

Mechanisms of Thermolytic Rearrangement of *cis*-Bis(silylmethyl)platinum(II) Complexes: β -Carbon Transfer Predominates over Hydrogen Transfer

Bernardeta C. Ankianiec, Victor Christou, David T. Hardy, S. Katherine Thomson, and G. Brent Young*¹

Contribution from the Inorganic Chemistry Laboratories, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.

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Abstract: Thermolytic rearrangement of bis((trimethylsilyl)methyl)platinum(II) complexes with phosphine ligands, *cis*-Pt(CH₂SiMe₃)₂L₂ [L = PMe₃, PEt₃, PPhMe₂, PPh₂Me, PPh₃], results in a novel migratory isomerization which yields the asymmetric organoplatinum(II) products *cis*-Pt(CH₃)(CH₂SiMe₂CH₂SiMe₃)L₂. Similarly, most analogous bis((aryldimethylsilyl)methyl)platinum(II) complexes, *cis*-Pt(CH₂SiMe₂C₆H₄R)₂L₂ [R = H, L = PMe₃, PEt₃, PMe₂-Ph, PPh₃, P-4-tolyl, PPh₂C₆H₄-2-CF₃; L₂ = 1,2-bis(dicyclohexylphosphino)ethane, dcpe; R = 2-Me, 3-Me, 4-Me, 4-OMe, 4-Bu¹, 4-F, 2-CF₃, 3-CF₃, 4-CF₃, 4-NMe₂, L = PPh₃] and *cis*-Pt(CH₂SiMe₂C₆F₅)₂(PPh₃)₂, react to give *cis*-Pt(C₆H₄R)(CH₂SiMe₂CH₂SiMe₂C₆H₄R)L₂ and *cis*-Pt(C₆F₅)(CH₂SiMe₂CH₂SiMe₂C₆F₅)(PPh₃)₂, respectively. In some cases, the *trans*-isomer is formed, either as primary product [R = H, L = PEt₃] or after prolonged thermolysis [R = H, L = PMe₃, PPhMe₂]. Reaction of the deuterium labeled analogues, *cis*-Pt[CH₂Si(CD₃)₃]₂L₂ [L = PPh₃, PPh₂Me, PEt₃], gives only *cis*-Pt(CD₃)[CH₂Si(CD₃)₂CH₂Si(CD₃)₃]₂L₂, establishing that it is a silicon-methyl bond which cleaves during the rearrangement, with secondary isotope effects, $k^H/k^D = 1.4-1.7$. Thermolysis of *cis*-Pt(CH₂SiMe₂C₆D₅)₂L₂ [L = PPh₃, PPhMe₂] reveals similar isotopic inhibition ($k^H/k^D = 1.2-1.4$). Rearrangement of *cis*-Pt(CH₂SiMe₃)(CH₂-SiMe₂Ph)(PPh₃)₂ affords only *cis*-Pt(Ph)(CH₂SiMe₂CH₂SiMe₃)(PPh₃)₂, confirming further that phenyl migration is more facile than methyl migration. Aryl migration is regiospecific, is accelerated by electron-withdrawing substituents, and is retarded by electron-donating groups. Linear Hammett correlation emerges, with $\rho = +0.9$. Where L is monodentate, lability increases with increasing steric bulk of L, and the presence of free phosphine inhibits reaction. Deuteration of PPh₃ in both *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ and *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃)₂ also slows isomerization ($k^H/k^D = 1.5$ and 2.1, respectively). A mechanism is proposed in which phosphine dissociation—possibly accompanied by development of intramolecular agostic interaction with a neighboring C-H bond—is an energetically important (though not rate-limiting) prerequisite to β -carbon migration from Si to Pt, generating an (η^2 -silene) platinum derivative. The intermediate subsequently undergoes regiospecific migration of the second pendant silylmethyl group to the S₁ terminus. Phosphine reassociation yields the products. Reactivity differences between individual complexes appear to stem chiefly from variations in the appreciable, positive ΔS^\ddagger . In contrast, *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₂-2-tolyl)₂ rearranges via cyclometalation on the 2-methyl substituent of the phosphine. Pyridine analogues, *cis*-Pt(CH₂SiMe₂-Ar)₂py₂, also prefer cyclometalation, this time via aromatic δ C-H activation and transfer, to give platinumindans. Implications for these and related systems are discussed.

Introduction

Intramolecular hydrogen migrations continue to provide useful information about the mechanism(s) of C-H bond activation by organometallic centers. Neopentyl derivatives of Os,² Ru,³ Rh,^{3a,4} Ir,⁵ Ni,⁶ and Pt⁷ have been reported to undergo thermolytic rearrangement via intramolecular aliphatic C-H activation and transfer, generating 3,3-dimethylmetallacyclobutanes. The mechanism has been explored in detail for platinum complexes.⁷ Many (trimethylsilyl)methyl analogues react similarly though, in

general, less readily.^{3,6,8} It seems to be assumed widely that the mechanistic controls on these systems are similar, irrespective of metal. In parallel, neophyl [CH₂CMe₂Ph] complexes of Ir,^{6a} Ni,⁹ and Pt¹⁰ rearrange by distal aromatic H migration to form 3,3-dimethylmetallaindanes. Again, the mechanistic details are best understood for platinum derivatives,¹⁰ and, where comparisons have been made, the reaction of corresponding silaneophyl [CH₂-SiMe₂Ph] species is analogous but slower.¹¹ Organof-block metal compounds—notably Th(CH₂EMe₂R)₂(η^5 -C₅Me₅)₂ [R = Me, Ph; E = C, Si]—show similar tendencies (although the kinetic preference in the silaneophylthorium system is for *aliphatic* H transfer and formation of the thoracyclobutane which subsequently rearranges to the thermodynamically favored thoraindan).¹² Our interest in understanding the generally greater inertness of β -silaalkyl systems led us to synthesize a range of

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bis(trimethylsilyl)methyl)platinum(II)¹³ and bis(aryldimethylsilyl)methyl)platinum(II)^{11,14} [silaneophyl] complexes. The unexpected results of thermolytic rearrangement of several of these with tertiary phosphine ligands suggests that mechanistic analogies cannot be assumed, even for the same metal. In contrast to their neopentylplatinum analogues, ((trimethylsilyl)methyl)platinum complexes do not yield metallacycles. Instead, they undergo a novel linkage isomerization, involving Si-C scission and transfer, to afford the unusual methylplatinum(II) products *cis*-Pt(CH₃)(CH₂SiMe₂CH₂SiMe₃)L₂. Silaneophyl analogues react similarly, usually to give *cis*-Pt(Ar)(CH₂SiMe₂CH₂SiMe₂-Ar)L₂, although *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₂C₆H₄-2-Me)₂ and *cis*-Pt(CH₂SiMe₂C₆H₄-4-R)₂(py)₂ both favor (alternative) cyclometalation options. A preliminary account of some of these results has appeared.¹⁵

Experimental Section

General. The syntheses and spectroscopic characteristics of the complexes *cis*-Pt(CH₂SiMe₃)₂L₂ [L = PMe₃, PEt₃, PPhMe₂, PPh₂Me, PPh₃; L₂ = cod, nbd] and *cis*-Pt(CH₂SiMe₂Ph)₂L₂ [L = PMe₃, PEt₃, PPh₂Me, PPh₃, P(4-tolyl)₃, PPh₂C₆H₄-2-CF₃] have been reported previously.^{11,13,14} Syntheses and spectroscopic characterizations of ring-substituted (aryldimethylsilyl)methyl)platinum(II) derivatives are described in full elsewhere.¹⁶ All reactions were carried out under argon, using standard anaerobic techniques.¹⁷ Apparatus was thoroughly flame-dried prior to use, and solvents were distilled under nitrogen; diethyl ether, and *n*-hexane from sodium/benzophenone, toluene from sodium.

Elemental analyses were performed by Imperial College Microanalytical Laboratories and by Butterworth Laboratories Ltd. NMR spectra were recorded on Jeol GSX 270 (¹H, 270.17 MHz, ¹³C, 67.94 MHz), Brüker WM250 (¹H, 250.13 MHz, ¹³C, 62.9 MHz), and Jeol FX90Q (¹H, 89.55 MHz, ¹⁹F, 84.27 MHz, ³¹P, 36.21 MHz) spectrometers. GCMS analyses were conducted using a Perkin-Elmer Sigma 3 gas chromatograph coupled to a Kratos MS25 quadrupole mass spectrometer. Bromine, phosphorus trichloride, triphenylphosphine, pyridine-*d*⁵, benzene-*d*⁶, [2.2.1]bicyclohepta-2,5-diene, cycloocta-1,5-diene, 2-bromotoluene, 4-bromobenzene trifluoride, 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 Chemical Co. Triethylphosphine, trimethylphosphine, dimethylphenylphosphine, diphenylmethylphosphine, and 1,2-bis(dicyclohexylphosphino)ethane were supplied by Strem Chemicals and stored under argon but were normally used without further purification. Prior to addition to thermolytic reactions, liquid alkylphosphines were distilled, and triphenylphosphine was recrystallized from propan-2-ol. Pyridine, supplied by Rose Chemicals, was dried over sodium hydroxide and distilled under argon prior to use. Chloromethyl(dimethyl)chlorosilane supplied by Aldrich Chemical Co. was stored under argon but used without further purification. 3-Bromotoluene, 4-bromotoluene, 2-bromobenzene trifluoride, 3-bromobenzene trifluoride, 4-bromoanisole, 4-bromo-*tert*-butylbenzene, and 4-bromofluorobenzene, supplied by Lancaster Synthesis, were also used without further purification.

Preparation of (Silaneophyl)((trimethylsilyl)methyl)(cycloocta-1,4-diene)platinum(II). A solution of Mg(CH₂SiMe₂Ph)Cl (2.75 mmol) in diethyl ether (25 cm³) was added dropwise to a stirred suspension of PtCl(CH₂SiMe₃)(cod)¹³ (0.565 g, 1.30 mmol) in the same solvent (15 cm³) at -78 °C. After addition, the reaction mixture was allowed to reach ambient temperature and was stirred for 17 h. The mixture was cooled to -20 °C, at which temperature a deoxygenated, saturated aqueous solution of NH₄Cl was added, and the whole was allowed to reattain ambient temperature. The aqueous layer was extracted with diethyl ether, 5 × 20 cm³, and these washings were combined with the original ether extract, washed once with distilled water, and dried over MgSO₄ and activated charcoal. Filtration and evaporation of solvent at reduced pressure afforded the crude product as a white solid. Recrystallization from hexane yielded pure Pt(CH₂SiMe₃)(CH₂SiMe₂Ph)(cod) as colorless crystals (yield 0.343 g, 47.9%). ¹H NMR: -0.06, s, [Si-CH₃]; 0.23, s, [Si-CH₃]; 0.93 (²J_{H-Pt} = 93.9 Hz), [Pt-CH₂-Si]; 0.78 (²J_{H-Pt} = 92.6

Hz), [Pt-CH₂-Si]; 4.34 (²J_{H-Pt} = 41.4 Hz), [Pt-CH(alkene)]; 4.57 (²J_{H-Pt} = 43.7 Hz), [Pt-CH(alkene)]; 2.22-2.25, m, [Pt-CH₂(alkene)]; 7.22-7.35, m, [H_{3,4,5}(aryl)]; 7.59, d (³J_{H-H} = 6.3 Hz), [H_{2,6}(aryl)] ppm. Anal. Calcd: C, 46.73; H, 6.72. Found: C, 46.53; H, 6.70. ¹³C NMR: 3.24 (³J_{C-Pt} = 30.9 Hz), [Si-CH₃]; 1.75 (³J_{C-Pt} = 30.3 Hz), [Si-CH₃]; 11.66 (¹J_{C-Pt} = 717.3 Hz), [Pt-CH₂-Si]; 17.36 (¹J_{C-Pt} = 706.7 Hz), [Pt-CH₂-Si]; 97.9 (¹J_{C-Pt} = 61.3 Hz), [Pt-CH(alkene)]; 97.23 (¹J_{C-Pt} = 66.1 Hz), [Pt-CH(alkene)]; 29.91, [Pt-CH₂(alkene)]; 29.87, [Pt-CH₂(alkene)]; 144.58 (³J_{C-Pt} = 24.0 Hz), [C₁(aryl)]; 133.72 [C_{2,6}(aryl)]; 127.36, [C_{3,5}(aryl)]; 127.88, [C₄(aryl)] ppm. All NMR data were recorded with chloroform-*d* as solvent. The deuterated analogue Pt(CH₂SiMe₃)(CH₂-SiMe₂Ph-*d*₅)(cod) was prepared and characterized by an identical procedure.

Preparation of *cis*-Bis(triphenylphosphine)(silaneophyl)((trimethylsilyl)methyl)platinum(II). Pt(CH₂SiMe₃)(CH₂SiMe₂Ph)(cod) (0.20 g, 0.37 mmol) and PPh₃ (0.20 g, 0.76 mmol) were dissolved together in diethyl ether (15 cm³) and heated in a Teflon-stoppered vessel at 60 °C for 14 days. Evaporation of the solvent at reduced pressure left a white solid, which was recrystallized from dichloromethane/methanol (1.5 cm³/0.8 cm³) to give pure *cis*-Pt(CH₂SiMe₃)(CH₂SiMe₂Ph)(PPh₃)₂ as colorless crystals (yield 0.159 g, 44.8%). ¹H NMR: 0.19, s, [Si-CH₃]; 0.14, s, [Si-CH₃]; 0.78 (²J_{H-Pt}, ³J_{H-P} obscd), [Pt-CH₂-Si]; 0.87 (²J_{H-Pt}, ³J_{H-P} obscd), [Pt-CH₂-Si]; 7.05-7.18, m, [H_{3,4,5}(Si-aryl)]; 7.48, d, (³J_{H-H} = 7.02 Hz), [H_{2,6}(Si-aryl)]; 7.21-7.47, m, [H₂-H₆(P-aryls)] ppm. ¹³C NMR: 3.91 (³J_{C-Pt} = 28.0 Hz), [Si-CH₃]; 2.90 (³J_{C-Pt} = 25.3 Hz), [Si-CH₃]; 8.92 (¹J_{C-Pt} obscd, ²J_{C-P} = 86.1 Hz, *trans*), [Pt-CH₂-Si]; 6.78 (¹J_{C-Pt} obscd, ²J_{C-P} = 87.3 Hz, *trans*), [Pt-CH₂-Si]; 146.04 (³J_{C-Pt} obscd), [C₁(Si-aryl)]; 134.85, [C_{2,6}(Si-aryl)]; 126.90, [C_{3,5}(Si-aryl)]; 127.01, [C₄(Si-aryl)]; 133.73 (³J_{C-Pt} = 26.0 Hz, [C_{1,1'}(P-aryl)]); 134.86, [C_{2,2',6,6'}(P-aryl)]; 127.43, [C_{3,3',5,5'}(P-aryl)]; 129.19, [C_{4,4'}(P-aryl)] ppm. ³¹P NMR: 24.6 (¹J_{P-Pt} = 1973 Hz, ²J_{P-P} = 8.9 Hz), [P_a, *trans* to CH₂-SiMe₃]; 25.0 (¹J_{P-Pt} = 2058 Hz), [P_b, *trans* to CH₂SiMe₂Ph] ppm. Anal. Calcd: C, 61.55; H, 5.69. Found: C, 61.48; H, 5.99. All NMR data were recorded with chloroform-*d* as solvent. Deuterated analogues *cis*-Pt(CH₂SiMe₃)(CH₂SiMe₂Ph-*d*₅)(PPh₃)₂ and *cis*-Pt(CH₂SiMe₃)(CH₂-SiMe₂Ph)(PPh₃-*d*₁₅)₂ were prepared and characterized by identical procedures.

Preparation of (Chloromethyl)dimethylphenylsilane.¹⁸ A solution of PhMgBr (167 mmol) in diethyl ether (200 cm³) was added slowly dropwise to ClCH₂SiMe₂Cl (22 cm³, 167 mmol) in diethyl ether (50 cm³). Upon stirring, the initially colorless solution gradually turned pale yellow, and a white precipitate of magnesium halides was produced. After addition was complete, the mixture was refluxed for 24 h. The resulting stirred suspension was cooled to -15 °C and hydrolyzed by dropwise addition of degassed saturated aqueous ammonium chloride solution (100 cm³). The pale yellow ethereal layer was separated, and the aqueous phase was washed with diethyl ether (3 × 20 cm³). The ether extracts were combined, dried over magnesium sulfate, and decolorized with activated charcoal to give an almost colorless solution. Removal of the diethyl ether *in vacuo* afforded a pale yellow oil of the crude product. Distillation under reduced pressure gave silaneophyl chloride as a colorless liquid (bp 114 °C/10 mmHg; yield 22.6 g, 77%). ¹H NMR (CDCl₃): 0.32, [CH₃]; 2.85, [CH₂] ppm.

Preparation of Diphenyl-2-tolylphosphine.¹⁹ To a stirred solution of PPh₂Cl (2.00 g, 9.1 mmol) in Et₂O (15 cm³) cooled to 0 °C was added dropwise a solution of BrMgC₆H₄-2-CH₃ in diethyl ether (50 cm³). Upon addition, the reaction mixture was stirred vigorously for 24 h and then cooled to -25 °C and quenched with saturated ammonium chloride solution (30 cm³). The organic layer was separated, and the aqueous phase was repeatedly washed with diethyl ether (3 × 15 cm³) until the washings were colorless. The ether extracts were combined, dried over MgSO₄, decolorized with activated charcoal, filtered, and evaporated to dryness *in vacuo*, yielding a pale yellow crystalline solid. The solid was dissolved in hot ethanol (10 cm³) and cooled slowly to ambient temperature. The white crystalline solid was filtered, washed with cold ethanol (2 × 4 cm³), and dried *in vacuo* (yield 2.26 g, 90%). ³¹P NMR (CDCl₃): -14.1, s, ppm.

Preparation of *cis*-Bis(triethylphosphine-*d*₁₅)bis((trimethylsilyl)methyl)platinum(II). This was prepared in an analogous fashion to Pt(CH₂SiMe₃)₂(PEt₃)₂¹³ (yield 82%). Anal. Calcd: C, 37.76; H, 8.24. Found: C, 37.49; H, 8.32.

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Preparation of (Chloromethyl)trimethylsilane- d_3 .²⁰ A solution of (chloromethyl)trichlorosilane (5.0 g, 27.1 mmol) in Et₂O (30 cm³) was added dropwise to a solution of CD₃MgI (85.0 cm³ of 1.0 M in Et₂O, 85 mmol) at -78 °C, and the mixture was stirred overnight at ambient temperature. Air was admitted to the flask, and dilute aqueous HCl was added (Caution! Very vigorous reaction.) until all solids present had dissolved. The ethereal phase was separated and the aqueous phase extracted with Et₂O (2 × 20 cm³). The combined organic phases were then washed with dilute aqueous Na₂S₂O₃ (2 × 20 cm³ of 0.1 M) and dried overnight over CaCl₂. Ether was then removed *in vacuo* until ca. 20 cm³ of solution remained, and then the product was distilled (bp 98–99 °C). The pale yellow liquid was freeze-pump-thaw degassed over activated charcoal to remove any traces of iodine remaining and then trap-to-trap distilled into a dry, tared, sealed vessel (yield 1.89 g, 53%).

