of possibilities. Direct resistivity measurements on these two phases will not be easy because of their extreme sensitivity to moisture, air, cements, etc.

(2) The structure of the d^1 binary ZrI$_3$ is a continuation of the metal-metal bonding seen in Na$_{0.5}$ScI$_3$, achieving complete filling of the d$_{z^2}$ band and paired metal atoms. Increased metal pairing and broadening of the M-M σ bands are evident.

(3) The low-lying bands that are antibonding for M-M π and δ interactions in LiScI$_3$ and ZrI$_3$ change with increased metal pairing to afford relatively localized π and δ bonding in NbI$_3$. A further increase in the number of d electrons combined with substantial iodine matrix effects and shrinking orbitals should lessen M-M bonding markedly for isostructural MI$_3$ compounds of later elements.

Acknowledgment. We are indebted to A. Lachgar for preliminary calculations, to A. Guloy and G. J. Miller for valuable advice on several points, and to B. Krebs and G. Thiele for sharing their unpublished structural data. This research was supported by the National Science Foundation, Solid State Chemistry, via Grant DMR-8902954 and was carried out in facilities of the Ames Laboratory, DOE.

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(Phosphinoalkyl)silyl Complexes. 10.[1] Formation of Chelated Bis[(diphenylphosphinoethyl)diorganosilyl]platinum(II) Complexes. Precoordination through Phosphorus, Intermediacy of a Platinum(IV) Disilyl, and Diastereoisomerism at Planar Platinum(II) in "Chelate-Assisted" Hydrosilylation

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Addition of the silane PPh$_2$CH$_2$CH$_2$SiMe$_2$H (chelH, **1a**) to Pt(COD)$_2$ (COD = cycloocta-1,5-diene) affords in high yield the cis-bis chelate Pt(chel)$_2$ (**2**); formation of the same product from Pt(COD)(X)Y (X = Y = Me; X = Me, Y = Cl) has been shown by NMR spectroscopy (^{1}H, ^{31}P, ^{195}Pt) to proceed via prior coordination of chelH through P to afford Pt(chelH)$_2$(X)(Y) (cis and trans isomers) and through intermediacy of PtH(chel)$_2$Cl (**22**) in which P trans to Si at Pt(IV) leads to an exceptionally low ^2J(Pt-P) = 1084 Hz. Cleavage of Pt-Si bonds in **2** by HCl can be controlled to give the monochelate species Pt(chel)(chelH)Cl (**7**), from which chelH is displaced by PMe$_2$Ph, or *trans*-PtH(PPh$_2$CH$_2$CH$_2$SiMe$_2$Cl)$_2$Cl (**9**). Products related to **9** result from Pt-Si bond cleavage by I$_2$ or MeI. Using the analogue PPh$_2$CH$_2$CH$_2$SiMe(Ph)H (**1c**) of **1a**, the analogue Pt[PPh$_2$CH$_2$CH$_2$SiMe(Ph)]$_2$ (**4**) of **2** is obtained as a mixture of meso and racemic diastereomers in which the latter predominates, as is established by its separation and then reaction with optically pure (+)-2-methylbutyl iodide to give two diastereomeric products of Pt-Si bond cleavage as well as by single-crystal X-ray diffraction.

Introduction

Some time ago we began to examine the usefulness of simultaneous silyl and phosphorus ligation as a methodology for modifying the molecular geometry of a transition-metal silyl complex to "anchor" the silicon center in the vicinity of a metal site.[2] This was conceived as a design for developing a configuration in which electron release from Si might exaggerate the electron-rich character of catalytically reactive platinum-group metal centers, and wherein nucleophilic substrate activation by the latter could cycle without concomitant capture and subsequent elimination of the silyl fragment in a classical "leaving group" sense. The objective was thus to retain the silyl group as an electronic influence within a complex coordination sphere by incorporating it into a polydentate ligand framework, the spatial demands of which might be separately tailored to contribute to catalytic selectivity or extended in an approach to catalyst immobilization. Hydrosilylation (i.e. Si-H bond oxidative addition) of low-valent metal complexes by the bifunctional silane PPh$_2$CH$_2$CH$_2$SiMe$_2$H ("chelH") or related (phosphinoalkyl)silanes[3] has provided a general synthetic route to mono- and bischelate derivatives of the silyl PPh$_2$CH$_2$CH$_2$SiMe$_2$- (i.e. "chel"), in which a silicon-transition-element bond is supported by simultaneous phosphine coordination to the metal atom. The (chel)$_2$ assembly so obtained is represented by diastereoisomeric planar platinum(II) complexes,[2] enantiomeric 5- and 6-coordinate rhodium(III) and iridium(III) geometries,[4] and conformationally distinct dispositions around octahedral ruthenium(II) and osmium(II) centers.[5] While our primary concern has lain with elaboration toward more rigid polydentate (cage) coordination[1] and with catalysis,[6] formation of the (chel)$_2$ species focuses attention on two interesting considerations, viz (a) the relationship between the "chelate-assisted" addition step and precoordination through the donor (P) heteroatom and (b) the way in which approach of a second chel skeleton to the metal site is oriented by prior attachment of the first. These effects are discernible in chemistry that has led to the isolation[2] of Pt(chel)$_2$ and related molecules and has established conclusively that Pt(IV) species are indeed involved in the formation of these silyl-platinum(II) complexes, i.e., that a "chelate-assisted" addition is followed by elimination of HCl, although the mechanism of subsequent cleavage of Pt-Si bonds by this latter reagent remains uncertain. We have also used NMR spectroscopy to monitor the course of COD displacement from [Pt(COD)Cl$_2$] (COD = cycloocta-1,5-diene), which is the most convenient synthetic route to the chelate ring structure in [Pt(chel)$_2$]; in this reaction, initial coordination through P can clearly be distinguished, confirming that the double Si-H bond addition at Pt does indeed constitute a "chelate-assisted" process. Existence[2] of the analogues [Pt(PPh$_2$CH$_2$CH$_2$SiR^{1}R^2)$_2$] in an unequal diastereoisomer ratio that depends on the nature of R^1 vs R^2 further demonstrates the significance of ligand orientation effects around the reacting Pt center.

