Highly Stereospecific Carbene Insertions into Platinum–Halide Bonds. Crystal Structure of [PtCl(*S*-CHClSiMe$_3$)(*S*,*S*-Ph$_2$PCHMeCH$_2$CHMePPh$_2$)]†

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Trimethylsilyldiazomethane reacted with [PtX$_2$L$_2$] [X = Cl, Br or I; L$_2$ = cycloocta-1,5-diene (cod) or Ph$_2$P(CH$_2$)$_n$PPh$_2$ where *n* = 1–4] to give the corresponding [PtX(CHXSiMe$_3$)L$_2$] as a racemic mixture in high yields. The cod ligands in [PtX(CHXSiMe$_3$)(cod)] were readily displaced by diphosphines. When optically active complexes [PtX$_2$L$_2$] [X = Cl, Br or I; L$_2$ = (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane, (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (*S*,*S*-skewphos) or (4*R*,5*R*)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] were treated with trimethylsilyldiazomethane the products [PtX(CHXSiMe$_3$)L$_2$] were mixtures of diastereoisomers in different proportions ranging from 1:1 to 15:1. The major diastereoisomer of [PtCl(CHClSiMe$_3$)(*S*,*S*-skewphos)] was readily separated by fractional crystallisation and its crystal structure revealed that the configuration at the α-carbon was *S*. This compound is configurationally stable for at least 14 d in CDCl$_3$ solution as shown by ^{31}P NMR spectroscopy. The high diastereoselectivities obtained in some of the reactions may originate from steric effects.

Chloromethylplatinum(II) complexes[1] have been used for the synthesis of co-ordinated phosphorus ylides,[2] platinaoxacyclobutanes,[3] platinaazacyclobutanes[4] and for some novel C–C bond-forming reactions.[5] We have previously shown[6] that diazocarbonyl compounds react with complexes of the type [PtX$_2$L$_2$] (X = Cl or I, L$_2$ = cyclooctadiene or a diphosphine) to give functionalised chloromethylplatinum(II) complexes containing an asymmetric carbon atom α to the platinum and that this reaction is diastereoselective when L$_2$ is a chiral diphosphine (diastereomeric ratios of up to 7:1). We now report that, in the absence of water, the readily available diazo compound Me$_3$SiCHN$_2$ reacts similarly with complexes of the type [PtX$_2$L$_2$] to give [PtCl(CHClSiMe$_3$)L$_2$] and when L$_2$ = chiral diphosphine diastereomeric ratios of up to 15:1 have been achieved. A preliminary account of part of this work has been given previously[7] and recently McCrindle and McAlees[8] have also reported observations on some of these reactions.

Results and Discussion

Treatment of [PtX$_2$(cod)] (X = Cl, Br or I; cod = cycloocta-1,5-diene) with 1.1 equivalent or an excess of Me$_3$SiCHN$_2$ gave the monoinsertion products [PtX(CHXSiMe$_3$)(cod)] (X = Cl, **1a**; Br, **1b**; or I, **1c**) in high yields which have been fully characterised (see Tables 1 and 2 and Experimental section for details). The ^{1}H NMR spectrum of **1a** shows four distinct resonances for the alkenyl protons of the co-ordinated cod (multiplets of δ 4.84, 4.97, 5.51 and 5.62), consistent with the presence of the asymmetric CHClSiMe$_3$ group which renders these protons diastereotopic. Similarly, treatment of [PtX$_2$L$_2$] [X = Cl or I; L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$, *n* = 1 (dppm), 2 (dppe), 3 (dppp) or 4 (dppb)] with Me$_3$SiCHN$_2$ gave the monoinsertion products **1d**–**1i** (see Tables 1–3 for characterising data); some of these compounds have also been made by substitution of the cod ligands in complexes **1a** and **1c** by the appropriate diphosphine (see Scheme 1 and Experimental section). Complexes **1a**–**1i** are racemic mixtures.