Preparation of (Chloromagnesiomethyl)trimethylsilane- d_3 . This was prepared in an analogous fashion to Mg(CH₂SiMe₃)Cl (yield 100%).

Preparation of (Cycloocta-1,5-diene)bis(trimethylsilyl)methyl- d_3 -platinum(II). This was prepared as for Pt(CH₂SiMe₃)₂(cod)¹³ (yield 0.75 g, 76%). Anal. Calcd: C, 38.75; H, 6.91. Found: C, 38.71; H, 7.14.

The following compounds were also prepared in an analogous fashion to their undeuterated analogues.

***cis*-Bis(triethylphosphine)bis(trimethylsilyl)methyl- d_3 -platinum(II)** (yield 85%). Anal. Calcd: C, 38.46; H, 8.39. Found: C, 39.02; H, 8.59.

***cis*-Bis(diphenylmethylphosphine)bis(trimethylsilyl)methyl- d_3 -platinum(II)** (yield 87%). Anal. Calcd: C, 51.82; H, 6.14. Found: C, 51.90; H, 6.18.

***cis*-Bis(triphenylphosphine)bis(trimethylsilyl)methyl- d_3 -platinum(II)** (yield 79%). Anal. Calcd: C, 57.80; H, 5.73. Found: C, 57.73; H, 5.72.

Preparation of Bromobenzene- d_5 .²¹ Dry pyridine (0.2 cm³, 2.5 mmol) was added to a stirred solution of benzene- d_6 (15.0 g, 178 mmol). Bromine (34.8 g, 218 mmol) was carefully poured down a condenser. A vigorous reaction ensued, and HBr was evolved. After formation of HBr had ceased, the mixture was heated to 30 °C for 3 h and then to 70 °C for a further 2 h. The cooled dark orange mixture was washed with dilute sodium metabisulfite solution (3 × 20 cm³) until the washings were alkaline to litmus and the solution was straw yellow. The organic layer was then washed with water (1 × 20 cm³), dried over MgSO₄, and filtered, and the residues were washed with diethyl ether (2 × 15 cm³). The solvent was removed *in vacuo*, yielding a pale yellow liquid, which was distilled to afford BrC₆D₅ as a colorless liquid (bp 155–158 °C; yield 18.78 g, 65%). MS:M⁺ = 162; >98% C₆D₅Br.

Preparation of (Chloromethyl)dimethylphenylsilane- d_5 . A solution of C₆D₅MgBr in diethyl ether (20 cm³) was added slowly to a stirred solution of ClCH₂SiMe₂Ph (8.1 cm³, 61.8 mmol) in Et₂O (10 cm³). Upon complete addition, the mixture was gently refluxed for 24 h. After this time, a white precipitate of MgClBr and a pale yellow solution had formed, which was cooled to -78 °C and quenched with degassed saturated ammonium chloride solution (60 cm³). The organic layer was separated and the aqueous phase washed with diethyl ether (3 × 20 cm³). The ether extracts were combined, dried over MgSO₄, and filtered, and the inorganic residues were washed with Et₂O (2 × 10 cm³). Removal of the solvent *in vacuo* afforded a pale yellow liquid. Distillation of this liquid gave ClCH₂SiMe₂Ph- d_5 , a colorless liquid, as the main fraction (bp 115–116 °C/10 mmHg; yield 7.9 g, 67%). MS:M⁺ = 190; >97% ClCH₂SiMe₂C₆D₅. ¹H NMR (CDCl₃): 0.30, [CH₃]; 2.91, [CH₂] ppm.

Preparation of Triphenylphosphine- d_15 .¹⁹ A solution of Mg(C₆D₅)Br (60 mmol) in Et₂O (60 cm³) was added slowly to a stirred solution of PCl₃ (2.1 g, 15.0 mmol) in diethyl ether (20 cm³) at 0 °C. On warming to ambient temperature, the mixture was stirred for a further 16 h and then cooled to -78 °C and quenched with degassed saturated ammonium chloride solution (30 cm³). The organic layer was separated and the aqueous phase washed with diethyl ether (3 × 20 cm³). The ether extracts were combined, dried over MgSO₄, and decolorized with activated charcoal. After filtration and washing of the residues with Et₂O (2 × 7 cm³), evaporation to dryness yielded a pale yellow solid. This solid was dissolved in the minimum quantity of hot ethanol (20 cm³) and cooled slowly to room temperature. The solid was filtered, washed with cold ethanol (2 × 5 cm³) and *n*-hexane (10 cm³), and dried *in vacuo* to give

a white crystalline solid (yield 2.99 g, 72%). MS:M⁺ = 277; >96% PPh₃- d_{15} . ³¹P NMR (CDCl₃): -6.22 ppm.

Preparation of Bis(silaneophyl- d_5)([2.2.1]bicyclohepta-2,5-diene)platinum(II). A solution of Mg(CH₂SiMe₂Ph- d_5)Cl (8.4 mmol) in Et₂O (25 cm³) was added dropwise to a stirred suspension of PtCl₂(nbd) (1.00 g, 2.8 mmol) in diethyl ether (10 cm³) at -78 °C. The mixture was gradually warmed to room temperature and then stirred for a further 16 h. The dark colored reaction mixture was cooled to -78 °C and quenched with degassed saturated ammonium chloride solution (20 cm³). The organic layer was separated and the aqueous phase washed with Et₂O (2 × 10 cm³). The ether extracts were combined, dried over MgSO₄, and decolorized with activated charcoal. After filtering and washing of the residues with diethyl ether (2 × 8 cm³), the solvent was removed *in vacuo* to yield a white oil, which was dissolved in the minimum amount of *n*-hexane (3 cm³) and cooled to -20 °C. The solid was filtered, washed with cold *n*-hexane (2 × 3 cm³), and dried *in vacuo*, affording the product as a white crystalline solid (yield 1.48 g, 89%). Anal. Calcd: C, 50.39; H, 5.75. Found: C, 50.08; H, 5.76.

Preparation of *cis*-Bis(triphenylphosphine)bis(silaneophyl- d_5)platinum(II). Triphenylphosphine (0.18 g, 0.68 mmol) was added to Pt(CH₂SiMe₂C₆D₅)₂(nbd) (0.20 g, 0.34 mmol) in diethyl ether (7 cm³), and the mixture was allowed to stand at ambient temperature for 7 days. Removal of the ether *in vacuo* afforded a pale yellow solid, which was dissolved in the minimum quantity of benzene (2 cm³). *n*-Hexane (2 cm³) was added, and the solution was cooled to -20 °C. The solid was filtered, washed with *n*-hexane (2 × 3 cm³), and dried *in vacuo*, giving the product as a white crystalline solid (yield 0.32 g, 0.31 mmol, 92%). Anal. Calcd: C, 63.38; H, 5.52. Found: C, 62.93; H, 5.40.

The following compounds were prepared by analogous methods.

***cis*-Bis(diphenylmethylphosphine)bis(silaneophyl- d_5)platinum(II).** Product: white solid from benzene and *n*-hexane (yield 0.27 g, 88%). Anal. Calcd: C, 58.46; H, 6.91. Found: C, 58.63; H, 7.04.

***cis*-Bis(dimethylphenylphosphine)bis(silaneophyl- d_5)platinum(II).** Product: white crystalline plates from benzene and *n*-hexane (yield 0.26 g, 97%). Anal. Calcd: C, 52.35; H, 6.20. Found: C, 52.68; H, 6.12.

***cis*-Bis(triphenylphosphine- d_15)bis(silaneophyl)platinum(II).** Product: white crystalline solid from benzene and *n*-hexane (yield 0.33 g, 93%). Anal. Calcd: C, 61.86; H, 5.38. Found: C, 61.77 H, 5.54.

[1,2-Bis(dicyclohexylphosphino)ethane]bis(silaneophyl)platinum(II). Product: white crystalline solid from dichloromethane and methanol (yield 80 mg, 70%). ¹H NMR: 0.65, s, [SiCH₃]; 0.95–2.05, m, [C₆H₁₂]; 7.62, dd, [aromatic H₂, H₆]; 7.32, m, [aromatic H₃, H₅]; 7.18, m, [aromatic H₄] ppm. ¹³C NMR: -3.70, t''t', (¹J_{Pt-C} = 531 Hz, ²J_{Pt-C} = 90 Hz), [PtCH₂]; 4.62, d, (²J_{Pt-C} = 31 Hz), [SiCH₃]; 147.91, d, (⁴J_{Pt-C} = 10 Hz), [aromatic C₁]; 134.43 [aromatic C₂, C₆]; 128.19 [aromatic C₄]; 127.78 [aromatic C₃, C₅]; 34.31, d, (¹J_{Pt-C} = 23 Hz), [cyclohexyl-CH]; 23.0–30.4 [cyclohexyl-CH₂] ppm. ³¹P NMR: 58.88 (¹J_{Pt-P} = 2025 Hz) ppm. [Shift standards and conventions as in Tables 1–9.] Anal. Calcd: C, 58.78; H, 7.94. Found: C, 58.92; H, 8.09. All NMR data were recorded with chloroform-*d* as solvent.

Preparation of *cis*-Bis(triphenylphosphine)(phenyl){[(dimethylphenylsilyl)methyl]dimethylsilyl}methylplatinum(II). *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃)₂ (0.15 g, 0.15 mmol) was dissolved in toluene (6 cm³) and freeze-thaw degassed through three cycles. The colorless solution was heated to 100 °C for 24 h and cooled, and the resultant yellow solution was filtered through a plug of florisil and activated charcoal. The solvent was evaporated to dryness and the solid recrystallized from the minimum amount of benzene (1 cm³) and *n*-hexane (1 cm³), yielding a white crystalline solid (yield 0.14 g, 92%). Anal. Calcd: 63.70; H, 5.54. Found: C, 63.68; H, 5.61.

Preparation of *cis*-Bis(diphenylmethylphosphine)(phenyl){[(dimethylphenylsilyl)methyl]dimethylsilyl}methylplatinum(II). This complex was obtained as a white solid from *n*-hexane by heating a toluene solution of *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₂Me)₂ to 135 °C for 24 h by a procedure similar to that described above (yield 0.13 g, 87%).

Preparation of *cis*-Bis(triphenylphosphine)(2-methylphenyl){[(dimethyl(2-methylphenyl)silyl)methyl]dimethylsilyl}methylplatinum(II). The title compound was synthesised as a white crystalline solid by heating a toluene solution to 70 °C for 16 h by a procedure essentially identical to that described above (yield 0.14 g, 95%).

Preparation of *cis*-Bis(triphenylphosphine)(pentafluorophenyl){[(dimethyl(pentafluorophenyl)silyl)methyl]dimethylsilyl}methylplatinum(II). Triphenylphosphine (0.14 g, 0.52 mmol) was added to a solution of Pt(CH₂SiMe₂C₆F₅)₂(cod) (0.20 g, 0.24 mmol) in Et₂O (5 cm³) and heated to 60 °C for 35 days. Removal of the solvent *in vacuo* afforded the product as a white solid (yield 0.24 g, 77%).

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Table 1. ^1H NMR Characteristics of *cis*-Pt(R)(CH₂SiMe₂CH₂SiMe₂R')L₂

R,R'	L	δ ^1H ppm					ancillary ligands [assignment]
		geometry	hydrocarbyl ligands ($J_{\text{Pt-H}}$)/Hz [assignment]			R	
			Pt-CH ₂	Si-CH ₂	Si-CH ₃		
Me	PMePh ₂	<i>cis</i>	<i>d</i>	-0.07	0.18	1.09 (67.0) [<i>H</i>];	1.42, 1.60 [<i>P-CH</i>] 6.92-7.02 [<i>H</i> _{3,4,5}]; 7.39-7.51 [<i>H</i> _{2,6}] 7.00-7.33 [<i>H</i> _{3,4,5}]; 7.38-7.48 [<i>H</i> _{2,6}]
Me	PPh ₃	<i>cis</i>	<i>d</i>	-0.53	0.14	0.45 (68.8) [<i>H</i>];	
Ph	PMe ₃ ^a	<i>cis</i>	0.65 (67.8)	-0.09	0.08	6.93 m, [<i>H</i> ₄]; 7.09-7.20 m, [<i>H</i> ₃ , <i>H</i> _{3'} , <i>H</i> ₄ , <i>H</i> ₅ , <i>H</i> _{5'}]; 7.51 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]; 7.56 t ^{tt} , (64.4) [<i>H</i> ₂ , <i>H</i> ₆]	0.76 m, [<i>P-CH</i>]; 0.98 m, [<i>P'-CH</i>]
Ph	PEt ₃ ^a	<i>trans</i>	0.34 (79.6)	-0.18	-0.08	6.83 m, [<i>H</i> ₄]; 6.91 m, [<i>H</i> ₃ , <i>H</i> ₅]; 7.11-7.16 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.37 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]; 7.42 t ^{tt} , (56.7) [<i>H</i> ₂ , <i>H</i> ₆]	0.86 m, [<i>P-CH</i> ₂ CH ₃]; 1.47 m, [<i>P-CH</i> ₂ CH ₃]
Ph	PMe ₂ Ph ^c	<i>cis</i>	0.69 <i>d</i>	-0.18	-0.08	<i>d</i> [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; <i>d</i> [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.51 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]; 7.65 t ^{tt} , (56.7) [<i>H</i> ₂ , <i>H</i> ₆]	0.83 m, [<i>P-CH</i>]; 1.12 m, [<i>P'-CH</i>]; 6.89-6.98 m, [<i>H</i> ₃ , <i>H</i> _{3'} , <i>H</i> ₄ , <i>H</i> _{4'} , <i>H</i> ₅ , <i>H</i> _{5'}]; 7.12-7.22 m, [<i>H</i> ₂ , <i>H</i> ₂ , <i>H</i> ₆ , <i>H</i> _{6'}];
Ph	PMe ₂ Ph ^{a,e}	<i>cis</i>	0.74	-0.08	0.12		0.83 m, [<i>P-CH</i>]; 1.09 m, [<i>P'-CH</i>]; 6.90-6.96 m, [<i>H</i> ₃ , <i>H</i> _{3'} , <i>H</i> ₄ , <i>H</i> _{4'} , <i>H</i> ₅ , <i>H</i> _{5'}]; 7.18-7.23 m, [<i>H</i> ₂ , <i>H</i> ₆]; 7.25-7.34 m, [<i>H</i> ₂ , <i>H</i> _{6'}]
Ph	PPh ₂ Me ^a	<i>cis</i>	0.85 (85.2)	-0.39	-0.17	7.15-7.18 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; <i>d</i> [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.43 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]; 7.48 t ^{tt} , (50.5) [<i>H</i> ₂ , <i>H</i> ₆]	1.11 m, (24.7) [<i>P-CH</i>]; 1.25 m, (20.3) [<i>P'-CH</i>]; 6.86-6.91 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 6.96-6.99 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.35-7.37 m, [<i>H</i> ₂ , <i>H</i> ₆]; 7.37-7.39 m, [<i>H</i> ₂ , <i>H</i> _{6'}]
Ph	PPh ₃ ^f	<i>cis</i>	0.41 (81.1)	-0.97	-0.72	6.36 m, [<i>H</i> ₄]; 6.44 m, [<i>H</i> ₃ , <i>H</i> ₅]; <i>d</i> [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.04 t ^{tt} , (64.2) [<i>H</i> ₂ , <i>H</i> ₆]; 7.09 dd, [<i>H</i> ₂ , <i>H</i> _{6'}];	6.88-6.92 m, [<i>H</i> ₂ , <i>H</i> ₆]; 6.96-7.00 m, [<i>H</i> ₂ , <i>H</i> _{6'}]; 7.11-7.15 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.18-7.24 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅];
Ph	PPh ₃ ^{a,e}	<i>cis</i>	0.92 (83.4)	-0.58	-0.19		6.73-6.81 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 6.82-6.88 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.31-7.47 m, [<i>H</i> ₂ , <i>H</i> ₂ , <i>H</i> ₆ , <i>H</i> _{6'}]
Ph	PPh ₃ - <i>d</i> ₁₅ ^a	<i>cis</i>	0.91 (85.9)	-0.58	-0.19	6.66 m, [<i>H</i> ₄]; 6.75 m, [<i>H</i> ₃ , <i>H</i> ₅]; 7.11-7.19 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.40 t ^{tt} , (58.6) [<i>H</i> ₂ , <i>H</i> ₆]; 7.43 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]	
Ph	P-4-tol ₃ ^c	<i>cis</i>	1.05 (88.7)	-0.48	0.00	<i>d</i> [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; <i>d</i> [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 6.90 t ^{tt} , (62.3) [<i>H</i> ₂ , <i>H</i> ₆]; 7.24 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]	2.06 s, [<i>Ar-CH</i>]; 2.07 s, [<i>Ar'-CH</i>]; 6.76 d, [<i>H</i> ₃ , <i>H</i> ₅]; 6.84 d, [<i>Ar</i> , <i>H</i>]; 7.45 dd, [<i>H</i> ₂ , <i>H</i> ₆] ($J_{\text{P-H}} = 10.2$ Hz); 7.56 dd, [<i>H</i> ₂ , <i>H</i> _{6'}] ($J_{\text{P-H}} = 9.5$ Hz)
Ph	L' ^{a,b}		0.95 (88.7)	-0.45	-0.15	6.60 m, [<i>H</i> ₄]; 6.73 m, [<i>H</i> ₃ , <i>H</i> ₅]; 7.12-7.17 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.52 dd, [<i>H</i> ₂ , <i>H</i> _{6'}]; 8.02 t ^{tt} , (125.9) [<i>H</i> ₂ , <i>H</i> ₆]	6.85-6.93 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 6.99-7.02 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.42-7.49 m, [<i>H</i> ₆]; 7.56-7.63 m, [<i>H</i> ₆]
Ph, Me	PPh ₃	<i>cis</i>	0.93 <i>d</i>	-0.88	-0.02	<i>d</i>	6.74-7.0 m, [<i>H</i> ₃ , <i>H</i> ₄ , <i>H</i> ₅]; 7.31-7.50 m [<i>H</i> ₂ , <i>H</i> ₆]
Ph, Me	PMe ₃	<i>cis</i>	0.25 (62.5)	-0.73	-0.08	6.8 m [<i>H</i> ₄]; 7.06-7.20 m [<i>H</i> ₃ , <i>H</i> ₅]; 7.28 t ^{tt} [<i>H</i> ₂ , <i>H</i> ₆]	1.04 m [<i>P-CH</i>]; 1.36 m [<i>P'-CH</i>]

^a Toluene-*d*₆. ^b L' = PPh₂C₆H₄-2-CF₃. ^c Benzene-*d*₆. ^d Obscured. ^e L₂Pt(Ph-*d*₅)(CH₂SiMe₂CH₂SiMe₂Ph-*d*₅). ^f Chloroform-*d*.