Experimental Section

Synthetic manipulations were conducted under an atmosphere of dry dinitrogen gas, using standard vacuum/purge techniques. All solvents

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[1] Part 9: Joslin, F. L.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 504.

[2] Holmes-Smith, R. D.; Stobart, S. R.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Chem. Commun.* **1981**, 937.

[3] Holmes-Smith, R. D.; Osei, R. D.; Stobart, S. R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 861.

[4] Auburn, M. J.; Stobart, S. R. *Inorg. Chem.* **1985**, *24*, 318.

[5] Holmes-Smith, R. D.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J.; Jochem, K.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1987**, 969.

[6] Stobart, S. R.; Grundy, S. L.; Joslin, F. L. U.S. Patent 4,950,798 1990.

were dried and distilled immediately before use. The (phosphinoalkyl)silanes $PPh_2CH_2CH_2SiR^1R^2H$ (**1a**, $R^1 = R^2 =$ Me; **1b**, $R^1 = R^2 =$ Ph; **1c**, $R^1 =$ Me, $R^2 =$ Ph; **1d**, $R^1 =$ Me, $R^2 =$ H; **1e**, $R^1 =$ Ph, $R^2 =$ H) as well as $[PtCl_2(COD)]$, $[PtMe_2(COD)]$, $[PtMeCl(COD)]$, and $[Pt(COD)_2]$ were prepared by literature methods.[3,7,8] IR spectra were recorded by using a Perkin-Elmer 283 instrument; the ^1H, $^{31}P\{^1H\}$, and ^{195}Pt NMR data were measured with a Bruker WM-250 Fourier-transform NMR spectrometer. The ^{31}P chemical shifts are expressed as δ in ppm vs external trimethyl phosphite. ^{195}Pt chemical shifts are reported in ppm relative to $\Xi(^{195}Pt) = 21.4$ MHz.[9] All NMR data reported in the tables were recorded at ambient temperature in $CDCl_3$ solution. Microanalytical data were supplied by Canadian Microanalytical Service Ltd., Vancouver, BC.

Synthesis of Complexes. $[Pt(PPh_2CH_2CH_2SiMe_2)_2]$ (2). Dropwise addition of $PPh_2CH_2CH_2SiMe_2H$ (**1a**) (0.58 g, 2.13 mmol) dissolved in dry benzene (10 mL) over 60 min to a slurry of $[PtCl_2(COD)]$ (0.39 g, 1.05 mmol) in benzene (15 mL) and NEt_3 (10 mL) was followed by stirring (25 °C/2 h); then all volatile material was removed in vacuo, and the residue was extracted with hexane (4 × 5 mL). Filtration through a Florisil column (2.5 cm × 7 cm) followed by evaporation of the solvent gave the white, crystalline *product* (0.30 g, 48%). Anal. Calcd for $PtC_{32}H_{40}Si_2P_2$: C, 52.10; H, 5.43. Found: C, 52.46; H, 5.63.

$[Pt(PPh_2CH_2CH_2SiPh_2)_2]$ (3). A solution of $[Pt(COD)_2]$ (0.18 g, 0.44 mmol) in Et_2O (20 mL) was added slowly to the silane (**1b**) (0.35 g, 0.88 mmol) also dissolved in Et_2O (15 mL). After stirring (25 °C/10 min), volatiles were removed in vacuo and the solid residue was extracted with 50:50 CH_2Cl_2/pentane (3 × 10 mL). Filtration followed by removal of the solvent gave the white crystalline *product* (0.38 g, 86%). Anal. Calcd for $PtC_{52}H_{48}Si_2P_2$: C, 63.35; H, 4.87. Found: C, 63.57; H, 5.06.

$[Pt(PPh_2CH_2CH_2SiMePh)_2]$ (4). A solution of $[Pt(COD)_2]$ (0.20 g, 0.47 mmol) in hexane (50 mL) was added to the silane (**1c**) (0.32 g, 0.96 mmol) dissolved in a mixture of hexane (10 mL) and THF (10 mL). After the mixture was stirred (2 h), filtration through a Florisil column (2.5 cm × 7 cm) was followed by removal of volatiles in vacuo to afford a pale yellow solid (mixture of diastereoisomers). Recrystallization from CH_2Cl_2/hexane gave white crystals of the pure *racemic* diastereoisomer, (0.092 g, 41%). Anal. Calcd for $PtC_{42}H_{44}Si_2P_2$: C, 58.54; H. 5.11. Found: C, 58.72; H, 5.27.

$[Pt(PPh_2CH_2CH_2SiMeH)_2]$ (5) and $[Pt(PPh_2CH_2CH_2SiPhH)_2]$ (6). Reactions conducted in a manner similar to those described above by using the (phosphinoethyl)monoorganosilanes **1d** or **1e** afforded solutions, which were shown (^1H and ^{31}P NMR) to contain platinum(II) products having analogous characteristics to the diastereomer mixture that yielded complex **4**; however, attempts at isolation and recrystallization produced insoluble materials which could not be properly characterized.