Table 1 Elemental analytical[a] and IR data (cm^{-1})[b]

Complex	Analysis (%) C	H	ν(Pt–Cl)
1a	31.10 (31.30)	4.75 (4.80)	300
1b	26.45 (26.45)	4.10 (4.00)	
1c	23.05 (22.40)	3.55 (3.45)	
1d	47.25 (47.30)	4.30 (4.40)	290
1e	37.80 (37.90)	3.40 (3.50)	
1f	48.00 (48.00)	4.50 (4.55)	280
1g	38.85 (38.60)	3.60 (3.65)	
1h	48.05 (48.75)	4.70 (4.75)	280
2a, **3a**[c]	47.30 (47.20)	4.95 (4.80)	290
2b, **3b**[c]	43.00 (42.90)	4.50 (4.30)	
2c, **3c**[d]	37.35 (37.90)	3.90 (3.80)	
4a, **5a**[d]	45.95 (46.40)	4.70 (4.80)	290
4c, **5c**[c]	39.90 (39.50)	4.25 (4.05)	
6a, **7a**	49.00 (49.40)	5.55 (5.00)	290
6b, **7b**	44.85 (44.75)	4.55 (4.50)	
6c, **7c**[e]	42.00 (42.30)	4.25 (4.70)	

[a] Calculated values in parentheses. [b] Spectra measured in CsI pellets. [c] Contains 0.5 CH$_2$Cl$_2$. [d] Contains 1 CH$_2$Cl$_2$. [e] Contains 1 Et$_2$O.

Treatment of complex **1a** with (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (*S*,*S*-chiraphos) in CDCl$_3$ gave a 1:1 mixture of diastereoisomers **2a** and **3a** (Scheme 2). The presence of the two isomers is particularly evident in the ^{31}P NMR spectrum which shows two equally intense AX patterns, the parameters for which are closely similar (see Table 2). In the same manner, 1:1 mixtures of diastereoisomers **2b** with **3b**, **2c** with **3c** and the corresponding complexes of (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (*S*,*S*-skewphos) (**4a**–**4c** with **5a**–**5c**) and (4*R*,5*R*)-4,5-bis(diphenylphosphinomethyl)-2,2-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 2 ^{31}P NMR data[a]

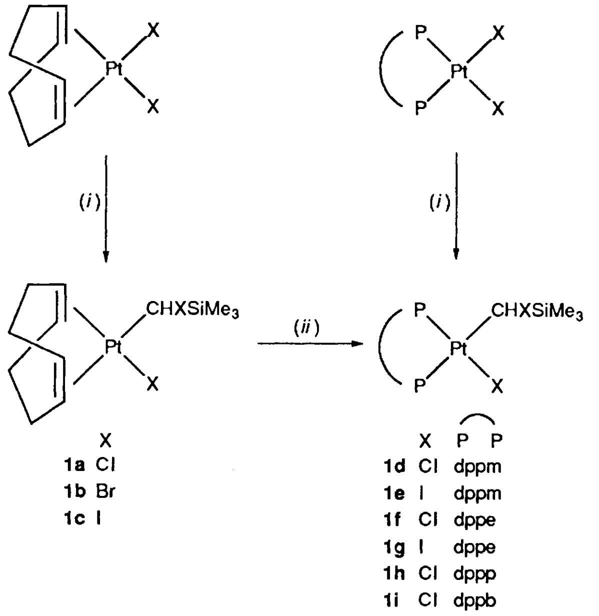
Complex	δ(P_A)	^1J(PtP_A)	δ(P_B)	^1J(PtP_B)	^2J(P_AP_B)	Ratio[b]
1d	−42.8	4050	−42.8	1362	49	
1e	−52.8	3614	−57.2	1457	50	
1f	40.8	4177	40.8	1816	0	
1g	42.6	3910	40.5	1851	0	
1h	2.5	4109	−0.8	1675	24	
1i	15.6	4257	13.4	1738	17	
2a, 3a	41.3	4089	41.7	1767	15	10
	42.5	4255	43.2	1734	15	
2b, 3b	41.6	4030	40.5	1795	13	5
	44.1	4130	43.2	1781	13	
2c, 3c	39.1	3828	37.1	1818	12	5
	41.7	3923	41.3	1808	12	
4a, 5a	13.3	4116	14.1	1719	24	15
	14.4	4128	10.7	1660	24	
4b, 5b	12.8	4066	12.1	1760	23	2
	13.7	4074	8.7	1707	24	
4c, 5c	8.8	3896	7.5	1820	22	2
	9.7	3902	5.9	1792	24	
6a, 7a	2.1	4252	4.0	1677	15	2
	5.0	4269	3.9	1695	15	
6b, 7b	4.1	4128	−0.5	1714	15	1
	2.2	4226	−0.9	1724	17	
6c, 7c	0.1	4045	−8.1	1772	17	1
	−1.3	4075	−6.0	1796	17	

[a] Spectra (36.2 MHz) measured in $CDCl_3$ at 28 °C unless otherwise stated. Chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. Coupling constants (J) in Hz (±3). Atom P_A is *trans* to the halogen and P_B *trans* to the carbon. [b] In cases where two diastereoisomers are formed numbers in this column refer to ratios of the intensities of the ^{31}P NMR signals (data for the major isomer are given first).

