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SYNTHESES AND SPECTROSCOPIC CHARACTERISTICS OF BIS-[DIMETHYL(ARYL)SILYLMETHYL]-PLATINUM(II) AND BIS-[DIMETHYL(BENZYL)-SILYLMETHYL]PLATINUM(II) COMPLEXES WITH DIENE-, NITROGEN-, AND PHOSPHORUS-DONOR LIGANDS

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Abstract—The preparations and spectroscopic characteristics of a range of aromatic ring-substituted aryl(dimethyl)silylmethyl (sila-neophyl) complexes of platinum(II) with diene-, nitrogen-, and phosphorus-donor ancillary ligands, *cis*-$Pt(CH_2SiMe_2C_6H_4R)_2L_2$ (R = H, 2-Me, 3-Me, 4-Me, 4-OMe, 4-^tBu, 4-F, 2-CF_3, 3-CF_3, 4-CF_3, 4-NMe_2) and *cis*-$Pt(CH_2SiMe_2C_6F_5)_2L_2$ [L = PPh_3, pyridine (py); L_2 = cycloocta-1,5-diene (cod), bicyclo[2.2.1]hepta-2,5-diene (nbd)] are reported. Corresponding characteristics for benzylsilylmethylplatinum analogues, *cis*-$Pt(CH_2SiMe_2CH_2C_6H_4R)_2L_2$, (R = H, 4-Me; L_2 = cod; L = PPh_3) are also presented.

Recently, we reported on the syntheses and spectroscopic characteristics of a range of aryl(dimethyl) silylmethyl (sila-neophyl) complexes of platinum (II) with diene-, nitrogen-, and phosphorus-donor ancillary ligands, *cis*-$Pt(CH_2SiMe_2Ph)_2L_2$.[1] Some of these undergo thermolytic rearrangement *via* metallacyclization at an aromatic ring site.[1,2] Others—primarily those with phosphorus-donor ligands—favour a more unusual rearrangement to $Pt(Ph)(CH_2SiMe_2CH_2SiMe_2Ph)L_2$ via β-aryl migration to the metal, followed by migration of the remaining pendant sila-neophyl group in the resulting (η^2-silene)platinum intermediate.[3] The rate-sensitivities of reactions of aromatic carbon are among the best understood in mechanistic chemistry and so it was of clear interest to investigate such rate-structure relationships for these modes of organometallic rearrangement. Here, we present the preparative and spectroscopic characteristics of a range of suitably aryl-substituted analogues, *cis*-$Pt(CH_2SiMe_2C_6H_4R)_2L_2$ (R = 2-Me, 3-Me, 4-Me, 4-OMe, 4-^tBu, 4-F, 2-CF_3, 3-CF_3, 4-CF_3, 4-NMe_2) and *cis*-$Pt(CH_2SiMe_2C_6F_5)_2L_2$ [L = PPh_3, pyridine (py); L_2 = cycloocta-1,5-diene (cod), bicyclo[2.2.1]hepta-2,5-diene (nbd)]. A related benzylsilylmethylplatinum system, *cis*-$Pt(CH_2SiMe_2CH_2C_6H_4R)_2L_2$, (R = H, 4-Me; L_2 = cod; L = PPh_3) is also reported.

EXPERIMENTAL.

General and instrumental

Elemental analyses were undertaken by Imperial College Microanalytical Laboratories and by Butterworth Laboratories Ltd. NMR spectra were recorded on a Jeol GSX 270 (^1H, 270.17 MHz; ^{13}C, 67.94 MHz), Brüker WM250 (^1H, 250.13 MHz; ^{13}C, 62.9 MHz) and Jeol FX90Q (^1H, 89.55 MHz; ^{19}F, 84.27 MHz; ^{31}P, 36.21 MHz) spectrometers.

All reactions were carried out under argon using

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standard anaerobic techniques.[3] Solvents were distilled under nitrogen prior to use.

Chloromethyl(dimethyl)chlorosilane supplied by Aldrich Chem. Co. was stored under argon but used without further purification. Bicyclo[2.2.1]hepta-2,5-diene, cycloocta-1,5-diene, 2-bromotoluene, 4-bromobenzotrifluoride, 4-bromo-*N*,*N*-dimethylaniline, bromopentafluorobenzene, benzyl bromide, α-bromo-*p*-xylene, triphenylphosphine,bis-(1,1′-diphenylphosphino)ferrocene and 4-tert-butylpyridine were all used as supplied by Aldrich Chem. Co. 3-Bromotoluene, 4-bromotoluene, 2-bromobenzotrifluoride, 3-bromobenzotrifluoride, 4-bromoanisole, 4-bromo-tert-butylbenzene and 4-bromofluorobenzene, supplied by Lancaster Synthesis, were used without further purification.

Most aryllithium reagents were prepared *in situ* by metal–halogen exchange of n-butyllithium with the corresponding aryl bromide in diethyl ether by an established route.[4]

Syntheses

Preparation of pentafluorophenylmagnesium bromide.[5] To a stirred solution of C_2H_5MgBr (60.8 mmol) at 0°C in THF (40 cm^3) was added dropwise a solution of C_6F_5Br (15.00 g, 60.8 mmol) in THF (60 cm^3). The mixture was gradually warmed to ambient temperature and then stirred for a further 4 h. Filtration of this solution afforded C_6F_5MgBr (yield: 58.4 mmol, 96%).

Preparation of o^2*-tolyllithium.* A solution of 2-bromotoluene (20.00 g, 116.9 mmol) in n-hexane (60 cm^3) was added to a stirred solution of ^{t}BuLi (116.9 mmol) in n-hexane (60 cm^3) cooled to 0°C. A white precipitate formed immediately. After stirring for a further 16 h, the mixture was filtered; the solid washed with n-hexane (4×30 cm^3) and dried *in vacuo*, yielding LiC_6H_4-2-CH_3 as a white powdery solid (yield: 10.55 g, 107.5 mmol, 92%).

Preparation of chloromethyl(dimethyl)(4-tert-butylphenyl)silane. To a stirred solution of chloromethyl(dimethyl)chlorosilane (10.5 cm^3, 80.0 mmol) in Et_2O (50 cm^3) was added dropwise a solution of $BrMgC_6H_4$-4-^{t}Bu (80.0 mmol) in diethyl ether (90 cm^3). Upon complete addition of alkylating reagent, the mixture was refluxed for 24 h, then cooled to −20°C and quenched with aqueous ammonium chloride solution (80 cm^3). The organic layer was separated and the aqueous phase washed with Et_2O (2×20 cm^3). The combined ether extracts were dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* formed a pale yellow oil, which was distilled to afford chloromethyl(dimethyl)(4-tert-butylphenyl)silane as a low melting point, colourless crystalline solid (m.p. 30–31°C; yield: 13.36 g, 53.0 mmol, 70%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.21s, Si—CH_3; 1.13s, ^{t}Bu; 2.59s, CH_2Cl; 7.14d, 7.72d, aromatic.

Preparation of chloromethyl(dimethyl)(4-methoxyphenyl)silane. Chloromethyl(dimethyl)(4-methoxyphenyl)silane was prepared as a colourless liquid from chloromethyl(dimethyl)chlorosilane and 4-$OCH_3C_6H_4MgBr$ according to a similar procedure described above, (yield: 9.58 g, 45.1 mmol, 56%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.38s, Si—CH_3; 2.90s, CH_2Cl; 3.80s, OCH_3; 6.91d, 7.45d, aromatic.

Preparation of chloromethyl(dimethyl)(2-methylphenyl)silane. Chloromethyl(dimethyl)(2-methylphenyl)silane was obtained as a colourless liquid by the interaction of chloromethyl(dimethyl) chlorosilane and 2-$CH_3C_6H_4Li$, following a procedure similar to the one described above (yield: 7.89 g, 39.7 mmol, 50%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.52s, Si—CH_3; 2.51s, Ar—CH_3; 3.12s, CH_2Cl; 7.14–7.53m, aromatic.

Preparation of chloromethyl(dimethyl)(3-methylphenyl)silane. Chloromethyl(dimethyl)(3-methylphenyl)silane, a colourless liquid, was prepared by a procedure analogous to that described above from chloro(dimethyl)chlorosilane and 3-$CH_3C_6H_4Li$ (yield: 13.26 g, 66.7 mmol, 79%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.40s, Si—CH_3; 2.35s, Ar—CH_3; 2.91s, CH_2Cl; 7.17–7.36m, aromatic.

Preparation of chloromethyl(dimethyl)(4-methylphenyl)silane. Chloromethyl(dimethyl)(4-methylphenyl)silane was prepared as a colourless liquid from chloro(dimethyl)chlorosilane and 4-$CH_3C_6H_4Li$ by a method essentially identical to that described above (yield: 11.89 g, 59.8 mmol, 75%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.23s, Si—CH_3; 2.17s, Ar—CH_3; 2.73s, CH_2Cl; 7.01d, 7.25d, aromatic.

Preparation of chloromethyl(dimethyl)(2-trifluoromethylphenyl)silane. Chloromethyl(dimethyl)(2-trifluoromethylphenyl)silane was obtained as a colourless liquid, according to a similar procedure described above, from chloromethyl(dimethyl) chlorosilane and 2-$CF_3C_6H_4Li$ (yield: 16.23 g, 64.0 mmol, 77%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.49s, Si—CH_3; 3.07s, CH_2Cl; 7.49–7.75m, aromatic.

Preparation of chloromethyl(dimethyl)(3-trifluoromethylphenyl)silane. Chloromethyl(dimethyl) (3-trifluoromethylphenyl)silane, a colourless liquid, was prepared from chloromethyl (dimethyl) chlorosilane and 3-$CF_3C_6H_4Li$ by a similar method to that described above (yield: 14.58 g, 57.7 mmol, 72%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.42s, Si—CH_3; 2.93s, CH_2Cl; 7.31–7.50m, aromatic.