$[Pt(PPh_2CH_2CH_2SiMe_2)(PPh_2CH_2CH_2SiMe_2Cl)Cl]$ (7). To complex **2** (0.20 g, 0.27 mmol) dissolved in benzene (20 mL) was added dropwise a 0.1 M HCl solution in benzene (5.5 mL). Removal of volatiles afforded a residue, which was washed with hexane (3 × 10 mL) to yield the white crystalline *product* (0.19 g, 88%). Anal. Calcd for $PtC_{32}H_{40}Si_2P_2Cl_2$: C, 47.52; H, 4.95; Cl, 8.79. Found: C, 47.31; H, 4.82; Cl, 8.41.

$[Pt(PPh_2CH_2CH_2SiPh_2)(PPh_2CH_2CH_2SiPh_2Cl)Cl]$ (8) was isolated similarly, in 90% yield, by using complex **3** as precursor. Anal. Calcd for $PtC_{52}H_{48}Si_2P_2Cl_2$: C, 59.09; H, 4.54; Cl, 6.72. Found: C, 59.11; H, 4.59, Cl, 5.84.

$[PtH(PPh_2CH_2CH_2SiMe_2Cl)_2Cl]$ (9). Complex **2** (0.10 g, 0.13 mmol) was dissolved in Et_2O (10 mL), and then HCl gas was bubbled through the solution for 5 min. Evaporation of the solvent provided the white solid *product* (0.095 g, 85%). Anal. Calcd for $PtC_{32}H_{41}Si_2P_2Cl_3$: C, 45.57; H, 4.85; Cl, 12.61. Found: C, 45.41; H, 4.66; Cl, 12.07. The related, white product $[PtH(PPh_2CH_2CH_2SiPh_2Cl)_2Cl]$ (**10**) (88%) was obtained similarly from compound **3**. Anal. Calcd for $PtC_{52}H_{49}Si_2P_2Cl_3$: C, 57.12; H, 4.49; Cl, 9.75. Found: C, 57.33; H, 4.53; Cl, 9.21.

$[Pt(PPh_2CH_2CH_2SiMe_2)Cl(PMe_2Ph)]$ (11). A stirred solution of complex **7** (40 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was treated with a solution of PMe_2Ph (7 mg, 0.05 mmol) in CH_2Cl_2 (1 mL). Evaporation of the resulting solution to 1 mL followed by the addition of hexane (3 mL) precipitated the *product* as a white powder (30 mg, 96%). Anal. Calcd for $PtC_{24}H_{31}SiP_2Cl$: C, 45.04; H, 4.85; Cl, 5.55. Found: C, 45.19; H, 4.41; Cl, 5.69.

$[Pt(PPh_2CH_2CH_2SiPh_2)Cl(PMe_2Ph)]$ (12) (92%) was obtained in a similar fashion by using complex **8** in place of complex **7**. Anal. Calcd for $PtC_{34}H_{35}SiP_2Cl$: C, 53.44; H, 4.58; Cl, 4.64. Found: C, 53.14; H, 4.41; Cl, 4.45.

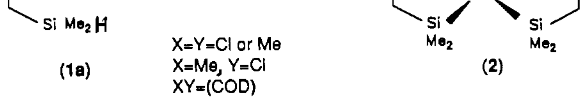
$[Pt(PPh_2CH_2CH_2SiMe_3)_2I_2]$ (13). Compound **2** (0.30 g, 0.40 mmol), hexane (10 mL), and MeI (0.4 mL, ca. 6 mmol) were sealed together in a small reaction tube then heated at 120 °C for 4 h. After cooling, the tube was opened and volatile material was removed in vacuo. This afforded a yellow solid, which was recrystallized from CH_2Cl_2/heptane to give the *product* (0.37 g, 89%). Anal. Calcd for $PtC_{34}H_{46}Si_2P_2I_2$: C, 39.96; H, 4.51. Found: C, 39.46; H, 4.32.

$[Pt(PPh_2CH_2CH_2SiMe_2I)_2I_2]$ (14). On addition of a solution of I_2 (0.068 g, 0.27 mmol) in Et_2O (15 mL) to complex **2** (0.20 g, 0.27 mmol) dissolved in the same solvent (10 mL), a yellow precipitate formed immediately. The supernatant was removed by using a syringe, and the solid was washed thoroughly with Et_2O (3 × 5 mL) to give the *product* (0.085 g, 32%). Anal. Calcd for $PtC_{32}H_{40}Si_2P_2I_2$: C, 30.84; H, 3.21. Found: C, 31.11; H, 3.36.

***trans*- and *cis*-$[Pt(PPh_2CH_2CH_2SiMe_2Cl)_2Cl_2]$ (15 and 16).** Complex **2** (0.10 g, 0.13 mmol) was refluxed for 5 h in CCl_4 (15 mL). After the reaction was cooled, the pale yellow *product* (0.088 g, 77%) was filtered off and washed thoroughly with hexane. Anal. Calcd for $PtC_{32}H_{40}Si_2P_2Cl_2$: C, 43.69; H, 4.55; Cl, 16.15. Found: C, 43.61; H, 4.33; Cl, 16.21.

Results

Addition of $PPh_2CH_2CH_2SiMe_2H$ (**1a**) to $[Pt(COD)_2]$ leads rapidly under mild conditions to virtually quantitative information of the colorless, crystalline bis-chelate $[Pt(PPh_2CH_2CH_2SiMe_2)_2]$, i.e. $Pt(chel)_2$ (**2**) (eq 1). Several alternate routes exist to the same complex, including addition of **1a** to (a) $[Pt(PPh_3)_4]$, although the product obtained in this way is difficult to free completely from residual PPh_3, to (b) $[Pt(COD)(Y)Cl]$ (Y = Cl or Me), where NEt_3 is required to intercept the HCl generated in the reaction mixture, or to (c) $[Pt(COD)Me_2]$, which again affords a pure product in excellent yield (eq 1).