Preparation of *cis*-Bis(triphenylphosphine)(methyl)((trimethylsilyl)methyl)dimethylsilyl)methyl)platinum(II). *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ (0.15 g, 0.17 mmol) was dissolved in toluene (6 cm³) and freeze-thaw degassed through three cycles. The colorless solution was heated to 125 °C for 24 h and cooled, and the resultant solution was evaporated to dryness and the colorless solid recrystallized from the minimum amount of toluene (yield 0.14 g, 93%). Anal. Calcd: C, 59.71; H, 5.86. Found: C, 59.57; H, 5.95.

Preparation of *cis*-Bis(diphenylmethylphosphine)(methyl)((trimethylsilyl)methyl)dimethylsilyl)methyl)platinum(II). This complex was obtained as a white solid (after recrystallization from toluene) by heating a toluene solution of *cis*-Pt(CH₂SiMe₃)₂(PPh₂Me)₂ at 125 °C for 24 h in similar fashion to that described above for *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ (yield 91%). Anal. Calcd: C, 53.04; H, 6.28. Found: C, 52.43; H, 6.07.

Preparation of *cis*-Bis(dimethylphenylphosphine)(methyl)((trimethylsilyl)methyl)dimethylsilyl)methyl)platinum(II). This complex was obtained as a white solid (after recrystallization from toluene) by heating a toluene solution of *cis*-Pt(CH₂SiMe₃)₂(PPhMe₂)₂ at 125 °C for 24 h in similar fashion to that described above for *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ (yield 95%). Anal. Calcd: C, 44.63; H, 6.87. Found: C, 44.58; H, 6.89.

Preparation of *cis*-(Diphenyl-2-tolylphosphine)(silaneophyl)-1,1-diphenylphosphine-2-platinaindan. *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₂-2-tol)₂ (0.09 g, 0.09 mmol) was dissolved in toluene (3 cm³) and freeze-thaw degassed through three cycles. The solution was heated to 40 °C for 16 h. Removal of the solvent *in vacuo* yielded the product as a white analytically pure solid (yield 0.06 g, 89%). Anal. Calcd: C, 63.35; H, 5.32. Found: C, 63.52; H, 5.14.

Preparation of *cis*-Bis(pyridine)platina-3-silaindan. *cis*-Pt(CH₂SiMe₂Ph)₂(py)₂ (0.10 g, 0.20 mmol) was dissolved in toluene (8 cm³) and left at ambient temperature for 4 days. Removal of toluene *in vacuo* afforded a yellow-brown oily residue, which was recrystallized from diethyl ether (1 cm³) and *n*-hexane (0.5 cm³) to give the product as pale yellow crystalline solid (yield 0.07 g, 91%). Anal. Calcd: C, 45.50; H, 4.42; N, 5.59. Found: C, 45.11; H, 4.63; N, 5.74.

Preparation of *cis*-Bis(pyridine)-1-platina-3-sila-7-(trifluoromethyl)indan. Pt(CH₂SiMe₂C₆H₄-CF₃)₂(cod) (0.20 g, 0.24 mmol) was dissolved in excess pyridine (10 cm³) and heated to 60 °C for 24 h. Excess pyridine was removed *in vacuo* to give an off-white oil, which was recrystallized from diethyl ether (1 cm³) and *n*-hexane (0.3 cm³) to afford the product as colorless plates (yield 0.12 g, 88%). Anal. Calcd: C, 42.18; H, 3.72; N, 5.19. Found: C, 41.87; H, 3.54; N, 5.19.

Table 2. ^{13}C NMR Characteristics of *cis*-Pt(R)(CH₂SiMe₂CH₂SiMe₂R)L₂^a

R	L	δ ^{13}C ppm				phosphine ligands ($J_{\text{Pt-C}}$)/ Hz [assignment] ($J_{\text{P-C}}$)/Hz
		hydrocarbyl ligands ($J_{\text{Pt-C}}$)/Hz [assignment]			R	
		Pt-CH ₂	Si-CH ₂	Si-CH ₃		
Me	PPh ₃	14.05 (645.0) ($J_{\text{C-P}_{\text{trans}}} = 80.0$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 4.8$ Hz)	8.80 (30.7)	1.99 6.28 (26.1)	7.75 (595.7) [Pt-CH ₃]	127.57 [C ₃ , C ₅] (17.9); 127.81 [C ₃ , C ₅] (18.0); 129.21 [C ₄]; 129.48 [C ₄]; 134.62 (21.9) [C ₁ , C _{1'}] (39.0); 134.95 (15.9) [C ₂ , C ₆] (11.6); 134.90 (13.1) [C ₂ , C ₆] (10.7); 14.63 (22.2) [P-CH ₃] (22.2); 16.29 (29.8) [P-CH ₃] (35.1); 127.91 [C ₃ , C ₅]; 128.06 [C ₃ , C ₅]; 129.34 [C ₄]; 129.43 [C ₄]; 132.61 (14.3) [C ₂ , C ₆] (11.5); 132.91 (14.8) [C ₂ , C ₆] (10.6); 134.90 (16.5) [C ₁ , C _{1'}] (22.2)
Me	PPh ₂ Me	11.55 (557.9) ($J_{\text{C-P}_{\text{trans}}} = 85.0$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 5.9$ Hz)	8.54 (30.7)	1.74 4.92 (25.9)	4.81 (604.5) [Pt-CH ₃]	127.33 [C ₃ , C ₅] (9.8); 127.61 [C ₃ , C ₅] (9.7); 128.90 [C ₄]; 129.90 [C ₄]; 133.63 (16.9) [C ₁ , C _{1'}] (39.0); 134.15 (15.9) [C ₂ , C ₆] (11.6); 134.90 (13.1) [C ₂ , C ₆] (10.7) 14.63 (22.2) [P-CH ₃] (22.2); 16.29 (29.8) [P-CH ₃] (35.1); 127.91 [C ₃ , C ₅]; 128.06 [C ₃ , C ₅]; 129.34 [C ₄]; 129.43 [C ₄]; 132.61 (14.3) [C ₂ , C ₆] (11.5); 132.91 (14.8) [C ₂ , C ₆] (10.6); 134.90 (16.5) [C ₁ , C _{1'}] (22.2)
Ph	PPh ₃	14.08, 15.40 (567.5) ($J_{\text{C-P}_{\text{trans}}} = 83.0$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 5.8$ Hz)	5.45 (27.7)	0.02 3.30 (24.1)	120.56 [C ₄]; 126.60 (55.7) [C ₃ , C ₅] ($J_{\text{C-P}} = 6.6$ Hz); 127.84 [C ₄]; 128.34 [C ₃ , C ₅]; 133.40 [C ₂ , C ₆]; 138.41 (32.4) [C ₂ , C ₆]; 143.34 [C ₁]; 159.36 (875.8) [C ₁] ($J_{\text{C-P}_{\text{trans}}} = 114.9$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 11.8$ Hz)	127.33 [C ₃ , C ₅] (9.8); 127.61 [C ₃ , C ₅] (9.7); 128.90 [C ₄]; 129.90 [C ₄]; 133.63 (16.9) [C ₁ , C _{1'}] (39.0); 134.15 (15.9) [C ₂ , C ₆] (11.6); 134.90 (13.1) [C ₂ , C ₆] (10.7) 14.63 (22.2) [P-CH ₃] (22.2); 16.29 (29.8) [P-CH ₃] (35.1); 127.91 [C ₃ , C ₅]; 128.06 [C ₃ , C ₅]; 129.34 [C ₄]; 129.43 [C ₄]; 132.61 (14.3) [C ₂ , C ₆] (11.5); 132.91 (14.8) [C ₂ , C ₆] (10.6); 134.90 (16.5) [C ₁ , C _{1'}] (22.2)
Ph	PPh ₂ Me	12.02, 13.35 (535.9) ($J_{\text{C-P}_{\text{trans}}} = 83.6$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 4.8$ Hz)	5.64 (27.6)	-0.01 3.62 (25.5)	121.39 [C ₄]; 126.80 (64.5) [C ₃ , C ₅] ($J_{\text{C-P}} = 6.1$ Hz); 126.95 [C ₄]; 127.21 [C ₃ , C ₅]; 133.38 [C ₂ , C ₆]; 138.17 (30.9) [C ₂ , C ₆] ($J_{\text{C-P}} = 2.1$ Hz); 143.20 [C ₁]; 160.96 (807.6) [C ₁] ($J_{\text{C-P}_{\text{trans}}} = 117.4$ Hz; $J_{\text{C-P}_{\text{cis}}} = 12.4$ Hz)	127.33 [C ₃ , C ₅] (9.8); 127.61 [C ₃ , C ₅] (9.7); 128.90 [C ₄]; 129.90 [C ₄]; 133.63 (16.9) [C ₁ , C _{1'}] (39.0); 134.15 (15.9) [C ₂ , C ₆] (11.6); 134.90 (13.1) [C ₂ , C ₆] (10.7) 14.63 (22.2) [P-CH ₃] (22.2); 16.29 (29.8) [P-CH ₃] (35.1); 127.91 [C ₃ , C ₅]; 128.06 [C ₃ , C ₅]; 129.34 [C ₄]; 129.43 [C ₄]; 132.61 (14.3) [C ₂ , C ₆] (11.5); 132.91 (14.8) [C ₂ , C ₆] (10.6); 134.90 (16.5) [C ₁ , C _{1'}] (22.2)
2-tol	PPh ₃	9.45, 10.85 (501.5) ($J_{\text{C-P}_{\text{trans}}} = 88.0$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 4.5$ Hz)	6.13 (26.6)	1.09 2.78 (17.4) 3.29 (22.4)	23.19 [CH ₃]; 26.88 (60.7) [CH ₃]; 121.05 [C ₄]; 122.32 [C ₂] ($J_{\text{C-P}} = 69.3$ Hz); 124.04 (86.6) [C ₆]; ($J_{\text{C-P}} = 6.2$ Hz); 124.43 [C ₅]; 128.24 [C ₃]; 129.43 [C ₄]; 132.25 [C ₆]; 139.07 (25.7) [C ₃]; 141.02 [C ₂]; 141.38 (25.3) [C ₃]; ($J_{\text{C-P}_{\text{trans}}} = 113.2$ Hz; $J_{\text{C-P}_{\text{cis}}} = 10.0$ Hz)	127.24 [C ₃ , C ₅] (9.4); 127.62 [C ₃ , C ₅] (9.1); 128.94 [C ₄]; 129.18 [C ₄]; 133.65 (17.5) [C ₁] (43.6); 133.72 (14.2) [C ₁] (34.9); 134.20 (13.0) [C ₂ , C ₆] (11.5); 134.87 (10.3) [C ₂ , C ₆] (10.7)
Ph	dcpe	14.98 (580.0) ($J_{\text{C-P}_{\text{trans}}} = 84.7$ Hz)	3.84 (27.8)	1.36 (27.1) -1.10	120.98 (11.9) [C ₄]; 126.84 (58.2) [C ₂ , C ₆]; 126.94 [C ₃ , C ₅]; 127.77 [C ₄]; 133.34 [C ₁]; 133.76 [C ₂ , C ₆]; 138.82 (34.2) [C ₃ , C ₅]; 158.71 (1060.0) [C ₁]	25.90–26.71 m; 26.91–27.36 m 28.06–28.63 m; 29.75 m [dcpe]
C ₆ F ₅	PPh ₃	6.35, 7.81 (538.3) ($J_{\text{C-P}_{\text{trans}}} = 89.7$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 7.0$ Hz)	6.42 (23.5)	1.00 2.63 (22.1)	138.84 m, 139.26 m, 139.91 m, 143.58 m, 146.96 m, 147.35 m, 150.44 m, 151.60 m, [aromatic]	127.63 [C ₃ , C ₅] (8.7); 127.80 [C ₃ , C ₅] (3.7); 129.64 [C ₄]; 129.77 [C ₄]; 131.14 (17.0) [C ₁] (46.5); b [C ₁]; 133.94 (18.8) [C ₂ , C ₆] (17.9);

^a Measured in chloroform-*d*. ^b Obscured.

Preparation of *cis*-Bis(pyridine)(2-methylphenyl){[(dimethyl(2-methylphenyl)silyl)methyl]dimethylsilyl}methyl}platinum(II). Pt(CH₂SiMe₂C₆H₄-2-Me)₂(cod) (0.20 g, 0.32 mmol) was dissolved in excess pyridine (15 cm³) and heated to 60 °C for 24 h. Excess pyridine was removed *in vacuo*, yielding a pale yellow oily residue, which was dissolved in Et₂O (1 cm³). *n*-Hexane was (0.2 cm³) added, and the solution was cooled to -20 °C. The solid was filtered, washed with cold *n*-hexane (2 × 2 cm³), and dried *in vacuo* to give a pale yellow crystalline solid of the product (yield 0.17 g, 85%). Anal. Calcd: C, 52.99; H, 5.93; N, 4.12. Found: C, 52.71; H, 5.84; N, 4.10.

Thermolyses. (a) Kinetic Scale. Toluene-*d*₈ and benzene-*d*₆, supplied by MSD Isotopes, were distilled from Na and Na/K alloy, respectively, and were stored under argon prior to use. Measurements were performed in 5-mm-diameter, medium-walled NMR tubes equipped with sealable Teflon valves (J. Young Scientific Ltd., Acton, London). Samples were prepared by freeze-thaw degassing of toluene-*d*₈ or benzene-*d*₆ solutions (either prepared fresh or from a stock solution stored under argon) through five deoxygenating cycles and then sealed under argon.

Reaction progress was monitored periodically by either ¹H, ¹⁹F, or ³¹P NMR spectroscopy, as described previously.¹⁰ For reactions monitored by ³¹P NMR, solutions whose concentrations were 0.02 mol-dm⁻³ in organoplatinum were prepared. Solutions 0.01 mol-dm⁻³ in organoplatinum were adequate for reactions followed by ¹H or ¹⁹F NMR spectroscopy. The tube was maintained at the required temperature (calibrated ±0.1 °C) either in the Jeol FX90Q spectrometer or by immersion in a Haake W13 thermoregulated silicone oil bath (±0.1 °C). Where thermolyses were conducted in the presence of added phosphine,

a standard solution of PR₃ in toluene-*d*₈ was transferred *via* microsyringe to the reaction tubes. Standard errors (where quoted) were derived using (appropriately) linear or nonlinear regression software, as supplied by Applied Photophysics Laboratories, with the SF17 stopped-flow kinetic spectrometer workstation.

(b) Analytical Scale. A deoxygenated toluene solution of the appropriate PtR₂L₂ complex was prepared in a grease-free, Teflon-sealed vessel and heated to 125 °C for 24 h. The solvent was then removed *in vacuo*, and the product was recrystallized prior to characterization.

Results

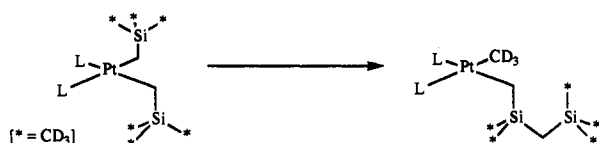
1. Thermolytic Product Analyses. (a) *cis*-Pt(CH₂SiMe₂)₂L₂. Thermolyses of toluene-*d*₈ solutions of the complexes *cis*-Pt(CH₂SiMe₂)₂L₂ [L = PEt₃, PPhMe₂, PPh₂Me, PPh₃] each resulted in quantitative rearrangement to a single, asymmetric organoplatinum(II) complex, most immediately evident from ³¹P NMR spectra (nonequivalent ligating phosphines). Mass spectra of products displayed molecular ions whose composition corresponded with the parent compound, Pt(CH₂SiMe₂)₂L₂. Elemental analyses of these compounds also accorded with this formulation. With L = PEt₃, the product could not be isolated in pure form. Rearrangement of the trimethylphosphine analogue required appreciably higher temperatures (>130 °C), and secondary reactions were evident. Though the predominant reaction was clearly parallel to that of the others, it was not

Table 3. ^{31}P NMR Characteristics of $\text{Pt}(\text{Ph})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{R})\text{L}_2$

complex	δ^a/ppm	$J_{\text{Pt-P}}/\text{Hz}$	$J_{\text{P-P}}/\text{Hz}$	$J_{\text{P-F}}/\text{Hz}$
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PMe ₃) ₂ ^b	-28.0, -24.5	1891, 1718	11	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ Ph)(PEt ₃) ₂ ^b	4.2, 4.8	2003, 1737	13	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PMe ₂ Ph) ₂ ^b	-14.8, -13.3	1947, 1749	13	
<i>cis</i> -Pt(Ph- <i>d</i> ₅)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph- <i>d</i> ₅)(PMe ₂ Ph) ₂ ^b	-14.8, -13.2	1945, 1747	11	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PPh ₂ Me) ₂ ^b	2.75, 4.61	1973, 1765	11	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PPh ₃) ₂ ^b	24.0, 25.3	2082, 1670	11	
<i>cis</i> -Pt(Ph- <i>d</i> ₅)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph- <i>d</i> ₅)(PPh ₃) ₂ ^b	23.8, 25.0	2082, 1674	9	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PPh ₃ - <i>d</i> ₁₅) ₂ ^b	23.4, 24.8	2084, 1665	9	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(P-4-tolyl) ₂ ^c	22.2, 23.2	2092, 1697	9	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PPh ₂ C ₆ H ₄ -2-CF ₃) ₂ ^c	28.6, 30.4	2036, 1726	11	13
Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(dcpe) ^c	56.4, 58.9	2001, 1757	0	
<i>trans</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PMe ₃) ₂ ^b	-19.8	2783		
<i>trans</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PEt ₃) ₂ ^b	14.5	2800		
<i>trans</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ Ph)(PMe ₂ Ph) ₂ ^c	-9.2	2887		
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₃)(PPh ₃) ₂ ^b	25.72, 24.51	2075, 1672	10	
<i>cis</i> -Pt(Ph)(CH ₂ SiMe ₂ CH ₂ SiMe ₃)(PMe ₃) ₂ ^b	-24.14, -27.25	1868, 1709	13	

^a Relative to 85% H₃PO₄/D₂O. ^b Toluene-*d*₈. ^c Benzene-*d*₆.

Scheme 1



quantified in detail. The products are indefinitely air-inert as solids and also as solutions in deoxygenated halo- or hydrocarbons. Available ^1H , ^{13}C , and ^{31}P NMR spectroscopic characteristics appear in Tables 1, 2, and 3, respectively.

Formation, to any detectable extent, either of symmetric metallacycles, $\text{Pt}(\text{CH}_2\text{SiMe}_2\text{CH}_2)\text{L}_2$, or of asymmetric metallacycles—via metalation on a phosphine substituent—was discounted. Production of *cis*-Pt(C₆H₄-4-Me)(CH₂SiMe₃)L₂ by solvent C-H activation, was also excluded; an independently synthesized sample (L = PEt₃) displayed distinctive ^{31}P NMR characteristics [4.89 ppm (coincident), $^1J_{\text{Pt-P}} = 1967$ and 1761 Hz.]