Preparation of chloromethyl(dimethyl)(4-trifluoromethylphenyl)silane. Chloromethyl(dimethyl) (4-trifluoromethylphenyl)silane was obtained as a colourless liquid from chloromethyl(dimethyl) chlorosilane and 4-$CF_3C_6H_4Li$ by a procedure similar to that outlined above (yield: 12.33 g, 48.8 mmol, 61%). ^1H NMR ($CDCl_3$): δ (ppm) = 0.35s, Si—CH_3; 2.95s, CH_2Cl; 7.62d, 7.68d, aromatic.

Preparation of chloromethyl(dimethyl)(4-fluorophenyl)silane. Chloromethyl(dimethyl)(4-fluorophenyl)silane was prepared by an analogous procedure from chloromethyl(dimethyl)chlorosilane and 4-FC_6H_4MgBr and obtained as a colourless liquid (yield: 11.94 g, 58.9 mmol, 68%). ^1H NMR ($CDCl_3$): δ (ppm) = 0.35s, Si—CH_3; 2.84s, CH_2Cl; 6.96m, 7.44m, aromatic.

Preparation of chloromethyl(dimethyl)(4-N,N-dimethylaminophenyl)silane. Chloromethyl(dimethyl) (4-*N*,*N*-dimethylaminophenyl)silane was obtained by a method essentially identical to that described previously from the reaction of chloromethyl (dimethyl)chlorosilane with 4-$NMe_2C_6H_4Li$, affording a white low melting point solid (m.p. 18–21°C; yield: 14.82 g, 65.1 mmol, 76%). ^1H NMR ($CDCl_3$): δ (ppm) = 1.09s, Si—CH_3; 3.63s, CH_2Cl; 3.67s, NCH_3; 7.44d, 8.12d, aromatic.

Preparation of chloromethyl(dimethyl)(pentafluorophenyl)silane. Chloromethyl(dimethyl)(pentafluorophenyl)silane was prepared as a colourless liquid from chloromethyl(dimethyl)chlorosilane and C_6F_5MgBr by a procedure similar to that described above (yield: 9.36 g, 34.1 mmol, 71%). ^1H NMR ($CDCl_3$): δ (ppm) = 0.51d, Si—CH_3; 3.08s, CH_2Cl.

Preparation of chloromethyl(dimethyl)(benzyl) silane. Chloromethyl(dimethyl)(benzyl)silane, a colourless liquid, was obtained from chloromethyl (dimethyl)chlorosilane and $C_6H_5CH_2MgBr$ by a method identical to that described above (yield: 18.77 g, 94.4 mmol, 65%). ^1H NMR ($CDCl_3$): δ (ppm) = 0.35s, Si—CH_3; 2.48s, Ar—CH_2; 2.96s, CH_2Cl; 7.23–7.51m, aromatic.

Preparation of chloromethyl(dimethyl)(4-methylbenzyl)silane. Chloromethyl(dimethyl)(4-methylbenzyl)silane was prepared analogously to the procedure adopted above from chloromethyl(dimethyl) chlorosilane and 4-$CH_3C_6H_4CH_2MgBr$ and was obtained as a colourless liquid (yield: 7.71 g, 36.2 mmol, 67%). ^1H NMR ($CDCl_3$): δ (ppm) = 0.13s, Si—CH_3; 2.19s, Ar—CH_2; 2.34s, Ar—CH_3; 2.74s, CH_2Cl; 6.91d, 7.06d, aromatic.

Preparation of bis-[(2-methylphenyl)(dimethyl) silylmethyl](cycloocta-1,5-diene)platinum(II). A solution of 2-$CH_3C_6H_4SiMe_2CH_2MgCl$ (6.0 mmol) in Et_2O (40 cm^3) was added dropwise to a stirred suspension of $PtCl_2$(cod) (0.69 g, 1.84 mmol) in diethyl ether (20 cm^3) at −78°C. After complete addition of the Grignard reagent, the mixture was gradually warmed to ambient temperature and stirred for a further 16 h. The stirred suspension was cooled to −25°C and hydrolysed dropwise with saturated aqueous ammonium chloride solution (30 cm^3). The organic layer was separated and the aqueous phase washed with diethyl ether (2 × 10 cm^3). The combined ether extracts were dried over $MgSO_4$ and decolourized with activated charcoal to give a colourless solution after filtration. Removal of the solvent *in vacuo* gave a white crystalline solid, which was recrystallized from the minimum amount of n-hexane (5 cm^3) to afford colourless rhomboid crystals of the product (yield: 1.01 g, 1.60 mmol, 87%).

Prepared according to a similar procedure were:

Bis-[(3-methylphenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: colourless plates from n-hexane (yield: 0.89 g, 1.41 mmol, 78%).

Bis-[(4-methylphenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: colourless crystalline solid from n-hexane (yield: 1.44 g, 2.29 mmol, 96%).

Bis-[(4-methylphenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: colourless rods from n-hexane (yield: 0.98 g, 1.48 mmol, 81%).

Bis-[(4-tert-butylphenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: white crystalline solid from n-hexane (yield: 1.09 g, 1.53 mmol, 84%).

Bis-[(4-fluorophenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: colourless crystallline solid from n-hexane (yield: 1.16 g, 1.82 mmol, 97%).

Bis-[(2-trifluoromethylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II). Product: colourless rods from n-hexane (yield: 1.81 g, 2.46 mmol, 92%).

Bis-[(3-trifluoromethylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II). Product: white crystalline solid from n-hexane (yield: 1.73 g, 2.35 mmol, 88%).

Bis-[(4-trifluoromethylphenyl)(dimethyl)silylmethyl](cycloocta-1,5-diene)platinum(II). Product: colourless crystalline solid from n-hexane (yield: 1.30 g, 1.76 mmol, 88%).

Bis-[(4-*N*,*N*-dimethylaminophenyl)(dimethyl) silylmethyl](cycloocta-1,5-diene)platinum(II). Product: buff crystalline solid from n-hexane (yield: 1.56 g, 2.27 mmol, 85%).

Bis-[(pentafluorophenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: white crystalline solid from chloroform (yield: 1.52 g, 1.94 mmol, 73%).

Bis-[benzyl(dimethyl)silylmethyl](cycloocta-1,5-

diene)platinum(II). Product: colourless blocks from n-hexane (yield: 0.94 g, 1.43 mmol, 80%).

Bis - [(4 - methylphenyl)(dimethyl)silylmethyl] (cycloocta-1,5-diene)platinum(II). Product: colourless sticky solid (yield: 1.16 g, 1.76 mmol, 94%).

Bis - [(2 - methylphenyl)(dimethyl)silylmethyl] (bicyclo[2.2.1]hepta-2,5-diene)platinum(II). Product: white solid from n-hexane (yield: 1.63 g, 2.65 mmol, 95%).

Bis - [(3 -methylphenyl)(dimethyl)silylmethyl] (bicyclo[2.2.1]hepta-2,5-diene)platinum(II). Product: white crystalline solid from n-hexane (yield: 1.32 g, 2.14 mmol, 77%).

Bis - [(4 - methylphenyl)(dimethyl)silylmethyl] (bicyclo[2.2.1]hepta-2,5-diene)platinum(II). Product: white crystalline solid from n-hexane (yield: 1.51 g, 2.45 mmol, 88%).

Preparation of cis-*bis*-[(4-*methylphenyl*) (*dimethyl*)*silylmethyl*] - *bis* - (*pyridine*)*platinum*(II). $Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CH_3)_2(cod)$ (0.21 g, 0.33 mmol) was dissolved in pyridine (15 cm^3, 186.0 mmol) and the resulting solution stirred at 60°C for 24 h. Unreacted pyridine was removed *in vacuo* and the yellow solid residue recrystallized from diethyl ether (3 cm^3) and n-hexane (1 cm^3) affording the product as a pale yellow–brown solid (yield: 0.17 g, 0.25 mmol, 76%).

Prepared according to an essentially identical method were:

cis-Bis-[(3-methylphenyl)(dimethyl)silylmethyl]-bis-(pyridine)platinum(II). Product: pale yellow liquid (yield: 0.19 g, 0.29 mmol, 100%).

cis - Bis - [(4 - methoxyphenyl)(dimethyl) silylmethyl]-bis-(pyridine)platinum(II). Product: pale yellow–brown crystalline solid from diethyl ether and n-hexane (yield: 0.18 g, 0.25 mmol, 84%).

cis - Bis - [(4 - tert - butylphenyl)(dimethyl) silylmethyl]-bis-(pyridine)platinum(II). Product: pale yellow crystalline solid from diethyl ether and n-hexane (yield: 0.165 g, 0.22 mmol, 75%).

cis-Bis-[(4-fluorophenyl)(dimethyl)silylmethyl]-bis-(pyridine)platinum(II). Product: pale yellow liquid (yield: 0.21 g, 0.31 mmol, 100%).

cis - Bis - [(benzyl)(dimethyl)silylmethyl] - bis - (pyridine)platinum(II). Product: pale yellow crystalline solid from diethyl ether and n-hexane (yield: 0.16 g, 0.23 mmol, 74%).

Preparation of cis-*bis*-[(4-*methylphenyl*)(*dimethyl*) *silylmethyl*] - *bis* - (4 - *tert* - *butylpyridine*) *platinum* (II).$Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CH_3)_2(cod)$ (0.18 g, 0.29 mmol) was dissolved in excess 4-tert-butylpyridine (10 cm^3, 68.1 mmol) and the solution stirred for 24 h at 60°C. Excess ligand was removed by vacuum distillation, during which the pale yellow solution turned orange. The oily residue was dissolved in Et_2O (2 cm^3), n-hexane (1 cm^3) added, then cooled to -20°C. Filtration of the solid and drying *in vacuo* afforded the product as a pale orange crystalline solid (yield: 0.19 g, 2.40 mmol, 83%).

Preparation of cis-*bis*-[(2-*methylphenyl*) (*dimethyl*)*silylmethyl*]-*bis*-(*triphenylphosphine*) *platinum*(II). To a solution of $Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CH_3)_2(nbd)$ (0.42 g, 0.68 mmol) in diethyl ether (6 cm^3) was added triphenylphosphine (0.362 g, 1.36 mmol). After 15 min a white crystalline solid began forming. The solution was allowed to stand at ambient temperature for 5 days to ensure that the reaction was complete. The solvent was removed *in vacuo* giving white needles of the product as the etherate. The solid was dissolved in the minimum amount of cold toluene (60 cm^3) and flash evaporated to afford the product as a white microcrystalline solid (yield: 0.70 g, 0.67 mmol, 98%).