Table 3 Selected proton NMR data[a]

Complex	δ(PtCH)	^2J(PtCH)[b]	^3J(PPtCH)	δ($SiCH_3$)
1a	4.48	91.0		+0.22
1b	4.38	84.2		+0.26
1c	2.4[c]			+0.30
1d	4.12	48.9	7.3	−0.12
1e	3.48	52.0	11.5, 7.2	−0.10
1f	3.50	31.0	10.0, 7.3	−0.12
1g	3.10	33.5	12.9, 5.9	−0.05
1h	2.98	34.8	13.2, 6.0	−0.05
1i	3.03	37.2	14.1, 6.3	−0.12
2a, 3a	3.30	29.3	10.6, 8.0	−0.12
2b, 3b	3.31	32.7	11.7, 7.3	−0.12
2c, 3c	3.03	35.7	13.1, 6.8	−0.08
4a, 5a	2.92	24.5	14.0, 7.0	−0.10
4b, 5b	2.89	n.o.		0.00
4c, 5c	2.80	n.o.		0.00
6a, 7a	3.32[d]	n.o.		−0.10, −0 .11
6b, 7b	3.65[d]	n.o.		−0.00, −0 .02
6c, 7c	3.84[d]	n.o.		0.00, −0 .02

[a] Spectra (300 MHz) measured in $CDCl_3$ at 25 °C; chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz (±0.1). [b] n.o. = Not observed because signal is obscured. [c] Signal obscured but assigned on the basis of observed nuclear Overhauser enhancement between this signal and that of $SiMe_3$. [d] Assignment confirmed by correlation spectroscopy.



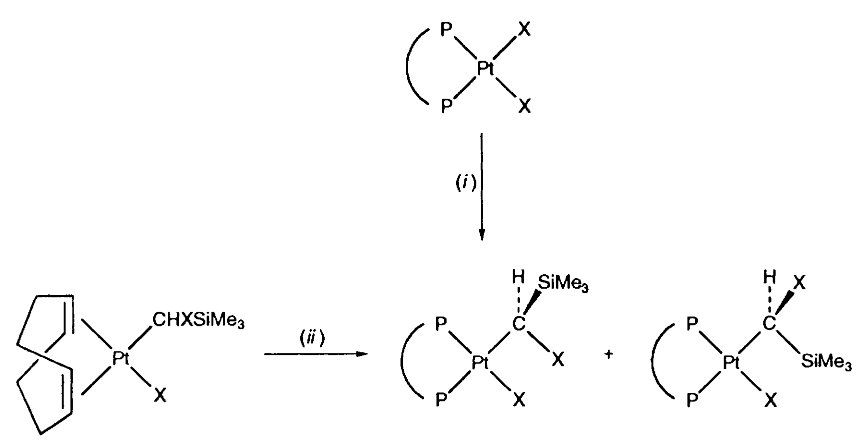
Scheme 1 (*i*) $N_2CHSiMe_3$; (*ii*) diphosphine

dimethyl-1,3-dioxolane (*R*,*R*-diop) (**6a–6c** with **7a–7c**) have been made and characterised (Tables 1–3).

When the optically active complexes [PtX_2L_2] (X = Cl, Br or I; L_2 = *S*,*S*-chiraphos, *S*,*S*-skewphos or *R*,*R*-diop) were treated with Me_3SiCHN_2 the same diastereomers **2–7** were formed (see Scheme 2) but in the proportions shown in Table 2, as determined by integration of the ^{1}H NMR signals for the Me_3Si groups or integration of ^{31}P NMR signals corrected for Nuclear Overhauser and relaxation effects by comparison with spectra measured under the same conditions of 1 : 1 mixtures generated from **1a–1c** and the chiral diphosphine.

