

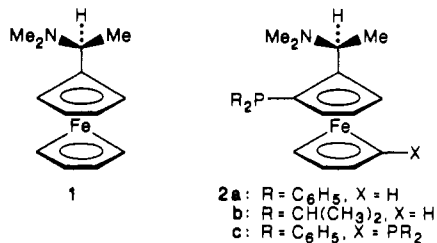
Platinum(II) Complexes of Ferrocenylphosphines as Hydrosilylation Catalysts. Crystal Structure of (P-N)PtCl₂ (P-N = Fe(η⁵-C₅H₅)(η⁵-C₅H₃(P(CHMe₂)₂)CHMeNMe₂-1,2))

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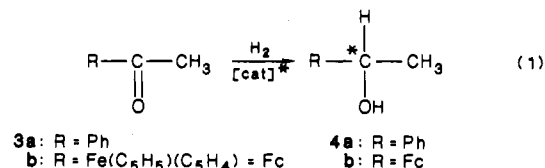
Platinum(II) complexes (P-N)PtCl₂ and (P-P)PtCl₂ (P-N = (S,R)-Fe(C₅H₅)(C₅H₃(CHMeNMe₂)PR₂-1,2), R = Ph (**2a**), CHMe₂ (**2b**); P-P = (S,R)-Fe(C₅H₄PPh₂)(C₅H₃(CHMeNMe₂)PPh₂-1,2) (**2c**)) are effective catalyst precursors for the hydrosilylation of the ketones PhCOR by Ph₂SiH₂ (R = CH₃, CH₂CH₂CH₃, CH(CH₃)₂). Chemical yields of the alcohols obtained following hydrolysis are high (100%), but optical yields are low (13.2% ee maximum). (P-N)PtCl₂ complexes are better catalyst precursors than (P-P)PtCl₂. Diphenylsilane reacts with (P-N)PtCl₂, yielding the stable Pt(IV) hydride. This eliminates Ph₂SiHCl in solution to afford (P-N)PtClH. Ferrocenyl ketones, FcCOR (R = CH₃, Ph) under the same conditions, with (P-N)PtCl₂ (P-N = **2a**) as catalyst precursor, afford FcCHOHR (R = CH₃) and FcCH₂R, the major product (R = CH₃, Ph), directly without a hydrolysis step. The optical yield of FcCHOHCH₃ is low (1.5%). The stable carbonium ion FcCHCH₃⁺ is reduced by Ph₂SiH₂ to FcCH₂CH₃ in a thermal reaction that is catalyzed by the complex (P-N)PtCl₂ (P-N = **2a**). The mechanistic implications of these observations are discussed. The structure of the hydrosilylation catalyst precursor (P-N)PtCl₂ (P-N = (S,R)-**2b**) has been determined. Crystals are orthorhombic, space group P2₁2₁2₁, with a = 11.000 (1) Å, b = 11.358 (1) Å, c = 17.998 (2) Å, V = 2248.6 (4) Å³, Z = 4, and D_{expl} = 1.888 g cm⁻³. The Pt atom has cis-square-planar coordination, which shows a significant distortion toward tetrahedral geometry with Cl-Pt-P and Cl-Pt-N trans angles of 169.7 (1) and 171.8 (2)°. The two Pt-Cl bond distances differ significantly with 2.394 (3) Å for Pt-Cl(1) trans to P and 2.288 (3) Å for Pt-Cl(2) trans to N.

Metal complexes of chiral phosphines and arsines have increasing importance as catalysts for the asymmetric hydrogenation, hydrosilylation, and hydroformylation of unsaturated substrates such as olefins, ketones, and imines.^{1,2} The aminoferrocene derivative **1**, which is easily resolved via its tartrate salt, is an important precursor for the synthesis of chiral ligands such as **2**.³⁻⁷



The catalytic hydrogenation of unactivated ketones generally does not proceed with high optical yield. For example if cat* is a rhodium(I) derivative of the ligand BPPFOH (**2c** with the -NMe₂ group replaced by -OH), the optical yield for eq 1 (R = Ph) is 43%.⁸ Recently other workers have improved this using Rh(I)/DIOP complexes with added amine as a promoter.^{9,10} Optical yields as high as 74% can be achieved.

The reduction of **3a** via asymmetric hydrosilylation has also been investigated with use of Rh(I)-based complexes.^{1,2} Again, a combination Rh(I)/MPFA complex (MPFA = **2a** with R =



Me) affords good results (52% ee). Recently Brunner and co-workers have found that very good optical yields for ketone hydrosilylation (88%) are obtainable using Rh(I) derivatives of "harder" (non-phosphine-containing) chiral ligands.¹¹

Derivatives of other metals such as Pt(II) have received little attention. Kumada and co-workers¹² found that chiral monodentate phosphine/Pt(II) combinations catalyze the hydrosilylation of ketones, including **3a**, in good chemical yield but the optical yield is low (18.6% maximum). Brunner and co-workers¹³ report low optical yields from catalysts based on Pt(II)/chelating amines.

The present investigation on the asymmetric hydrosilylation of ketones such as **3** was initiated because of our interest in the catalytic activity of platinum(II) complexes of "hard-soft" ligands such as **2a**^{5,6} and because of our desire to prepare chiral **4b**. Successful use of metal complexes of ligands such as **2** in this particular reaction would effectively enable the catalyst to breed its own chirality, an objective that has been achieved for some chiral bis(tertiary phosphines).¹⁴ This would be viable because **4b** is easily transformed into **1**.¹⁵

Experimental Section

¹H NMR spectra were recorded on Bruker WP-80 and WH-400 spectrometers operating at 80 and 400 MHz, respectively. ³¹P{¹H} NMR spectra were recorded on a Bruker WP-80 spectrometer operating at 32.3 MHz. ³¹P shifts are given relative to 85% H₃PO₄ with P(OMe)₃ (δ = 141.0) used as an external reference. A Hewlett-Packard 5880A gas chromatograph with a Carbowax column was used to identify the reaction products. Optical rotations were measured in a 1-dm cell with a Perkin-Elmer 141 polarimeter. Melting points were determined with a Gallenkamp melting point apparatus and are reported without correction. Microanalyses were performed by P. Borda of the University of British Columbia.

Chiral ligands **2a-c** were prepared according to literature procedures.³⁻⁵ Platinum(II) complexes of **2a-c** were prepared according to

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literature methods¹⁶ with some modification.