Preparation of cis-*bis*-(3-*methylphenyl*) (*dimethyl*) *silylmethyl*] - *bis* - (*triphenylphosphine*)*platinum*(II). Triphenylphosphine (0.17 g, 0.66 mmol) was added to a solution of $Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CH_3)_2(nbd)$ (0.20 g, 0.33 mmol) in diethyl ether (6 cm^3), which was then heated to 60°C for 14 days. The solvent was removed *in vacuo* forming a white solid, which was recrystallized from benzene (2 cm^3) and n-hexane (1 cm^3) to afford the product as a white crystalline solid (yield: 0.30 g, 0.29 mmol, 88%).

Preparation of cis-*bis*-[(4-*methylphenyl*) (*dimethyl*) *silylmethyl* - *bis* - (*triphenylphosphine*)*platinum*(II). *cis* - Bis - [(4-methylphenyl)(dimethyl)silylmethyl]-bis-(triphenylphosphine)platinum(II) was prepared in an analogous fashion from $Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CH_3)_2(nbd)$ and triphenylphosphine, forming a white crystalline solid from benzene and n-hexane (yield: 0.29 g, 0.28 mmol, 85%).

Preparation of cis-*bis*-[(2-*trifluoromethylphenyl*) (*dimethyl*)*silylmethyl*] - *bis* - (*triphenylphosphine*) *platinum*(II). To a solution of $Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2(cod)$ (0.20 g, 0.28 mmol) in diethyl ether (7 cm^3) was added triphenylphosphine (0.14 g, 0.56 mmol) and the solution was heated to 60°C for 21 days. The colourless rods which had formed were filtered, washed with n-hexane (3 × 2 cm^3) and dried *in vacuo* to give analytically pure $(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$. A second crop of sample was obtained by recrystallizing the filtrate from benzene (1 cm^3) and n-hexane (1 cm^3) as a white crystalline solid (yield: 0.25 g, 0.22 mmol, 82%).

Preparation of cis-*bis*-[(4-*tert*-*butylphenyl*) (*dimethyl*)*silylmethyl*] - *bis* - (*triphenylphosphine*) *platinum*(II). Triphenylphosphine (0.14 g, 0.56 mmol) was added to a solution of $Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2(cod)$ (0.20 g, 0.28 mmol) in diethyl ether (7 cm^3), which was then heated to

60°C for 28 days. Removal of the solvent *in vacuo* yielded a solid residue. Dissolution in benzene (2 cm^3), addition of n-hexane (1 cm^3), cooling to -20°C followed by filtration and drying *in vacuo*, afforded the product as a white crystalline solid (yield: 0.26 g, 0.23 mmol, 82%).

Prepared according to essentially an analogous procedure were:

cis - Bis - [(3 - trifluoromethylphenyl)(dimethyl) silylmethyl]-bis-(triphenylphosphine)platinum(II). Product: white crystalline solid from benzene and n-hexane (yield: 0.23 g, 0.20 mmol, 74%).

cis - Bis - [(4 - trifluoromethylphenyl)(dimethyl) silylmethyl]-bis-(triphenylphosphine)platinum(II). Product: colourless plates from benzene and methanol (yield: 0.26 g, 0.23 mmol, 84%).

cis - Bis - [(4 - methoxyphenyl)(dimethyl)silylmethyl] - bis - (triphenylphosphine)platinum(II). Product: colourless aggregates from benzene and n-hexane (yield: 0.29 g, 0.27 mmol, 90%).

cis-Bis-[(4-fluorophenyl)(dimethyl)silylmethyl]-bis-(triphenylphosphine)platinum(II). Product: colourless crystalline solid from benzene and n-hexane (yield: 0.27 g, 0.26 mmol, 83%).

cis - Bis-[(4-*N*,*N* - dimethylaminophenyl) (dimethyl)silylmethyl] - bis - (triphenylphosphine) platinum(II). Product: white solid from benzene and n-hexane (yield: 0.25 g, 0.23 mmol, 78%).

cis - Bis - [(benzyl)(dimethyl)silylmethyl] - bis - (triphenylphosphine)platinum(II). Product: white crystalline solid from benzene and n-hexane (yield: 0.32 g, 0.30 mmol, 96%).

cis-Bis-[(4-methylbenzyl)(dimethyl)silylmethyl]-bis-(triphenylphosphine)platinum(II). Product: white solid from n-hexane (yield: 0.26 g, 0.24 mmol, 80%).

Preparation of cis-*bis*-[(4-*methylphenyl*) (*dimethyl*)*silylmethyl*][(1,1′-*diphenylphosphino*)*ferrocene*]*platinum*(II). To a solution of $Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CH_3)_2(cod)$ (0.21 g, 0.34 mmol) in toluene (6 cm^3) was added dppf (0.19 g, 0.34 mmol) and the solution heated to 50°C for 21 days. Removal of the solvent *in vacuo* yielded an amber residue, which was dissolved in the minimum amount of toluene (2 cm^3), n-hexane added (2 cm^3) and cooled to -20°C. Filtration followed by drying *in vacuo* gave an amber microcrystalline powder of the product (yield: 0.26 g, 0.28 mmol, 83%).

RESULTS AND DISCUSSION

Synthesis

Chloromethyl(*dimethyl*)*arylsilanes and chloromethyl*(*dimethyl*)*benzylsilanes.* Series of chloromethyl(dimethyl)arylsilanes and chloromethyl(dimethyl)benzylsilanes have been prepared by modifications of a published procedure.[6] In general, *para*-substituted derivatives could be prepared in moderately good yields by the interaction of chloromethyl(dimethyl)chlorosilane with the appropriate arylmagnesium bromide, generated *in situ* by the reaction of magnesium shot and aryl bromide.

Although *meta*- and *ortho*-substituted arylsilanes could also be prepared analogously, yields were poor. Improved yields were obtained by reacting chloromethyl(dimethyl)chlorosilane with the corresponding aryllithium reagent. Silanes with *N*,*N*-dimethylamino or trifluoromethyl group substituents on the aromatic ring were also synthesized by this route. In these cases corresponding Grignard reagents could only be obtained in poor yields, due to intermolecular coupling reactions.

With the exception of chloromethyl(dimethyl) (4-tert-butylphenyl)silane and chloromethyl(dimethyl)(4 - *N*, *N* - dimethylaminophenyl)silane—which are low melting, colourless solids—they are high boiling, colourless liquids.

Diene and pyridine complexes. The synthesis of diene complexes has been achieved in > 70% yield by treatment of either $PtCl_2(cod)$ or $PtCl_2(nbd)$ with the appropriate Grignard reagent. These colourless or white solids are air-inert; $Pt(CH_2SiMe_2C_6H_4R)_2(nbd)$ were stored at -20°C to prevent thermolytic decomposition, and have satisfactory analyses (Table 1).

Subsequent replacement of the diene by pyridine or 4-tert-butylpyridine yielded mostly pale yellow or orange crystalline solids. *cis*-$Pt(CH_2SiMe_2C_6H_4R)_2(py)_2$ ($R = 3\text{-}CH_3$, 4-F) could only be isolated as pale yellow liquids. Elemental analyses are detailed in Table 2. Diene displacement is generally complete in 24 h in neat ligand solution. Although stable as solids, at room temperature benzene or toluene solutions rapidly undergo rearrangement forming, in most cases, a platinasilaindan and liberating trimethylarylsilane (*vide infra*). *cis*-$Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2(py)_2$ could not be isolated but has been characterized by ^1H NMR spectroscopy as its pyridine-d_5 analogue.

Phosphine complexes. The majority of complexes were synthesized by displacement of cod by triphenylphosphine at 60°C in diethyl ether. Substitution of diene is characteristically slow, often taking *ca* 28 days for completion. Displacement of nbd was more facile, generally complete within 14 days at 60°C. In the case of $Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CH_3)_2(nbd)$, this metathesis was carried out at ambient temperature to preclude any thermolytic rearrangement of the dialkyl complex.

Table 1. Analytical data for bis-[dimethyl(aryl)silylmethyl]platinum(II) and bis-[dimethyl(benzyl)silylmethyl] platinum(II) complexes with diene-, nitrogen-, and phosphorus-donor ligands

Complex	Colour	Found (calculated) (%) C	H	N
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$	Colourless	53.4 (53.4)	6.8 (6.7)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$	Colourless	53.0 (53.4)	6.7 (6.7)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Colourless	53.1 (53.4)	6.7 (6.7)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$	Colourless	50.6 (50.8)	6.4 (6.4)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2$	Colourless	56.9 (57.2)	7.6 (7.6)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$	Colourless	49.3 (49.0)	5.7 (5.7)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$	Colourless	45.6 (45.6)	4.9 (4.9)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$	Colourless	45.3 (45.6)	4.9 (4.9)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$	Colourless	45.4 (45.6)	4.9 (4.9)	—
$(cod)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$	Colourless	52.5 (52.4)	7.2 (7.0)	4.1 (4.0)
$(cod)Pt(CH_2SiMe_2C_6F_5)_2$	Colourless	39.8 (39.9)	3.6 (3.6)	—
$(cod)Pt(CH_2SiMe_2CH_2C_6H_5)_2$	Colourless	53.2 (53.4)	6.8 (6.7)	—
$(cod)Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$	Colourless	54.8 (54.8)	6.9 (7.0)	—
$(nbd)Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$	Colourless	52.6 (52.8)	6.1 (6.2)	—
$(nbd)Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$	Colourless	52.7 (52.8)	6.4 (6.2)	—
$(nbd)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Colourless	52.9 (52.8)	6.3 (6.2)	—
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Pale yellow	53.0 (52.9)	5.9 (5.9)	4.1 (4.1)
$({}^tBupy)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Pale orange	57.4 (57.6)	7.2 (7.1)	3.5 (3.5)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$	Pale yellow	50.8 (50.6)	5.7 (5.7)	4.0 (3.9)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2$	Pale yellow	56.8 (56.6)	6.9 (6.9)	3.7 (3.7)
$(py)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2$	Pale yellow	52.9 (52.9)	5.8 (5.9)	4.1 (4.1)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$	Colourless	64.3 (64.3)	5.9 (5.8)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$	Colourless	64.4 (64.3)	5.5 (5.8)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Colourless	64.0 (64.3)	5.6 (5.8)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2 \cdot 2/3C_6H_6$	Colourless	63.7 (63.7)	5.9 (5.7)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2$	Colourless	65.9 (65.9)	6.5 (6.4)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$	Colourless	61.3 (61.5)	5.2 (5.1)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$	Colourless	58.2 (58.3)	4.6 (4.7)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$	Colourless	58.2 (58.3)	4.7 (4.7)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$	Colourless	58.5 (58.3)	4.8 (4.7)	—
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$	Colourless	62.8 (63.1)	6.8 (7.2)	2.7 (2.5)
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2$	Colourless	63.9 (64.3)	5.9 (5.8)	—
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$	Colourless	65.1 (64.8)	6.1 (6.0)	—
$(Dppf)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$	Amber	60.6 (60.3)	5.5 (5.4)	—