^1H NMR spectra of products (Table 1) displayed indicative features, most notably two distinct silicon-bound methyl resonances and a characteristic singlet upfield of 0.00 ppm (Table 1). The aromatic patterns supported the inequivalence of the phosphine ligands.

The $^{13}\text{C}\{^1\text{H}\}$ spectra (Table 2) confirmed the absence of any aromatic *ortho*-metalation (C₂ is essentially unaffected by reaction) and allowed unequivocal assignment of the structures. Two distinct Pt-CH_n resonances were observed. From the signal phases obtained from ADEPT measurements, the lower field resonance could be attributed to a Pt-CH₂ grouping, while the higher field signal clearly corresponded to Pt-CH₃. Two Si-CH₃ environments were also evident, one displaying $^3J_{\text{Pt-C}}$ interaction (comparable to that in the parent complex), and a second, more intense, with no observable coupling. An additional upfield resonance, showing $^3J_{\text{Pt-C}}$ coupling, was identified as a Si-CH₂-Si group.

The novel, methyl({[(trimethylsilyl)methyl]dimethylsilyl}methyl)platinum(II) complex *cis*-Pt(CH₃)(CH₂SiMe₂CH₂SiMe₃)L₂ is consistent with all the foregoing observations. The structure has been confirmed (L = PPh₃) by X-ray diffractometry.²²

An important aspect of product analysis is the origin of the methyl group bound ultimately to platinum. Accordingly, we synthesized and thermolyzed the selectively deuterated analogues *cis*-Pt[CH₂Si(CD₃)₃]₂L₂ (L = PPh₃, PPh₂Me). Though rearrangement of each is retarded (*vide infra*), exactly analogous products arise whose ^{13}C NMR spectra reveal the presence only of Pt-CD₃ and Pt-CH₂-Si groups. Superficially, at least, the rearrangement features an effective β -methyl migration from

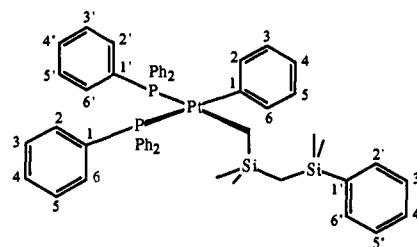


Figure 1. NMR numbering conventions for $\text{Pt}(\text{Ph})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PR}_3)_2$.

silicon (Scheme 1). Treatment of a toluene solution of *cis*-Pt(CH₃)(CH₂SiMe₂CH₂SiMe₃)(PPh₃)₂ with HCl in toluene yielded *bis*(trimethylsilyl)methane and methane as sole organic products. After thermolysis of an equimolar solution of *cis*-Pt[CH₂Si(CH₃)₃]₂(PPh₃)₂ and *cis*-Pt[CH₂Si(CD₃)₃]₂(PPh₃)₂ and subsequent treatment with HCl, Me₃SiCH₂SiMe₃ and Me₃SiCH₂-SiMe₃-*d*₁₅ were the only significant isotopomers detected by GCMS, indicating a strictly intramolecular rearrangement.

(b) *cis*-Pt(CH₂SiMe₂Ph)₂L₂. Thermolysis of *cis*-Pt(CH₂SiMe₂Ph)₂L₂ [L = PMe₃, PEt₃, PMe₂Ph, PPh₂Me, PPh₃, *P-p*-tolyl, PPh₂C₆H₄-2-CF₃; L₂ = 1,2-*bis*(dicyclohexylphosphino)ethane, dcpe] in toluene resulted, likewise, in rearrangement to a species containing two nonequivalent phosphorus nuclei coupled to platinum. Full spectroscopic assignments are summarized in Tables 1–3. A numbering convention is shown in Figure 1.²³

In ^{31}P NMR spectra, the magnitudes of $^1J_{\text{Pt-P}}$ are consistent with one phosphorus *trans* to an aryl group and the other *trans* to a β -silaalkyl fragment. ^1H NMR spectra (Table 1) of these products have many of the distinctive features of *cis*-Pt(CH₃)(CH₂SiMe₂CH₂SiMe₃)L₂—notably two silicon-methyl environments and a singlet further upfield attributable to the Si-CH₂-Si group. A multiplet at *ca.* 1.00 ppm, showing coupling to ^{195}Pt and to ^{31}P , originates from the Pt-CH₂ group. The aromatic region (where not obscured by ancillary ligand resonances) exhibits three multiplets with integral ratios of 2:1:2; the resonance at lowest field displays coupling to both ^{195}Pt and ^{31}P , typical for a platinum-bound aryl group. In addition, two further resonances, a doubled doublet and a higher field multiplet, are observed with chemical shifts consistent with a phenyl substituent of a β -silaalkyl group. Two distinct resonance sets are evident for each phosphine ligand environment.

Unequivocal structural indications again are obtained from the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Table 2). Two Si-CH₃ groups emerge, only one of which displays significant $^3J_{\text{Pt-C}}$ interaction. An additional aliphatic carbon showing similar coupling to platinum

(23) Transferred aryl group carbon atoms are designated C_n and the remaining carbon atoms as C_n'. Carbon atoms on the phosphine ligand *trans* to the aryl group and *trans* to the silaalkyl fragment are also designated as C_n and C_n' respectively.

(22) Hursthouse, M. B.; Karulov, A., to be published elsewhere.

Table 4. ^1H NMR Characteristics of *cis*-Pt(Ar)(CH₂SiMe₂CH₂SiMe₂Ar)(PPh₃)₂

Ar	δ ^1H ppm				
	Pt-CH ₂	Si-CH ₂	Si-CH ₃	hydrocarbyl ligands ($J_{\text{Pt-H}}$)/Hz [assignment] ($J_{\text{P-H}}$)/Hz	ancillary ligands [assignment]
C ₆ H ₄ -2-Me ^a	0.83	-0.64 ^b	-0.39	2.28 [CH ₃]; 2.78 [CH ₃]; 6.50 m, [H ₅];	6.70-6.80 m, [H ₃ , H ₄ , H ₅];
	(86.0)	-0.42	-0.18	6.63 dd, [H ₃];	6.81-6.88 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -2-CF ₃ ^a	0.93		0.23	6.90-7.12 m, [H ₃ , H ₄ , H ₄ , H ₅]; c [H ₆];	7.26-7.36 m, [H ₂ , H ₆];
	(86.0)		0.26	7.51 t ^u , (51.3) [H ₆]	7.38-7.47 m, [H ₂ , H ₆]
C ₆ H ₄ -3-Me ^a	0.70 ^d	-0.71 ^e	-0.52	6.45 m, [H ₅]; 6.50 m, [H ₃];	6.70-6.80 m, [H ₃ , H ₄ , H ₅];
	(85.0)	-0.31	-0.18	6.92-7.07 m, [H ₃ , H ₄ , H ₄ , H ₅]; c [H ₆];	6.81-6.89 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -3-CF ₃ ^a	1.08 ^f		0.21	7.57 t ^u , (49.9) [H ₆];	7.29-7.36 [H ₂ , H ₆];
	(82.5)		0.27		7.42-7.49 [H ₂ , H ₆]
C ₆ H ₄ -4-Me ^a	0.94	-0.54	-0.17	1.98 [CH ₃], 2.18 [CH ₃]; 6.49 m, [H ₅];	6.72-6.81 m, [H ₃ , H ₄ , H ₅];
	(85.9)		0.22	6.87-7.15 m, [H ₄ , H ₄ , H ₅ , H ₆ , H ₆];	6.82-6.88 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -4-CF ₃ ^a	0.79	-0.81	-0.26	c [H ₂ , H ₂]	7.27-7.50 m, [H ₂ , H ₂ , H ₆ , H ₆]
	(83.6)		0.07	c	6.53-6.84 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -4-Me ^a	1.05	-0.47	-0.04	6.74 dd, [H ₃ , H ₅]; c [H ₃ , H ₅];	6.87-6.97 m, [H ₃ , H ₄ , H ₅];
	(84.8)		0.20	c [H ₂ , H ₆]; 7.42 t ^u , (58.5) [H ₂ , H ₆]	7.03-7.15 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -4-CF ₃ ^a	0.90	-0.70	-0.13	c [H ₃ , H ₅]; 7.13 m, [H ₃ , H ₅];	7.44-7.52 m, [H ₂ , H ₆];
	(83.5)		0.20	c [H ₂ , H ₆]; 7.56 t ^u , (51.3) [H ₂ , H ₆]	7.55-7.60 m, [H ₂ , H ₆];
C ₆ H ₄ -4-Bu ¹ ^a	0.96	-0.52	-0.20	1.21 [C-CH ₃]; 6.73 m, [H ₃ , H ₅];	6.76-6.81 m, [H ₃ , H ₄ , H ₅];
	(85.7)		0.22	7.06 d, [H ₃ , H ₅]; 7.22 d, [H ₂ , H ₆];	6.83-6.89 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -4-OMe ^a	0.94	-0.58	-0.14	7.25 t ^u , (55.0) [H ₂ , H ₆]	7.31-7.36 m, [H ₂ , H ₆];
	(82.5)		0.22	3.33 [O-CH ₃]; 3.38 [O-CH ₃];	7.37-7.44 m, [H ₂ , H ₆]
C ₆ H ₄ -4-F ^a	0.82	-0.73	-0.20	6.47 m, [H ₃ , H ₅]; 6.90 d, [H ₃ , H ₅];	6.74-6.80 m, [H ₃ , H ₄ , H ₅];
	(84.4)		0.12	7.24 t ^u , (56.9) [H ₂ , H ₆];	6.81-6.89 m, [H ₃ , H ₄ , H ₅];
C ₆ H ₄ -4-NMe ₂ ^a	1.01	-0.12	0.21	7.50 d, [H ₂ , H ₆]	7.33-7.42 m, [H ₂ , H ₆];
	(82.7)		0.24	6.54 m, [H ₃ , H ₅]; 6.73 m, [H ₃ , H ₅]	7.43-7.51 m, [H ₂ , H ₆]
C ₆ F ₅ ^g	0.85	-0.53	-0.10	($J_{\text{H-F}} = 16.6$ Hz); 7.20 m, (43.5) [H ₂ , H ₆];	6.72-6.79 m, [H ₃ , H ₄ , H ₅];
	(81.2)		0.19 ^h	7.24 m, [H ₂ , H ₆]; ($J_{\text{H-H}_3} = 8.8$ Hz)	6.80-6.88 m, [H ₃ , H ₄ , H ₅];
	(10.2)			($J_{\text{H-F}} = 11.0$ Hz)	7.25-7.36 m, [H ₂ , H ₆];
				2.50 [N-CH ₃]; 2.54 [N-CH ₃];	7.38-7.44 m [H ₂ , H ₆]
				6.31 m, [H ₃ , H ₅]; 6.54 d, [H ₃ , H ₅]	6.84-6.87 m, [H ₃ , H ₄ , H ₅];
				($J_{\text{H-H}_3} = 8.7$ Hz); c [H ₂ , H ₆];	6.93-6.99 m, [H ₃ , H ₄ , H ₅];
				7.27 t ^u , (59.2) [H ₂ , H ₆]	7.34-7.40 m, [H ₂ , H ₆];
					7.42-7.48 m, [H ₂ , H ₆]
					6.91-7.05 m, [H ₃ , H ₄ , H ₅];
					7.07-7.16 m, [H ₃ , H ₄ , H ₅];
					7.30-7.36 m, [H ₂ , H ₆];
					7.39-7.46 m, [H ₂ , H ₆]

^a Toluene-*d*₈. ^b $J_{\text{H-H}} = 14.2$ Hz. ^c Obscured by phosphine resonances. ^d $J_{\text{H-F}} = 28.2$ Hz. ^e $J_{\text{H-H}} = 13.5$ Hz. ^f $J_{\text{H-F}} = 6.0$ Hz. ^g Benzene-*d*₆. ^h $J_{\text{H-H}} = 3.4$ Hz.

is assigned as a Si-CH₂-Si group. A Pt-CH₂ group is also evident. The aromatic region (in addition to resonances due to the nonequivalent phosphines) comprises eight distinct aromatic resonances, three of which are coupled to platinum. Rearrangement of *cis*-Pt(CH₂SiMe₂Ph)₂L₂ has produced *cis*-Pt(Ph)(CH₂-SiMe₂CH₂SiMe₂Ph)L₂ by β -aryl migration. There was no evidence for competitive operation of, for example, β -methyl migration or metallacyclization at sites on the silaneophyl or phosphine ligands.

In one case, the primary product does not have the *cis*-configuration, however. Where L = PEt₃, *trans*-Pt(Ph)(CH₂-SiMe₂CH₂SiMe₂Ph)(PEt₃)₂ is produced. The ³¹P NMR spectrum comprises a singlet with ¹⁹⁵Pt satellites ($J_{\text{Pt-P}} = 2800$ Hz). In the ¹H NMR spectrum (Table 1), the signals due to hydrocarbyl components are very similar to those noted for *cis*-Pt(Ph)(CH₂-SiMe₂CH₂SiMe₂Ph)L₂, except that the Pt-CH₂ group generates a binomial triplet (with ¹⁹⁵Pt satellites) instead of an apparent quartet.²⁴ Resonances assignable to triethylphosphine, on the other hand, indicate a single phosphine environment. All these features are characteristic of the *trans*-configuration. Prolonged thermolysis also of Pt(CH₂SiMe₂Ph)₂L₂ [L = PMe₃, PMe₂Ph]—or of *cis*-Pt(Ph)(CH₂SiMe₂CH₂SiMe₂Ph)L₂—results, ultimately, in formation of the *trans*-products.

(c) *cis*-Pt(CH₂SiMe₂C₆H₄R)₂(PPh₃)₂ and *cis*-Pt(CH₂SiMe₂-C₆F₅)₂(PPh₃)₂. Thermolysis, between 60 °C and 90 °C, of a variety of aryl-substituted silaneophyl complexes, *cis*-Pt(CH₂-SiMe₂C₆H₄R)₂(PPh₃)₂ [R = 2-Me, 3-Me, 4-Me, 4-OMe, 4-Bu¹, 4-F, 2-CF₃, 3-CF₃, 4-CF₃, 4-NMe₂]; led, quantitatively, to corresponding products of aryl transfer, *cis*-Pt(C₆H₄R)(CH₂-SiMe₂CH₂SiMe₂C₆H₄R)(PPh₃)₂. Though not isolable, *cis*-Pt(CH₂SiMe₂C₆F₅)₂(PPh₃)₂ could be characterized as a transient species which rearranged at ambient temperature, affording *cis*-Pt(C₆F₅)(CH₂SiMe₂CH₂SiMe₂C₆F₅)(PPh₃)₂.

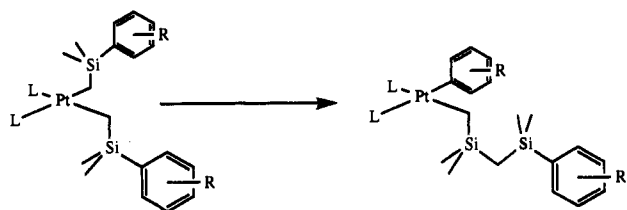
Most ¹H and ³¹P NMR characteristics of these complexes (Tables 4 and 5) are similar to those observed for *cis*-Pt(Ph)-(CH₂SiMe₂CH₂SiMe₂Ph)L₂. It is immediately clear from ¹H NMR evidence that the aryl group is transferred regiospecifically (Scheme 2). For example, *para*-substituted silaneophyl complexes exhibited two doublets—attributable to protons of the alkyl-bound aryl group—as well as two similar multiplets, one of which shows

(24) This "quartet" pattern—often comprising a central doublet, with less intense flanking signals—is a common ¹H NMR characteristic of *cis*-(R₃P)₂Pt-(CH₂)₂ fragments (cf. also ref 10, 11, 13, 14, and 16) and has been analyzed in some detail elsewhere; see Goodfellow, R. J.; Hardy, M. J.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* 1973, 2450-2555 and references cited therein. Values for the two disparate couplings ³ $J_{\text{P-H}}$ are not directly accessible from the spectra.

Table 5. ^{31}P NMR Characteristics of $\text{cis-Pt}(\text{R})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{R}')(\text{PPh}_3)_2$

R,R'	δ^a/ppm	$J_{\text{Pt-P}}/\text{Hz}$	$J_{\text{P-P}}/\text{Hz}$
$\text{C}_6\text{H}_4\text{-2-Me}^b$	22.1, 25.1	1653, 2080	9
$\text{C}_6\text{H}_4\text{-3-Me}^b$	24.0, 25.5	1660, 2086	9
$\text{C}_6\text{H}_4\text{-4-Me}^b$	24.2, 24.8	1675, 2076	10
$\text{C}_6\text{H}_4\text{-4-OMe}^b$	24.6, 25.1	1703, 2060	11
$\text{C}_6\text{H}_4\text{-4-Bu}^1b$	24.1, 25.3	1664, 2087	9
$\text{C}_6\text{H}_4\text{-4-F}^b$	24.0, 24.9	1740, 2060	10
$\text{C}_6\text{H}_4\text{-2-CF}_3^c$	22.3, 24.2	1890, 2043	13
$\text{C}_6\text{H}_4\text{-3-CF}_3^b$	23.5, 25.0	1707, 2056	11
$\text{C}_6\text{H}_4\text{-4-CF}_3^b$	23.6, 25.3	1744, 2074	13
$\text{C}_6\text{H}_4\text{-4-NMe}_2^b$	24.5, 25.3	1710, 2113	11
C_6F_5^d	21.9, 25.3	2040, 2546	13
C_6H_5^b	24.0, 25.3	1670, 2082	11

^a Relative to 85% $\text{H}_3\text{PO}_4/\text{D}_2\text{O}$. ^b Toluene- d_8 . ^c Benzene- d_6 . ^d Chloroform- d .

Scheme 2

coupling to both ^{195}Pt and ^{31}P —assigned to H_2 , H_6 of the transferred aryl group.

There is also indication of restricted rotation about the platinum–aryl bond in the products where $\text{R} = 2\text{-CH}_3$ and 2-CF_3 . Both of these complexes exhibit four distinct silicon-bound methyl groups. Both the Pt-CH_2 and the $\text{Si-CH}_2\text{-Si}$ groups have nonequivalent hydrogen pairs. The latter hydrogens exhibit two doublets with $J_{\text{H-H}} = 14$ Hz, while the two separate platinum–methylene signals are multiplets with platinum satellites. Remarkably, also, for $\text{R} = 2\text{-CF}_3$, both hydrogens of Pt-CH_2 experience (presumably through-space) coupling to ^{19}F , one to a greater extent than the other, implying closer approach to the *o*-trifluoromethyl group.