One millimole of K_2PtCl_4 in 5 mL of H_2O was treated with 1 mmol of **2a** (**2b** or **2c**) in 10 mL of CH_2Cl_2 . The solution mixture was stirred for about 3 h until the aqueous phase became colorless. The organic phase was separated and dried ($MgSO_4$), and the solvent was reduced to small volume. The solid product was precipitated by dropwise addition of diethyl ether. The solid was isolated and recrystallized from CH_2Cl_2 or $CHCl_3$ by precipitation with diethyl ether.

(P-N)PtCl₂ (P-N = (S,R)-**2a**): yield 63%; mp 191–193 °C dec. Anal. Calcd for $C_{26}H_{28}NCl_2PtFe \cdot H_2O$: C, 43.06; H, 4.14; N, 1.93. Found: C, 43.16; H, 3.83; N, 1.90. ¹H NMR (δ , $CDCl_3$): 1.39 (d, $J_{HH} = 7.2$ Hz, CCH_3); 2.97, 3.77 (2 × s, NMe_2); 3.57–3.62 (m, $CHCH_3$); 3.81 (s, FeC_5H_5); 4.25, 4.47 (2 × b s, FeC_5H_5); 7.31–7.57; 8.19–8.25 (m, P-(C_6H_5)₂). ³¹P{¹H} NMR (δ , $CDCl_3$): -11.89 ($J_{P-P} = 3981.9$ Hz).

(P-N)PtCl₂ (P-N = (S,R)-**2b**): yield 47%; mp 195–197 °C dec. Anal. Calcd for $C_{20}H_{32}NCl_2PtFe$: C, 37.59; H, 5.01; N, 2.19. Found: C, 37.49; H, 5.23; N, 2.05. ¹H NMR (δ , $CDCl_3$): 1.26–1.70 (m, $CHCH_3$, $CH(CH_3)_2$); 2.45, 3.45 (2 × b s, $N(CH_3)_2$); 2.68, 3.08 (2 × b m, $CH(CH_3)_2$); 3.96–4.20 (m, $CHCH_3$); 4.25 (s, FeC_5H_5); 4.32–4.64 (m, FeC_5H_5). ³¹P{¹H} NMR (δ , $CDCl_3$): 9.51 ($J_{P-P} = 3889.3$ Hz).

(P-P)PtCl₂ (P-P = (S,R)-**2c**): yield 66%; mp 187–189 °C dec. Anal. Calcd for $C_{38}H_{37}NCl_2P_2FePt$: C, 50.20; H, 4.29; N, 1.54. Found: C, 50.78; H, 4.32; N, 1.55. ¹H NMR (δ , $CDCl_3$): 1.31 (d, $J_{HH} = 7.2$ Hz, $CHCH_3$); 2.32 (s, $N(CH_3)_2$); 3.42–3.58, 4.11–4.63 (m, $C_5H_4FeC_5H_5$); 5.89–5.97 (m, $CHCH_3$); 7.00–8.53 (m, P(C_6H_5)₂). ³¹P{¹H} NMR (δ , $CDCl_3$): 15.49 ($J_{P-P} = 3860.5$ Hz, $J_{PP} = 8$ Hz); 8.70 ($J_{P-P} = 3720.3$ Hz, $J_{PP} = 8$ Hz).

Experiments. 1. Reaction of Acetylferrocene with Diphenylsilane. The catalyst precursor (P-N)PtCl₂ (P-N = **2a**, 0.04 mmol) in 10 mL of degassed CH_2Cl_2 , acetylferrocene (4 mmol), and diphenylsilane (8 mmol) were mixed in a Carius tube under N_2 . The tube was sealed with a Teflon valve and heated (60 °C) with stirring for ~24 h. The reaction was monitored by TLC until there was no acetylferrocene remaining. Diethyl ether (100 mL) was added to precipitate out any metal complexes, and the solution was filtered and evaporated to leave a red-brown oil. Column chromatography on neutral alumina ($CHCl_3$ eluent) revealed the presence of first ethylferrocene followed by ferrocenylethanol. The ethylferrocene was an orange oil: bp 88–90 °C (1 mm), lit.¹⁷ bp 108.9 °C (5.5 mm); isolated yield 60%. Anal. Calcd for $C_{12}H_{14}Fe$: C, 67.38; H, 6.54. Found: C, 67.68; H, 6.30. ¹H NMR (δ , $CDCl_3$): 1.22 (t, $J_{HH} = 7$ Hz, CH_2CH_3); 2.35 (q, $J_{HH} = 7$ Hz, CH_2CH_3); 4.21 (s, C_5H_5); 4.75–4.70 (m, C_5H_5). The alcohol, isolated yield 18%, had mp 75–77 °C (lit.¹⁸ mp 78–79 °C). Anal. Calcd for $C_{12}H_{14}OFe$: C, 62.67; H, 6.09. Found: C, 62.77; H, 6.04. ¹H NMR (δ , $CDCl_3$): 1.45 (d, $J_{HH} = 7$ Hz, CH_3); 1.93 (b s, OH); 4.21 (s, C_5H_5); 4.25–4.75 (m, CH).

2. Reaction of Benzoylferrocene with Diphenylsilane. The conditions were essentially as in experiment 1 except that 2 mol % of the catalyst precursor was employed and the reaction time was 67 h. Only benzylferrocene was isolated (85%) as product after workup by column chromatography: mp 76–79 °C (lit.¹⁹ mp 76 °C). Anal. Calcd for $C_{17}H_{16}Fe$: C, 73.97; H, 5.80. Found: C, 73.58; H, 5.91. ¹H NMR (δ , $CDCl_3$): 3.75 (s, CH_2); 4.20 (s, C_5H_5); 7.28 (b s, C_6H_5).

3. Other Hydrosilylation Reactions. The catalyst precursor (1 mol %), CH_2Cl_2 (3 mL), ketone (1 mol), and diphenylsilane (1 or 2 mol) in a stirred sealed tube under nitrogen were treated as shown in Tables III–V. Acetone (20 mL) containing 4 mL of aqueous HCl solution (10%) was added to the reaction mixture. After 2 h at 20 °C with stirring, the organic phase was extracted with diethyl ether, dried ($MgSO_4$), and evaporated. The residue was distilled under vacuum to afford a mixture of ketone and alcohol. These were identified by GLC (Carbowax column) and by their known ¹H NMR spectra.

4. Reaction of Diphenylsilane with (P-N)PtCl₂ (P-N = **2a,b).** A solution of (P-N)PtCl₂ in CH_2Cl_2 was treated with 2 mol of Ph_2SiH_2 . After 2 days at 20 °C anhydrous diethyl ether was added to the reaction mixture to precipitate the platinum(IV) hydride product from **2a**; yield 30%. Anal. Calcd for $C_{38}H_{40}NCl_2SiP_2FePt$: C, 51.20; H, 4.49; N, 1.57; Cl, 7.45. Found: C, 50.43; H, 4.79; N, 1.76; Cl, 7.18.