These complexes are air-inert, colourless crystalline solids with satisfactory microanalytical characteristics (Table 1). Only *cis*-$Pt(CH_2SiMe_2C_6F_5)_2(PPh_3)_2$ was not isolated, although it was observed by ^1H and ^{31}P NMR spectroscopy. They do not decompose at room temperature in deoxygenated hydrocarbon solvents but do react slowly with chlorocarbons, affording *cis*-$PtCl_2(PPh_3)_2$.

Spectroscopic characteristics

Conventions. The numerical conventions employed for the aromatic ring are shown in Fig. 1. In all cases, the silicon-bound carbon of the aromatic ring is designated C_1, while the substituents are attached either to C_2, C_3 or C_4.

^1H *NMR.* Common features in all these spectra detailed in Table 2 are the characteristic singlet near 0.0 ppm for the silicon-bound methyl hydrogens and a 1:4:1 "triplet" for the platinum-bound methylene hydrogens (L = diene or py), as a result of spin–spin coupling to ^{195}Pt. An apparent quartet with satellites is observed for L = PPh_3.[7] The magnitude of $^2J_{Pt-H}$ is generally of the order 84–102 Hz, depending on the *trans* ligand, and decreases in the order:

$$nbd > cod > py > PPh_3$$

Table 2. ^1H NMR characteristics of bis-[dimethyl(aryl)silylmethyl]platinum(II) and bis-[dimethyl(benzyl)silylmethyl]platinum(II) complexes with diene-, nitrogen- and phosphorus-donor ligands

Complex	δ ^1H (ppm): hydrocarbyl ligands (J_{Pt-H}) (Hz) (*assignment*) (J_{H-F}) (Hz)				δ ^1H (ppm): ancillary ligands (J_{Pt-H}) (Hz) (*assignment*)
	Pt—CH_2	Si—CH_3	Substituent	Aromatic	
(cod)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2$^{a}	1.15 (**92.3**)	0.59	2.57 [CH_3]	7.09–7.25m, [H_3, H_4, H_5]; 7.70dd, [H_6] ($J_{H_2-H_3}$ = 7.0 Hz)	1.46–1.71m,^{b} [CH_2]; 4.26 "t", (**42.3**)[CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-3-Me)$_2$^{a}	1.37 (**92.0**)	0.60	2.26 [CH_3]	7.10dd, [H_4] ($J_{H_4-H_5}$ = 7.7 Hz); 7.27t, [H_5] ($J_{H_5-H_6}$ = 7.1 Hz); 7.61dd, [H_6]; 7.66dd, [H_2]	1.55–1.67m,^{b} [CH_2]; 4.31 "t", (**41.7**)[CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2$^{c}	1.19 (**92.2**)	0.44	2.13 [CH_3]	7.01d, [H_3, H_5]; 7.53d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.6 Hz)	1.39–1.63m,^{b} [CH_2]; 4.19 "t", (**41.9**)[CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-OMe)$_2$^{a}	1.38 (**97.6**)	0.60	3.40 [OCH_3]	6.96d, [H_3, H_5]; 7.70d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.5 Hz)	1.50–1.74m,^{b} [CH_2]; 4.36 "t", (**42.0**)[CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-^tBu)$_2$^{a}	1.49 (**85.8**)	0.62	1.31 [C-CH_3]	7.41d, [H_3, H_5]; 7.77d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.9 Hz)	1.51–1.74m,^{b} [CH_2]; 4.33 "t", (**40.7**)[CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-F)$_2$^{c}	1.05 (**93.0**)	0.35	—	6.85m, [H_3, H_5] (*9.3*); 7.43m, [H_2, H_6] (*6.4*) ($J_{H_2-H_3}$ = 8.5 Hz)	1.41–1.63m,^{b} [CH_2]; 4.11 "t", (**39.4**)[CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-2-CF_3)$_2$^{d}	1.07 (**92.5**)	0.36	—	7.34–7.46m, [H_4, H_5]; 7.62dd, [H_3] ($J_{H_3-H_4}$ = 7.5 Hz); 7.73dd, [H_6] ($J_{H_5-H_6}$ = 7.1 Hz)	2.03 "t", (**17.0**) [CH_2]; 4.49 "t", (**42.1**) [CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-3-CF_3)$_2$^{d}	0.96 (**92.6**)	0.31	—	7.40t, [H_3]; 7.53d, [H_4] ($J_{H_4-H_5}$ = 7.8 Hz); 7.71d, [H_6] ($J_{H_5-H_6}$ = 7.4 Hz); 7.79d, [H_2]	1.96–2.04m,^{b} [CH_2]; 4.45 "t", (**42.6**)[CH]

Table 2—*continued*

Complex	δ ^{1}H (ppm) : hydrocarbyl ligands (J_{Pt-H}) (Hz) (*assignment*) (J_{H-F}) (Hz) Pt—CH$_2$	Si—CH$_3$	Substituent	Aromatic	δ ^{1}H (ppm) : ancillary ligands (J_{Pt-H}) (Hz) (*assignment*)
(cod)Pt($CH_2SiMe_2C_6H_4$-4-$CF_3)_2$[d]	0.97 **(92.4)**	0.30	—	7.52d, [H_3, H_5] ; 7.69d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.7 Hz)	2.02 "t", **(17.3)** [CH_2] ; 4.49 "t", **(42.4)** [CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-$NMe_2)_2$[d]	1.05 **(92.3)**	0.26	2.92 [N—CH_3]	6.71d, [H_3, H_5] ; 7.43d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.6 Hz)	1.97–2.05m,[b] [CH_2] ; 4.48 "t", **(42.2)** [CH]
(cod)Pt($CH_2SiMe_2C_6F_5)_2$[d]	0.98 **(91.6)**	0.40 *(3.6)*	—	—	2.19–2.26m,[b] [CH_2] ; 4.68 "t", **(42.4)** [CH]
(cod)Pt($CH_2SiMe_2CH_2C_6H_5)_2$[d]	0.81 **(93.5)**	0.02	2.06 [CH_2]	6.98–7.04m, [H_3, H_4, H_5] ; 7.18m, [H_2, H_6]	2.11–2.24m,[b] [CH_2] ; 4.51 "t", **(42.0)** [CH]
(cod)Pt($CH_2SiMe_2CH_2C_6H_4$-4-$Me)_2$[d]	0.92 **(93.5)**	0.09	2.12 [CH_2] 2.36 [CH_3]	6.99d, [H_3, H_5] ; 7.18d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.0 Hz)	2.18–2.31m,[b] [CH_2] ; 4.68 "t", **(41.4)** [CH]
(nbd)Pt($CH_2SiMe_2C_6H_4$-2-$Me)_2$[d]	1.15 **(102.0)**	0.33	2.51 [CH_3]	7.09–7.16m, [H_4, H_5] ; 7.20dd, [H_3] ($J_{H_3-H_4}$ = 7.4 Hz) ; 7.52dd, [H_6] ($J_{H_5-H_6}$ = 7.1 Hz)	1.31m, [H_C] ; 3.61m,[b] [H_B] ; 4.42 "t", **(41.1)** [H_A]
(nbd)Pt($CH_2SiMe_2C_6H_4$-3-$Me)_2$[d]	1.11 **(101.2)**	0.27	2.36 [CH_3]	7.11d, [H_4] ($J_{H_4-H_5}$ = 7.6 Hz) ; 7.22t, [H_5] ($J_{H_5-H_6}$ = 7.2 Hz) ; 7.41d, [H_6] ; 7.43d, [H_2]	1.33m, [H_C] ; 3.59m,[b] [H_B] ; 4.44 "t", **(42.4)** [H_A]
(nbd)Pt($CH_2SiMe_2C_6H_4$-4-$Me)_2$[d]	1.11 **(101.2)**	0.26	2.34 [CH_3]	7.15d, [H_3, H_5] ; 7.50d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.0 Hz)	1.34m, [H_C] ; 3.62m,[b] [H_B] ; 4.48 "t", **(42.4)** [H_A]
(py)$_2$Pt($CH_2SiMe_2C_6H_4$-4-$Me)_2$[c,e]	0.95 **(88.8)**	0.49	2.11 [CH_3]	6.88d, [H_3, H_5] ; 7.63d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.7 Hz)	6.05m, [H_3, H_5] ($J_{H_2-H_3}$ = 6.2 Hz) ; 6.60m, [H_4] ($J_{H_3-H_4}$ = 7.6 Hz) ; 8.05dd, **(22.6)** [H_2, H_6]
(^{t}Bupy)$_2$Pt($CH_2SiMe_2C_6H_4$-4-$Me)_2$[c,e]	1.17 **(89.1)**	0.68	2.18 [CH_3]	7.03d, [H_3, H_5] ; 7.80d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.8 Hz)	0.86s, [CH_3] ; 6.39d, [H_3, H_5] ; 8.28d, **(22.6)** [H_2, H_6] ($J_{H_2-H_3}$ = 6.9 Hz)