A single recrystallisation of the mixture of *S*,*S*-skewphos complexes **4a** and **5a** from CH_2Cl_2 and Et_2O gave pure **4a**. No epimerisation of the α-carbon configuration was observed when pure **4a** or a 1 : 1 mixture of **4a** and **4b** was redissolved in $CDCl_3$, over a period of 14 d even in the presence of [$AsPh_4$]Cl. This demonstrates that under these conditions this compound is optically stable for kinetic reasons.

Crystals of complex **4a** suitable for X-ray crystallography were grown from CH_2Cl_2–Et_2O. The molecular structure is shown Fig. 1 and selected molecular dimensions are listed in Table 4. The crystal structure consists of isolated molecules of **4a** separated by normal contacts. The molecule consists of a platinum atom which is chelated by a skewphos ligand and further ligated by a chloride ligand and σ bonded to the chiral



	X			X	P P
1a	Cl	**2a**	**3a**	Cl	*S*,*S*-chiraphos
1b	Br	**2b**	**3b**	Br	*S*,*S*-chiraphos
1c	I	**2c**	**3c**	I	*S*,*S*-chiraphos
		4a	**5a**	Cl	*S*,*S*-skewphos
		4b	**5b**	Br	*S*,*S*-skewphos
		4c	**5c**	I	*S*,*S*-skewphos
		6a	**7a**	Cl	*R*,*R*-diop
		6b	**7b**	Br	*R*,*R*-diop
		6c	**7c**	I	*R*,*R*-diop

Scheme 2 (*i*) N$_2$CHSiMe$_3$; (*ii*) diphosphine

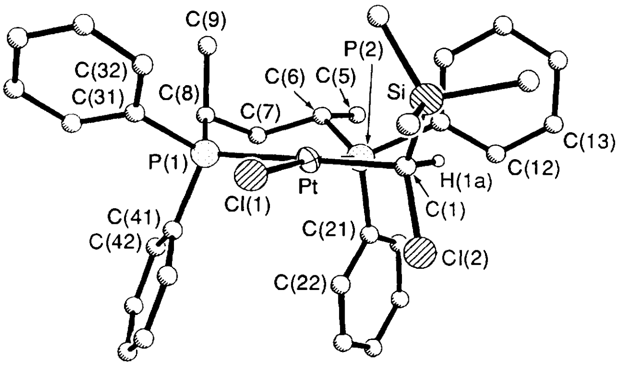


Fig. 1 Molecular geometry of complex **4a**, showing the atom labelling scheme. The platinum atom is represented as an ellipsoid enclosing 50% probability density. All hydrogens other than H(1a) have been omitted for clarity

alkyl ligand through C(1) [Pt-C(1) 2.104(12) Å]. The variation in *trans* influence is indicated by the different Pt-P distances for the two skewphos phosphorus atoms [Pt-P(2) 2.232(4) *trans* to Cl(1) and Pt-P(1) 2.318(4) *trans* to C(1); Pt-Cl(1) 2.360(4)Å]. As is to be expected for a platinum(II) complex the co-ordination at Pt is close to planar (mean deviation 0.057 Å) with a slight twist (6.0°) in the co-ordination plane between the PtP$_2$ and the PtCCl units. The *cis* and *trans* angles deviate slightly from 90 and 180°, the largest deviation for a *cis* angle being for the skewphos ligand [P(2)-Pt-P(1) 94.0(1)°]. The conformation adopted by the chiral alkyl has the α-hydrogen near the co-ordination plane of the platinum and pointing towards P(2) [torsion angle P(2)-Pt-C(1)-H(1a) 7°]. This orientation allows the bulkier Cl and SiMe$_3$ substituents at C(1) to avoid the crowded co-ordination plane with the larger SiMe$_3$ group between the pseudo-equatorial phenyl groups [*cf.* Cl(2) which is closer to the pseudo-axial phenyl rings, see Fig. 1]. Rather similar gross geometries have been observed in [PtCl(*R*-CHClCO$_2$Et)(*R*,*R*-diop)][6] and in [PtCl(*R*-CHMeCO$_2$Et)(*S*,*S*-diop)].[9] The skewphos six-membered ring adopts a flattened chair conformation (see Fig. 1) with the methyl substituents in axial [C(9)] and equatorial [C(5)] sites respectively.