(1)

A chelate ring-structure for (phosphinoalkyl)silyl coordination in **2** is suggested by the observation of platinum coupling to silylmethyl protons, as well as by deshielding of the P nucleus, δ −82.5 ppm relative to corresponding chemical shifts[10] in the family of complexes $[Pt(SiR_3)_2(PR'_3)_2]$ (SiR_3 = triorganosilyl, PR'_3 = tertiary phosphine). A cis arrangement of the chelated ligands in compound **2** is indicated by $^1J(PtP) = 1608$ Hz, which closely compares with that reported for $[Pt(PMe_2Ph)_2(SiMePh_2)_2]$ (1559 Hz), which has mutually cis phosphines. This conclusion has been corroborated by the results[2] of an X-ray crystal structure determination. Treatment of the precursors $[Pt(COD)_2]$ or $[Pt(COD)Cl_2]$ (eq 2) with other (phosphinoethyl)silanes (**1b–1e**) led to formation of analogous products **3–6** respectively, which were characterized in the first instance in solution by using NMR spectroscopy (Table I); while compounds **3** or **4** could be obtained as crystalline solids without difficulty, attempts to isolate complexes **5** and **6** resulted in formation of insoluble materials that could not be satisfactorily identified.

(2)

In the absence of NEt_3, reactions involving $[Pt(COD)Cl_2]$ (eqs 1 and 2) are complicated by Pt–Si bond cleavage that occurs through attack by HCl, which is generated as a result of the silane addition. Accordingly, on treatment with excess HCl, both Pt–Si bonds in compound **2** are broken, giving a trans platinum(II) hydrochloride $[Pt(H)Cl(PPh_2CH_2CH_2SiMe_2Cl)_2]$ (**9**) (eq 3).

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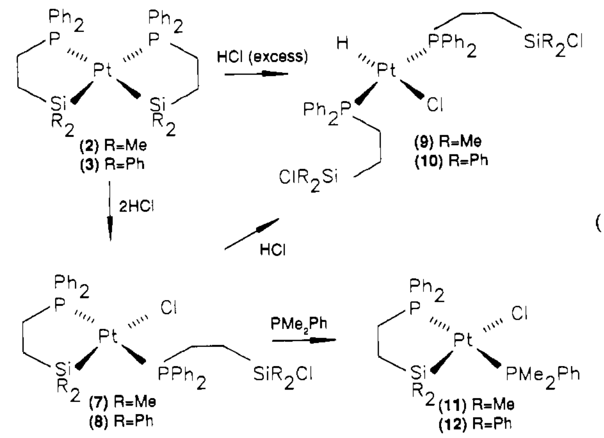
(7) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(8) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271.

(9) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 249.

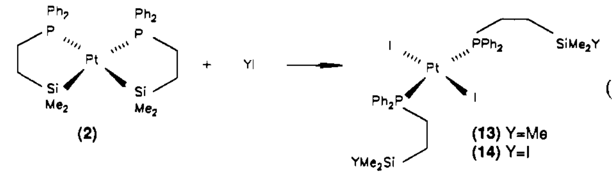
(10) Heaton, B. T.; Pidcock, A. *J. Organomet. Chem.* **1968**, *14*, 235.



(3)

Absorption at 2200 cm^{-1} in the IR spectrum is attributable to ν(PtH), and a hydride resonance appears at $\delta = -16.1$ ppm in the ^{1}H NMR spectrum as a triplet flanked by triplet ^{195}Pt "satellites", ^1J(PtH) and ^2J(PH) (Table II), establishing a stereochemistry in which H is cis to two phosphine ligands and trans to Cl. Analogous Pt–Si bond cleavage in **3** yields **10**. Controlled addition of HCl (2 molar equiv) to **2** or **3** via titration with HCl-saturated benzene solution results in quantitative formation of the related monochelate species [Pt(chel)(PPh$_2$CH$_2$CH$_2$SiR$_2$Cl)Cl] (R = Me (**7**); R = Ph (**8**)). The latter were characterized by microanalytical data and the absence in IR or NMR spectra of features attributable to Si–H or Pt–H bonds; they also give rise to a distinctive ^{31}P NMR spectrum (Table II), in which an AB pattern, ^2J(PP) = 388.9 Hz, ^1J(PtP) = 3101, 3018 Hz for complex **7** and ^2J(PP) = 392.7 Hz, ^1J(PtP) = 2956, 2837 Hz for complex **8**, establishes that a trans relationship exists between the P nuclei. Such selective cleavage of one Pt–Si bond in **2** may offer the most convenient route to a Pt(II) species possessing a single chelated silyl ligand, since we have been unable to separate the mixtures of corresponding mono- and bis-chelate derivatives that are formed from reaction of **1a** with [PtCl$_2$(PR'$_3$)$_2$] (PR'$_3$ = tertiary phosphine). It is further possible to displace the non-chelate (phosphinoalkyl)chlorosilane ligand in **7** or **8** by using the more basic PMe$_2$Ph, to give compounds **11** and **12**, respectively, for which ^{31}P chemical shifts and coupling constants are consistent with a trans disposition for the two different phosphines (Table II).