Product from **2b**: yield 25%. Anal. Calcd for $C_{32}H_{44}NCl_2SiP_2FePt$: C, 46.68; H, 5.34; N, 1.70; Cl, 8.61. Found: C, 46.36; H, 5.52; N, 1.64; Cl, 8.44.

5. Reaction of Sodium Borohydride with (P-N)PtCl₂. To a suspension of (P-N)PtCl₂ (P-N = **2a**, 0.4 g) in 15 mL of methanol was added

Table I. Final Positional (Fractional, $\times 10^4$; Pt and Fe, $\times 10^5$) and Isotropic Thermal Parameters (U , $\times 10^3 \text{ \AA}^2$)^a with Estimated Standard Deviations in Parentheses

| atom | x | y | z | U_{eq} |
|-------|------------|------------|-----------|----------|
| Pt | 47359 (4) | 54337 (3) | 10112 (2) | 33 |
| Fe | 85801 (14) | 61688 (13) | 25256 (9) | 33 |
| Cl(1) | 2637 (3) | 4880 (2) | 1041 (2) | 54 |
| Cl(2) | 4676 (4) | 4893 (4) | -213 (2) | 78 |
| P | 6754 (3) | 5620 (2) | 915 (2) | 33 |
| N | 4564 (7) | 6084 (7) | 2124 (4) | 30 |
| C(1) | 7358 (8) | 5374 (8) | 1842 (5) | 27 |
| C(2) | 6751 (9) | 5836 (8) | 2479 (5) | 27 |
| C(3) | 7276 (10) | 5294 (9) | 3111 (6) | 39 |
| C(4) | 8177 (10) | 4505 (10) | 2876 (6) | 43 |
| C(5) | 8241 (9) | 4547 (10) | 2091 (6) | 37 |
| C(6) | 9508 (12) | 7489 (11) | 1996 (8) | 56 |
| C(7) | 8956 (12) | 7914 (10) | 2669 (9) | 62 |
| C(8) | 9399 (13) | 7272 (14) | 3267 (8) | 68 |
| C(9) | 10270 (14) | 6447 (12) | 2952 (9) | 68 |
| C(10) | 10274 (14) | 6607 (11) | 2209 (9) | 65 |
| C(11) | 5701 (9) | 6689 (8) | 2476 (6) | 26 |
| C(12) | 5520 (10) | 7232 (9) | 3233 (6) | 41 |
| C(13) | 4161 (12) | 5138 (9) | 2626 (7) | 48 |
| C(14) | 3608 (11) | 7011 (10) | 2089 (8) | 51 |
| C(15) | 7281 (12) | 7036 (10) | 503 (6) | 46 |
| C(16) | 6849 (13) | 8134 (9) | 905 (8) | 58 |
| C(17) | 7026 (17) | 7055 (12) | -323 (7) | 77 |
| C(18) | 7502 (11) | 4485 (11) | 333 (6) | 45 |
| C(19) | 8872 (12) | 4634 (15) | 253 (7) | 66 |
| C(20) | 7157 (13) | 3235 (10) | 557 (7) | 56 |

^a U_{eq} = one-third of the trace of the diagonalized U matrix.

dropwise a methanol solution of sodium borohydride (0.01 g/mL) at 0 °C with stirring under N_2 until the reaction mixture changed to a brown color.²⁰ The mixture was stirred for about 15 min, acidified with methanolic HCl, and extracted with benzene (3×10 mL). The benzene extract was reduced in volume, and *n*-pentane was added to give a pale orange solid, yield 43%. Anal. Calcd for $C_{26}H_{29}NClP_2FePt$: C, 46.42; H, 4.31; N, 2.08. Found: C, 46.80; H, 4.65; N, 2.30. ¹H NMR (δ , CD_2Cl_2): -18.55 ($J_{PtH} = 1341$ Hz, $J_{PH} = 14$ Hz). ³¹P{¹H} NMR (δ , $CDCl_3$): 9.69 ($J_{P-P} = 4392$ Hz).

X-ray Crystal Analysis of (P-N)PtCl₂ (P-N = (S,R)-2b**).** A red crystal of *cis*-dichloro[1-(diisopropylphosphino)-2-(1-(dimethylamino)ethyl)ferrocene]platinum(II) of dimensions $0.4 \times 0.2 \times 0.05$ mm, with {100}, {001}, and {001} forms was mounted on an Enraf-Nonius CAD4-F diffractometer. Unit cell parameters were refined by least-squares methods on $\sin \theta$ values for 25 reflections with $\theta = 12$ – 19° (Mo $K\alpha_1$ radiation, $\lambda = 0.70930$ Å). Crystal data at 22 °C: $C_{20}H_{32}Cl_2FePt$, $M_r = 639.3$, orthorhombic, $P2_12_12_1$, $a = 11.000$ (1) Å, $b = 11.358$ (1) Å, $c = 17.998$ (2) Å, $V = 2248.6$ Å³, $Z = 4$, D_{exp} = 1.888 g cm⁻³, $F(000) = 1248$, μ (Mo $K\alpha$) = 72 cm⁻¹.

Intensities were measured with Mo $K\alpha$ radiation (graphite monochromator) for $\theta \leq 30^\circ$, ω - 2θ scan, ω -scan width $(0.65 + 0.35 \tan \theta)^\circ$, extended 25% on each side for background counts, scan speeds 1– 10° min⁻¹, horizontal and vertical apertures $(2.00 + \tan \theta)$ mm and 4 mm, respectively, intensity checks every 1 h, and orientation checks every 150 reflections. Intensities were corrected for Lorentz, polarization, and absorption (transmission factors 0.17–0.61). Of 3660 reflections measured, 2217 (61%) had $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, S = scan count, and B = time-averaged background count.