$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[a]	1.10 **(84.2)**	0.62	2.17 [CH_3]	6.99dd, [H_4] ($J_{H_4-H_5}$ = 7.9 Hz); 7.18m, [H_5]; 7.62d, [H_2]; 7.71dd, [H_6] ($J_{H_5-H_6}$ = 7.3 Hz)	6.18m, [H_3, H_5] ($J_{H_2-H_3}$ = 6.4 Hz); 6.69m, [H_4] ($J_{H_3-H_4}$ = 7.6 Hz); 8.19dd, **(21.7)** [H_2, H_6] ($J_{H_2-H_4}$ = 1.5 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$[c,e]	0.94 **(88.2)**	0.48	3.29 [OCH_3]	6.67d, [H_3, H_5]; 7.61d, [H_2, H_6] ($H_{H_2-H_3}$ = 8.4 Hz)	6.12m, [H_3, H_5] ($J_{H_2-H_3}$ = 6.4 Hz); 6.65m, [H_4] ($J_{H_3-H_4}$ = 7.5 Hz); 8.09dd, **(21.4)** [H$_2$, H_6] ($J_{H_2-H_4}$ = 1.2 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2$[c,e]	0.97 **(89.5)**	0.50	1.19 [CH_3]	7.11d, [H_3, H_5]; 7.63d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.2 Hz)	6.11m, [H_3, H_5] ($J_{H_2-H_3}$ = 6.3 Hz); 6.63m, [H_4] ($J_{H_3-H_4}$ = 7.6 Hz); 8.09dd, **(22.8)** [H_2, H_6] ($J_{H_2-H_4}$ = 1.5 Hz)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[c]	0.76 **(89.4)**	0.35	—	6.73m, [H_3, H_5] *(10.1)*; 7.48m, [H_2, H_6] *(6.5)* ($J_{H_2-H_3}$ = 7.8 Hz)	6.30m, [H_3, H_5] ($J_{H_2-H_3}$ = 6.6 Hz); 7.04m, [H_4] ($J_{H_3-H_4}$ = 7.7 Hz); 8.07dd, **(23.1)** [H_2, H_6] ($J_{H_2-H_4}$ = 1.5 Hz)
$(py\text{-}d^5)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$[f]	0.84 **(88.5)**	0.36	—	7.52d, [H_3, H_5]; 7.81d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.0 Hz)	—
$(py)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2$[c]	0.63 **(87.1)**	−0.04	2.19 [CH_2]	6.82–6.92m, [H_3, H_4, H_5]; 7.06d, [H_2, H_6] ($J_{H_2-H_3}$ = 4.6 Hz)	6.34m, [H_3, H_5] ($J_{H_2-H_3}$ = 6.6 Hz); 6.70m, [H_4] ($J_{H_3-H_4}$ = 7.1 Hz); 8.24dd, **(23.1)** [H_2, H_6] ($J_{H_2-H_4}$ = 1.6 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$[a]	0.87 —[b]	0.08	2.03 [CH_3]	6.92t, [H_5]; 7.01t, [H_4]; 7.16dd, [H_3] ($J_{H_3-H_4}$ = 7.3 Hz); 7.23dd, [H_6] ($J_{H_5-H_6}$ = 7.5 Hz)	7.02–7.07m, [H_3, H_4, H_5]; 7.32m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$[d]	0.91 —[b]	0.17	2.37 [CH_3]	7.22–7.32m, [H_4, H_5, H_6]; *g* [H_2]	7.11–7.19m, [H_3, H_4, H_5]; 7.39m, [H_2, H_6]

Table 2—*continued*

Complex	δ ^{1}H (ppm) : hydrocarbyl ligands (J_{Pt-H}) (Hz) (*assignment*) (J_{H-F}) (Hz)				δ ^{1}H (ppm) : ancillary ligands (J_{Pt-H}) (Hz) (*assignment*)
	Pt—CH$_2$	Si—CH$_3$	Substituent	Aromatic	
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-4-Me})_2{}^d$	0.89 —^{b}	0.11	2.37 [CH_3]	7.23d, [H_3, H_5]; 7.36d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.0 Hz)	7.06–7.14m, [H_3, H_4, H_5]; 7.34m, [H_2, H_6]
$(Dppf)Pt(CH_2SiMe_2C_6H_4\text{-4-Me})_2{}^a$	1.25 —^{b}	0.48	2.37 [CH_3]	7.09d, [H_3, H_5]; 7.62d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.5 Hz)	3.78s, [H_Y, $H_{Y'}$]; 4.08s, [H_Z, $H_{Z'}$]; 6.96–7.08m, [H_3, H_4, H_5]; 7.83m,^{h} [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-4-OMe})_2{}^a$	1.54 —^{b}	0.50	3.42 [OCH_3]	6.89d, [H_3, H_5]; 7.67d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.5 Hz)	6.84–6.89m, [H_3, H_4, H_5] 7.48m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-4-}^tBu)_2{}^a$	0.91 —^{b}	0.57	1.36 [CH_3]	7.38d, [H_3, H_5]; 7.73d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.0 Hz)	6.90–6.95m, [H_3, H_4, H_5]; 7.51m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-4-F})^{2a}$	1.31 —^{b}	0.44	—	7.01q, [H_3, H_5] (*17.1*); 7.61q, (H_2, H_6] (*14.2*) ($J_{H_2-H_3}$ = 8.4 Hz)	6.89–6.96m, [H_3, H_4, H_5]; 7.52m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-2-CF}_3)_2{}^d$	0.79 **(84.1)**	0.06	—	6.88–6.94m, [H_3, H_5]; *g* [H_4]; 7.21m, [H_6]	7.00–7.07m, [H_3, H_4, H_5]; 7.29m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-3-CF}_3)_2{}^d$	1.08 —^{b}	0.41	—	7.40^h [H_5]; *g* [H_4]; 7.62dd, [H_6] ($J_{H_5-H_6}$ = 7.5 Hz); 7.92d, [H_2]	6.82–6.97m, [H_3, H_4, H_5]; 7.47m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-4-CF}_3)_2{}^c$	1.10 —^{b}	0.35	—	7.32d, [H_3, H_5]; 7.44d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.6 Hz)	6.76–6.87m, [H_3, H_4, H_5]; 7.35m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-4-NMe}_2)_2{}^a$	1.43 —^{b}	0.57	2.63 [N—CH$_3$]	6.74d, [H_3, H_5]; 7.74d, [H_2, H_6] ($J_{H_2-H_3}$ = 8.6 Hz)	6.89–6.96m, [H_3, H_4, H_5]; 7.52m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6F_5)_2{}^d$	0.84 —^{b}	0.19 (*3.4*)	—	—	6.89–7.01m, [H_3, H_4, H_5]; 7.51m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2{}^a$	1.05 **(84.4)**	0.26	2.13 [CH_2]	7.01m, [H_4] ($J_{H_3-H_4}$ = 5.3 Hz); 7.07dd, [H_2, H_6] ($J_{H_2-H_3}$ = 8.1 Hz); 7.19m, [H_3, H_5]	6.89–6.92m, [H_3, H_4, H_5]; 7.58m, [H_2, H_6]
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-4-Me})_2{}^a$	1.06 **(92.1)**	0.25	2.13 [CH_2] 2.23 [CH_3]	*g* [H_3, H_5]; 7.09d, [H_2, H_6] ($J_{H_2-H_3}$ = 7.9 Hz)	6.94–7.04m, [H_3, H_4, H_5]; 7.61m, [H_2, H_6]

^{a} Benzene-d^6; ^{b} broad resonance; ^{c} toluene-d^8; ^{d} chloroform-d^1; ^{e} run at −20°C; ^{f} pyridine-d^5; ^{g} obscured; ^{h} partially obscured by ligand peak.

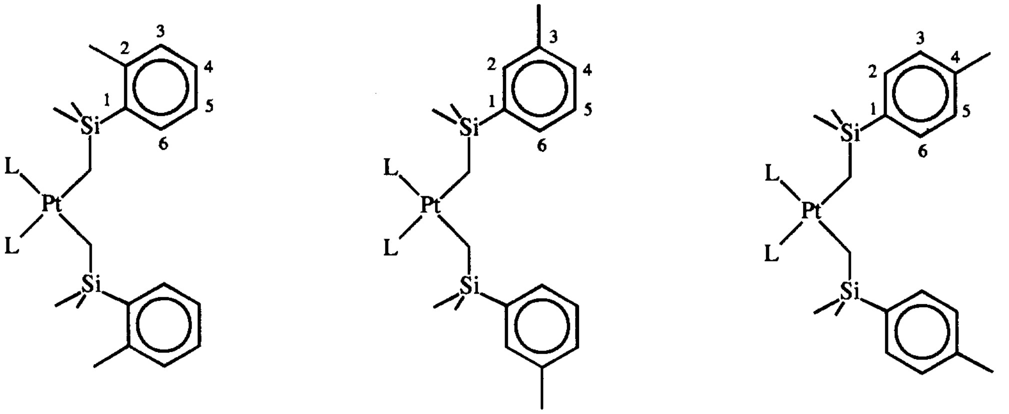

Fig. 1. Numerical conventions for NMR discussions.

This implies that there is more *s*-orbital character in the Pt—CH_2 skeleton of η^2-diene complexes, reflecting the weaker *trans* influence[8] of diene relative to nitrogen- and phosphorus-donor ligands.

Within each series there is little variation in the magnitude of $^2J_{Pt—H}$ as the substituent is changed, indicating that the ring substituents are too distant to exert any appreciable steric or electronic effects at the metal. This is also reflected in the magnitude of $^2J_{Pt—H}$ for olefinic hydrogens in the diene and $^2J_{Pt—H}$ for the *ortho* protons in the pyridine ring, which show a corresponding lack of variation.