Table 4 Bond lengths (Å) and selected bond angles (°) for complex **4a**

Pt-Cl(1)	2.360(4)	Pt-P(1)	2.318(4)
Pt-P(2)	2.232(4)	Pt-C(1)	2.104(12)
Cl(2)-C(1)	1.843(13)	P(1)-C(8)	1.846(14)
P(1)-C(31)	1.824(11)	P(1)-C(41)	1.811(11)
P(2)-C(6)	1.838(14)	P(2)-C(11)	1.848(12)
P(2)-C(21)	1.829(8)	Si-C(1)	1.890(14)
Si-C(2)	1.847(18)	Si-C(3)	1.854(18)
Si-C(4)	1.886(17)	C(5)-C(6)	1.548(22)
C(6)-C(7)	1.521(20)	C(7)-C(8)	1.508(20)
C(8)-C(9)	1.534(21)		
Cl(1)-Pt-P(1)	89.1(1)	Cl(1)-Pt-P(2)	173.3(1)
P(1)-Pt-P(2)	94.0(1)	Cl(1)-Pt-C(1)	88.4(4)
P(1)-Pt-C(1)	177.5(4)	P(2)-Pt-C(1)	88.5(4)
Pt-P(1)-C(8)	116.6(5)	Pt-P-C(31)	118.7(3)
C(8)-P(1)-C(31)	99.9(5)	Pt-P-C(41)	111.0(4)
C(8)-P(1)-C(41)	105.4(6)	C(31)-P(1)-C(41)	103.5(5)
Pt-P(2)-C(6)	115.8(5)	Pt-P(2)-C(11)	115.0(4)
C(6)-P(2)-C(11)	100.6(6)	Pt-P(2)-C(21)	109.7(3)
C(6)-P(2)-C(21)	107.6(6)	C(11)-P(2)-C(21)	107.4(4)
C(1)-Si-C(2)	114.7(7)	C(1)-Si-C(3)	110.8(7)
C(2)-Si-C(3)	110.3(8)	C(1)-Si-C(4)	106.9(7)
C(2)-Si-C(4)	105.8(8)	C(3)-Si-C(4)	108.0(8)
Pt-C(1)-Cl(2)	111.2(6)	Pt-C(1)-Si	115.1(7)
Cl(2)-C(1)-Si	108.3(6)	P(2)-C(6)-C(5)	115.1(10)
P(2)-C(6)-C(7)	112.9(10)	C(5)-C(6)-C(7)	109.1(12)
C(6)-C(7)-C(8)	116.8(13)	P(1)-C(8)-C(7)	113.0(10)
P(1)-C(8)-C(9)	108.9(10)	C(7)-C(8)-C(9)	111.9(12)

It had been reasoned that if steric effects influence the ratio of diastereoisomers, higher diastereoselectivity should be obtained using N$_2$CHSiMe$_3$ as a consequence of the bulkiness of the SiMe$_3$ substituent. Indeed the diastereoselectivities of some of these insertion reactions are high (see Table 2) and, for the chlorides, higher than for the corresponding reactions with ethyl diazoacetate or diazoacetophenone[6] consistent with steric effects being one factor in determining the diastereoselection. For the bromides and iodides, where the difference in size between the halogen and the trimethylsilyl substituents is less, the diastereoselectivity is less than for the corresponding chlorides as would be expected on steric grounds. However there appear to be no consistent trends in diastereoselectivity among the different diphosphines and further work is in progress to probe the other factors that are important in determining the diastereoselectivities of these insertions.

It is known[10] that CH_2N_2 and Me_3SiCHN_2 have similar chemical reactivity but the corresponding reaction of $[PtX_2$(diphosphine)] with diazomethane gives the bis insertion products $[Pt(CH_2X)_2$(diphosphine)].[11] This contrasting behaviour is most likely a consequence of kinetics {hindered approach of Me_3SiCHN_2 to the bulky $[PtX(CHXSiMe_3)$(diphosphine)]} and thermodynamics {unfavourable steric congestion that would be present in the product, $[Pt(CHXSiMe_3)_2$(diphosphine)]}.[8]

It has been shown that the bulky diazoalkane $N_2CHSiMe_3$ reacts smoothly with complexes of the type $[PtX_2$(diphosphine)] to give the products of monoinsertion into the Pt–X bonds. When X = Cl and the diphosphine is chiral, unprecedentedly high diastereoselectivity is obtained. Single isomers which are configurationally stable are readily separated which should make these species valuable for mechanistic studies.

