane precipitated the residual *trans*-$[PtH(Cl)(PMe_2Ph)_2]$ which was filtered off, and the mother-liquor was concentrated to give an oil. This was recrystallised from benzene–light petroleum to give *solid* (+)-*trans*-$[PtCl\{GeEt(1\text{-}C_{10}H_7)Ph\}(PMe_2Ph)_2]$, m.p. 145—146 °C, $[\alpha]_D^{25}$ +12·9° (*c*, 2·3 g/100 ml in benzene) (Found: C, 50·25; H, 4·9. Calc. for $C_{34}H_{39}GeP_2Pt$: C, 50·25; H, 4·9%).

Preparation of (−)-cis-*Hydrido[ethyl-*(1-*naphthyl*)*phenylgermyl]bis(triphenylphosphine)platinum*(II).—A mixture of (+)-R'_3Ge^*H (0·10 g, 0·31 mmol), $[\alpha]_D^{25}$ +15·0°, with a suspension of $[Pt(PPh_3)_2C_2H_4]$ (0·20 g, 0·27 mmol) in degassed hexane (5 ml) was stirred under dry nitrogen for 6 days at room temperature, during which ethylene was evolved and the colour of the suspended solid changed to pale yellow. The *solid* was filtered off, and washed with hexane (5 ml) to give (−)-*cis*-$[PtH\{GeEt(1\text{-}C_{10}H_7)Ph\}(PPh_3)_2]$ (0·25 g, 90%), m.p. 84—88 °C (decomp.), $[\alpha]_D^{25}$ −6·0° (*c*, 1·7 g/100 ml in benzene); ν(Pt–H), 2070 cm^{-1} (Nujol mull) (Found: C, 61·3; H, 4·9. Calc. for $C_{54}H_{48}GeP_2Pt$: C, 63·2; H, 4·7%).

Interaction of (+)-R'_3Ge^*H *and* cis-$[PtCl_2(PMe_2Ph)_2]$ *in the Presence of Triethylamine.*—A mixture of (+)-R'_3Ge^*H (0·12 g, 0·37 mmol), $[\alpha]_D^{25}$ +15·0°, *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0·20 g, 0·37 mmol), benzene (10 ml), and triethylamine

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(5 ml) was heated under reflux in dry nitrogen for 60 h. The mixture was then cooled and the solid which separated was filtered off, and shown by its i.r. spectrum to be unchanged *cis*-[$PtCl_2(PMe_2Ph)_2$]. The i.r. spectrum also indicated that no triethylamine hydrochloride had been formed. No germylplatinum complex could be isolated from the filtrate.

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