The aromatic region of *para*-substituted derivatives appears as a set of two AB doublets, characteristic of 1,4-disubstituted benzenes. These resonances are readily assigned; the signal occurring at higher field is due to *meta* hydrogens, the one at lower field due to *ortho* hydrogens. These assignments were further verified in the case of *cis*-$Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2L_2$ (L_2 = cod; L = py, PPh_3) by comparison of the magnitudes of $J_{F—H}$ coupling constants. Values of $^3J_{F—H}$, in the range 9–18 Hz, due to a spin–spin interaction of the ^{19}F nucleus ($I = 1/2$, 100% abundant) with the *meta* hydrogens were observed. Interaction of ^{19}F with the *ortho* hydrogens gave $^4J_{F—H}$ between 6 and 14 Hz.

More complicated patterns were observed for *ortho*- and *meta*-substituted arene rings. H_2 could usually be distinguished from H_6 in *meta*-substituted derivatives; the former appearing as a doublet, due to coupling of H_2 with H_4, and the latter as a doubled doublet. Often, H_5 could also be assigned as the resonance which occurs furthest upfield. For complexes with *ortho*-substituted phenyl rings only H_6 could be assigned unequivocally, occurring as a doubled doublet at low field (δ = 7.5–7.7 ppm). The remaining protons appear as a complicated multiplet.

For complexes *cis*-$Pt(CH_2SiMe_2C_6H_4R)_2L_2$ (R = 2-CF_3, 3-CF_3, 4-CF_3; L_2 = cod; L = PPh_3), no coupling was observed between the fluorine nuclei and protons on the aromatic ring, presumably since the magnitude of $^4J_{F—H}$ is so small that it remains unresolved. However, $^5J_{F—H}$ is observed due to ^{19}F interacting with the silicon-methyl hydrogens in *cis*-$Pt(CH_2SiMe_2C_6F_5)_2L_2$ (L_2 = cod; L = PPh_3).

^{13}C *NMR*. All isolated compounds have been characterized by $^{13}C\{^1H\}$ NMR spectroscopy (Table 3). Assignments are based on comparison with free ligands,[9] with corresponding XCH_2SiMe_2Ar compounds (X = H or Cl),[10] platinum–carbon and/or fluorine–carbon coupling constants and on the intensity of the peaks. The two quaternary carbon atoms on the aromatic ring could be distinguished readily. The silicon-bound carbon, C_1, is coupled to ^{195}Pt, typically giving $^3J_{Pt—C}$ of 20–35 Hz, while the substituent-bearing carbon appears as a singlet. The remaining aromatic carbons were assigned on the basis that *meta*-carbon atoms are least affected by changing the substituent.[11] Hence, lower frequency resonances were usually designated as C_3 and C_5; those at higher frequency C_2 and C_6.

Complexes with either a fluorine or trifluoromethyl substituent all exhibited coupling to ^{19}F. For diene complexes the magnitude of $^1J_{F—C}$ to the quaternary carbon of the CF_3 group was *ca* 280 Hz, while for $^2J_{F—C_4}$ a smaller value of 250 Hz was observed. The magnitude of $^2J_{F—C_4}$ is larger than expected and is in accord with more *s* character deployed at an sp^2-carbon atom. Replacing the diene by triphenylphosphine in *cis*-$Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)L_2$, however, results in an anomalously low value of $^1J_{F—C}$ of 154.7 Hz, possibly explained by a lengthening of the carbon–fluorine bonds in response to a greater steric demand by triphenylphosphine.

A very complicated pattern for the aromatic

Table 3. ^{13}C NMR characteristics of bis-[dimethyl(aryl)silylmethyl]platinum(II) and bis-[dimethyl(benzyl)silylmethyl]platinum(II) complexes with diene-, nitrogen-, and phosphorus-donor ligands

Complex	δ ^{13}C(ppm) : hydrocarbyl ligands (J_{Pt-C}) (Hz) (*assignment*) (J_{C-F}) (Hz)				δ ^{13}C(ppm) : ancillary ligands (J_{Pt-C})(Hz)(*assignment*)
	Pt—CH$_3$	Si—CH$_3$	Substituent	Aromatic	
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-2-Me)$_2$[a]	12.31 **(713.4)**	3.04 **(32.6)**	23.63 [*CH$_3$*]	124.67 [*C$_5$*] ; 128.33 [*C$_3$*] ; 129.70 [*C$_4$*] ; 134.42 [*C$_6$*] ; 142.13 **(20.3)** [*C$_1$*] ; 143.43 [*C$_2$*]	29.83 [*CH$_2$*] ; 97.85 **(63.4)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-3-Me)$_2$[b]	12.51 **(711.4)**	2.17 **(32.1)**	21.61 [*CH$_3$*]	127.79 [*C$_5$*] ; 129.12 [*C$_4$*] ; 131.30 [*C$_6$*] ; 134.85 [*C$_2$*] ; 136.67 [*C$_3$*] ; 144.41 **(22.6)** [*C$_1$*]	29.78 [*CH$_2$*] ; 97.83 **(64.5)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-4-Me)$_2$[b]	12.64 **(710.5)**	2.25 **(31.7)**	21.40 [*CH$_3$*]	128.59 [*C$_3$*, *C$_5$*] ; 134.23 [*C$_2$*, *C$_6$*] ; 137.67 [*C$_4$*] ; 140.94 **(22.6)** [*C$_1$*]	29.78 [*CH$_2$*] ; 97.77 **(64.3)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-4-OMe)$_2$[a]	12.04 **(710.4)**	1.88 **(31.0)**	55.04 [*OCH$_3$*]	113.26 [*C$_3$*, *C$_5$*] ; 135.01 [*C$_2$*, *C$_6$*] ; 135.41 **(25.4)** [*C$_1$*] ; 159.82 [*C$_4$*]	29.80 [*CH$_2$*] ; 97.64 **(64.1)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-4-^{t}Bu)$_2$[a]	11.78 **(710.4)**	1.66 **(29.6)**	31.36 [*C—CH$_3$*] 31.36 [C—*CH$_3$*]	124.26 [*C$_3$*, *C$_5$*] ; 133.60 [*C$_2$*, *C$_6$*] ; 140.84 **(25.9)** [*C$_1$*] ; 150.78 [*C$_4$*]	29.69 [*CH$_2$*] ; 97.65 **(64.6)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-4-F)$_2$[a]	11.59 **(711.0)**	1.83 **(30.5)**	—	114.36 [*C$_3$*, *C$_5$*] (*19.1*) ; 135.46 [*C$_2$*, *C$_6$*] (*7.4*) ; 139.78 **(26.1)** [*C$_1$*] (*3.6*) ; 163.55 [*C$_4$*] **(246.6)**	29.81 [*CH$_2$*] ; 97.98 **(64.1)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-2-CF$_3$)$_2$[a]	12.97 **(713.5)**	3.29 **(27.0)**	125.32 [*CF$_3$*] (*274.0*)	125.75 [*C$_3$*] (*5.6*) ; 128.01 [*C$_5$*] ; 130.32 [*C$_4$*] ; 134.54 [*C$_2$*] (*30.7*) ; 136.29 [*C$_6$*] ; 142.86 **(28.0)** [*C$_1$*]	29.82 [*CH$_2$*] ; 97.97 **(63.9)** [*CH*]
(cod)Pt(CH$_2$SiMe$_2$C$_6$H$_4$-3-CF$_3$)$_2$[a]	10.95 **(708.5)**	1.52 **(29.8)**	124.77 [*CF$_3$*] (*272.5*)	124.70 [*C$_4$*] (*3.2*) ; 127.56 [*C$_5$*] ; 129.68 [*C$_3$*] (*31.3*) ; 130.17 [*C$_2$*] (*2.6*) ; 137.02 [*C$_6$*] ; 145.76 **(26.3)** [*C$_1$*]	29.73 [*CH$_2$*] ; 98.24 **(64.9)** [*CH*]

(cod)Pt($CH_2SiMe_2C_6H_4$-4-CF_3)$_2{}^a$	10.79 **(707.9)**	1.48 **(29.5)**	124.54 [CF_3] (*271.9*)	123.88 [C_3, C_5] (*3.0*) ; 129.69 [C_4] (*32.1*) ; 133.90 [C_2, C_6] ; 149.45 **(26.3)** [C_1]	29.77 [CH_2] ; 98.24 **(64.9)** [CH]
(cod)Pt($CH_2SiMe_2C_6H_4$-4-NMe_2)$_2{}^a$	12.58 **(713.1)**	[1.99] **(31.0)**	40.42 [N—CH_3]	112.25 [C_3, C_5] ; 130.40 **(25.2)** [C_1] ; 134.73 [C_2, C_6] ; 150.80 [C_4]	29.85 [CH_2] ; 97.52 **(63.8)** [CH]
(cod)Pt($CH_2SiMe_2C_6F_5$)$_2{}^a$	10.33 **(701.3)**	3.01 **(26.1)** (3.6)	—	114.47 **(36.7)** [C_1] (*67.3*) ; 137.22m, [C_3, C_5] ; 141.35m, [C_4] ; 148.73m, [C_2, C_6]	29.95 [CH_2] ; 99.22 **(65.6)** [CH]
(cod)Pt($CH_2SiMe_2CH_2C_6H_5$)$_2{}^a$	10.79 **(709.0)**	1.16 **(23.3)**	30.29 **(38.4)** [CH_2]	123.43 [C_4] ; 127.83 [C_3, C_5] ; 128.26 [C_2, C_6] ; 141.84 [C_1]	29.90 [CH_2] ; 97.46 **(64.3)** [CH]
(cod)Pt($CH_2SiMe_2CH_2C_6H_4$-4-Me)$_2{}^a$	11.04 **(708.4)**	1.13 **(25.2)**	20.83 [CH_3] 29.63 **(36.5)** [CH_2]	128.15 [C_3, C_5] ; 128.57 [C_2, C_6] ; 132.56 [C_4] ; 138.53 [C_1]	29.92 [CH_2] ; 97.35 **(63.6)** [CH]
(nbd)Pt($CH_2SiMe_2C_6H_4$-2-Me)$_2{}^a$	[15.22] **(755.5)**	2.90 **(35.7)**	23.55 [CH_3]	124.75 [C_5] ; 128.41 [C_3] ; 129.69 [C_4] ; 134.42 [C_6] ; 142.14 **(20.8)** [C_1] ; 143.46 [C_2]	48.80 **(40.5)** [C_B] ; 72.65 **(52.7)** [C_c] ; 85.68 **(54.4)** [C_A]
(nbd)Pt($CH_2SiMe_2C_6H_4$-3-Me)$_2{}^a$	14.36 **(752.7)**	1.62 **(32.9)**	21.60 [CH_3]	127.34 [C_5] ; 128.83 [C_4] ; 130.66 [C_6] ; 134.40 [C_2] ; 136.50 [C_3] ; 144.39 **(24.8)** [C_1]	48.74 **(40.7)** [C_B] ; 72.52 **(53.3)** [C_c] ; 85.38 **(54.6)** [C_A]
(nbd)Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2{}^a$	14.48 **(752.3)**	1.70 **(32.9)**	21.37 [CH_3]	128.23 [C_3, C_5] ; 133.66 [C_2, C_6] ; 137.61 [C_4] ; 140.84 **(25.9)** [C_1]	48.74 **(40.7)** [C_B] ; 72.53 **(53.2)** [C_C] ; 85.35 **(54.9)** [C_A]
(py)$_2$Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2{}^b$	−13.03 **(743.2)**	1.73 **(35.3)**	21.45 [CH_3]	128.21 [C_3, C_5] ; 134.17 [C_2, C_6] ; 136.32 [C_4] ; 142.81 **(35.4)** [C_1]	127.68 **(20.8)** [C_3, C_5] ; 134.51 [C_4] ; 150.74 **(24.8)** [C_2, C_6]
(^{t}Bupy)$_2$Pt($CH_2SiMe_2C_6H_4$-4-Me)$_2{}^c$	−12.74 **(743.4)**	1.87 **(37.1)**	21.49 [CH_3]	128.06 [C_3, C_5] ; 134.03 [C_2, C_6] ; 135.79 [C_4] ; 142.88 **(35.1)** [C_1]	29.74 [C—CH_3] ; 34.40 [C—CH_3] ; 121.71 **(18.5)** [C_3, C_5] ; 137.4 **(25.2)** [C_2, C_6] 158.73 [C_4]