Experimental

All reactions were carried out under an atmosphere of nitrogen, though the products could be handled in air. All the diphosphines (Aldrich or Strem), and a 2 mol dm^{-3} hexane solution of $N_2CHSiMe_3$ (Aldrich) were used as purchased. The FT-IR spectra (CsI discs) were obtained using a Nicolet 510P spectrometer, $^{31}P-\{^1H\}$ NMR spectra at 81 MHz and 28 °C using a Bruker AM200 spectrometer and ^1H NMR spectra at 300 MHz at 25 °C using a Varian Gemini 300 spectrometer.

Preparations.—$[PtCl(CHClSiMe_3)(cod)]$ **1a**. A solution of $N_2CHSiMe_3$ (0.29 cm^3 of a 2 mol dm^{-3} solution in hexane, 0.58 mmol) was added over 5 min under nitrogen to a solution of $[PtCl_2(cod)]$ (200 mg, 0.53 mmol) in CH_2Cl_2 (15 cm^3), the mixture was stirred for 2 h and then the volume was reduced to 1 cm^3. Addition of diethyl ether (25 cm^3) precipitated the off-white product (220 mg, 90%). The bromo (**1b**) and iodo (**1c**) analogues were made similarly in 84 and 82% yield respectively. ^{13}C NMR ($CDCl_3$): **1a**, δ 53.12, [^1J(PtC) 750, CPt] and 0.01 (CH_3Si); **1b**, δ 41.07 [^1J(PtC) 750 Hz, CPt] and 0.90 (CH_3Si); **1c**, δ 30.22 [^1J(PtC) not observed, obscured by allylic cod resonances, CPt] and 1.97 (CH_3Si).

$[PtCl(CHClSiMe_3)(dppm)]$ **1d** *from* $[PtCl_2(dppm)]$. A solution of $N_2CHSiMe_3$ (0.69 cm^3 of a 2 mol dm^{-3} solution in hexane, 1.38 mmol) was added over 5 min under nitrogen to a solution of $[PtCl_2(cod)]$ (300 mg, 0.46 mmol) in dry CH_2Cl_2 (20 cm^3), the mixture was stirred for 18 h and then the volume was reduced to 1 cm^3. Addition of diethyl ether (30 cm^3) precipitated the off-white product (307 mg, 91%). Complexes **1e**–**1i** were made similarly from the appropriate $[PtX_2$(diphosphine)] in the following yields: **1e**, 74; **1f**, 73; **1g**, 71; **1h**, 97; **1i**, 94%.

$[PtI(CHISiMe_3)(dppe)]$ **1g** *from* $[PtI(CHISiMe_3)(cod)]$ **1c**. A solution of dppe (124 mg, 0.31 mmol) in CH_2Cl_2 (30 cm^3) was added dropwise to a vigorously stirred solution of $[PtI(CHISiMe_3)(cod)]$ (200 mg, 0.31 mmol) in CH_2Cl_2 (20 cm^3). The resulting yellow solution was stirred for 1 h and then the solvent was evaporated to dryness under reduced pressure. Addition of pentane (50 cm^3) to the residue gave the yellow product (270 mg, 93%). Complexes **1d** and **1f** have also been prepared in this way in > 90% yields.

$[PtCl(CHClSiMe_3)$(*S*,*S*-skewphos)] *as a mixture of diastereoisomers* **4a** *and* **5a** *and the separation of pure* **4a**. A solution of $N_2CHSiMe_3$ (0.32 cm^3 of a 2 mol dm^{-3} solution in hexane, 0.64 mmol) was added over 5 min under nitrogen to a solution of $[PtCl_2$(*S*,*S*-skewphos)] (150 mg, 0.21 mmol) in dry CH_2Cl_2 (5 cm^3), the mixture was stirred for 16 h and then the volume was reduced to 1 cm^3. Addition of diethyl ether (20 cm^3) precipitated the off-white product (120 mg, 72%) which is a 15:1 mixture of diastereoisomers **4a** and **5a**; one recrystallisation from CH_2Cl_2–Et_2O gave pure **4a**. The complexes **2**–**7** were all made similarly (though reaction times varied from 30 min to 16 h) in the following yields: **2a**, **3a**, 76; **2b**, **3b**, 74; **2c**, **3c**, 79; **4a**, **5a**, 72; **4b**, **5b**, 79; **4c**, **5c**, 61; **6a**, **7a**, 75; **6b**, **7b**, 63; **6c**, **7c**, 74%. The isomer ratios obtained by this method are given in Table 2. In each case a 1:1 mixture of diastereoisomers has been generated by adding 1 equivalent of the appropriate diphosphine to **1a**–**1c** in $CDCl_3$.