Table 6. ^1H NMR Characteristics of $\text{cis-Pt}(\text{CH}_2\text{-2-C}_6\text{H}_4\text{PPh}_2)(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PPh}_2\text{C}_6\text{H}_4\text{-2-Me})$

δ ^1H ppm ^a				
hydrocarbyl ligands ($J_{\text{Pt-H}}/\text{Hz}$ [assignment] ($J_{\text{P-H}}/\text{Hz}$				
Pt-CH ₂	Si-CH ₃	Ar-CH ₃	aromatic	phosphine [assignment]
1.25 (83.6) [CH ₂ -Si] (11.4)	0.37	2.08	7.02 m, [H ₃ , H ₅]; 7.06 m, [H ₄]; 7.76 dd, [H ₂ , H ₆] ($J_{\text{H}_2\text{-H}_3} = 7.1$ Hz)	6.75–6.90 m, [most meta and para phosphine signals]; 7.20 dd, [H ₃ -metallacycle]; 7.24–7.41 m, [H ₂ , H ₆ and H ₆ -metallacycle]; 7.44–7.48 m, [H ₂ , H ₆]
4.01 (76.0); [CH ₂ -P] (8.9)				

^a Benzene- d_6 .

Table 7. ^{13}C NMR Characteristics of $\text{cis-Pt}(\text{CH}_2\text{-2-C}_6\text{H}_4\text{PPh}_2)(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PPh}_2\text{C}_6\text{H}_4\text{-2-Me})$

δ ^{13}C ppm ^a				
hydrocarbyl ligands ($J_{\text{Pt-C}}/\text{Hz}$ [assignment] ($J_{\text{P-C}}/\text{Hz}$				
Pt-CH ₂	Si-CH ₃	Ar-CH ₃	aromatic	phosphine ligand ($J_{\text{Pt-C}}/\text{Hz}$ [assignment] ($J_{\text{P-C}}/\text{Hz}$
4.35, 5.63 (571.6) ($J_{\text{C-P}_{\text{trans}}} = 83.6$ Hz) ($J_{\text{C-P}_{\text{cis}}} = 5.1$ Hz) [CH ₂ -Si] 33.31, 34.82 (596.1) ($J_{\text{C-P}_{\text{trans}}} = 96.9$ Hz) [CH ₂ -P]	2.41 (27.2)	22.67 (8.8)	126.93 [C ₃ , C ₅]; 127.14 [C ₄]; 133.91 [C ₂ , C ₆]; 146.58 (24.7) [C ₁]	124.51 [C ₅ -P _A] (5.7); 125.14 [C ₅ -P _B]; 127.59 [C ₃ , C ₅ -P _B] (9.5); 127.88 [C ₃ , C ₅ -P _A] (9.4); 129.16, 129.24 [C ₄ -P _A , C ₄ -P _B]; 129.75 [C ₄ -P _B]; 130.18 [C ₄ -P _A]; 131.27 [C ₃ -P _A]; 131.46 [C ₃ -P _B] (9.7); 133.06 (13.3) [C ₂ , C ₆ -P _A] (11.8); 134.49 [C ₆ -P _B] (8.1); 134.58 [C ₆ -P _A]; 135.04 (14.6) [C ₂ , C ₆ -P _B] (12.0); 139.12 [C ₁ -P _B] (10.1); 140.02 (124.9) [C ₁ -P _A] (11.0); 142.38 [C ₂ -P _B] (10.3); 160.94 [C ₂ -P _A] (36.3)

^a Chloroform- d .

Further proof of regioselectivity is furnished by ^{13}C NMR spectroscopy (Table 2). For instance, $\text{cis-Pt}(\text{C}_6\text{H}_4\text{-2-Me})(\text{CH}_2\text{-SiMe}_2\text{CH}_2\text{SiMe}_2\text{C}_6\text{H}_4\text{-2-Me})(\text{PPh}_3)_2$ displays two aryl–methyl resonances. The downfield signal shows $^3J_{\text{Pt-C}}$, characteristic of an *o*-methyl substituent on the transferred aryl group (*m*- or *p*-methyl substituents reveal negligible $J_{\text{Pt-C}}$).

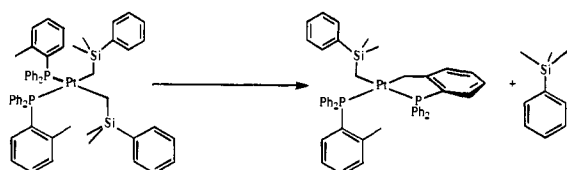
(d) $\text{cis-Pt}(\text{CH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_2\text{Ph})\text{L}_2$. The ^{31}P NMR spectrum of the single thermolytic product from $\text{cis-Pt}(\text{CH}_2\text{-SiMe}_3)(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PPh}_3)_2$ is very similar to that of $\text{cis-Pt}(\text{Ph})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PPh}_3)_2$ (Table 3). ^1H NMR measurements (Table 1) reveal the high field resonance (−0.88 ppm) characteristics of $\text{Si-CH}_2\text{-Si}$ and two Si-CH_3 environments in 3:2 ratio. In addition, while there is a Pt-CH_2 feature, there is no indication of Pt-CH_3 . The only significant product is, therefore, assigned the structure $\text{cis-Pt}(\text{Ph})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{-SiMe}_3)(\text{PPh}_3)_2$. On similar evidence (Tables 1 and 3), $\text{cis-Pt}(\text{CH}_2\text{-SiMe}_3)(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PMe}_3)_2$ rearranges to $\text{cis-Pt}(\text{Ph})(\text{CH}_2\text{-SiMe}_2\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)_2$.

(e) $\text{cis-Pt}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{PPh}_2\text{C}_6\text{H}_4\text{-2-Me})_2$. The thermolysis product from $\text{cis-Pt}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{PPh}_2\text{C}_6\text{H}_4\text{-2-Me})_2$ does not have the same ^{31}P NMR characteristics as those obtained from β -phenyl transfer. Two distinct, mutually *cis*, P-resonances are observed, and the $^1J_{\text{Pt-P}}$ values of 1891 and 2170 Hz are indicative of alkyl and silylalkyl fragments *trans* to phosphorus. In contrast to $\text{cis-Pt}(\text{Ph})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{Ph})\text{L}_2$, there is a substantial chemical shift difference between the two phosphorus nuclei. The relative upfield shift [Δ_R] of +19.3 ppm implies the formation of a five-membered phosphametallacycle.²⁵

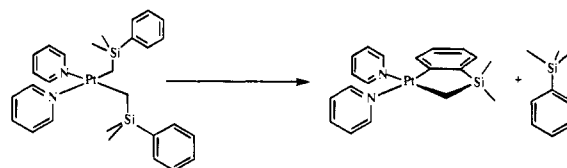
Characteristic ^1H NMR features (Table 6) of this complex are a high-field singlet due to Si-Me groups, an apparent quartet with ^{195}Pt satellites, typical for Pt-CH_2 , and a low-field singlet, which can be attributed to CH_3 hydrogens of an *o*-tolylphosphine group. Additionally, a doublet with satellites at ca. 4.0 ppm, which corresponds to two hydrogens, strongly implies a second platinum-bound methylene group.

Further, the ^{13}C NMR spectrum (Table 7) exhibits several interesting features, in addition to resonances typical of a coordinated silaneophyl skeleton, notably the doublet centered at 39.0 ppm, which arises from a Pt-CH_2 group coupled to a

Scheme 3



Scheme 4



trans-phosphorus nucleus. The aromatic region is complicated, but assignments due to aromatic ring carbons coupled to platinum and/or phosphorus can be made. A multiplet at *ca.* 140 ppm with $J_{\text{Pt-C}} = 124.9$ Hz and $J_{\text{P-C}} = 11.0$ Hz may be attributed to C₁ of the metallated ring; similarly, the doublet at 161 ppm with $J_{\text{Pt-C}} = 36.3$ Hz is due to C₂ bound to P of the metallacycle. C₃, C₅, and C₆ of this ring also appear as doublets coupled to ³¹P.

The new complex is identified as *cis*-Pt(CH₂-2-C₆H₄PPH₂)(CH₂-SiMe₂Ph)(PPH₂C₆H₄-2-Me), a five-membered metallacycle formed as a result of aliphatic δ-C-H activation on an *o*-CH₃ on the phosphine, with concomitant loss of 1 equiv of trimethylphenyl-

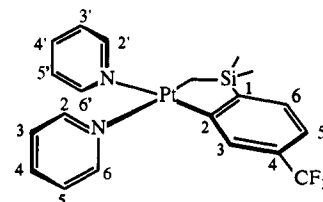


Figure 2. NMR numbering conventions for platinum-silaindanes.

silane (Scheme 3). The presence of the latter product was confirmed by GCMS.

(f) *cis*-Pt(CH₂SiMe₂C₆H₄-4-R)₂py₂. These complexes were considerably more labile than their phosphine analogues. Indeed, *cis*-Pt(CH₂SiMe₂C₆H₄-4-CF₃)₂(py)₂ was too labile for isolation and was generated *in situ* (see Experimental Section). Ultimately, in consequence, only product analyses were carried out. At (or above) ambient temperature, toluene solutions of *cis*-Pt(CH₂-SiMe₂C₆H₄-4-R)₂(py)₂ [R = H, OMe, Bu^t, F, CF₃]—like their carbon analogues, *cis*-Pt(CH₂CMe₂Ph)₂L₂—undergo δ-aromatic C-H bond activation, generating the corresponding platinum-silaindane and 1 equiv of trimethylarylsilane (Scheme 4). *cis*-Pt(CH₂SiMe₂-2-C₆H₄)(py)₂ and *cis*-Pt(CH₂SiMe₂-2-C₆H₃-4-CF₃)(py)₂ could be isolated as pale yellow and white crystalline solids, respectively. Other metallacycles were identified in solution only, by their characteristic ¹H NMR spectra. (For Table 8, the numbering convention previously adopted¹⁰ for platinum-silaindanes appears in Figure 2. Hydrogen and carbon atoms *trans* to the aryl fragment are designated H_{*n*'} and C_{*n*'}, respectively.)

Table 8. ¹H NMR Characteristics of *cis*-Bis(pyridine)-1-platina-3-silaindanes and Related Complexes

complex	δ ¹ H ppm			
	hydrocarbyl ligands ($J_{\text{Pt-H}}$)/Hz [assignment]			ancillary ligands ($J_{\text{Pt-H}}$)/Hz [assignment]
	Pt-CH ₂	Si-CH ₃	aromatic substituents	
(py) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₄) ^a	0.86 (100.4)	0.07	7.01–7.19 m, [H ₄ , H ₅]; 7.46 dd, [H ₆] ($J_{\text{H}_2-\text{H}_4} = 7.5$ Hz); 7.68 dd, (67.0) [H ₃] ($J_{\text{H}_2-\text{H}_4} = 7.9$ Hz)	6.20 m, [H ₃ , H ₅] ($J_{\text{H}_2-\text{H}_4} = 6.4$ Hz); 6.39 m, [H _{3'} , H _{5'}] ($J_{\text{H}_2-\text{H}_4} = 6.4$ Hz); 6.65 m, [H ₄] ($J_{\text{H}_2-\text{H}_4} = 1.6$ Hz); 6.77 m, [H _{4'}] ($J_{\text{H}_2-\text{H}_4} = 1.4$ Hz); 8.31 dd, (25.7) [H ₂ , H ₆] ($J_{\text{H}_2-\text{H}_3} = 7.6$ Hz); 8.47 dd, (20.0) [H ₂ , H _{6'}] ($J_{\text{H}_2-\text{H}_3} = 7.6$ Hz)
(py- <i>d</i> ₅) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₄) ^b	0.97 (98.4)	0.31	7.36–7.43 m, [H ₄ , H ₅ , H ₆]; 7.89 dd, (62.4) [H ₃] ($J_{\text{H}_2-\text{H}_4} = 7.9$ Hz)	
(py) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₃ -4-OMe) ^a	1.09 (100.1)	0.45	3.41 [O-CH ₃]; 6.98 d, [H ₅] ($J_{\text{H}_2-\text{H}_4} = 7.5$ Hz); 7.56 dd [H ₆]; 7.75 d, (67.1) [H ₃] ($J_{\text{H}_2-\text{H}_3} = 7.9$ Hz)	6.28 m, [H ₃ , H ₅] ($J_{\text{H}_2-\text{H}_4} = 7.2$ Hz); 6.45 m, [H _{3'} , H _{5'}] ($J_{\text{H}_2-\text{H}_4} = 7.1$ Hz); 6.73 m, [H ₄] ($J_{\text{H}_2-\text{H}_4} = 1.0$ Hz); 6.82 m, [H _{4'}] ($J_{\text{H}_2-\text{H}_4} = 0.9$ Hz); 8.45 dd, (24.1) [H ₂ , H ₆] ($J_{\text{H}_2-\text{H}_3} = 7.5$ Hz); 8.62 dd, (20.8) [H ₂ , H _{6'}] ($J_{\text{H}_2-\text{H}_3} = 7.4$ Hz)
(py) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₃ -4-Bu ^t) ^a	1.11 (100.3)	0.44	1.38 [C-CH ₃]; 7.28 dd, [H ₅]; ($J_{\text{H}_2-\text{H}_4} = 7.6$ Hz); 7.64 d, [H ₆]; 7.83 d, (63.2) [H ₃] ($J_{\text{H}_2-\text{H}_3} = 7.7$ Hz)	6.19 m, [H ₃ , H ₅] ($J_{\text{H}_2-\text{H}_4} = 7.9$ Hz); 6.42 m, [H _{3'} , H _{5'}] ($J_{\text{H}_2-\text{H}_4} = 8.0$ Hz); 6.67 m, [H ₄] ($J_{\text{H}_2-\text{H}_4} = 2.0$ Hz); 6.81 m, [H _{4'}] ($J_{\text{H}_2-\text{H}_4} = 1.4$ Hz); 8.44 dd, (22.1) [H ₂ , H ₆] ($J_{\text{H}_2-\text{H}_3} = 8.0$ Hz); 8.59 dd, (23.9) [H ₂ , H _{6'}] ($J_{\text{H}_2-\text{H}_3} = 8.0$ Hz)
(py) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₃ -4-F) ^a	0.99 (100.4)	0.22	7.17 m, [H ₅] ($J_{\text{H}_2-\text{H}_4} = 7.0$ Hz) ($J_{\text{H-F}} = 14.1$ Hz); 7.40 m, [H ₆] ($J_{\text{H-F}} = 7.5$ Hz); 7.71 m, (64.8) [H ₃] ($J_{\text{H}_2-\text{H}_3} = 7.8$ Hz) ($J_{\text{H-F}} = 14.9$ Hz)	6.15 m, [H ₃ , H ₅] ($J_{\text{H}_2-\text{H}_4} = 7.8$ Hz); 6.24 m, [H _{3'} , H _{5'}] ($J_{\text{H}_2-\text{H}_4} = 7.7$ Hz); 6.52 m, [H ₄] ($J_{\text{H}_2-\text{H}_4} = 1.1$ Hz); 6.69 m, [H _{4'}] ($J_{\text{H}_2-\text{H}_4} = 1.5$ Hz); 8.29 dd, (35.3) [H ₂ , H ₆] ($J_{\text{H}_2-\text{H}_3} = 7.9$ Hz); 8.62 dd, (19.9) [H ₂ , H _{6'}] ($J_{\text{H}_2-\text{H}_3} = 7.7$ Hz)
(py) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₃ -4-CF ₃) ^a	1.00 (100.0)	0.24	7.31–7.37 m, [H ₅ , H ₆]; 7.83 d, (66.8) [H ₃] ($J_{\text{H}_2-\text{H}_3} = 7.8$ Hz)	6.20 m, [H ₃ , H ₅] ($J_{\text{H}_2-\text{H}_3} = 6.4$ Hz); 6.42 m, [H _{3'} , H _{5'}]; 6.68 m, [H ₄] ($J_{\text{H}_2-\text{H}_4} = 7.7$ Hz); 6.78 m, [H _{4'}]; 8.18 m, (30.0) [H ₂ , H ₆]; 8.53 dd, (25.6) [H ₂ , H _{6'}]
(py) ₂ Pt(C ₆ H ₄ -2-Me) (CH ₂ SiMe ₂ CH ₂ SiMe ₂ C ₆ H ₄ -2-Me) ^a	0.78 (100.5)	-0.10 0.22 0.36 (CH ₃) 0.06	2.36 [CH ₃]; 2.79 [CH ₃]; 6.93–7.13 m, [H ₄ , H _{4'} , H ₅ , H _{5'}]; 7.50 dd, [H _{6'}] ($J_{\text{H}_2-\text{H}_4} = 7.0$ Hz); 7.98 dd, (67.0) [H ₆] ($J_{\text{H}_2-\text{H}_4} = 12.8$ Hz)	6.00 m, [H ₃ , H ₅] ($J_{\text{H}_2-\text{H}_4} = 6.4$ Hz); 6.27 m, [H _{3'} , H _{5'}] ($J_{\text{H}_2-\text{H}_4} = 6.4$ Hz); 6.50 m, [H ₄] ($J_{\text{H}_2-\text{H}_4} = 1.2$ Hz); 6.65 m, [H _{4'}] ($J_{\text{H}_2-\text{H}_4} = 1.1$ Hz); 8.18 dd, (26.6) [H ₂ , H ₆] ($J_{\text{H}_2-\text{H}_3} = 7.5$ Hz); 8.38 dd, (18.2) [H ₂ , H _{6'}] ($J_{\text{H}_2-\text{H}_3} = 7.5$ Hz)

^a Toluene-*d*₈. ^b Pyridine-*d*₅.

Common to all these species is a singlet due to silicon–methyl groups (0.0–0.5 ppm) and a 1:4:1 pattern at ca. 1.0 ppm originating from the Pt–CH₂ group ($^2J_{\text{Pt-H}} \approx 100$ Hz). The most characteristic feature of the aromatic region is a doubled doublet (7.7–7.9 ppm) with platinum satellites, assigned to H₃ of the metallacyclic ring. Here, $^3J_{\text{Pt-H}} \approx 62.0$ – 67.0 Hz, similar to that for *cis*-PtAr₂(py)₂ [Ar = Ph, C₆H₄-4-Bu^t, C₆H₄-4-CF₃].²⁶ The asymmetry of these complexes is clear from the pyridine signals, which reveal six environments, three for each ring. The doubled doublets at lowest field both show coupling to platinum. The two values of $^3J_{\text{Pt-H}}$ are ca. 20 and 25 Hz, respectively—the larger assigned to the ligand *trans* to the alkyl moiety. A useful feature of the aromatic region of *cis*-Pt(CH₂SiMe₂-2-C₆H₃-4-CF₃)(py)₂ is splitting of the resonances of the pyridine ring *trans* to Pt–methylene by long-range coupling to ¹⁹F, which allows unequivocal assignment of pyridine resonances in this case.

The ¹³C NMR spectrum of *cis*-Pt(CH₂SiMe₂-2-C₆H₄)(py)₂ (Table 9) also demonstrates the nonequivalence of the ligands. Both C₂(C₆) and C₃(C₅) show interactions with ¹⁹⁵Pt; the larger coupling constant in each case is assigned to pyridine *trans* to the alkyl group, consistent with a *trans*-influence weaker than that of an aryl group.