Table 3—*continued*

Complex	δ ^{13}C(ppm) : hydrocarbyl ligands (J_{Pt-C}) (Hz) (*assignment*) (J_{C-F}) (Hz) Pt—CH$_3$	Si—CH$_3$	Substituent	Aromatic	δ ^{13}C(ppm) : ancillary ligands (J_{Pt-C})(Hz)(*assignment*)
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$ [c,d]	−12.58 **(736.6)**	1.84 **(30.6)**	54.19 [*OCH*$_3$]	113.03 [C_3, C_5]; 135.13 [C_2, C_6]; 136.96 **(21.0)** [C_1]; 159.49 [C_4]	124.68 [C_3, C_5]; 134.58 [C_4]; 150.61*e* [C_2, C_6]
$(py)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2$ [c,d]	−12.80 **(735.2)**	1.74 **(20.1)**	31.42 [*C*—*CH*$_3$] 34.36 [C—*CH*$_3$]	124.63 [C_3, C_5]; 133.76 [C_2, C_6]; 135.41 **(27.5)** [C_1]; 149.13 [C_4]	124.14 [C_3, C_5]; 134.50 [C_4]; 150.60*e* [C_2, C_6]
$(py)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2$ [c,d]	−13.06 **(742.1)**	1.55 **(28.7)**	30.43 **(41.8)** [*CH*$_2$]	123.27 [C_4]; 127.99 [C_3, C_5]; 128.58 [C_2, C_6]; 143.26 [C_1]	124.89 [C_3, C_5]; 134.95 [C_4]; 150.79*e* [C_2, C_6]
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2$ [a]	6.70, 8.16 **(577.8)** ($J_{C-P_{trans}}$ = 91.4 Hz) ($J_{C-P_{cis}}$ = 6.1 Hz)	3.26 **(24.7)**	15.23 [*CH*$_3$]	124.08 [C_5]; 127.32 [C_3]; 129.16 [C_4]; 134.19 [C_6]; 143.37 [C_2]; 143.90 **(22.5)** [C_1]	127.44 [C_3, C_5] (J_{C-P} = 4.0 Hz); 129.16 [C_4]; 133.56 **(19.5)** [C_1] (J_{C-P} = 43.6 Hz); 134.69 **(21.1)** [C_2, C_6] (J_{C-P} = 10.8 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2$ [a]	6.43, 7.89 **(575.5)** ($J_{C-P_{trans}}$ = 92.2 Hz) ($J_{C-P_{cis}}$ = 6.4 Hz)	2.69 **(24.7)**	21.60 [*CH*$_3$]	126.84 [C_5]; 128.00 [C_4]; 128.32 [C_3]; 131.26 [C_6]; 135.67 [C_5]; 145.68 **(28.4)** [C_1]	127.38 **(8.6)** [C_3, C_5] (J_{C-P} = 8.6 Hz); 129.13 [C_4]; 133.55 **(18.3)** [C_1] (J_{C-P} = 34.4 Hz); 134.78 **(11.1)** [C_2, C_6] (J_{C-P} = 10.5 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2$ [a]	6.71, 8.18 **(576.9)** ($J_{C-P_{trans}}$ = 92.2 Hz) ($J_{C-P_{cis}}$ = 6.0 Hz)	2.72 **(24.1)**	21.37 [*CH*$_3$]	127.73 [C_3, C_5]; 134.27 [C_2, C_6]; 136.55 [C_4]; 142.18 **(28.5)** [C_1]	127.38 **(8.6)** [C_3, C_5] (J_{C-P} = 8.6 Hz); 129.13 [C_4]; 133.58 **(18.3)** [C_1] (J_{C-P} = 44.5 Hz); 134.84 **(11.6)** [C_2, C_6] (J_{C-P} = 10.8 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2$ [a]	6.73, 8.19 **(566.1)** ($J_{C-P_{trans}}$ = 92.2 Hz) ($J_{C-P_{cis}}$ = 5.9 Hz)	2.88 **(24.1)**	54.98 [*OCH*$_3$]	112.82 [C_3, C_5]; 135.51 [C_2, C_6]; 136.95 **(28.4)** [C_1]; 159.31 [C_4]	127.43 [C_3, C_5] (J_{C-P} = 3.4 Hz); 129.17 [C_4]; 133.58 **(18.0)** [C_1] (J_{C-P} = 44.4 Hz); 134.84 **(11.5)** [C_2, C_6] (J_{C-P} = 10.3 Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2$ [a]	6.80, 8.26 **(601.1)** ($J_{C-P_{trans}}$ = 100.3 Hz) ($J_{C-P_{cis}}$ = 8.2 Hz)	2.79 **(28.0)**	31.87 [*C*—*CH*$_3$] 34.51 [C—*CH*$_3$]	124.97 [C_3, C_5]; 134.19 [C_2, C_6]; 142.27 **(21.4)** [C_1]; 149.79 [C_4]	127.51 **(12.7)** [C_3, C_5] (J_{C-P} = 7.3 Hz); 129.13 [C_4]; 133.72 **(14.1)** [C_1] (J_{C-P} = 35.9 Hz); 134.84 **(12.3)** [C_2, C_6] (J_{C-P} = 8.7 Hz)

$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2$[b]	6.84, 8.31 **(574.5)** $(J_{C-P_{trans}} = 92.1\ Hz)$ $(J_{C-P_{cis}} = 6.2\ Hz)$	3.39 **(24.5)**	—	114.31 $[C_3, C_5]$ *(19.6)*; 136.38 $[C_2, C_6]$ *(7.0)*; 141.40 **(27.0)** $[C_1]$; 149.79 $[C_4]$ *(245.7)*	127.78 $[C_3, C_5]$ $(J_{C-P} = 5.0\ Hz)$; 129.59 $[C_4]$; 133.92 **(18.3)** $[C_1]$ $(J_{C-P} = 44.7\ Hz)$; 135.12 **(11.8)** $[C_2, C_6]$ $(J_{C-P} = 10.8\ Hz)$
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2$[a]	6.02, 7.37 **(577.5)** $(J_{C-P_{trans}} = 91.9\ Hz)$ $(J_{C-P_{cis}} = 6.3\ Hz)$	3.22 **(27.4)**	121.85 $[CF_3]$ *(154.7)*	125.26 $[C_3]$ *(5.2)*; 127.06 $[C_5]$; 130.02 $[C_4]$; 137.21 $[C_2]$ *(11.4)*; 136.26 $[C_6]$; 144.31 **(30.6)** $[C_1]$	127.38 **(8.4)** $[C_3, C_5]$ $(J_{C-P} = 9.4\ Hz)$; 129.26 $[C_4]$; 133.19 **(18.7)** $[C_1]$ $(J_{C-P} = 44.7\ Hz)$; 134.84 **(12.5)** $[C_2, C_6]$ $(J_{C-P}\ 11.4\ Hz)$
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2$[a]	5.39, 6.86 **(837.4)** $(J_{C-P_{trans}} = 92.4\ Hz)$ $(J_{C-P_{cis}} = 6.7\ Hz)$	2.47 **(23.7)**	110.96 $[CF_3]$ *(309.9)*	124.74 $[C_3]$ *(125.8)*; 128.95 $[C_5]$; 129.72 $[C_4]$; 134.15 $[C_2]$ *(23.1)*; 137.45 $[C_6]$; 147.38 **(31.0)** $[C_1]$	127.51 **(7.8)** $[C_3, C_5]$ $(J_{C-P} = 8.4\ Hz)$; 129.41 $[C_4]$; 133.24 **(18.2)** $[C_1]$ $(J_{C-P} = 50.1\ Hz)$; 134.70 **(10.7)** $[C_2, C_6]$ $(J_{C-P} = 10.7\ Hz)$
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2$[a]	5.48, 7.98 **(567.7)** $(J_{C-P_{trans}} = 92.6\ Hz)$ $(J_{C-P_{cis}} = 7.1\ Hz)$	2.42 **(24.2)**	124.70 $[CF_3]$ *(306.0)*	123.32 $[C_3, C_5]$ *(4.5)*; 129.30 $[C_4]$ *(35.7)*; 134.15 $[C_2, C_6]$; 151.09 **(27.0)** $[C_1]$	127.33 **(11.9)** $[C_3, C_5]$ $(J_{C-P} = 11.0\ Hz)$; 129.39 $[C_4]$; 133.18 **(21.0)** $[C_1]$ $(J_{C-P} = 51.9\ Hz)$; 134.68 **(11.2)** $[C_2, C_6]$ $(J_{C-P} = 12.6\ Hz)$
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2$[a]	7.33, 8.80 **(581.5)** $(J_{C-P_{trans}} = 91.9\ Hz)$ $(J_{C-P_{cis}} = 6.2\ Hz)$	2.95 **(23.2)**	40.59 $[N-CH_3]$	112.02 $[C_3, C_5]$; 133.96 **(18.4)** $[C_1]$; 135.28 $[C_2, C_6]$; 150.69 $[C_4]$	127.35 **(16.2)** $[C_3, C_5]$ $(J_{C-P} = 8.3\ Hz)$; 129.04 $[C_4]$; 133.76 **(18.6)** $[C_1]$ $(J_{C-P} = 44.0\ Hz)$; 134.90 **(12.4)** $[C_2, C_6]$ $(J_{C-P} = 10.7\ Hz)$
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2$[b]	7.56, 9.01 **(583.1)** $(J_{C-P_{trans}} = 94.4\ Hz)$ $(J_{C-P_{cis}} = 6.0\ Hz)$	2.10 **(23.2)**	31.32 **(36.1)**$[CH_2]$	123.57 $[C_4]$; 128.11 $[C_3, C_5]$; 128.67 $[C_2, C_6]$; 142.82 $[C_1]$	127.82 $[C_3, C_5]$ $(J_{C-P} = 4.5\ Hz)$; 129.61 $[C_4]$; 134.22 **(18.3)** $[C_1]$ $(J_{C-P} = 44.2\ Hz)$; 135.20 **(10.6)** $[C_2, C_6]$ $(J_{C-P} = 10.7\ Hz)$
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2$[a]	6.75, 8.21 **(574.8)** $(J_{C-P_{trans}} = 91.7\ Hz)$ $(J_{C-P_{cis}} = 5.8\ Hz)$	1.47 **(23.0)**	20.81 $[CH_2]$ 30.07 **(36.0)** $[CH_3]$	128.05 $[C_3, C_5]$; 128.33 $[C_2, C_6]$; 128.55 $[C_4]$; 139.37 $[C_1]$	127.49 $[C_3, C_5]$ $(J_{C-P} = 3.3\ Hz)$; 129.29 $[C_4]$; 133.62 **(17.9)** $[C_1]$ $(J_{C-P} = 43.2\ Hz)$; 134.79 **(9.8)** $[C_2, C_6]$ $(J_{C-P} = 10.3\ Hz)$