The structure was determined by Patterson and Fourier methods and refined by full-matrix least-squares techniques, with H atoms fixed in calculated positions: final $R = 0.035$ (0.056 for the refined enantiomer, which can therefore be rejected); $R_w = 0.036$; goodness of fit 1.20, for 2217 reflections; $R = 0.085$ for all data; $w = 1/\sigma^2(F)$ gave uniform values of $\sum w(\Delta F)^2$ as a function of F_o and $\sin \theta$; maximum shift in final cycle 0.036σ, maximum fluctuations in final difference synthesis -0.92 and +0.86 e Å⁻³. Atomic scattering factors from ref 21a were used with locally written or locally modified versions of standard computer pro-

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 (21) (a) *International Tables for X-ray Crystallography*; and 149. Kynoch: Birmingham, England, 1974; Vol. IV, pp 99–102, 149. (b) Programs used: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

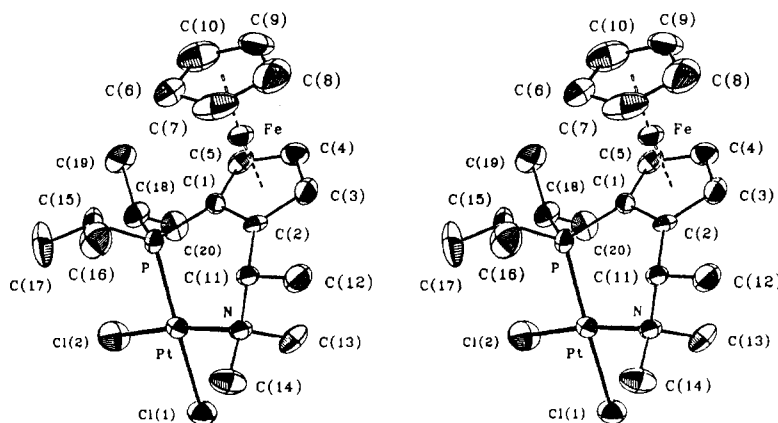


Figure 1. Structure of (P-N)PtCl₂ (P-N = (S,R)-2b).

Table II. Summary of Molecular Dimensions (Distances, Å; Angles, deg)

| | | | |
|------------|-----------|----------------|-----------|
| Pt-Cl(1) | 2.394 (3) | Pt-P | 2.237 (3) |
| Pt-Cl(2) | 2.287 (3) | Pt-N | 2.144 (8) |
| Cl(1)-Pt-P | 169.7 (1) | Cl(1)-Pt-Cl(2) | 85.6 (1) |
| Cl(2)-Pt-N | 171.8 (2) | Cl(1)-Pt-N | 89.1 (2) |
| P-Pt-N | 97.3 (2) | Cl(2)-Pt-P | 88.8 (1) |

Fe-C: 2.01–2.05 (1), mean 2.037 (4)
 P-C(1): 1.82 (1)
 P-C(propyl): 1.85 (1), 1.86 (1), mean 1.858 (6)
 angles at P: 103.8–114.9 (3–5)
 N-C(11): 1.56(1)
 N-C(Me): 1.47 (1), 1.49 (1), mean 1.480 (9)
 Pt-N-C(11): 117.4 (6)
 other angles at N: 105.5–110.4 (6–9)
 C-C (Cp rings): 1.35–1.45 (2), mean 1.408 (6)
 C-C-C (Cp rings): 105.6–112.0 (8–14), mean 108.0 (4)

grams.^{21b} Final positional parameters are in Table I, and significant bond distances and angles are summarized in Table II.

Results and Discussion

The three new chiral complexes of Pt(II) used in this investigation are the compounds (P-N)PtCl₂ and (P-P)PtCl₂ where P-N = (S,R)-2a and (S,R)-2b and P-P = (S,R)-2c. Two descriptors for configuration are necessary because of the presence of a chiral center ((S,R)) and planar chirality ((S,R)). The analytical data show that the formulation of the complexes is correct. The NMR spectra reveal that the -NMe₂ group is bound in the case of the complexes of 2a and 2b since two NMe resonances are present. The complex containing 2c shows only a sharp singlet for the NMe₂ group, and the ³¹P NMR spectrum shows platinum coupling to both PPh₂ groups; thus, the ligand is bound through both phosphorus atoms.²²

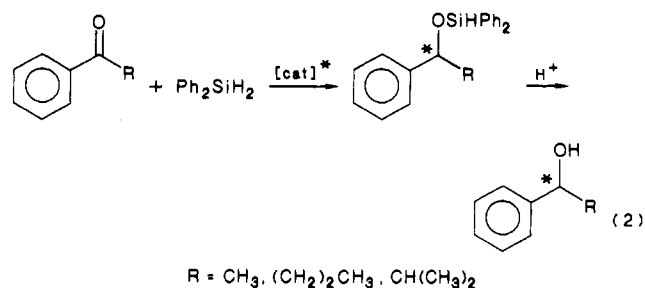
The resonances of the NMe₂ groups are sharp in the ambient-temperature spectrum of the complexes of 2a and 2c but are broad in the complex of 2b. This broadening is probably associated with a conformational nonrigidity as found previously for the complexes [(P-N)RhNBD]ClO₄, where P-N denotes ligands analogous to 2 but with -P(CMe₃)₂ replacing the -PPh₂ groups.^{6a}

In the solid state the molecule of 2b (Figure 1) is chiral, with an S configuration for the amine-substituted C(11) atom and an R configuration for the asymmetrically substituted ferrocene moiety as anticipated from the preparation procedure used.^{18,23} The iron atom is sandwiched between two cyclopentadienyl rings, which are planar within experimental error, deviate slightly from

coplanarity (angle between ring planes 5.7°), and are separated by an average of 3.29 Å. The orientation of the rings is close to an eclipsed conformation (rotation from eclipsed 3.7°, defined in terms of vectors from each ring atom to the mean ring center). The Pt atom has cis-square-planar coordination, to two Cl atoms and the P and N atoms of the ferrocene ligand; the coordination shows a significant distortion toward tetrahedral geometry, with Cl-Pt-P and Cl-Pt-N trans angles of 169.7 (1) and 171.8 (2)°, respectively. The six-membered chelate ring is a boat, with P and C(11) at prow and stern. This ring does not seem to have much vibrational motion in the solid state, although as mentioned above, it could be conformationally mobile in solution and involved in a chair-boat equilibrium.