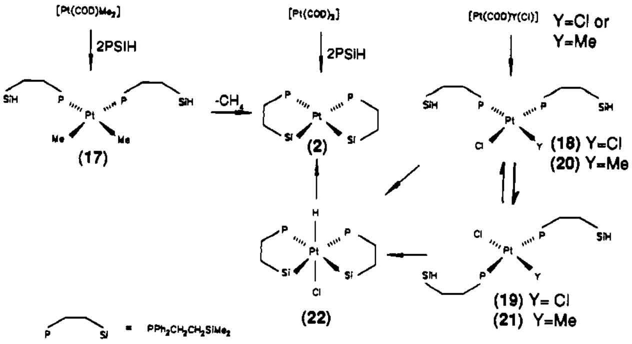
When [Pt(chel)$_2$] (**2**) was heated with MeI in hexane solution, cleavage of both of the Pt–Si bonds again resulted, with quantitative formation of the complex [Pt(PPh$_2$CH$_2$CH$_2$SiMe$_3$)$_2$I$_2$] (**13**) (eq 4), i.e., methylation at Si with conversion of the chelated (phosphinoalkyl)silyl group to a monodentate phosphinoalkylsilane ligand. A trans stereochemistry for this diiodoplatinum(II) product (**13**) was assigned on the basis of the ^{31}P NMR spectrum, which showed ^1J(PtP) = 2405 Hz. Rapid disruption of Pt–Si bonds in **2** was also apparent on treatment with diiodine, the yellow product (**14**) being readily identifiable (Table II) as *trans*-[Pt(PPh$_2$CH$_2$CH$_2$SiMe$_2$I)$_2$I$_2$]. Similarly, but more slowly, in boiling CCl$_4$ the chloro analogue of complex **14**, [Pt(PPh$_2$CH$_2$CH$_2$SiMe$_2$Cl)$_2$Cl$_2$], was formed but this time as a mixture of trans (**15**) and cis (**16**) isomers, distinguishable by ^1J(PtP) at 2549 and 3606 Hz, respectively.



(4)

The reaction of **1a** with each of the precursor Pt complexes represented as [Pt(COD)XY] in eq 1 was also followed by using NMR spectroscopy. The transformations identified in this manner are arranged in Scheme I; the spectroscopic data are listed in Table III. With [Pt(COD)$_2$], diolefin displacement occurred very rapidly and [Pt(chel)$_2$] (**2**), recognizable from its characteristic ^{31}P NMR spectrum,[2] was the only platinum-containing product detectable in solution. Starting with [Pt(COD)Me$_2$], complex **2** was again formed rapidly as the ultimate product, but its appearance in the ^{31}P NMR spectrum was preceded by that of a transient resonance with ^1J(PPt) = 1699 Hz, an observation suggesting the intermediacy of a cis complex [Pt(PPh$_2$CH$_2$CH$_2$SiMe$_2$H)$_2$Me$_2$], i.e. [Pt(chelH)$_2$Me$_2$] (**17**). This conclusion was subsequently substantiated by ^{1}H NMR spectroscopy: resolution of a quartet multiplicity and associated ^{195}Pt "satellite" structure in a resonance centered at 0.42 ppm, [^2J(HPt) = 69.4 Hz], which is characteristic[7] of a methylplatinum species, was accompanied by a multiplet pattern at δ 3.77 ppm attributable to the silyl hydrogen in the free silane function.

Scheme I



In contrast with its action on [Pt(COD)$_2$] or [Pt(COD)Me$_2$], addition of **1a** to [Pt(COD)(Y)Cl] (Y = Cl or Me) led to production of [Pt(chel)$_2$] (**2**) much more slowly. In the absence of NEt$_3$, non-chelated complexes analogous to **17** are formed initially, which undergo cis–trans isomerization: this is followed by further reaction to yield, from either system (Scheme I), the same Pt(IV) intermediate, whereupon HCl is then released in a reductive step to give the product (**2**). Thus COD displacement from the dichloro complex [Pt(COD)Cl$_2$] affords the cis isomer of [Pt(chelH)$_2$Cl$_2$] (**18**), ^1J(PtP) = 3662 Hz, which over 30 min equilibrates to a mixture containing ca. 30% of the corresponding trans isomer (**19**), ^1J(PtP) = 2917 Hz. In a similar manner the cis isomer of [Pt(chelH)$_2$(Me)Cl] (**20**) with ^1J(PtP) = 4266, 1699 Hz appears first from the chloro(methyl) precursor [Pt(COD)MeCl], but then rapidly (15 min) rearranges almost completely (ca. 90%) to the trans isomer (**21**) with ^1J(PtP) = 3011 Hz. Further characterization of these phosphinoalkylsilane intermediates **18**, **19**, and **21** was provided by ^{195}Pt NMR spectroscopy, which showed triplet resonances confirming attachment of two P atoms at Pt, and by ^{1}H NMR measurements (Table III). Subsequently, and more slowly (>60 min), a common product is formed from mixtures of either **18** and **19** or **20** and **21**. The ^{31}P NMR spectrum of this new species is immediately distinguishable from those of **18**–**21**, with a conspicuously low value for ^1J(PtP) = 1084 Hz that is typical for a Pt(IV) complex,[11] the identity of which was deduced from its ^{1}H NMR spectrum: this showed a hydride resonance, δ −10.00 ppm, split by coupling to two equivalent, cis P atoms and by coupling to ^{195}Pt with ^1J(PtH) = 770 Hz. These data are entirely consistent with a trans relationship between H and Cl in an octahedral platinum(IV) configuration, [Pt(chel)$_2$(H)(Cl)] (**22**); see Scheme I.

