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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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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 Alcohol[1]

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The synthesis of a number of platinum(II) complexes of the hybrid ligand $Ph_2PCH_2C(CF_3)_2OH$ (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*-$[PtCl_2(HL^1)_2]$, *cis*- and *trans*-$[PtCl(L^1)(HL^1)]$, *cis*-$[Pt(L^1)_2]$, *cis*-$[PtCl(L^1)(PR_3)]$, *trans*-$[Pt(CH_3)(L^1)(HL^1)]$, and the platinum(IV) complex $[PtCl_2(L^1)_2]$. Complete crystal and molecular structural determinations have been made on two complexes. *trans*-$[PtCl_2(HL^1)_2]$ 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) Å^3, and $Z = 2$. Least-squares refinement on F of 232 variables using 3234 observations converged at a conventional agreement factor of 0.039. *cis*-$[Pt(L^1)_2]$ ($CHCl_3$ 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) Å^3, 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 $-CH_2C(CF_3)_2OH$ substituent on phosphorus has a bulk comparable to that of *tert*-butyl or $-C_6F_5$. 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 $[PtCl_2(HL^1)_2]$, 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 $Ph_2PCH_2C(CF_3)_2OH$ (HL^1, **1**) and its coordination (in the ionized form) to Ni^{2+}, Pd^{2+}, and Pt^{2+} to give neutral bis complexes $[M(L^1)_2]$.[2] These square-planar complexes have the cis configuration for M = Pd or Pt, while for M = 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 $[(L^1)Pd(\mu\text{-}Cl)_2Pd(L^1)]$.[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 $PPh_2CH_2C(CF_3)_2OH$ (HL^1, **1**) and the complex *cis*-$[Pt(L^1)_2]$ (**2**) have been described previously.[2]

***cis*-[PtCl(L¹)(HL¹)] (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*-$[PtCl(L^1)(HL^1)]$, 64%.

***cis*-[PtCl₂(HL¹)₂] (4).** $[Pt(L^1)_2]$ (**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*-$[PtCl_2(HL^1)_2]$, 89%.

***trans*-[PtCl₂(HL¹)₂] (5).** $[PtCl_2(CH_3CN)_2]$ (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*-$[PtCl_2(HL^1)_2]$, 70%.

***trans*-[PtCl(L¹)(HL¹)] (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*-$[PtCl(L^1)(HL^1)]$, 20%.

***cis*-[PtCl(L¹)(PPh₃)] (7a).** Either *cis*- or *trans*-$[PtCl(L^1)(HL^1)]$ (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*-$[PtCl(L^1)(PPh_3)]$ 87%.

***cis*-[PtCl(L¹)(PPh₂Me)] (7b) and *cis*-[PtCl(L¹)(PPhMe₂)] (7c)** were prepared by the same route as **7a**, the phosphine being added in 30–50% excess. For the trimethylphosphine complex *cis*-$[PtCl(L^1)(PMe_3)]$ (**7d**),

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

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Table I. Analytical Data on Complexes

		anal.					
		% C		% H		% P	
compd	formula	calcd	found	calcd	found	calcd	found
cis-PtCl(L^1)(HL^1) (**3**)	$C_{32}H_{25}ClF_{12}O_2P_2Pt$	39.95	40.17	2.62	2.58	6.44	7.44
trans-PtCl$_2$(HL^1)$_2$ (**5**)	$C_{32}H_{26}Cl_2F_{12}O_2P_2Pt$	38.49	38.16	2.62	2.64	6.20	7.78
trans-PtCl(L^1)(HL^1) (**6**)	$C_{32}H_{25}ClF_{12}O_2P_2Pt$	39.95	39.81	2.62	2.72	6.44	6.27
cis-PtCl(L^1)(PPh$_3$) (**7a**)	$C_{34}H_{27}ClF_6OP_2Pt$	47.54	47.04	3.17	3.24	7.21	7.73
cis-PtCl(L^1)(PPh$_2$Me) (**7b**)	$C_{29}H_{25}ClF_6OP_2Pt$	43.76	43.21	3.16	3.41	7.78	7.97
cis-PtCl(L^1)(PPhMe$_2$) (**7c**)	$C_{24}H_{23}ClF_6OP_2Pt$	39.28	39.54	3.16	3.09	8.44	8.37
cis-PtCl(L^1)(PMe$_3$) (**7d**)	$C_{19}H_{21}ClF_6OP_2Pt$	34.80	33.76	3.23	2.99	9.44	9.03
trans-PtMe(L^1)(HL^1) (**8**)	$C_{33}H_{28}F_{12}O_2P_2Pt$	42.09	41.98	3.00	3.01	6.59	6.63
PtCl$_2$(L^1)$_2$ (**9**)	$C_{32}H_{24}Cl_2F_{12}O_2P_2Pt$	38.57	37.96	2.43	2.78	6.23	5.43
PdCl$_2$(HL^1)$_2$ (**10**)	$C_{32}H_{26}Cl_2F_{12}O_2P_2Pd$	42.24	42.36	2.88	3.09	6.81	7.66