Bond lengths and angles (Table II) are generally close to expected values. The two Pt-Cl bond distances differ significantly, presumably as a result of the differing influences of the trans substituents (2.394 (3) Å for Pt-Cl(1) trans to P, 2.288 (3) Å for Pt-Cl(2) trans to N).²⁴ In *cis*-PtCl₂(PEt₂Ph)(CNEt), the two bond lengths are 2.390 (8) Å (trans to P) and 2.314 (10) Å²⁵ a difference of 0.076 Å. Larger differences (0.17 Å) are found in chlorine-bridged species.²⁶

The use of Ph₂SiH₂ in the catalyzed hydrosilylation of aromatic ketones is well-established.¹ In the present work the same silane was used (eq 2) and found to be effective in terms of chemical



yield of the alcohol isolated after the necessary hydrolysis step.²⁷ The P...N bound catalyst precursors (P-N)PtCl₂ are more active than (P-P)PtCl₂ (P-P = 2c) (Tables III–V). For example 3a is 100% hydrosilylated at 60 °C with the aid of (P-N)PtCl₂; the yield is 0% when the conditions are the same but the catalyst is (P-P)PtCl₂. This may be a further instance of the efficacious combination of “hard-soft” mixed ligands with the appropriate metal.^{13,28–31}

(22) In ligands such as 2c, where there is a choice of P...N binding, the only exceptions to the P...P mode found to date are in Rh(I) complexes of ligands where PPh₂ groups are replaced by -P(CMe₃)₂.^{6a}

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Table III. Asymmetric Hydrosilylation of Ketones with Ph₂SiH₂ Catalyzed by (P-N)PtCl₂ (P-N = (S,R)-2a)^a

| ketone | silane:ketone | product | yield, % ^b | optical yield, % ^c |
|---|------------------|---|-----------------------|-------------------------------|
| C ₆ H ₅ COCH ₃ | 1:1 | C ₆ H ₅ CHOHCH ₃ | 85 | 3.8 (S) |
| C ₆ H ₅ COCH ₃ | 2:1 | C ₆ H ₅ CHOHCH ₃ | 100 | 4.2 (S) |
| C ₆ H ₅ CO(CH ₂) ₂ CH ₃ | 1:1 | C ₆ H ₅ CHOH(CH ₂) ₂ CH ₃ | 30 | 9.4 (S) |
| C ₆ H ₅ CO(CH ₂) ₂ CH ₃ | 2:1 | C ₆ H ₅ CHOH(CH ₂) ₂ CH ₃ | 52 | 7.1 (S) |
| C ₆ H ₅ COCH(CH ₃) ₂ | 1:1 | no product | 0 | |
| C ₆ H ₅ COCH(CH ₃) ₂ | 2:1 ^d | C ₆ H ₅ CHOHCH(CH ₃) ₂ | 27 | 1.2 (S) |

^a Conditions: ketone:Pt = 100:1; solvent, 3 mL of CH₂Cl₂; temperature, 20 °C; time, 48 h. ^b GLC yield based on starting ketone. ^c Optical yields are calculated with respect to optically pure 1-phenylethanol ([α]_D = -52.5° (C 2.27, CH₂Cl₂): Nagar, U.; Shishido, T.; Chiba, R.; Mitsushashi, H. *Tetrahedron* **1965**, *21*, 1701), *n*-propylphenylcarbinol ([α]_D = -45.9° (C 6.1, benzene): Mislow, K.; Hamermesh, C. L. *J. Am. Chem. Soc.* **1955**, *77*, 1590), and phenylisopropylcarbinol ([α]_D = -48.3° (C 7, ether): Cram, D. J.; McCarty, J. E. *J. Am. Chem. Soc.* **1957**, *79*, 2866) and calibrated for the optical purity of the chiral ligand used (90%). ^d Reaction time 90 h.

Table IV. Asymmetric Hydrosilylation of Ketones with Ph₂SiH₂ Catalyzed by (P-N)PtCl₂ (P-N = (S,R)-2b)^a

| ketone | silane:ketone | temp, °C | time, h | product | yield, % | optical yield, % |
|---|---------------|----------|---------|---|----------|------------------|
| C ₆ H ₅ COCH ₃ | 2:1 | 60 | 48 | C ₆ H ₅ CHOHCH ₃ | 100 | 1.2 (S) |
| C ₆ H ₅ COCH ₃ | 2:1 | 60 | 24 | C ₆ H ₅ CHOHCH ₃ | 100 | 1.9 (S) |
| C ₆ H ₅ COCH ₃ | 2:1 | 20 | 48 | C ₆ H ₅ CHOHCH ₃ | 100 | 1.2 (R) |
| C ₆ H ₅ COCH ₃ | 2:1 | 20 | 24 | C ₆ H ₅ CHOHCH ₃ | 29 | 3.9 (R) |
| C ₆ H ₅ COCH ₃ | 1:1 | 20 | 45 | C ₆ H ₅ CHOHCH ₃ | 69 | 4.2 (R) |
| C ₆ H ₅ CO(CH ₂) ₂ CH ₃ | 2:1 | 20 | 66 | C ₆ H ₅ CHOH(CH ₂) ₂ CH ₃ | 100 | 2.8 (S) |
| C ₆ H ₅ CO(CH ₂) ₂ CH ₃ | 1:1 | 20 | 65 | C ₆ H ₅ CHOH(CH ₂) ₂ CH ₃ | 21 | 3.0 (S) |
| C ₆ H ₅ CO(CH ₂) ₂ CH ₃ | 1:1 | 60 | 48 | C ₆ H ₅ CHOH(CH ₂) ₂ CH ₃ | 97 | 1.5 (S) |
| C ₆ H ₅ COCH(CH ₃) ₂ | 2:1 | 20 | 66 | C ₆ H ₅ CHOHCH(CH ₃) ₂ | 3 | ^b |
| C ₆ H ₅ COCH(CH ₃) ₂ | 1:1 | 60 | 68 | C ₆ H ₅ CHOHCH(CH ₃) ₂ | 100 | 1.1 (S) |

^a See Table III for footnotes *b* and *c* explaining the yield and optical yield, columns, respectively. ^b Not recorded.

Table V. Asymmetric Hydrosilylation of Butyrophenone with Ph₂SiH₂ Catalyzed by (P-N)PtCl₂ (P-N = (S,R)-2a)^a

| silane:ketone | temp, °C | time, h | yield, % | optical yield, % |
|---------------|-----------------|---------|----------|------------------|
| 2:1 | 20 | 48 | 52 | 7.1 (S) |
| 2:1 | 20 | 70 | 86 | 7.2 (S) |
| 1:1 | 20 | 48 | 30 | 9.4 (S) |
| 1:1 | 20 ^b | 48 | 10 | 12.6 (S) |
| 1:1 | 4 | 93 | 10 | 13.2 (S) |
| 1:1 | 4 ^c | 93 | 29 | 9.1 (S) |
| 1:1 | 60 | 48 | 98 | 1.6 (S) |

^a See Table III for footnotes *b* and *c* explaining the yield and optical yield columns, respectively. ^b P-N:(P-N)PtCl₂ = 5:1. ^c HCl:(P-N)PtCl₂ = 10:1.