Displacement of COD from Pt(COD)$_2$ by the chelH analogues PPh$_2$CH$_2$CH$_2$SiMe(Ph)H (**1c**) or PPh$_2$CH$_2$CH$_2$SiRH$_2$ (**1d**, R = Me; **1e**, Ph) (which are respectively chiral or prochiral at Si) afforded analogues **4**–**6** of Pt(chel)$_2$ (**2**) as diastereoisomeric mixtures, so that the ^{31}P NMR spectra appeared as duplicate overlapping patterns (Table I) as has been depicted[2] previously. Unequal diastereomer ratios were evident in all three instances [ca. 60:40 (**4**), 80:20, (**5**), and 75:25, (**6**)]. Recrystallization of

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[11] Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1973**, 854. Belluco, U. *Organometallic and Coordination Chemistry of Platinum*; Academic: New York, 1974. Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

Table I. NMR Data for Bis-Chelate Platinum Complexes **2–6**

compound	δ(P)	^1J(PtP), Hz	$\delta(H_{SiMe})$	^4J(PH), Hz	^3J(PtH), Hz
$[Pt(chel)_2]$ (**2**)	−82.1	1613	0.28	2.5	28.0
$[Pt(PPh_2CH_2CH_2SiPh_2)_2]$ (**3**)	−83.6	1696		*b*	
$[Pt(PPh_2CH_2CH_2SiMePh)_2]$ (**4**)	−81.8[a]	1677	0.46	2.0	29.0
	81.5	1677	0.14	2.0	29.0
$[Pt(PPh_2CH_2CH_2SiMeH)_2]$ (**5**)	−84.0[a]	1724	0.35	2.2	33.0
	−84.3	1708			
$[Pt(PPh_2CH_2CH_2SiPhH)_2]$ (**6**)	−79.8[a]	1838		*b*	
	−80.3	1815			

[a] Major isomer. [b] ^{1}H NMR spectrum not observed.

Table II. NMR and IR Data for Pt–Si Bond Cleavage Products **7–16**

compound	δ(P)	^1J(PtP), Hz	^2J(PP) Hz	$\delta(H_{SiMe})$	$\delta(H_{PtH})$	^2J(PH), Hz	^1J(PtH), Hz	ν(PtH), cm^{-1}
$[Pt(chel)(PPh_2CH_2CH_2SiMe_2Cl)Cl]$ (**7**)	−85.5[a]	3101	388.8	0.12[c]				
	−114.1[b]	3018		0.08				
$[Pt(PPh_2CH_2CH_2SiPh_2)(PPh_2CH_2CH_2SiPh_2Cl)Cl]$ (**8**)	−87.2[a]	2956	392.7					
	−113.5[b]	2837						
$[PtH(PPh_2CH_2CH_2SiMe_2Cl)_2Cl]$ (**9**)	−112.6	2972		0.07	−16.84	12.9	1240	2200
$[PtH(PPh_2CH_2CH_2SiPh_2Cl)_2Cl]$ (**10**)	−111.6	2857			−17.22	12.2	12.82	2211
$[Pt(chel)Cl(PMe_2Ph)]$ (**11**)[d]	−86.2[e]	2988	399	0.20				
	−141.7[f]	2915						
$[Pt(PPh_2CH_2CH_2SiPh_2)Cl(PMe_2Ph)]$ (**12**)[g]	−88.6[e]	2861	400					
	−144.5[f]	2915						
$[Pt(PPh_2CH_2CH_2SiMe_3)_2I_2]$ (**13**)	−133.7	2409		−0.52				
$[Pt(PPh_2CH_2CH_2SiMe_2I)_2I_2]$ (**14**)	−131.9	2405		0.02				
trans-$[Pt(PPh_2CH_2CH_2SiMe_2Cl)_2Cl_2]$ (**15**)	−124.4	2549		0.09				
cis-$[Pt(PPh_2CH_2CH_2SiMe_2Cl)_2Cl_2]$ (**16**)	−129.9	3606		0.07				

[a] $PPh_2CH_2CH_2SiR_2$. [b] $PPh_2CH_2CH_2SiR_2Cl$. [c] ^3J(PtH) = 28.5 Hz. [d] ^{1}H NMR: $\delta(H_{PMe})$ = 1.78, J(PH) = 7.39 Hz (triplet, coupling to both P atoms), ^3J(PtH) = 34 Hz. [e] $PPh_2CH_2CH_2SiR_2$. [f] PMe_2Ph. [g] ^{1}H NMR: $\delta(H_{PMe})$ = 1.81, J(PH) = 7.21 Hz (triplet, coupling to both P atoms), ^3J(PtH) = 33.51 Hz.

Table III. NMR Data for Compounds **17–22**

compound	δ(P)	^1J(PtP), Hz	^2J(PP), Hz	$\delta(H_{SiMe})$	J(SiH),[a] Hz	^3J(HH), Hz	^1J(PtMe), Hz	^3J(HP), Hz	^2J(PtH), Hz
$[Pt(chelH)_2Me_2]$ (**17**)	−133.7	1699		0.06	3.77	3.7	0.41	*b*	69.4
cis-$[Pt(chelH)_2Cl_2]$ (**18**)[c]	−130.4	3662		0.22	3.60	4.8			
trans-$[Pt(chelH)_2Cl_2]$ (**19**)[d]	−121.3	2917		0.18	*e*	4.1			
cis-$[Pt(chelH)_2Cl(Me)]$ (**20**)	−126.9[j]	4266	12.5	0.07	3.67[i]	3.9	0.48	3.8	54.5
	−136.1[g]	1699		0.12[h]		4.1		7.2	
trans-$[Pt(chelH)_2Cl(Me)]$ (**21**)[f]	−122.9	3011		0.15	3.84	4.4	0.06	6.0	85.6
$[Pt(chel)_2H(Cl)]$ (**22**)[k]	−133.1	1084		0.53[l]		2.4			