All of this series of *para*-substituted aromatic rings underwent facile metallacyclization. In contrast, *cis*-Pt(C₆H₄-2-Me)(CH₂SiMe₂CH₂SiMe₂C₆H₄-2-Me)(py)₂ is the only apparent product from the reaction of *cis*-Pt(CH₂SiMe₂C₆H₄-2-Me)₂(cod) with pyridine. In evidence, the ¹H NMR spectrum indicates three silicon–methyl environments in the ratio 2:1:1. Additionally, a less intense signal (0.06 ppm, 2H) may be attributed to a Si–CH₂–Si fragment. Two singlets (2.36 and 2.79 ppm) due to arene-bound methyl groups are also evident. The two most characteristic resonances in the aromatic region are the doubled doublet for H₆ and a lower field resonance ($^3J_{\text{Pt-H}} = 67.0$ Hz) due to H₆. Signal-broadening for two of the Si–CH₃ groups and one aryl–methyl group was observed as temperature was increased, consistent with restricted rotation about the platinum–aryl bond, as noted for the triphenylphosphine analogue. These observations are consistent with β-aryl transfer, similar to *cis*-Pt(CH₂SiMe₂-Ar)₂(PR₃)₂.

The most notable feature of the ¹³C NMR spectrum is four Si–CH_n signals, three of which are coupled to ¹⁹⁵Pt (Table 9). The largest coupling is similar to that observed for Si–CH₂–Si in the phosphine analogues. The other two with smaller $^3J_{\text{Pt-C}}$ are attributed to Si–Me groups nearest to platinum. One aryl–methyl group also exhibits $^3J_{\text{Pt-C}}$ (31.3 Hz).

2. Kinetic Analyses. (A) Migratory Isomerizations. The kinetics of these reactions were monitored using either ³¹P or, where this was impractical, ¹H NMR spectroscopy. In the latter

Table 10. Rate Data for Thermolytic Rearrangement of *cis*-Pt(CH₂SiR₃)₂L₂

L	R	T/K	10 ⁵ k _{obs} /s ⁻¹
PPh ₃	Me	373.0	1.67 ± 0.09
PPh ₃	Me	375.5	2.49 ± 0.08
PPh ₃	Me	378.0	3.35 ± 0.09
PPh ₃	Me	380.5	4.45 ± 0.11
PPh ₃	Me	383.0	6.68 ± 0.10
PPh ₃	Me	385.5	9.91 ± 0.11
PPh ₃	Me	390.0	17.37 ± 0.10
PPh ₃	Me- <i>d</i> ₃	378.0	1.95 ± 0.01
PPh ₃ - <i>d</i> ₁₅	Me	385.5	4.77 ± 0.12
PEt ₃	Me	373.0	1.83 ± 0.07
PEt ₃	Me	385.5	2.25 ± 0.11
PEt ₃	Me	388.0	2.83 ± 0.12
PEt ₃	Me	393.0	5.52 ± 0.09
PEt ₃	Me	398.0	9.61 ± 0.10
PEt ₃	Me- <i>d</i> ₃	398.0	7.93 ± 0.11
PEt ₃	Me	398.0	3.67 ± 0.04 ^a
PEt ₃	Me	398.0	2.66 ± 0.08 ^b
PEt ₃	Me	398.0	2.11 ± 0.08 ^c
PPh ₂ Me	Me	373.0	0.73 ± 0.12
PPh ₂ Me	Me	378.0	1.22 ± 0.12
PPh ₂ Me	Me	381.0	2.05 ± 0.11
PPh ₂ Me	Me	385.0	3.70 ± 0.06
PPh ₂ Me	Me	391.0	7.72 ± 0.05
PPh ₂ Me	Me- <i>d</i> ₃	391.0	5.08 ± 0.11

^a 0.010 mol·dm⁻³ added PEt₃. ^b 0.015 mol·dm⁻³ added PEt₃. ^c 0.020 mol·dm⁻³ added PEt₃.

case, reaction was followed by comparing the relative integrals arising from silicon-bound methyl groups in parent and product complexes.¹⁰ The rearrangements were all kinetically first order in organoplatinum substrate for at least three half-lives, and their rates were independent of platinum concentration in the range 0.001–0.05 mol·dm⁻³. Three types of kinetic variation studies were employed to illuminate the mechanisms. The effects on reaction rate of (a) temperature, (b) concentration of ancillary ligand, L, and (c) substituent variations were examined in turn.

(a) Rate Dependence on Temperature. Representative data for β-methyl and β-phenyl migrations in *cis*-Pt(CH₂SiMe₂R)₂L₂ at various temperatures appear in Tables 10 and 11, respectively. The temperature dependence of k_{obs} for these systems conforms to the Arrhenius relationship, from which activation parameters ΔH[‡]_{obs} and ΔS[‡]_{obs} were extracted (Table 12). Several salient features are apparent. First, from comparison of absolute rates of rearrangements of *cis*-Pt(CH₂SiMe₃)₂L₂ and *cis*-Pt(CH₂SiMe₂-Ph)₂L₂, aryl migration appears to be quantitatively easier than methyl migration. All the reactions, however, are characterized by similar activation enthalpies and large, positive activation

Table 9. ¹³C NMR Characteristics of *cis*-Pt(CH₂SiMe₂-2-C₆H₄)(py)₂ and Pt(C₆H₄-2-Me)(CH₂SiMe₂CH₂SiMe₂C₆H₄-2-Me)(py)

complex	δ ¹³ C ppm			
	hydrocarbyl ligands ($J_{\text{Pt-C}}$)/Hz [assignment]			ancillary ligands ($J_{\text{Pt-C}}$)/Hz [assignment]
	Pt–CH ₂	Si–CH _n	aromatic	
(py) ₂ Pt(CH ₂ SiMe ₂ C ₆ H ₄) ^a	-8.56 (771.0)	4.29 (33.3) [CH ₃]	121.92 (12.9) [C ₆]; 126.80 (77.8) [C ₄]; 133.94 [C ₅]; 139.36 (33.5) [C ₃]; 142.04 (28.3) [C ₁]; 143.29 (841.2) [C ₂]	124.75 (20.6) [C ₃ , C ₅]; 124.91 (14.5) [C ₃ , C ₅]; 135.20 [C ₄]; 135.67 [C ₄]; 150.97 (14.2) [C ₂ , C ₆]; 151.57 (16.5) [C ₂ , C ₆]
(py) ₂ Pt(C ₆ H ₄ -2-Me)(CH ₂ SiMe ₂ CH ₂ SiMe ₂ C ₆ H ₄ -2-Me) ^a	-11.68 (772.0)	1.52 3.56 (27.0) 4.30 (23.9) (CH ₃) 6.30 (45.2) [CH ₂]	14.09 [CH ₃]; 22.68 (31.3) [CH ₃]; 122.00 [C ₄]; 124.30 [C ₄]; 125.03 (31.5) [C ₅]; 127.22 [C ₅]; 128.74 [C ₃]; 130.17 [C ₆]; 134.89 (32.4) [C ₃]; 139.29 (33.4) [C ₆]; 143.51 (19.6) [C ₂]; 143.68 [C ₂]; 143.82 (831.9) [C ₁]; 150.29 [C ₁]	124.60 (20.1) [C ₃ , C ₅]; 124.90 (19.3) [C ₃ , C ₅]; 134.89 [C ₄]; 134.97 [C ₄]; 150.56 (17.2) [C ₂ , C ₆]; 151.58 (15.0) [C ₂ , C ₆]

^a Benzene-*d*₆.

Table 11. Rate Data for Thermolytic Rearrangement of Pt(R)(CH₂SiMe₂Ph)L₂

R	L	[L]/M	T/K	10 ⁵ k _{obs} /s ⁻¹
CH ₂ SiMe ₂ Ph	PMe ₂ Ph	0.0	388.0	1.75 ± 0.07
CH ₂ SiMe ₂ Ph	PMe ₂ Ph	0.0	390.5	2.58 ± 0.11
CH ₂ SiMe ₂ Ph	PMe ₂ Ph	0.0	393.0	3.44 ± 0.04
CH ₂ SiMe ₂ Ph	PMe ₂ Ph	0.0	395.5	4.50 ± 0.12
CH ₂ SiMe ₂ Ph	PMe ₂ Ph	0.0	398.0	6.85 ± 0.09
CH ₂ SiMe ₂ Ph	PMe ₂ Ph	0.0	403.0	13.10 ± 0.10
CH ₂ SiMe ₂ Ph- <i>d</i> ₅ ^a	PMe ₂ Ph	0.0	125.0	5.59 ± 0.09
CH ₂ SiMe ₂ Ph	PPh ₃	0.0	344.0	0.85 ± 0.06
CH ₂ SiMe ₂ Ph	PPh ₃	0.0	348.0	1.60 ± 0.05
CH ₂ SiMe ₂ Ph	PPh ₃	0.0	350.5	2.64 ± 0.03
CH ₂ SiMe ₂ Ph	PPh ₃	0.0	353.0	3.65 ± 0.06
CH ₂ SiMe ₂ Ph	PPh ₃	0.0	355.5	5.39 ± 0.08
CH ₂ SiMe ₂ Ph	PPh ₃	0.0	358.0	8.61 ± 0.07
CH ₂ SiMe ₂ Ph- <i>d</i> ₅ ^a	PPh ₃	0.0	358.0	7.12 ± 0.09
CH ₂ SiMe ₂ Ph	PPh ₃ - <i>d</i> ₁₅	0.0	358.0	5.86 ± 0.12
CH ₂ SiMe ₂ Ph	PPh ₃	0.025	388.0	5.85 ± 0.06
CH ₂ SiMe ₂ Ph	PPh ₃	0.05	388.0	3.81 ± 0.07
CH ₂ SiMe ₂ Ph	PPh ₃	0.075	388.0	2.79 ± 0.07
CH ₂ SiMe ₂ Ph	PPh ₃	0.1	388.0	2.09 ± 0.08
CH ₂ SiMe ₂ Ph	P-4-tol ₃	0.0	358.0	1.36 ± 0.05
CH ₂ SiMe ₂ Ph	P-4-tol ₃	0.0	360.5	2.41 ± 0.05
CH ₂ SiMe ₂ Ph	P-4-tol ₃	0.0	365.5	4.91 ± 0.08
CH ₂ SiMe ₂ Ph	P-4-tol ₃	0.0	368.0	6.57 ± 0.11
CH ₂ SiMe ₂ Ph	P-4-tol ₃	0.0	370.5	9.84 ± 0.10
CH ₂ SiMe ₂ Ph	PMe ₃	0.0	403.0	3.53 ± 0.09
CH ₂ SiMe ₂ Ph	PEt ₃ ^b	0.0	373.0	4.09 ± 0.13
CH ₂ SiMe ₂ Ph	PPh ₂ C ₆ H ₄ -2-CF ₃	0.15	298.0	0.33 ± 0.06
CH ₂ SiMe ₃	PPh ₃	0.0	358.0	2.12 ± 0.07
CH ₂ SiMe ₃	PPh ₃	0.0	363.0	4.71 ± 0.09
CH ₂ SiMe ₃	PPh ₃	0.0	365.0	5.05 ± 0.08
CH ₂ SiMe ₃	PPh ₃	0.0	368.0	9.20 ± 0.13
CH ₂ SiMe ₃ ^a	PPh ₃	0.0	368.0	7.77 ± 0.09

^a Other alkyl ligand is CH₂SiMe₂Ph-*d*₅. ^b Rearranges to the *trans* product.

entropies. Moreover, although the reaction outcomes differ, these data are broadly comparable to corresponding parameters for thermolytic rearrangements of the purely carboniferous analogues, notably, *cis*-Pt(CH₂CMe₃)₂(PEt₃)₂ [$\Delta H^\ddagger_{\text{obs}} = 203 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger_{\text{obs}} = +130 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]⁷ and *cis*-Pt(CH₂CMe₂Ph)₂(PEt₃)₂ [$\Delta H^\ddagger_{\text{obs}} = 174 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger_{\text{obs}} = +248 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$].^{10a}

(b) **Rate Dependence on Phosphine Concentration.** Inclusion of PPh₃ in solutions of *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃)₂ markedly retards rearrangement. Correlation of 1/*k*_{obs} with phosphine concentration is linear, with a non-zero intercept (Figure 3). Exactly parallel results were obtained for *cis*-Pt(CH₂SiMe₃)₂(PEt₃)₂ in the presence of additional PEt₃. Analogous rate dependencies have already been noted for cyclometalations of related complexes *cis*-Pt(CH₂CMe₃)₂L₂⁷ and *cis*-Pt(CH₂CMe₂-Ph)₂L₂.^{10a}

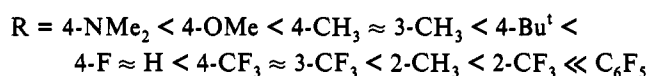
(c) **Rate Dependence on Substituent Variation.** (i) **Phosphine Substituents.** Ancillary ligand variations may have profound effects on rearrangement rates and pathways for dialkylplatinum systems. For *cis*-Pt(CH₂SiMe₃)₂L₂, reactivity increases in the order L = PMe₃ < PEt₃ < PPh₂Me < PPh₃. Activation parameters derived from Arrhenius correlations are presented in Table 12. The corresponding trend in lability of *cis*-Pt(CH₂-SiMe₂Ph)₂L₂ is L = PMe₃ < PEt₃ < PPhMe₂ < P(4-tolyl)₃ < PPh₃ < dcpe.

(ii) **Deuterium Labeling.** Besides isotopic substitution at selected sites being useful as a probe of migratory destination, the deuterium isotope effect on the rate (*k*^H_{obs}/*k*^D_{obs}) can provide valuable information about the intimate nature of the reaction mechanism.²⁷ Deuterium labeling was effected at two molecular

sites, namely, on the silylmethyl fragment and on the phosphine ligand. Rates of rearrangement were monitored for *cis*-Pt[CH₂-Si(CD₃)₃]₂L₂ [L = PEt₃, PPh₂Me, PPh₃] and *cis*-Pt(CH₂-SiMe₂C₆D₅)₂L₂ [L = PMePh₂, PPh₃] as well as for *cis*-Pt(CH₂SiMe₃)₂(PPh₃-*d*₁₅)₂ and *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃-*d*₁₅)₂. These measurements, recorded in Tables 10 and 11, show comparably small, though significant, isotopic inhibition upon deuteration of both the (trimethylsilyl)methyl and the silaneophyl ligands and, generally, somewhat larger effects in each case for phosphine deuteration (*vide infra*).

(iii) **Aromatic Ring Substituents.** Rearrangement kinetics were studied by ¹H or ¹⁹F NMR for *cis*-Pt(CH₂SiMe₂C₆H₄-4-R)₂(PPh₃)₂ [R = Bu^t, F] in detail. For the remaining complexes, the rate of reaction was measured at only one temperature. The reactions were first order in substrate for at least two half-lives. Rate data are presented in Table 13. Activation parameters appear in Table 12 and are very similar to those determined for rearrangement of *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃)₂.

The order of increasing reactivity for these substituted silaneophyl groups is as follows:



Linear free energy relationships (LFERs) have often been employed in rate-structure correlations of aromatic reactivity, for which substituent effects are most commonly assessed by the LFER expressed in the Hammett-Taft equation.^{28,29} The data best fit a correlation of log *k*/*k*₀ [at 85°C] against Hammett constants, σ_p , σ_m (Figure 4; greater scatter was observed with Taft σ_p^0 , σ_p^+ , σ_p^- parameters). An estimate of the substituent susceptibility of the reaction, $\rho = +0.9$, emerges from these data.

(B) **Cyclometalations.** The metallacyclization of *cis*-Pt(CH₂-SiMe₂Ph)₂(PPh₂-2-tol)₂ was monitored in the temperature range 32.5–45.0°C by ³¹P NMR. Appearance of phenyltrimethylsilane could be quantified by ¹H NMR or by HPLC. No product attributable to β-aryl migration was observed under these conditions. A first-order rate dependence on platinum substrate was observed for at least three half-lives. Rate data are presented in Table 14. The effect of temperature variation on the observed cyclometalation rate constant, *k*_{obs}, displayed a linear Arrhenius correspondence. Estimated activation parameters were $\Delta H^\ddagger_{298} = 102.7 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta S^\ddagger = 1.0 \pm 6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $\Delta G^\ddagger_{298} = 102.4 \pm 3 \text{ kJ}\cdot\text{mol}^{-1}$. Addition of diphenyl-2-tolylphosphine slowed metallacyclization, but the effect was not quantified.

Quantitative kinetic analyses of the cyclometalations of *cis*-Pt(CH₂SiMe₂Ar)₂(py)₂ also were not pursued, mainly because of their high lability, even at ambient temperatures, and poor kinetic reproducibility in preliminary studies.

Discussion

(1) **Migratory Isomerizations.** (a) **The Nature of C Transfer.** In the rearrangement of *cis*-Pt(CH₂SiMe₃)₂L₂, it was first important to distinguish which of the two Si-C bonds cleaves during rearrangement. The deuteration studies have established beyond doubt that the transferred substituent cannot originate as a platinum-bound methylene unit but—irrespective of mechanism—reflects an intact methyl migration from silicon. Formation of the new Pt-C bond, however, might occur, in principle, by attack of the metal on either a C-H bond or the C-Si bond of a methyl substituent (Scheme 5). The former option generates a platinasilacyclobutane which—rather than (the expected) reductive elimination of tetramethylsilane—could

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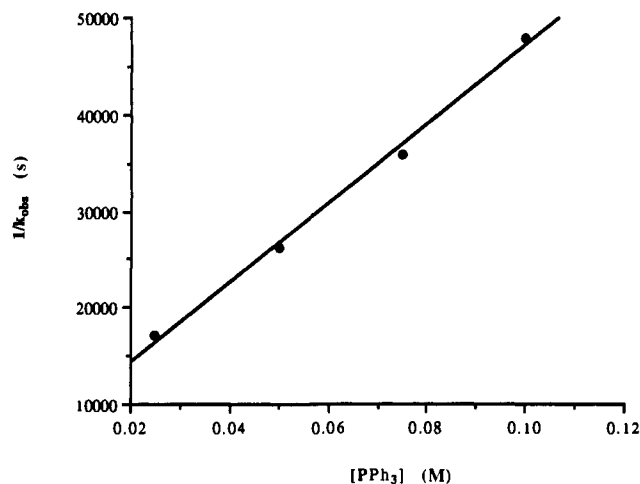
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(29) Where *k*₀ = rate of unsubstituted species at temperature *T*, *k* = rate of substituted species at *T*, ρ = reaction susceptibility constant, σ = substituent constant.