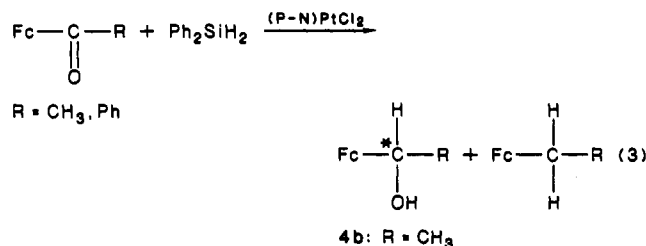
The hydrosilylation reaction of eq 2 is unsatisfactory in terms of the optical yield of the isolated alcohol. In general the best optical yields (e.g. 13.2% from butyrophenone) are obtained at low temperature and low conversion. The same effect was noted by Kolb and Hetflejš³² for the DIOP/Rh(I)-catalyzed hydrosilylation of PhCOCMe₃. The results in Table IV show that the configuration of the product is also temperature-dependent; *R* and *S* alcohols are obtained from the reaction of acetophenone at 20 and 60 °C, respectively. This may be due to a change in the relative populations of ligand conformations with temperature.^{6a} As noted above, when P-N = **2b** the NMR spectra of (P-N)PtCl₂ indicate that the complex is conformationally nonrigid.

The absolute configuration of the product from acetophenone (20 °C) is *S* for reactions catalyzed by derivatives of **2a** but is

R when the ligand is **2b**. A similar reversal has been noted in the asymmetric hydrogenation of prochiral olefins when the catalyst precursors are [(P-N)RhNBD]ClO₄ (P-N = **2a** or **2a** with R = CMe₃).³¹

The addition of excess ligand to the reaction mixture (Table V) increases the optical yield although it decreases the chemical yield. This may be because it discourages dissociation of the ligand from the metal complex,³⁰ thereby ensuring that the ligand is bound in the chelate mode which would be more favored to induce asymmetry into the reaction product. The lower yield could be due to the formation of (P-N)_xPt type complexes *x* > 1, with loss of catalytic activity. In the presence of excess HCl, the chemical yield is increased but the optical yield is decreased.

Reduction of Ferrocenyl Ketones. In contrast with the results described for eq 2, when acetylferrocene is heated with diphenylsilane in the presence of (P-N)PtCl₂ (P-N = **2a**), ethylferrocene (60% yield) and ferrocenylethanol (18% yield) are produced directly: no hydrolysis step is necessary (eq 3). Under the same conditions benzoylferrocene affords only benzylferrocene.



The minor product from acetylferrocene, **4b**, is chiral, but the optical yield is low (1.5%). This result seems to negate any hopes expressed in the introduction of producing this alcohol in useful optical yield via a catalyzed hydrosilylation reaction.

Although reduction of ketones to hydrocarbons during homogeneous catalyzed hydrosilylation is not common, poly(methylhydrosiloxane) will reduce nitrobenzene and benzaldehyde to aniline and toluene, respectively, in the presence of Pd/C.³³ Diethyl ether is obtained from the NiCl₂-catalyzed reaction of ethyl acetate with Et₃SiH.³⁴ Stoichiometric reductions of organic

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(30) Complexes of "hard-soft" ligands are often employed in catalysis in the hope of creating a vacant site on the metal by dissociation of one end of the ligand. A number of plausible mechanisms have been based on this concept, e.g. the asymmetric cross-coupling reaction studied by Kumada and co-workers,²⁹ but there is little direct experimental evidence in support of the phenomenon. It does seem that the complex [(As-N)RhNBD]ClO₄ (As-N = **2a** with AsPh₂ instead of PPh₂) is such an example.³¹

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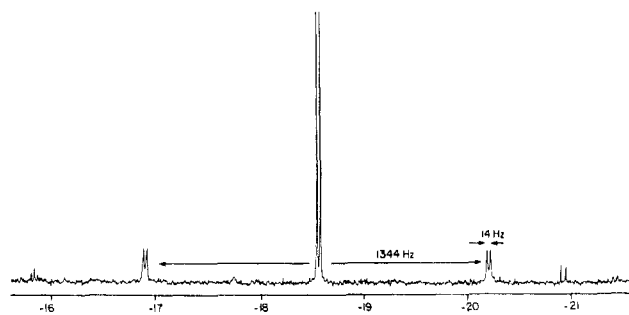


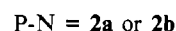
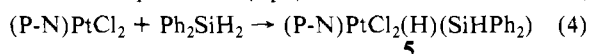
Figure 2. ^1H NMR spectrum of a solution (CD_2Cl_2) of **5**, ($\text{P-N} = \mathbf{2a}$) in the hydride region.

compounds by hydrosilanes are not unusual.^{35–38} For example, Gilman and Diehl³⁵ showed that benzophenone can be reduced to diphenylmethane by diphenylsilane at high temperature (270 °C). Other diaryl ketones react similarly although acetophenone is unaffected. In the case of benzophenone this uncatalyzed reaction is believed to proceed through a siloxy intermediate, $\text{Ph}_2\text{CHOSiHPh}_2$, which can be isolated when the ketone and silane are heated at slightly lower temperature.³⁶ Kazakova et al.³⁷ showed that treating stoichiometric amounts of acetylferrocene with $\text{Et}_3\text{SiH}/\text{CF}_3\text{CO}_2\text{H}$ also gave ethylferrocene. These reductions likely involve carbonium ion intermediates as does the $\text{LiAlH}_4/\text{AlCl}_3$ reduction of ferrocenyl ketones.^{39,40} One of the well-established features of the chemistry of ferrocene compounds is the stability of the α -ferrocenylcarbonium ion,^{40,41} and it seems likely that it is this which accounts for the different products formed by hydrosilylation of the ferrocenyl ketones. Thus, the hydrogenolysis could involve reaction of the carbonium ion $\text{FcC}^+(\text{H})\text{R}$ with diphenylsilane. The carbonium ion could be formed either from $\text{FcCHROSiPh}_2\text{H}$, the expected hydrosilylation product, or from an intermediate such as **9** earlier in the catalytic cycle. As a test, the preformed carbonium ion⁴² with $\text{R} = \text{CH}_3$ was treated with the silane in CH_2Cl_2 at 60 °C. The dark color of the solution gradually fades (2 days), and ethylferrocene can be isolated from the solution by following the same workup as used for experiment 1. When an identical reaction is carried out in the presence of 1 mol % of $(\text{P-N})\text{PtCl}_2$ ($\text{P-N} = \mathbf{2a}$), the color change is almost immediate (60 °C, 10 min) and ethylferrocene is again produced. The results provide support for the suggestion that the catalyzed hydrogenolysis of the ferrocenyl ketones by phenylsilane proceeds via the carbonium ion $\text{FcC}^+(\text{H})\text{R}$, and it should be noted that the reaction, which on this basis would involve the more stable ion ($\text{R} = \text{Ph}$), affords only the hydrocarbon product. Some alcohol is produced when $\text{R} = \text{CH}_3$.