Crystal Structure Determination of $[PtCl(S\text{-}CHClSiMe_3)$(*S*,*S*-skewphos)] **4a**.—*Crystal data.* $C_{33}H_{40}Cl_2P_2PtSi$, M_r = 792.7, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.152(5), b = 16.102(4), c = 19.021(5) Å, U = 3415(2) Å^3, Z = 4, D_c = 1.54 g cm^{-3}, λ = 0.710 73 Å, μ(Mo-Kα) = 44.1 cm^{-1}, $F(000)$ = 1576, T = 295 K.

A single crystal of complex **4a** (approximate dimensions 0.25 × 0.36 × 0.50 mm) was mounted in a thin-walled glass capillary under N_2 and held in place with epoxy glue. All diffraction measurements were made at room temperature (295 K) on a Siemens R3m/V diffractometer, using graphite-monochromated Mo-Kα X-radiation. Unit cell dimensions were determined from 34 centred reflections in the range

Table 5 Atomic coordinates (× 10^4) for complex **4a**

Atom	x	y	z
Pt	−59(1)	9 889(1)	1 009(1)
Cl(1)	−888(4)	9 086(3)	1 926(2)
Cl(2)	−2 769(4)	10 608(3)	1 214(3)
P(1)	1 823(3)	9 695(2)	1 500(2)
P(2)	598(3)	10 772(2)	191(2)
Si	−2 580(4)	9 033(3)	353(3)
C(1)	−1 799(11)	10 033(9)	599(6)
C(2)	−3 564(14)	8 600(11)	1 044(10)
C(3)	−1 480(16)	8 241(10)	61(10)
C(4)	−3 594(15)	9 277(11)	−413(8)
C(5)	2 555(14)	11 191(12)	−714(8)
C(6)	2 132(12)	10 592(10)	−128(7)
C(7)	3 055(14)	10 585(10)	461(7)
C(8)	3 119(12)	9 811(9)	905(7)
C(9)	3 231(16)	9 025(11)	454(8)
C(11)	−242	10 750	−646
C(12)	−937(11)	11 415(5)	−882(6)
C(13)	−1 526	11 365	−1 527
C(14)	−1 420	10 651	−1 938
C(15)	−725	9 986	−1 702
C(16)	−136	10 036	−1 057
C(21)	528	11 834	529
C(22)	230(8)	11 951(4)	1 234(4)
C(23)	257	12 746	1 525
C(24)	582	13 424	1 111
C(25)	880	13 308	406
C(26)	853	12 513	115
C(31)	2 176	8 691	1 892
C(32)	1 545(8)	7 971(7)	1 718(5)
C(33)	1 910	7 206	1 987
C(34)	2 905	7 160	2 430
C(35)	3 536	7 879	2 604
C(36)	3 171	8 645	2 334
C(41)	2 084	10 422	2 210
C(42)	3 084(8)	10 940(7)	2 251(5)
C(43)	3 200	11 496	2 810
C(44)	2 315	11 533	3 328
C(45)	1 315	11 015	3 287
C(46)	1 199	10 460	2 728

$16.0 < 2\theta < 30.0°$. A total of 3397 diffracted intensities, including check reflections, were measured in a unique octant of reciprocal space for $4.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Two check reflections (1 −6 3, 2 −2 10) remeasured after every 98 ordinary data showed a decay of *ca.* 6% over the period of data collection; an appropriate correction was therefore applied. Of the intensity data collected, 3373 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences, of these 2528 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 420 azimuthal scan data, maximum and minimum transmission coefficients being 0.438 and 0.301 respectively. Lorentz and polarisation corrections were applied.