Table 12. Activation Parameters for Formation of $\text{Pt}(\text{R}')(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{R})\text{L}_2$

R	R'	L	E_a (kJ·mol ⁻¹)	A	$\Delta H^\ddagger_{298\text{K}}$ (kJ·mol ⁻¹)	ΔS^\ddagger (J·mol ⁻¹ ·K ⁻¹)	ΔG^\ddagger (kJ·mol ⁻¹)	range ^a (K)
Me	Me	PEt ₃	145 ± 6	9.81 × 10 ¹⁴	143 ± 6	34 ± 15	131 ± 11	25
Me	Me	PPh ₂ Me	163 ± 8	5.45 × 10 ¹⁷	161 ± 8	86 ± 12	135 ± 12	18
Me	Me	PPh ₃	164 ± 2	1.43 × 10 ¹⁸	161 ± 3	94 ± 9	133 ± 6	17
Ph	Ph	PPh ₃	168 ± 2	2.55 × 10 ²⁰	166 ± 3	137 ± 9	125 ± 6	14
4-C ₆ H ₄ F	4-C ₆ H ₄ F	PPh ₃	169 ± 3	4.15 × 10 ²⁰	167 ± 3	142 ± 8	125 ± 5	10
4-C ₆ H ₄ Bu ^t	4-C ₆ H ₄ Bu ^t	PPh ₃	169 ± 4	2.26 × 10 ²⁰	167 ± 4	137 ± 8	126 ± 6	10
Ph	Ph	P(4-tolyl) ₃	167 ± 9	3.64 × 10 ¹⁹	165 ± 9	121 ± 9	129 ± 12	13
Ph	Ph	PPhMe ₂	173 ± 5	3.39 × 10 ¹⁸	170 ± 5	101 ± 6	140 ± 7	15
Me	Ph	PPh ₃	168 ± 3	5.70 × 10 ¹⁹	166 ± 3	125 ± 5	129 ± 5	10

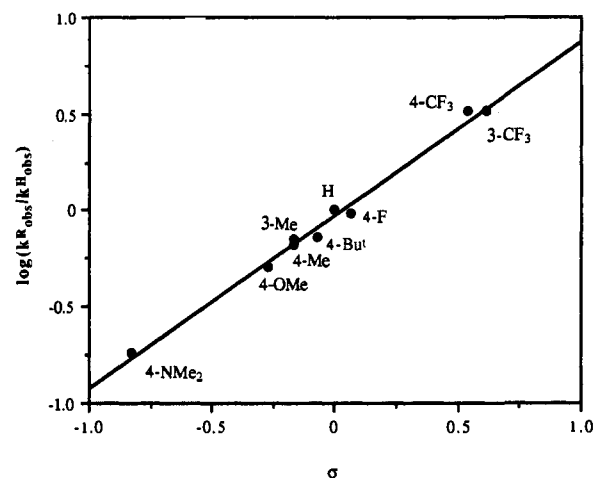
^a Over which activation parameters were measured.**Figure 3.** Reciprocal correlation of rate with concentration of added PPh₃ for rearrangement of *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃)₂.**Table 13.** Rate Data for Thermolytic Rearrangement of *cis*-Pt(CH₂SiMe₂Ar)₂(PPh₃)₂

Ar	T/K	10 ⁵ k _{obs} /s ⁻¹
C ₆ H ₄ -2-Me	338.0	3.13 ± 0.06
C ₆ H ₄ -2-CF ₃	338.0	20.42 ± 0.13
Ph	338.0	0.30 ± 0.07 ^a
C ₆ H ₄ -3-Me	363.0	15.85 ± 0.11
C ₆ H ₄ -3-CF ₃	363.0	30.53 ± 0.10
Ph	363.0	18.16 ± 0.09 ^a
C ₆ H ₄ -4-Me	358.0	7.18 ± 0.10
C ₆ H ₄ -4-OMe	358.0	6.41 ± 0.06
C ₆ H ₄ -4-Bu ^t	348.0	1.26 ± 0.08
C ₆ H ₄ -4-Bu ^t	350.5	1.88 ± 0.05
C ₆ H ₄ -4-Bu ^t	353.0	3.20 ± 0.09
C ₆ H ₄ -4-Bu ^t	355.5	4.68 ± 0.11
C ₆ H ₄ -4-Bu ^t	358.0	7.49 ± 0.11
C ₆ H ₄ -4-F	348.0	1.63 ± 0.08
C ₆ H ₄ -4-F	350.5	2.32 ± 0.06
C ₆ H ₄ -4-F	353.0	3.61 ± 0.09
C ₆ H ₄ -4-F	355.5	5.26 ± 0.10
C ₆ H ₄ -4-F	358.0	8.48 ± 0.12
C ₆ H ₄ -4-CF ₃	358.0	14.40 ± 0.08
C ₆ H ₄ -4-NMe ₂	358.0	4.12 ± 0.09

^a Calculated from Arrhenius correlation.

rearrange to the observed product, for instance, by a ring-scission reaction analogous to that invoked in the metallacycle-mediated mechanism for alkene dimerization. This step would have to be exclusively regioselective, though, to account for the formation only of *cis*-Pt(CD₃)[CH₂Si(CD₃)₂CH₂Si(CD₃)₃]L₂ from *cis*-Pt[CH₂Si(CD₃)₃]L₂. A simpler explanation is concerted methyl migration from Pt to Si, generating the η²-silene complex directly.

In the formation of *cis*-Pt(Ar)(CH₂SiMe₂CH₂SiMe₂Ar)L₂ by aryl migration, the carbon initially bound to Si is, unequivocally, ultimately bound to Pt. This universal regioselectivity of aryl-transfer rules out any corresponding pathway in which aromatic C-metalation precedes Si-C scission—as has been observed

**Figure 4.** Hammett correlation for aryl migration in *cis*-Pt(CH₂SiMe₂-*n*-C₆H₄R)₂(PPh₃)₂.**Table 14.** Rate Data for Thermolytic Rearrangement of Pt(CH₂SiMe₂Ph)₂(PPh₂-2-C₆H₄Me)₂

[L]/mol·dm ⁻³	T/K	10 ⁵ k _{obs} /s ⁻¹
0.00	305.5	1.96 ± 0.09
0.00	308.0	2.62 ± 0.12
0.00	310.5	3.92 ± 0.07
0.00	313.0	5.11 ± 0.07
0.00	315.5	7.27 ± 0.09
0.00	318.0	10.01 ± 0.11
0.05	338.0	5.96 ± 0.08

recently in a related system³⁰—and strongly indicates the concerted route. The broad similarity in activation parameters (and other characteristics, *vide infra*) for all the observed carbon transfers—irrespective of variations in silylmethyl and ancillary ligands—argues persuasively for a common mechanism. This general rearrangement, therefore, is attributed to a β-carbon transfer to the metal, with subsequent migration of the other silylmethyl substituent to the silicon center on the resulting coordinated silene.³¹ Silene–metal complexes have been proposed previously as intermediates in a variety of rearrangements of both (silylmethyl) and (methylsilyl)metal complexes.³² More recently, a number of isolable examples have been reported³³

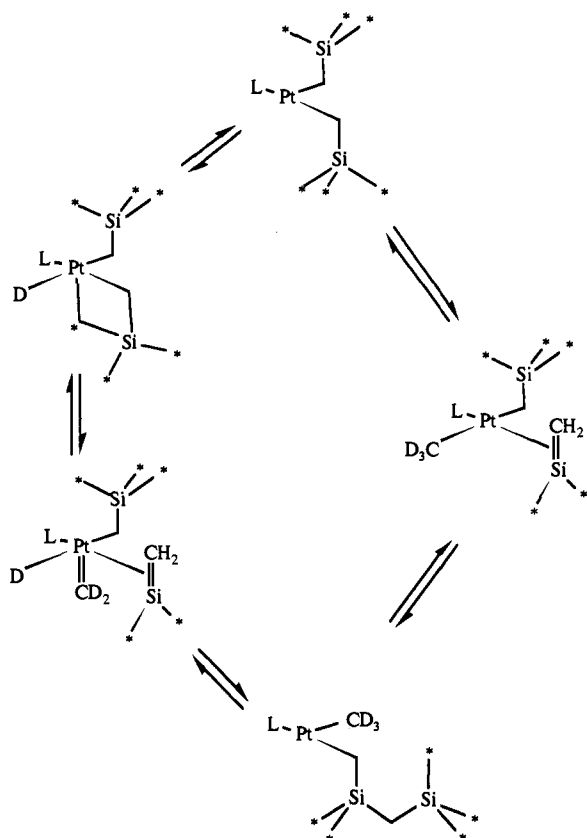
(30) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219–1221.

(31) The designation of the Pt(CH₂SiR₂) skeleton as a coordinated η²-silene—rather than a metallasilacyclopropane—is arbitrary, although we note that the behavior of W(η²-H₂C=SiMe₂)(η²-C₅H₅)₂ is consistent with such a description (ref 33). Studies aimed at detection or isolation of platinum examples are still in progress. Addy, N. J. A.; Young, G. B., unpublished work.

(32) See, for example: (a) Pannell, K. H. *J. Organomet. Chem.* **1970**, *21*, P17–P18. (b) Cundy, C. S.; Lappert, M. F.; Pearce, R. *J. Organomet. Chem.* **1973**, *59*, 161–166. (c) Pannell, K. H.; Rice, J. R. *J. Organomet. Chem.* **1974**, *78*, C35–C39. (d) Bulkowski, J. R.; Miro, N. D.; Sepelak, D.; Van Dyke, C. H. *J. Organomet. Chem.* **1975**, *101*, 267–277. (e) Lewis-Randolph, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 7768–7770. (f) Lewis-Randolph, C.; Wrighton, M. S. *Organometallics* **1987**, *6*, 365–371. (g) Berry, D. H.; Procopio, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 4099–4100.

(33) For a review, see: Lickiss, P. D. *Chem. Soc. Rev.* **1992**, *21*, 271.

Scheme 5



involving β -migration (or abstraction) of hydrogen or halogen from silicon. These include $\text{RuH}(\eta^2\text{-H}_2\text{C}=\text{SiMe}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)$,³⁴ $\text{Ir}(\eta^2\text{-H}_2\text{C}=\text{SiMe}_2)(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)$,³⁵ and $\text{W}(\eta^2\text{-H}_2\text{C}=\text{SiMe}_2)(\eta^5\text{-C}_5\text{H}_5)_2$.³⁶

Development of a $\beta\text{-Si-C}\cdots\text{Pt}$ agostic interaction also may be important in this rearrangement. Bonding of this type has been characterized recently in electron-deficient organolanthanide complexes—for example, $\text{La}(\eta^5\text{-C}_5\text{Me}_5)[\text{CH}(\text{SiMe}_3)_2]_2$ —although none of these has so far exhibited β -carbon transfer lability.³⁷

(b) Role of Pt-P Dissociation. As discussed elsewhere (by us and others), the rate retardation upon inclusion of free ligand, L, might be due either to (i) scavenging, equilibrium formation of a more inert pentacoordinate species $\text{Pt}(\text{CH}_2\text{SiMe}_2\text{R})_2\text{L}_3$, or else to (ii) inhibition of a normally prerequisite ligand dissociation step. Consistent with the latter explanation, the extent of the effect with varying ligand concentrations follows a pattern similar to those reported for rearrangement of *cis*- $\text{Pt}(\text{CH}_2\text{CMe}_3)_2\text{L}_2$ and *cis*- $\text{Pt}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{L}_2$ (although the outcomes differ from the current case), and no species other than reactants and products were detected at any time throughout the pertinent reactions. There is a reciprocal correlation between ligand concentration, [L], and k_{obs} . If the reaction is viewed as a series of simple steps (Scheme 6), a first-order rate law (eq 1) is predicted at constant concentrations of L (in accord with observations), assuming that steady state concentrations develop for all intermediates. The observed rate constant will have the form of eq 2. At constant temperature, by the same assumptions, k_{obs} should be inversely

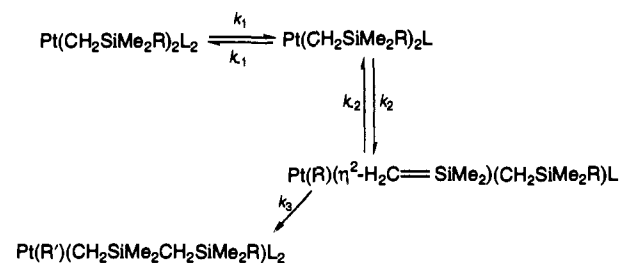
(34) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 7558–7560. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527–5534.

(35) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 4079–4081.

(36) (a) Berry, D. H.; Chey, J. H.; Zipin, H. S.; Carroll, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 452–453. (b) Kolowski, T. S.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 6405–6406.

(37) (a) Van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255–258. (b) Schaverien, C. J.; Nesbitt, G. J. *J. Chem. Soc., Dalton Trans.* **1992**, 157–167.

Scheme 6



proportional to the concentration of free ligand, eq 3.

$$-\frac{d[\text{Pt}(\text{CH}_2\text{SiMe}_2\text{R})_2\text{L}_2]}{dt} = \frac{k_1 k_2 k_3}{k_2 k_3 + k_{-1}(k_{-2} + k_3)[\text{L}]} \times [\text{Pt}(\text{CH}_2\text{SiMe}_2\text{R})_2\text{L}_2] = k_{\text{obs}}[\text{Pt}(\text{CH}_2\text{SiMe}_2\text{R})_2\text{L}_2] \quad (1)$$

$$k_{\text{obs}} = \frac{k_1 k_2 k_3}{k_2 k_3 + k_{-1}(k_{-2} + k_3)[\text{L}]} \quad (2)$$

$$1/k_{\text{obs}} = \left\{ \frac{k_{-1}(k_{-2} + k_3)}{k_1 k_2 k_3} \right\} [\text{L}] + 1/k_1 \quad (3)$$

Linear correlation is thus expected between $1/k_{\text{obs}}$ and [L], with an intercept of $1/k_1$, where k_1 is the first-order rate constant for ligand dissociation from the parent complex. For reactions of *cis*- $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PEt}_3)_2$ and *cis*- $\text{Pt}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{PPh}_3)_2$, comparable estimates, $10^{-4} \leq k_1 \leq 10^{-3}$, emerge for k_1 (in the range 115–125 °C). Even at their lower limits, these figures represent rates significantly greater than any of the overall rearrangement rates observed. On this basis, phosphine dissociation may also be excluded generally as a rate-limiting step.

This ligand loss—presumably not reversed until after the most energetic transition state—is undoubtedly a major contributor to the generally large positive activation entropy which characterizes each of these reactions. Variations in ΔS^\ddagger , moreover, appear to exert the greatest influence in determining the absolute magnitudes of rate constants as L varies (Table 12). The effect, most plausibly, mainly reflects the steric relief afforded by phosphine dissociation [see also 3, below]. Significantly, the increase in overall rate of reaction for a given silylmethyl ligand does correlate broadly with increasing steric bulk of the phosphine and, correspondingly, increase in ΔS^\ddagger . Indeed, the argument can be extended to explain the comparative, absolute labilities also of *cis*- $\text{Pt}(\text{CH}_2\text{CMe}_3)_2\text{L}_2$ and *cis*- $\text{Pt}(\text{CH}_2\text{CMe}_2\text{Ph})_2\text{L}_2$ (though the ultimate reaction modes of PtR_2L differ) on the assumption that the relative steric demand of alkyl ligands close to the metal center decreases in the order $\text{CH}_2\text{CMe}_2\text{Ph} > \text{CH}_2\text{CMe}_3 > \text{CH}_2\text{SiMe}_2\text{Ph} > \text{CH}_2\text{SiMe}_3$.

Phosphine dissociation most probably also mediates the secondary thermolytic *cis/trans* isomerization of *cis*- $\text{Pt}(\text{Ar})(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_2\text{Ar})\text{L}_2$.³⁸ Loss of one phosphine generates a tricoordinate T-shaped intermediate, which can equilibrate with a second distinct tricoordinate geometry. Reassociation of the ligand ultimately produces the thermodynamically preferred isomer. Few *trans*-platinum(II) complexes with alkyl groups have been reported, although *trans*-diarylplatinum(II) complexes are somewhat less rare.³⁹ More usually, though, such derivatives favor geometries in which the ligands of stronger *trans*-influence (such as alkyl or aryl substituents) are not mutually *trans* but are

(38) See, for example: (a) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. W. *J. Am. Chem. Soc.* **1981**, *103*, 1676–1678. (b) Alibrandi, G.; Cusumano, M.; Minniti, D.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 342–347.

(39) (a) Brune, H. A.; Ertl, J.; Graf, D.; Schmidtberg, G. *Chem. Ber.* **1982**, *115*, 1141–1153. (b) Ertl, J.; Debaerdemaeker, T.; Brune, H. A. *Chem. Ber.* **1982**, *115*, 3860–3874. (c) Brune, H. A.; Hess, R.; Schmidtberg, G. *Chem. Ber.* **1985**, *118*, 2011–2019.

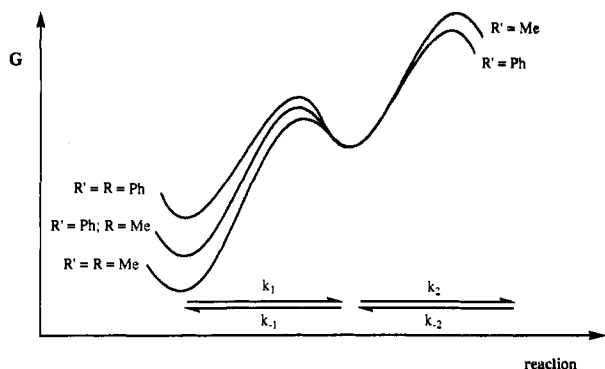


Figure 5. Idealized energy profile for initial stages of rearrangement of $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{R})(\text{CH}_2\text{SiMe}_2\text{R}')\text{L}_2$.

opposite groups of lower influence. Notably, though, $cis\text{-Pt}(\text{CH}_2\text{CMe}_2\text{Ph})(\text{C}_6\text{H}_4\text{-}2\text{-CMe}_3)(\text{PEt}_3)_2$ ⁴⁰ can rearrange to a *trans*-configuration, and related methyl(fluoroaryl)platinum(II) species, $trans\text{-Pt}(\text{CH}_3)(\text{Ar})(\text{PR}_3)_2$, have been characterized.⁴¹

(c) **Migratory Aptitudes of R in $\text{Pt}(\text{CH}_2\text{SiMe}_2\text{R})_2\text{L}_2$.** There are several indications that, in these rearrangements, aryl migration is generally more facile than methyl transfer.⁴² There is no detectable incidence of methyl migration in *any* silaneophyl rearrangement, irrespective of the individual variability of aryl transfer and in spite of the greater availability of methyl substituents. Direct comparison of rates and activation parameters between $cis\text{-Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PPh}_3)_2$ and $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{PPh}_3)_2$ clearly distinguishes the latter as more reactive, but, as discussed above, this may reflect energetic contributions other than those from R migration alone. A more reliable gauge is the result of competition between (trimethylsilyl)methyl and silaneophyl substituents as rearrangement sites in the *same* complex, $cis\text{-Pt}(\text{CH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PPh}_3)_2$. Again, phenyl migration is preferred exclusively, despite the even greater statistical predominance of methyl groups. The activation energy difference governing the different absolute reactivities of $cis\text{-Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PPh}_3)_2$ [$k_{373} = 1.56 \times 10^{-5} \text{ s}^{-1}$]⁴³ and $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{PPh}_3)_2$ [$k_{373} = 8.43 \times 10^{-4} \text{ s}^{-1}$]⁴³ appears, again, to be largely entropic in origin (Table 12). This would be consistent with greater steric congestion in $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{PPh}_3)_2$ and a correspondingly greater relief upon phosphine dissociation prior to attainment of the most energetic transition state [see 3, below]. While a similar entropic argument can be invoked to account for the intermediate absolute reactivity of $cis\text{-Pt}(\text{CH}_2\text{SiMe}_3)(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{PPh}_3)_2$ [$k_{373} = 1.91 \times 10^{-5} \text{ s}^{-1}$], it cannot readily explain the apparently *exclusive* preference for phenyl transfer once the Pt–P scission has occurred. This, more probably, arises from a (possibly) small—but nevertheless decisive—activation enthalpy advantage for aryl transfer (see below). A contribution by $\Delta\Delta H^\ddagger$ of only 8 kJ·mol⁻¹ at this stage⁴⁴ would be sufficient to ensure a relative transfer preference $k^{\text{Ph}}/k^{\text{Me}} \approx 25$, which is the estimated detectability threshold for a minor process using the analytical methods employed in this study.