Platinum Hydrides and Hydrosilylation. The oxidative addition of hydrogen halides to $\text{Pt}(\text{II})$ compounds results in the formation of $\text{Pt}(\text{IV})$ hydrides in solution.^{43,44} Similarly, group 14 hydrides add to diphosPtCl_2 , $\text{diphos} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.⁴⁵ The isolation and characterization of these and related $\text{Pt}(\text{IV})$ derivatives as solids are difficult, and the products readily decompose to the much

more stable $\text{Pt}(\text{II})$ species in solution.^{43–46}

In the present investigation it was found that reaction of diphenylsilane with $(\text{P-N})\text{PtCl}_2$ ($\text{P-N} = \mathbf{2a}$ or $\mathbf{2b}$) in CD_2Cl_2 solution takes place at ambient temperatures as judged by the ^1H NMR spectra of the mixtures. These spectra show a number of high-field metal hydride resonances; the absence of coupling to platinum shows that the species (unidentified) are exchanging hydride. Addition of diethyl ether to the reaction solution precipitates solids that, as judged by the microanalytical data ($\text{C}, \text{H}, \text{N}, \text{Cl}$), are the oxidative-addition products **5** (eq 4).

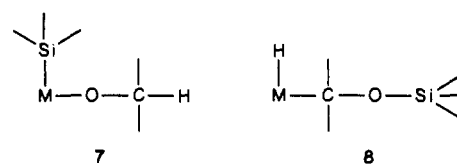


and the ^1H NMR spectrum (Figure 2) is essentially the same as that of **6** (^1H NMR (CD_2Cl_2) δ -18.56 ($J_{\text{PtH}} = 1344$ Hz, $J_{\text{PH}} = 14$ Hz); ^{31}P NMR δ 9.34 ($J_{\text{PtP}} = 4401$ Hz)), which can be independently synthesized from **2a** by using the procedure of Clark and co-workers.²⁰ The magnitude of $^2J_{\text{PH}}$ indicates that the hydride is cis to phosphorus.⁴³ Thus it seems that **5a** decompose to **6a** in solution in much the same manner as other isolated $\text{Pt}(\text{IV})$ hydride species.^{43,46}

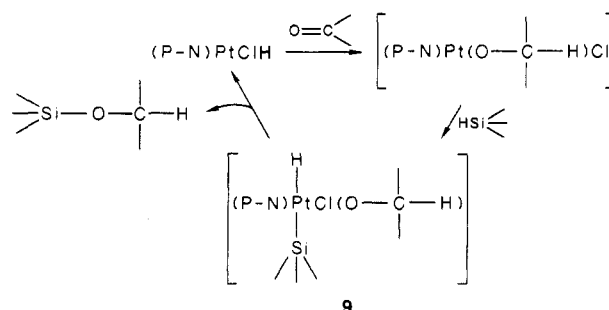
The complex **5b** ($\text{P-N} = \mathbf{2b}$) is also soluble in CD_2Cl_2 ; however, two $\text{Pt}(\text{II})$ hydrides are present (^1H NMR (CD_2Cl_2) δ -19.25 ($J_{\text{PtH}} = 1326$ Hz, $J_{\text{PH}} = 14$ Hz), -22.80 ($J_{\text{PtH}} = 1143$ Hz, $J_{\text{PH}} = 20$ Hz)) of relative intensity 2.5:1. The δ and J values indicate that either species could be a complex of type **6** ($\text{P-N} = \mathbf{2b}$) with hydride cis to phosphorus. In this case independent synthesis of **6b** was not successful.

The $(\text{P-P})\text{PtCl}_2$ derivatives ($\text{P-P} = \mathbf{2c}$ and 1,1'-bis(diphenylphosphino)ferrocene), do not react with diphenylsilane under the same conditions, again showing the difference in reactivities between $\text{P}\cdots\text{P}$ and $\text{P}\cdots\text{N}$ binding. The lack of reactivity with the silane is probably associated with the much lower catalytic activity of these species and strongly suggests that the true catalyst for these hydrosilylation and hydrogenolysis reactions is either a $\text{Pt}(\text{IV})$ hydride or, more likely, a $\text{Pt}(\text{II})$ hydride. Certainly we find that **6a** is an effective catalyst for the hydrosilylation of aromatic ketones.

The mechanism of the hydrosilylation of ketones catalyzed by metal complexes is not well-established. In order to obtain the final product, pathways involving intermediates of type **7** or **8** need



to be involved, and both have been proposed.^{1d,32,47} The present results seem to support a mechanism based on **7** since the catalyst is more likely to be a metal hydride. In its simplest form a likely mechanism can be written as



This could account for the low optical yields since the asymmetric

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center is developed further away from the metal atom. An intermediate such as **9** could also lead to direct alcohol formation as found for the acetylferrocene reaction and direct carbonium ion formation leading to hydrogenolysis of the ferrocenyl ketones.

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of unpublished work, and Johnson Matthey Chemicals Ltd. for the loan of platinum salts.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated final hydrogen atom positions, full bond lengths and angles, and important torsion angles together with a packing diagram (7 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Complexes of Hybrid Ligands. Synthesis, Reactions, and Structures of Platinum Complexes Derived from a Diphenylphosphino-Substituted Fluorinated Tertiary Alcohol¹

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The synthesis of a number of platinum(II) complexes of the hybrid ligand $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$ (HL^1) is described. The ligand interacts with Pt^{2+} in two ways: either unidentate and neutral, coordinating through phosphine, or bidentate and uninegative, (L^1), coordinating through phosphine and alkoxide to form a five-membered chelate ring. Complexes prepared include *cis*- and *trans*- $[\text{PtCl}_2(\text{HL}^1)_2]$, *cis*- and *trans*- $[\text{PtCl}(\text{L}^1)(\text{HL}^1)]$, *cis*- $[\text{Pt}(\text{L}^1)_2]$, *cis*- $[\text{PtCl}(\text{L}^1)(\text{PR}_3)]$, *trans*- $[\text{Pt}(\text{CH}_3)(\text{L}^1)(\text{HL}^1)]$, and the platinum(IV) complex $[\text{PtCl}_2(\text{L}^1)_2]$. Complete crystal and molecular structural determinations have been made on two complexes. *trans*- $[\text{PtCl}_2(\text{HL}^1)_2]$ is monoclinic, space group $P2_1/n$, with $a = 16.934$ (2) Å, $b = 10.320$ (1) Å, $c = 10.198$ (2) Å, $\beta = 90.32$ (1)°, $V = 1782.2$ (9) Å³, and $Z = 2$. Least-squares refinement on F of 232 variables using 3234 observations converged at a conventional agreement factor of 0.039. *cis*- $[\text{Pt}(\text{L}^1)_2]$ (CHCl_3 solvate) is monoclinic, space group $P2_1/c$, with $a = 20.036$ (3) Å, $b = 10.133$ (1) Å, $c = 19.517$ (3) Å, $\beta = 109.69$ (1)°, $V = 3731$ (2) Å³, and $Z = 4$. Least-squares refinement on F of 313 variables using 3030 observations converged at a conventional agreement factor of 0.045. Ligand profiles are calculated from the structural data, and monodentate HL^1 is assigned a cone angle of 159°; the $-\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$ substituent on phosphorus has a bulk comparable to that of *tert*-butyl or $-\text{C}_6\text{F}_5$. The C–OH bond length in coordinated HL^1 is 1.388 (7) Å, significantly less than those found in unfluorinated alcohols. It is concluded that the bulk of neutral HL^1 stabilizes the *trans* isomer of $[\text{PtCl}_2(\text{HL}^1)_2]$, while the effect of antisymbiosis is dominant in determining the geometry of complexes where the ligand is bidentate. Mechanisms for the formation and interconversion of the complexes are suggested.