Table II. Crystal Data and Experimental Conditions

	5	**2**
chem formula	$C_{32}H_{26}Cl_2F_{12}O_2P_2Pt$	$C_{33}H_{25}Cl_3F_{12}O_2P_2Pt$
fw	999.49	1044.94
space group	$P2_1/n$	$P2_1/c$
a, Å	16.934 (2)	20.036 (3)
b, Å	10.320 (1)	10.133 (1)
c, Å	10.198 (2)	19.517 (3)
β, deg	90.32 (1)	109.69 (1)
cell vol (22 °C), Å^3	1782.2 (9)	3731 (2)
D_{obsd}, D_{calcd}, g/cm^3	1.848 (1), 1.846	1.882, 1.860
cryst vol, mm^3	0.006 83	0.002 41
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα; 0.710 73
abs coeff, cm^{-1}	43.07	41.89
Gaussian grid	10 × 6 × 26	8 × 15 × 12
max, min. trans. factors	0.676, 0.460	0.743, 0.550
detector, mm	4.00 × (5.0 + 0.35 tan θ) at 205	
scan mode; scan speed, deg min^{-1}	$\omega/2\theta$; 1.1–1.3	$\omega/2\theta$; 1.3–3.3
scan width, deg	0.80 + 0.35 tan θ	0.70 + 0.35 tan θ
bkgd	*a*	*a*
data collcd	$-23 \le h \le 23$ $-1 \le k \le 14$ $0 \le l \le 14$	$-21 \le h \le 21$ $-10 \le k \le 0$ $0 \le l \le 21$
2θ range, deg	$0 \le 2\theta \le 60$	$0 \le 2\theta \le 45$
stds	(002), (200), (020), (004)	(0$\bar{2}$2), (002), (040), (200)
change in intens	+1.2% in 135 h	−5.3% in 83 h
no. of reflcns collcd; no. avgd	6057; 1042	5161; 246

[a] 25% above and below calculated scan width.

the phosphine was generated by heating AgI(PMe$_3$) in vacuo and transferred to the solution of [PtCl(L^1)(HL^1)] on a vacuum manifold.

[PtCH$_3$(L^1)(HL^1)] (8). The bridged complex [Me$_2$Pt(μ-SMe$_2$)$_2$PtMe$_2$] was prepared as reported[4] and an 0.175-g (0.30-mmol) portion was dissolved in CH$_2$Cl$_2$ (15 mL). HL^1 (0.54 g, 1.5 mmol) was added, the solution stirred for 1 h, solvent removed, and the resulting oil recrystallized from CHCl$_3$/hexanes to give white [PtCH$_3$(L^1)(HL^1)], in 31% yield.

[PtCl$_2$(L^1)$_2$] (9). [Pt(L^1)$_2$] (0.10 g, 0.11 mmol) was suspended in benzene (25 mL) and gaseous Cl$_2$ passed through with stirring. The solution immediately turned yellow, and [Pt(L^1)$_2$] dissolved. A yellow precipitate then appeared, at which point solvent was removed by rotary evaporation and the product washed with benzene to yield pure [PtCl$_2$(L^1)$_2$], in 87% yield. Attempts at recrystallization resulted in slow decomposition to regenerate [Pt(L^1)$_2$].