Figure 5 is a stylized profile, illustrating how the phosphine dissociation step—although it is not truly rate-determining—may be energetically dominant in determining the absolute rate of rearrangement of $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{R}')(\text{CH}_2\text{SiMe}_2\text{R})\text{L}_2$. The local bulk of the alkyl ligand (as well as that of L) labilizes the parent towards the initial Pt–P scission—reflected mainly in

ΔS^\ddagger —while the migratory preference for R or R' depends on the succeeding transition state.

The trends in aromatic substituent effect (for a given L) are most plausibly attributed to enthalpic disparities near the transition state for aryl migration; any effects on the subsequent migratory insertion step will be secondary, at best. Good Hammett–Taft correlations are usually associated with minimum variations in activation entropy,⁴⁵ and values of ΔS^\ddagger determined for several of this series of complexes are, indeed, similar (Table 12). Emergence of substituent sensitivity of the migrating aryl group confirms that this step precedes or comprises the most energetic transition state. The magnitude of ρ (+0.9) indicates a system in which substituent effects are experienced at the reaction site slightly less effectively than in the (acid dissociation) reactions on which the scale of σ -values is based, although the bond broken in the present case is closer to the source of aromatic influence.⁴⁶ The reactivity differences, however, cannot be attributed simplistically to substituent-induced variations in (initial) thermodynamic properties of the Si–C bonds; it has been estimated⁴⁷ that Si–Ph bonds are stronger than their Si–Me counterparts by *ca.* 38 kJ·mol⁻¹, but aryl groups, as noted, are always transferred in preference to methyl groups.

The positive value for ρ —and the notable acceleration of aryl migration by electron-withdrawing substituents—points to a reaction in which is facilitated by minimizing electron density at the reaction site. It is not clear whether, during this process, the Pt center is behaving as an effective nucleophile toward carbon or silicon or, indeed, the C–Si grouping as a whole.

(d) **Deuterium Labeling: (i) Silylmethyl Substituents.** The (relatively small) isotopic retardations on deuteration of the methyl groups in $cis\text{-Pt}(\text{CH}_2\text{SiMe}_3)_2\text{L}_2$ [$k^{\text{H}}_{\text{obs}}/k^{\text{D}}_{\text{obs}} = 1.7, 1.5, \text{ and } 1.4$ for L = PPh₃, PPh₂Me, and PEt₃, respectively; Table 10] could be interpreted as primary effects on γ -hydrogen transfer, partly diluted as a result of a phosphine reassociation rate (k_1), significant compared with that of successive steps (k_2 , *etc.*), as we have argued elsewhere.¹⁰ More plausibly, in concert with other evidence, it is a secondary effect on direct β -methyl migration (k_3). The rate inhibition observed for $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{C}_6\text{D}_5)_2\text{L}_2$ [$k^{\text{H}}_{\text{obs}}/k^{\text{D}}_{\text{obs}} = 1.2$ and 1.4 for L = PPh₃ and PPh₂Me, respectively; Table 11] and for $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{C}_6\text{D}_5)(\text{CH}_2\text{SiMe}_3)(\text{PPh}_3)_2$ [$k^{\text{H}}_{\text{obs}}/k^{\text{D}}_{\text{obs}} = 1.6$; Table 11] *cannot*, however, be due to primary isotopic inhibition. The sources of these observations are not easy to rationalize.

A major factor influencing α -secondary isotope effects has been suggested⁴⁸ to involve hybridization change at the α -carbon in the transition state—in this instance, that for methyl migration. For $cis\text{-Pt}[(\text{CH}_2\text{Si}(\text{CD}_3)_3)_2\text{L}_2$, the values of $k^{\text{H}}_{\text{obs}}/k^{\text{D}}_{\text{obs}}$ are somewhat larger than those expected for α -secondary isotope effects. An additional contribution to this secondary inhibition could arise from migration of the remaining(trimethylsilyl)-methyl-*d*₉ group to the silicon terminus of the η^2 -silene-*d*₆ ligand. The generally smaller β -isotope effects for $cis\text{-Pt}(\text{CH}_2\text{SiMe}_2\text{C}_6\text{D}_5)_2\text{L}_2$ most reasonably stem from inductive factors. Here, little or no isotope effect is expected on the migratory insertion rate.

(45) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; pp 223–229.

(46) Values greater than 1 indicate large charge density, and those less than 1 indicate relatively small effects. See ref 26.

(47) $D(\text{Si}-\text{CH}_3) = 314 \pm 4 \text{ kJ}\cdot\text{mol}^{-1}$; $D(\text{Si}-\text{C}_6\text{H}_5) = 352 \pm 8 \text{ kJ}\cdot\text{mol}^{-1}$; see: Tel'noi, V. I.; Rabinovich, I. B. *Russ. Chem. Rev. (Engl. Transl.)* **1980**, *49*, 603–618 and references cited therein. The difficulties in estimating Si–C bond energies are also assessed.

(48) Isotope effects are attributed to perturbations of the vibrational modes of the isotopically labeled site during the transformation from reactant to product. See ref 25 and: (a) Halveli, E. A. In *Progress in Physical Organic Chemistry*; Cohen, S. G.; Streitwieser, A.; Taft, R. W., Eds.; Wiley: New York, 1963; Vol. 1, Chapter 5. (b) Leffek, K. T. In *Isotopes in Organic Chemistry*; Buncl, E.; Lee, C. C., Eds.; Elsevier: New York and Amsterdam, 1976; Vol. 2, Chapter 3. (c) Saunders, W. H. In *Investigations of Rates of Reactions*; Lewis, E. S., Ed.; Wiley: New York, 1974; Part 1, Chapter 5.

(40) (a) Griffiths, D. C.; Joy, L. G.; Skapski, A. C.; Wilkes, D. J.; Young, G. B. *Organometallics* **1986**, *5*, 1744–1745. (b) Griffiths, D. C. Ph.D. Thesis, Imperial College, London, 1985.

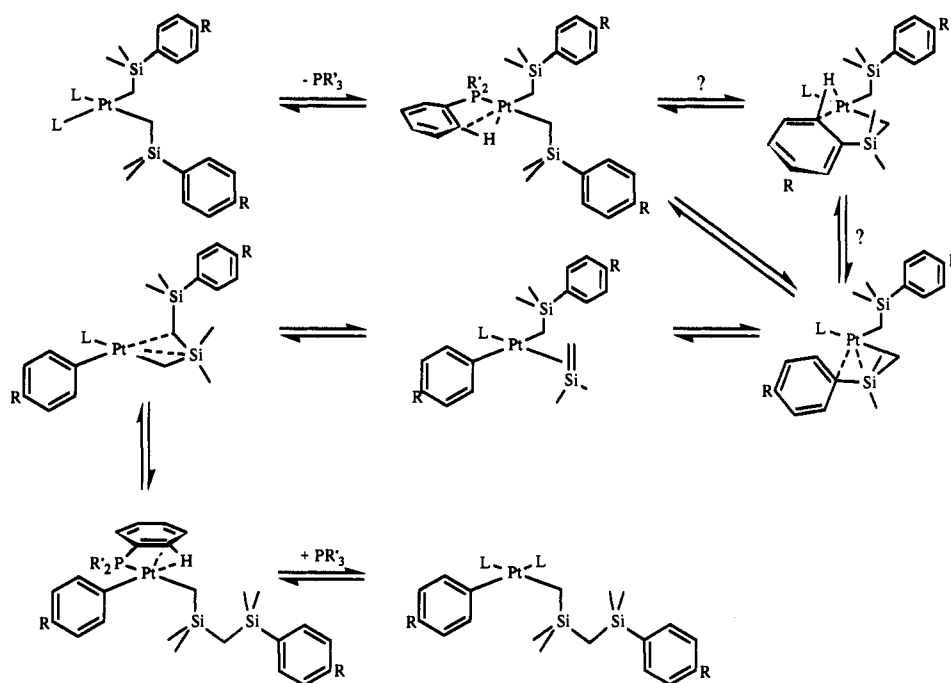
(41) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360–2366.

(42) Cf., for example: Ortiz, J. V.; Havlas, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1–17 and references cited therein.

(43) From extrapolation of Arrhenius data.

(44) Assuming $\Delta\Delta G^\ddagger = RT \ln(k_1/k_2)$; see: DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124–131 and references therein.

Scheme 7



(ii) **Phosphine Substituents.** The isotopic retardations upon deuteration of triphenylphosphine [$k^H/k^D = 1.5$ for *cis*-Pt(CH₂-SiMe₃)₂(PPh₃-*d*₁₅)₂ and 2.1 for *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃-*d*₁₅)₂] are also difficult to interpret by the reasoning normally applied to secondary inhibition. An alternative explanation is the development of a substantial agostic interaction⁴⁹ between platinum and a phosphine C-H bond as the neighboring ligand departs. Recently, similar isotope effect on ligand substitution in W(CO)₃(PCy₃)₂L [L = H₂, N₂, py, POME₃] ($k^H/k^D = 1.20$) has been attributed to development of an agostic link between a cyclohexyl C-H bond and the metal center as L dissociates.⁵⁰ It cannot be ruled out, therefore, that the inhibitory effects discussed in the previous section are due (in some part) to similar onset of agostic interaction between platinum and C-H bonds on methyl or phenyl groups of the trimethylsilyl and silaneophyl ligands.

(e) **Mechanism.** The above observations are consistent with the general rearrangement mechanism exemplified in Scheme 7 for *cis*-Pt(CH₂SiMe₂-4-C₆H₄R)₂(PPh₃)₂. There is preliminary—though not rate-limiting—dissociation of one Pt-P bond, possibly compensated by an agostic interaction between the coordinatively unsaturated metal and a phosphine substituent. We do not exclude similar interactions with C-H bonds on silicon substituents, although the absence of skeletal H/D scrambling (in any labeled complex) and of cyclometalation products indicate that no such interaction progresses to hydrogen transfer for this class of reactants. Instead, carbon migration to platinum—probably involving the most energetic transition state and perhaps *via* development of an agostic link between Pt and a C-Si bond—generates an (η²-silene)metal intermediate. This undergoes a ready, regiospecific migratory insertion to form the ((silylmethyl)silyl)methyl derivative, which—upon reassociation of phosphine—affords the observed product.

(2) **Cyclometalations of Pt(CH₂SiMe₂Ar)₂L₂.** (a) L = PPh₂(C₆H₄-2-Me). Although the kinetic effect has not been quantified in detail, the formation of phosphametallacyclic product, *cis*-

Pt(CH₂-2-C₆H₄PPH₂)(CH₂SiMe₂Ph)(PPh₂C₆H₄-2-Me), is also inhibited by the presence in solution of PPh₂(C₆H₄-2-Me). In principle, this might indicate either an associative or a dissociative role for L, but, in view of its steric bulk ($\theta = 161^\circ$) and the many other precedents, the latter seems more likely. The value of ΔS^\ddagger for this reaction is notably less positive, however.

(b) L = pyridine. The scarcity of quantitative data precludes firm mechanistic propositions at present [see 3, below].

(3) **General.** The intramolecular rearrangement displayed by the majority of bis(phosphine)bis(silylmethyl)platinum complexes is unique among organometals of this class. Though rare in general, β -alkyl transfers have been observed, notably in organoplatinum(II) systems which not only lack transferable β -hydrogen but also have strained alicyclic systems incorporating the β -carbon.⁵¹ Mechanistic information is lacking on a superficially similar reaction of a ((trimethylsilyl)methyl)ruthenium(IV) derivative, Ru(η^5 -C₅H₅)(η^3 -C₃H₅)(CH₂SiMe₃)Br, with F⁻ to form Ru(η^5 -C₅H₅)(η^3 -C₃H₅)(CH₂SiMe₂F)Me as a major product.⁵² It seems likely, though, that this reaction also has a powerful thermodynamic incentive by way of the fluorophilicity of silicon.

The fact that a given R-group in *cis*-PtR₂L₂ may favor alternative active roles or, indeed, passive participation, merely upon variation of L, serves to illustrate that (in these systems) reactivity is controlled by delicate energetic balances, about which presently we can only speculate. For example, it seems reasonable to suppose that phosphine loss from *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₂C₆H₄-2-Me)₂ is more ready than that from *cis*-Pt(CH₂SiMe₂Ph)₂(PPh₃)₂, but encroachment of the remaining *o*-methyl group is sufficient to discourage any reaction with the silaneophyl group in favor of aliphatic C-H activation and transfer from the methyl group itself. This may be related, of course, to the agostic role of phosphine-located C-H sites already suggested by the results of deuterium labeling studies (above). Where L is pyridine (or its relatives), we are attempting to elucidate whether steric or electronic properties of heterocyclic N-donor ligands are responsible for the favorability of aromatic δ -C-H transfer, this time from the silaneophyl ligand. Presumably, the steric

(49) See, for example: (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299-338. (b) Bercaw, J. E.; Burger, B. J.; Green, M. L. H.; Santisiero, B. D.; Sella, A.; Trimmer, M. S.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 734-736. (c) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172-1179 and references cited therein.

(50) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, S. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429-2435.

(51) (a) Flood, T. C.; Stadler, J. A. *Organometallics* **1984**, *3*, 1795-1803.

(b) (a) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076-6077.

(52) Itoh, K.; Fukahori, T. *J. Organomet. Chem.* **1988**, *349*, 227-230.

obstruction of the *o*-methyl substituent in *cis*-Pt(CH₂SiMe₂-2-C₆H₄Me)₂(py)₂ is sufficient to promote the reversion to β -carbon migration.

It would be tempting to propose that the ligand dissociations, which are a common prerequisite in reactions of planar tetra-coordinate d⁸ organometals, may be compensated generally by agostic interactions with remaining pendant groups. Although we note that no detectable isotope effect was reported for cyclometalation of *cis*-Pt(CH₂CMe₃)₂(PEt₃-d₁₅)₂,^{7b} it does seem likely that this phenomenon may emerge as more widespread than has been observed to date.⁵⁰

An important conclusion from this work is that the more general question of quantification of reactive differences between two different groups R and R' cannot, it is now clear, be addressed by kinetic comparison of PtR₂L₂ with PtR'L₂. This is because of the extent to which the energetics of Pt-L scission—though seldom rate-limiting—generally dominate the overall activation energies for rearrangements. These preponderantly entropic contributions—stemming from mutual steric interactions—are a simultaneous function of both R (or R') and L. In other words, both R (or R') and L can contribute to an entropic labilization of the parent complex relative to the (nominally) 14-electron intermediate, PtR₂L—which, in the current studies, normally swamps any more subtle contributions to the absolute reactivity of PtR₂L₂ or PtR'L₂ by individual reactive preferences of R and R'. The necessary requirement is to permit both R and R' to contribute to the energetics of Pt-L dissociation, while allowing the metal center arbitrary reactive choice between R and R', subsequent to departure of one L—as attempted for *cis*-Pt(CH₂-SiMe₃)(CH₂SiMe₂Ph)(PPh₃)₂, described above. Extensive studies of a series of asymmetric complexes PtRR'L₂ are now in progress in these laboratories in order to minimize differential entropy effects and allow more reliable quantification of relative reactive preferences.

The fact that this novel mode of thermolytic reaction is preferred to the cyclometalation expected by analogy with corresponding dineopentyl- and dineophylplatinum derivatives suggests that the β -Si-C interaction with Pt provides, ultimately, a more favorable entry to further rearrangement than the agostic C-H interactions which (assumedly) preface H migrations. The energetic balance is evidently fine, however, given that relatively minor variations in the ancillary ligands lead to a preference for cyclometalation routes. Why such β -carbon reactivity should be limited (so far) to organoplatinum(II) is more difficult to explain as yet. We have established that dialkylnickel(II) and dialkylpalladium(II) analogues rearrange via intramolecular reductive C-C elimination.⁵³ Various theoretical bases for the relative ease of reductive C-C elimination from many such Ni(II) and Pd(II) species have been argued.⁵⁴

A (germylmethyl)platinum(II) derivative, *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂, has also been prepared and studied. It is somewhat

more labile than *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ but reacts analogously, affording *cis*-Pt(CH₃)(CH₂GeMe₂CH₂GeMe₃)(PPh₃)₂.⁵⁵ The stannylmethyl analogue is much more reactive, but a corresponding product, *cis*-Pt(CH₃)(CH₂SnMe₂CH₂SnMe₃)(PPh₃)₂, cannot be isolated.

We are currently endeavoring to produce observable or isolable (η^2 -silene)platinum complexes in order to explore their reactivity more fully. Partly to this end, we have synthesized Pt(SiMe₃)₂(dcpe) and Pt(SiMe₃)H(dcpe) [dcpe = 1,2-bis(dicyclohexylphosphino)ethane], potential (η^2 -silene)metal precursors, via β -hydrogen transfer from carbon. Thermolysis, however, requires high temperatures and generates silylmethylene oligomers as the only tractable products, on which we shall report in due course.⁵⁶ We note that, in the course of this work, similar reactivity has emerged from a study of a related ruthenium system.⁵⁷

Conclusions

The salient features of this body of observations may be summarized as follows.

(1) Thermolytic rearrangements of most complexes of *cis*-Pt(CH₂SiMe₂R)₂L₂ (where L is a tertiary phosphine ligand) occur by β -carbon transfer, generating an (η^2 -silene)platinum intermediate. This subsequently rearranges *via* migration of the remaining silylmethyl ligand to the silicon terminus of the η^2 -silene. (2) Although it is not a rate-limiting process, the positive activation entropy associated with preliminary Pt-P scission may be a dominant contribution to overall activation energy, reflecting the relief of steric congestion introduced by both silylmethyl and phosphine ligands in the parent complexes. (3) Phosphine dissociation may be compensated by agostic interactions between the metal and ligand sites, most plausibly C-H bonds of phosphines, possibly also C-H bonds in silylmethyl groups, and, presumably, C-Si bonds prior to carbon transfer. (4) Phenyl migration is more facile than methyl transfer, and electron-withdrawing substituents accelerate the (regiospecific) shift of aryl groups, suggesting that platinum acts, superficially, as a nucleophile toward the migrating C-Si grouping. (5) Where L is pyridine and PPh(C₆H₄-2-Me), preferred thermolytic routes involve cyclometalations on silylmethyl and phosphine ligands, respectively.

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