[a]chloroform-d^1; [b]benzene-d^6; [c]toluene-d^8; [d]run at −25°C; [e]platinum satellites unresolved.

Table 4. ^{19}F NMR characteristics of bis-[dimethyl(aryl)silylmethyl]platinum(II) complexes with diene-, nitrogen-, and phosphorus-donor ligands

Complex	δ^a (ppm) : (J_{H-F}) (Hz) (*assignment*)
$ClCH_2SiMe_2C_6H_4$-4-F^b	51.3
$ClCH_2SiMe_2C_6H_4$-2-$CF_3{}^b$	104.0
$ClCH_2SiMe_2C_6H_4$-3-$CF_3{}^b$	99.4
$ClCH_2SiMe_2C_6H_4$-4-$CF_3{}^b$	99.0
$ClCH_2SiMe_2C_6F_5{}^b$	1.3m, [F_3, F_5] ; 11.7"t", (**19.5**) [F_4] ; 35.3dd, (**14.7**) [F_2, F_6]
(cod)Pt$(CH_2SiMe_2C_6H_4$-4-F$)_2{}^b$	48.1
(cod)Pt$(CH_2SiMe_2C_6H_4$-2-$CF_3)_2{}^b$	104.8
(cod)Pt$(CH_2SiMe_2C_6H_4$-3-$CF_3)_2{}^b$	100.1
(cod)Pt$(CH_2SiMe_2C_6H_4$-4-$CF_3)_2{}^b$	99.9
(cod)Pt$(CH_2SiMe_2C_6F_5)_2{}^b$	-0.2m, [F_3, F_5] ; 7.7"t", (**19.5**) [F_4] ; 35.1dd, (**19.5**) [F_2, F_6]
$(PPh_3)_2$Pt$(CH_2SiMe_2C_6H_4$-4-F$)_2{}^c$	47.5
$(PPh_3)_2$Pt$(CH_2SiMe_2C_6H_4$-2-$CF_3)_2{}^b$	104.9
$(PPh_3)_2$Pt$(CH_2SiMe_2C_6H_4$-3-$CF_3)_2{}^b$	100.5
$(PPh_3)_2$Pt$(CH_2SiMe_2C_6H_4$-4-$CF_3)_2{}^d$	100.0
$(PPh_3)_2$Pt$(CH_2SiMe_2C_6F_5)_2{}^b$	-0.2m, [F_3, F_5] ; 8.5"t", (**19.5**) [F_4] ; 35.1dd, (**14.7**) [F_2, F_6]

[a] Referenced to $CFCl_3$; [b] chloroform-d^1 ; [c] toluene-d^8 ; [d] benzene-d^6.

region is observed for Pt$(CH_2SiMe_2C_6F_5)_2$(cod), since each carbon atom experiences spin–spin coupling with more than one fluorine nucleus. Six multiplets are observed ; the two occurring at the lowest field may be attributed to C_2, C_6 and those furthest upfield correspond to C_3, C_5. The lowest intensity signal is due to C_1, which shows platinum satellites. In addition the signal due to the silicon-methyl groups is a "triplet" of doublets with $^4J_{F-C} = 7.3$ Hz.

The magnitude of $^1J_{Pt-C}$ for these compounds varies in the range 565–755 Hz. Smaller values are obtained for the phosphine complexes, again reflecting their stronger *trans* influence. A trend is also observed in the magnitude of $^3J_{Pt-C}$ to C_1 of the aromatic ring and to the silicon-bound methyl groups. When the ancillary ligand is a diene or pyridine, $^3J_{Pt-C_{methyl}}$ is larger than $^3J_{Pt-C_1}$, suggesting greater *s* character in the Si—CH_3 bond. If the ligand is triphenylphosphine, the converse is true. These changes in $^3J_{Pt-C}$ presumably reflect modifications in the bonding around the silicon atom as the steric demand of the ancillary ligand changes.

Resonances due to the ancillary ligand are largely as expected, though $^2J_{Pt-C}$ to C_2 and C_6 of pyridine could not always be determined, as the ^{195}Pt satellites were not well enough resolved at -20°C due to chemical shift anisotropy.[12]

^{19}F *NMR*. Most ^{19}F NMR spectra (Table 4) display a single resonance at lower field relative to $CFCl_3$. A chemical shift of *ca* $+100.0$ ppm was observed for complexes with trifluoromethyl groups, about 50.0 ppm to lower field than analogous *para*-fluoro derivatives. Three resonances were observed for *cis*-Pt$(CH_2SiMe_2C_6F_5)_2L_2$ (L_2 = cod ; L = PPh_3) and are similar to those observed previously for *trans*-Pt$(C_6F_5)X(PEt_3)_2$.[13] Both these complexes are thermolytically labile, readily rearranging to *cis*-Pt$(C_6F_5)(CH_2SiMe_2CH_2SiMe_2C_6F_5)L_2$. The ^{19}F NMR of these derivatives also consists of three distinct resonances. The multiplet at highest field is due to the *meta*-fluorine atoms. The signal due to F_4 appears as a triplet and that due to the *ortho*-fluorine atoms as a doubled doublet with platinum satellites. The magnitudes of $J_{F_2-F_3}$ and $J_{F_3-F_4}$ are between 15–20 Hz and $^3J_{Pt-F}$ is *ca* 50 Hz.

^{31}P *NMR*. ^{31}P{^{1}H} NMR data for the series of compounds *cis*-Pt$(CH_2SiMe_2C_6H_4R)_2(PPh_3)_2$ are detailed in Table 5. All complexes display the expected 1 : 4 : 1 "triplet" due to spin–spin coupling of the ^{31}P nucleus to ^{195}Pt. Since the ring substituents

Table 5. ^{31}P NMR characteristics of bis-[dimethyl(aryl)silylmethyl] platinum(II) and bis-[dimethyl(benzyl)silylmethyl]platinum(II) complexes with phosphorus-donor ligands

Complex	δ^a (ppm)	J_{Pt-P} (Hz)
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}Me)_2{}^b$	24.5	2013.7
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}Me)_2{}^c$	25.2	2018.1
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2{}^c$	24.1	2027.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}OMe)_2{}^c$	25.0	2027.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}{}^tBu)_2{}^c$	23.3	2029.2
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}F)_2{}^c$	23.1	2038.1
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}2\text{-}CF_3)_2{}^c$	24.0	2024.8
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}3\text{-}CF_3)_2{}^c$	24.7	2055.8
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}CF_3)_2{}^c$	24.8	2058.0
$(PPh_3)_2Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}NMe_2)_2{}^c$	24.7	2060.3
$(PPh_3)_2Pt(CH_2SiMe_2C_6F_5)_2{}^d$	23.6	2082.4
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_5)_2{}^c$	23.2	2022.6
$(PPh_3)_2Pt(CH_2SiMe_2CH_2C_6H_4\text{-}4\text{-}Me)_2{}^c$	25.1	2018.1
$(dppf)Pt(CH_2SiMe_2C_6H_4\text{-}4\text{-}Me)_2{}^b$	18.6	2044.7

[a] Referenced to 85% H_3PO_4/D_2O; [b] toluene-d^8; [c] benzene-d^6; [d] chloroform-d^1.

are so remote from both platinum and phosphorus nuclei, very little variation in either chemical shift or magnitude of $^1J_{Pt-P}$ is observed by changing the substituent.

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