Introduction

We have previously described the preparation of the potentially difunctional, hybrid, ligand $\text{Ph}_2\text{PCH}_2\text{C}(\text{CF}_3)_2\text{OH}$ (HL^1 , **1**) and its coordination (in the ionized form) to Ni^{2+} , Pd^{2+} , and Pt^{2+} to give neutral bis complexes $[\text{M}(\text{L}^1)_2]$.² These square-planar complexes have the *cis* configuration for $\text{M} = \text{Pd}$ or Pt , while for $\text{M} = \text{Ni}$, the complex is *trans* in the solid state but a *cis*–*trans* mixture in solution. (Throughout, we use the terms *cis* and *trans* with reference to the position of the two phosphino ligands in a complex.) The range of palladium complexes has been extended by the preparation and subsequent cleavage of the dinuclear complex $[(\text{L}^1)\text{Pd}(\mu\text{-Cl})_2\text{Pd}(\text{L}^1)]$.³

Because of the inert nature of platinum(II) complexes, it appeared that this metal would be suitable for a more extended investigation of the possible modes of coordination of the hybrid ligand. In this paper, we describe the preparation of a range of complexes, showing that the ligand may act either as a unidentate, neutral ligand, coordinating through phosphorus only, or as a bidentate, uninegative ligand, chelating to the metal through phosphine and alkoxide groups. Interchange between these two modes of coordination may be brought about by reaction with acid or base. Different geometries of coordination at Pt^{2+} are possible in mixed-ligand complexes; both *cis* and *trans* isomers have been isolated in some cases, and mechanisms for their formation and interconversion are suggested. In order to assess the importance of steric effects in determining the coordination geometry of this ligand, a complete structural determination has been made on two

complexes, one containing neutral, monodentate HL^1 coordinated to Pt^{2+} through phosphorus only and the other containing the bidentate, anionic ligand (L^1).

Experimental Section

General techniques and the preparation of the ligand $\text{PPh}_2\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$ (HL^1 , **1**) and the complex *cis*- $[\text{Pt}(\text{L}^1)_2]$ (**2**) have been described previously.²

cis- $[\text{PtCl}(\text{L}^1)(\text{HL}^1)]$ (**3**). PtCl_2 (0.40 g, 1.5 mmol) was suspended in DMF (100 mL), and excess HL^1 (1.50 g, 4.1 mmol) was added with stirring. Most of the PtCl_2 dissolved during addition of the ligand, and the remainder was dissolved by gentle heating. After the mixture was stirred for 3 h, solvent was removed by rotary evaporation, the remaining yellow oil was dissolved in CH_2Cl_2 , the solution was filtered, and hexanes were added to cause slow formation of white crystals of *cis*- $[\text{PtCl}(\text{L}^1)(\text{HL}^1)]$, 64%.

cis- $[\text{PtCl}_2(\text{HL}^1)_2]$ (**4**). $[\text{Pt}(\text{L}^1)_2]$ (**2**) (0.30 g, 0.32 mmol) was dissolved in acetone (60 mL) and gaseous HCl passed through with stirring for 5 min. Removal of solvent left a yellow oil, recrystallized from CHCl_3 /hexanes to yield pale yellow *cis*- $[\text{PtCl}_2(\text{HL}^1)_2]$, 89%.

trans- $[\text{PtCl}_2(\text{HL}^1)_2]$ (**5**). $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$ (0.46 g, 1.32 mmol) was dissolved in CH_3CN (60 mL) and HL^1 (0.98 g, 2.68 mmol) in EtOH (10 mL) added; the solution went yellow. Removal of solvent left a yellow oil, which solidified on addition of CHCl_3 to give *trans*- $[\text{PtCl}_2(\text{HL}^1)_2]$, 70%.

trans- $[\text{PtCl}(\text{L}^1)(\text{HL}^1)]$ (**6**). To PtCl_2 (0.30 g, 1.13 mmol) in DMF (60 mL) was added a stoichiometric amount of HL^1 (0.80 g, 2.16 mmol). Workup as performed for the *cis* isomer (**3**) yielded yellow crystals of *trans*- $[\text{PtCl}(\text{L}^1)(\text{HL}^1)]$, 20%.

cis- $[\text{PtCl}(\text{L}^1)(\text{PPh}_3)]$ (**7a**). Either *cis*- or *trans*- $[\text{PtCl}(\text{L}^1)(\text{HL}^1)]$ (0.20 g, 0.21 mmol) was dissolved in EtOH (25 mL) and triphenylphosphine (0.08 g, 0.31 mmol) added. After reflux for 3 h, solvent was removed and the residual oil recrystallized from CH_2Cl_2 /hexanes to give *cis*- $[\text{PtCl}(\text{L}^1)(\text{PPh}_3)]$ 87%.

cis- $[\text{PtCl}(\text{L}^1)(\text{PPh}_2\text{Me})]$ (**7b**) and *cis*- $[\text{PtCl}(\text{L}^1)(\text{PPhMe}_2)]$ (**7c**) were prepared by the same route as **7a**, the phosphine being added in 30–50% excess. For the trimethylphosphine complex *cis*- $[\text{PtCl}(\text{L}^1)(\text{PMe}_3)]$ (**7d**),

(1) Taken from: Montgomery, C. D. Ph.D. Thesis, Faculty of Graduate Studies, University of Western Ontario, 1986.

(2) Boeré, R. T.; Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* 1985, 24, 3680.

(3) Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chim. Acta* 1986, 117, 103.