The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms were refined without positional constraints except for the phenyl-group carbon atoms which were constrained to D_{6h} symmetry with C–C distances 1.395 Å. All hydrogen atoms were constrained to idealised geometries (C–H 0.96 Å, H–C–H 109.5°) with fixed isotropic displacement parameters. A parameter (η), defining the absolute structure and hence the molecular chirality,[12] refined to 1.07(4), thereby confirming the handedness of the molecules of complex **4a** in the crystal studied. An extinction parameter χ {where $F_{corr} = F[(1 + 0.002\chi F^2)/\sin 2\theta]^{-0.25}$} was refined to a value of 0.000 11(2). Full-matrix least-squares refinement of this model (186 parameters) converged to final residual indices $R = 0.044$, $R' = 0.046$, $S = 1.22$, where $R = \Sigma|\Delta|/\Sigma|F_0|$; $R' = (\Sigma w\Delta^2/\Sigma wF_0{}^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$ and N_o, N_v = numbers of observations and of variables. Weights, w, were set equal to $[\sigma_c{}^2(F_o) + gF_o{}^2]^{-1}$, where $\sigma_c{}^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0004$ was chosen to minimise the variation in S as a function of $|F_o|$. Final electron-density difference maps showed no features outside the range +1.1 to −0.7 e Å^{-3}, the largest of these being close to the platinum atom. Table 5 lists the final atomic positional parameters for the freely refined atoms, and Table 4 the selected bond lengths and inter-bond angles. All calculations were carried out on using programs of the SHELXTL-PLUS package.[13] Complex neutral-atom scattering factors were taken from ref. 14.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond angles.

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References

1 H. B. Friedrich and J. R. Moss, *Adv. Organomet. Chem.*, 1991, **33**, 235; D. Steinborn, *Angew. Chem., Int. Ed. Engl.*, 1992, 401.

2 N. J. Kermode, M. F. Lappert, B. W. Skelton, A. H. White and J. Holton, *J. Chem. Soc., Chem. Commun.*, 1981, 698; C. Engelter, J. R. Moss, L. R. Nassimbeni, M. L. Niven, G. Reid and J. C. Spiers, *J. Organomet. Chem.*, 1986, **315**, 255; J. F. Hoover and J. M. Stryker, *Organometallics*, 1988, **7**, 2082; R. McCrindle, G. J. Arsenault, A. Gupta, M. J. Hampden-Smith, R. E. Rice and A. J. McAlees, *J. Chem. Soc., Dalton Trans.*, 1991, 949.

3 J. F. Hoover and J. M. Stryker, *J. Am. Chem. Soc.*, 1989, **111**, 6466.

4 R. McCrindle, G. Ferguson and A. J. McAlees, *J. Chem. Soc., Chem. Commun*, 1990, 1524.

5 J. F. Hoover and J. M. Stryker, *J. Am. Chem. Soc.*, 1990, **112**, 464; R. McCrindle, G. J. Arsenault, R. Farwaha, M. J. Hampden-Smith and A. J. McAlees, *J. Chem. Soc., Chem. Commun.*, 1986, 943.

6 P. Bergamini, E. Costa, S. Sostero, A. G. Orpen and P. G. Pringle, *Organometallics*, 1992, **11**, 3879.

7 P. Bergamini, E. Costa, S. Sostero, C. Ganter, J. Hogg, A. G. Orpen and P. G. Pringle, *J. Organomet. Chem.*, 1993, **455**, C13.

8 R. McCrindle and A. J. McAlees, *Organometallics*, 1993, **12**, 2445; G. Ferguson, J. F. Gallagher, A. J. McAlees, R. McCrindle, J. Philips and G. J. B. Williams, *J. Organomet. Chem.*, 1992, **430**, C23.

9 P. Bergamini, E. Costa, P. Cramer, J. Hogg, A. G. Orpen and P. G. Pringle, *Organometallics*, in the press.

10 T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.*, 1981, **29**, 3249; *Aldrichim. Acta*, 1990, **23**, 55.

11 R. McCrindle, G. J. Arsenault, R. Farwaha, M. J. Hampden-Smith, R. E. Rice and A. J. McAlees, *J. Chem. Soc., Dalton Trans.*, 1988, 1773; N. W. Alcock, P. G. Pringle, P. Bergamini, S. Sostero and O. Traverso, *J. Chem. Soc., Dalton Trans.*, 1990, 1553.

12 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.

13 G. M. Sheldrick, SHELXTL-PLUS, Revision 2.4, Göttingen, 1988.

14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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