[a] Coupling to silyl hydride. [b] Complex pattern. [c] δ(Pt) = 110.3 ppm. [d] δ(Pt) = 560.5 ppm. [e] Not observed. [f] $PPh_2CH_2CH_2SiMe_2$ *trans* to Cl. [g] $PPh_2CH_2CH_2SiMe_2$ *trans* to Me. [h] Assignment of SiMe uncertain. [i] Only one SiH observed. [j] δ(Pt) = −106.6 ppm. [k] ^{1}H NMR: $\delta(H_{PtH})$ = −10.04, ^1J(PtH) = 770.1 Hz, ^2J(PH) = 14.5 Hz. [l] ^3J(PtH) = 23.0 Hz.

complex **4** resulted in recovery of the pure major isomer, with δ −81.8 ppm and ^1J(PtP) = 1677 Hz in the ^{31}P NMR spectrum. Further reaction of this material with optically active (+)-2-methylbutyl iodide (i.e. R*I) followed a similar course to that of $Pt(chel)_2$ (**2**) with MeI, yielding a yellow product that again showed a duplicate ^{31}P NMR spectrum, this time with δ −134.6, −133.7 ppm and ^1J(PtP) = 2396, 2408 Hz, and in nearly equal ratio. Relationship of these parameters with those for **13–16** (Table II) supports the conclusion that cleavage of Pt–Si bonds in the purified diastereomer (**4**) has led to formation of two diastereoisomeric complexes $[Pt[PPh_2CH_2CH_2Si^*MeR^*Ph]_2I_2]$ each as the trans geometric isomer. This identifies the precursor as the dissymmetric isomer of **4** (racemic, C_2 symmetry) rather than its planar symmetric counterpart (meso, C_s symmetry) from which a single trans product would be formed. Thus the major isomer of **4** is concluded to be that in which the Me and Ph substituents at Si are related by 2-fold rotation, with nonidentical groups opposing one another above and below the chelate frameworks. If such preference is sterically controlled, it is then logical to assume that the significantly more abundant diastereomer that results when either analogue **5** or **6** is formed is also that with the two SiH bonds on opposite faces of the molecule. Crystallization of the purified major diastereomer of **4** has in fact allowed it to be characterized unequivocally as the racemic modification by using single-crystal X-ray diffractometry.[12]

Discussion

The discovery that certain platinum compounds are effective catalysts for the addition of Si–H bonds to alkenes or alkynes[13] (behavior typified[14] by the activity of "Speier's catalyst" in olefin hydrosilylation) has led to continuing exploration of such behavior[15] and interest in the properties of molecules that contain Pt–Si bonds.[16] As a consequence, numerous mononuclear silyl–platinum complexes have been isolated, although in almost every case[17] only a single silyl group is attached to Pt and only one example[18] is not a planar derivative of platinum(II). This

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(12) Cameron, T. S. Personal communication. An X-ray crystal structure determination for compound **4** shows a molecular geometry conforming to idealized C_2 symmetry (i.e. enantiomeric) that is otherwise very similar in framework interatomic distances and angles to[2] complex **2**.

(13) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(14) Speier, J. L.; Webster, J. A.; Bournes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

(15) Lewis, L. N.; Uriate, R. J. *Organometallics* **1990**, *9*, 621.

(16) Mackay, K. M.; Nicholson, B. K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, England, 1982, Vol. 6, p 1043.

(17) Ang, H. G.; Lau, P. T. *Organomet. Chem. Rev. A* **1972**, *8*, 281.

(18) Bentham, J. E.; Cradock, S.; Ebsworth, E. A. V. *J. Chem. Soc. A* **1971**, 587.

exception is a six-coordinate species $[PtI_2(PEt_3)_2(H)(SiH_2I)]$, which has been recovered[12] as a yellow solid after addition of SiH_3I to *trans*-$[PtI_2(PEt_3)_2]$ or alternately by the action of HI on *trans*-$[PtI(PEt_3)_2(SiH_2I)]$; slow decomposition at ambient temperature to the four-coordinate complex *trans*-$[PtI(PEt_3)_2(SiHI_2)]$ has been ascribed[12] to rearrangement accompanied by elimination of H_2. Much more recently, the platinum(IV) congeners $[PtH_2(PMe_3)_2(MPh_3)_2]$ (M = Ge or Sn) have been characterized by Trogler et al.:[19] no evidence was encountered in parallel chemistry for the existence of a silyl analogue (i.e. M = Si), where instead the platinum(II) monosilyl $[PtH(SiPh_3)(PMe_3)_2]$ was recovered in spite of the low steric requirements of the phosphine ligands at Pt.

Identification of platinum(IV) silyls is thus an objective of fundamental interest: a number of key transformations in silyl–platinum(II) chemistry (notably hydrogenolysis of Pt–Si bonds, which is in some circumstances reversible and therefore relevant to catalysis) are believed to occur via oxidative addition, i.e., formation of transient Pt(IV) species;[20] however, the latter have not normally been detectable, even by using in situ NMR spectroscopy on reacting systems.[19,21] In a directly related mechanistic context, the importance of sequential oxidative addition/reductive elimination vs nucleophilic displacement at square Pt(II) as a vehicle for substitution reactions in Pt–Si chemistry has hitherto been difficult to assess, because of departure of the liberated silyl fragment from the Pt center during the elimination step. The synthetic methodology[2,6] described above has recently been adapted to obtain[22] a palladium congener $Pd(chel)_2$ of complex **2**, which is reported to be distinctly more stable than nonchelated bis(silyl) analogues.

Chelation at Pt by the phosphinoethylsilyl ligand chel is accompanied by a diagnostic[23] shift to high frequency (i.e. downfield), to about −80 ppm (Table I) compared with free chelH (−151 ppm) or with the latter coordinated through P only (Table II); this situation is typified by the shifts of −85.5 and −114.1 ppm for the complex $[PtCl(chel)(PPh_2CH_2CH_2SiMe_2Cl)]$ (**7**). Precoordination through P of chelH is evidently an important step in attachment of chel at Pt, as is illustrated by NMR characterization of the intermediates **17–21** although whether or not a similar profile is followed in related chemistry such as regiospecific addition[4] of chelH at Ir(I) remains unknown. Subsequent hydrosilylation at Pt has for the first time been shown to proceed through an octahedral silylplatinum(IV) configuration (**22**), in which the influence of a trans relationship with Si and the oxidized state of the metal combine to reduce $^1J(PtP)$ to an exceptionally low value (1084 Hz). Control of substrate orientation in the vicinity of the metal site that is implicit in selectivity toward a preferred diastereoisomer of complexes **4–6** may be significant in relation to asymmetric catalysis.

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Registry No. **2**, 80298-94-8; **3**, 80298-95-9; **4**, 134733-12-3; **5**, 134733-13-4; **6**, 134733-14-5; **7**, 134681-59-7; **8**, 134681-60-0; **9**, 134681-61-1; **10**, 134681-62-2; **11**, 134681-63-3; **12**, 134681-64-4; **13**, 80298-99-3; **14**, 134681-65-5; **15**, 134681-66-6; **16**, 134733-15-6; **17**, 134681-58-6; **18**, 134681-69-9; **19**, 134681-70-2; **20**, 134780-97-5; **21**, 134733-16-7; **22**, 134704-96-4; $[PtCl_2(COD)]$, 12080-32-9; $[Pt(COD)_2]$, 12130-66-4; CCl_4, 56-23-5; $PPh_2CH_2CH_2SiMe_2^-$, 134681-67-7; $PPh_2CH_2CH_2SiPh_2^-$, 134681-68-8; $[Pt(COD)Me_2]$, 12266-92-1; [Pt(COD)MeCl], 50978-00-2; $[Pt[PPh_2CH_2CH_2Si^*Me(C^*H(CH_3)(CH_2CH_3)(CH_2))Ph]_2I_2]$ (isomer 1), 134733-17-8; $[Pt[PPh_2CH_2Si^*Me(C^*H(CH_3)(CH_2CH_3)(CH_2))Ph]_2I_2]$ (isomer 2), 134733-18-9; ^{195}Pt, 14191-88-9.

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(19) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159.
(20) Chatt, J.; Eaborn, C.; Ibekwe, S. D.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343.
(21) Glockling, F.; Hooton, H. A. *J. Chem. Soc. A* **1968**, 826.
(22) Schubert, U.; Miller, C. *J. Organomet. Chem.* **1989**, *373*, 165.
(23) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

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Kinetics of the Electron-Exchange Reaction of the Hexacyanoosmate(II/III) Couple in Aqueous Media

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The kinetics of the electron self-exchange reaction of the $Os(CN)_6^{4-/3-}$ couple have been investigated in aqueous media by using ^{13}C NMR line-broadening techniques. The electron-exchange rate constant for the $Os(CN)_6^{4-/3-}$ couple at 25 °C, $I = 1.0$ M (Na^+), is $(8.9 \pm 0.5) \times 10^4$ M^{-1} s^{-1} with $\Delta H^* = 36 \pm 4$ kJ mol^{-1} and $\Delta S^* = -31 \pm 12$ J K^{-1} mol^{-1}. The rate constants display a first-order dependence on [Na^+] and are dependent on the nature of the cation of the electrolyte, with an observed order of $k_{11}(Li^+) < k_{11}(Na^+) < k_{11}(NH_4^+) < k_{11}(K^+)$. The acid dissociation constants for the $(HNC)_nOs(CN)_{6-n}^{(4-n)-}$ species, $pK_1 = 0.5 \pm 0.3$ and $pK_2 = 2.0 \pm 0.2$ ($I = 1.0$ M (Na^+)), were determined from cyclic voltammetry and ^{13}C NMR chemical shift measurements. The electron-exchange rate constants decrease with increasing acidity owing to the proton equilibria involving the $(HNC)_2Os(CN)_4^{2-}$ ($k_2 = 1.8 \times 10^3$ M^{-1} s^{-1}, $I = 1.0$ M (Na^+)) and $(HNC)Os(CN)_5^{3-}$ ($k_1 = 2.8 \times 10^4$ M^{-1} s^{-1}) species. The exchange rate constants are discussed in terms of the inner-sphere and solvent reorganization barriers and compared with the corresponding parameters for other $M(CN)_n^{4-/3-}$ couples.

Introduction

Kinetic investigations of the electron-exchange and electron-transfer reactions of the $M(CN)_6^{4-/3-}$ couples of the iron triad have been almost exclusively limited to the $Fe(CN)_6^{4-/3-}$ system.[1] The $Fe(CN)_6^{n-}$ species are well-characterized outer-sphere cross-reactants and have been extensively employed in electron-transfer kinetics studies with organic compounds,[2] transition-metal complexes,[3] and metalloproteins.[4] Recently, in this laboratory,

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(1) (a) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: London, 1976. (b) Sieklucka, B. *Prog. React. Kinet.* **1989**, *15*, 175.
(2) For recent examples see: (a) Anast, J. M.; Margerum, D. W. *Inorg. Chem.* **1982**, *21*, 3494. (b) Toma, H. E.; Batista, A. A. *J. Inorg. Biochem.* **1984**, *20*, 53. (c) Krack, I.; van Eldik, R. *Inorg. Chem.* **1986**, *25*, 1743.

0020-1669/91/1330-3337$02.50/0