[PdCl$_2$(HL^1)$_2$] (10). [PdCl$_2$(PhCN)$_2$] (0.155 g, 0.40 mmol) was dissolved in CHCl$_3$ (20 mL) and HL^1 (0.30 g, 0.82 mmol) in CHCl$_3$ (10 mL) added with stirring, causing a change in color from deep red to orange. Removal of solvent left a yellow oil, which solidified on addition of a small amount of CHCl$_3$ to give [PdCl$_2$(HL^1)$_2$], in 75% yield.

Complexes were characterized by elemental analysis (Table I) and mass spectra.

Infrared spectra were consistent with proposed structures, being dominated by strong C–F absorptions in the region 1160–1190 cm^{-1}. NMR spectra are discussed later in this paper.

Structure Determination

Yellow crystals of *trans*-[PtCl$_2$(HL^1)$_2$] (**5**) were grown by slow evaporation of a solution in CHCl$_3$/acetone, while colorless needles of *cis*-[Pt(L^1)$_2$] (**2**) were obtained from a solution in CHCl$_3$ as a monosolvate.

Preliminary photographs showed that both crystals belong to the monoclinic crystal system. For **5**, systematic absences were observed that uniquely determined the space group as $P2_1/n$, a nonstandard setting of $P2_1/c$, and for **2**, the space group is $P2_1/c$—C_{2h}^5-No. 14.[5a] Crystal densities were determined by using the method of neutral buoyancy in mixtures of cyclohexane and 1,2-dibromoethane. There are two formula weights of **5** per unit cell, requiring the platinum atom to lie on a center of inversion. For **2**, there are four formula units of [Pt(L^1)$_2$]·CHCl$_3$ per unit cell, with no site symmetry imposed. It was necessary to cleave a crystal of **2** for data collection and to take precautions against loss of the solvent molecule.

For both **5** and **2**, data collection was performed with Mo Kα radiation on an Enraf-Nonius CAD4F diffractometer.[6a] ω-Scan widths at half-height for three intense, low-angle reflections averaged 0.18° for **5** and 0.11° for **2**. Data were collected by the θ–2θ scan technique, and in each case, four reflections were monitored as a check on crystal and electronic stability. For **5**, no correction was considered necessary. The four standards for **2** showed an overall loss in intensity of 5.3%, presumably due to solvent loss, and a linear correction for decay was applied. Crystal faces were identified by optical goniometry, and dimensions were measured by using a microscope fitted with a filar eyepiece. A Gaussian absorption correction was applied in each case.[7] The averaging of symmetry-equivalent data for **5** gave agreement factors based on intensity of 0.019 before and 0.014 after the correction, and values of 0.024 and 0.018 respectively for **2** were obtained. The crystal data and the conditions for data collection are summarized for both studies in Table II.

Structure Solution and Refinement

Both structures were solved and refined by using the SDP-Plus software of Enraf-Nonius along with several local programs on a PDP-11/23+ computer.[6b] Refinement was by full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where w, the weighting factor, is defined as $4F_o/\sigma(F_o)^2$. The neutral, non-hydrogen atom scattering factors used were those of Cromer and Waber.[5b] The real parts of anomalous dispersion effects were included in the structure factor calculations; the values of $\Delta f'$ were those of Cromer.[5b]

Compound 5. In space group $P2_1/n$, equivalent positions $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$, the molecule must lie on an inversion center. All 26 non-hydrogen atoms were located by the heavy-atom method, and all 13 hydrogen atoms were found in a difference Fourier map at peak heights ranging from 0.6 (1) to 0.5 (1) e Å^{-3}. In subsequent cycles of refinement the hydrogen atoms were included in idealized positions using the scattering factors of Stewart, Davidson, and Simpson.[8] The refinement converged with agreement factors of $R_1 = 0.031$ and $R_2 = 0.039$ respectively, based on 232 variables, 3234 independent observations for which $F_o > 3\sigma(F_o)$ and a $p = 0.05$.[9] The esd on an observation of unit weight was 1.04 e. A statistical analysis showed no unusual trends, and the highest peak in a difference Fourier synthesis had a height

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Table III. Atomic Positional ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for Compound **5**

atom	x	y	z	U_{eq},[a] Å^2
Pt	0	0	0	32.93 (4)
Cl	469.6 (8)	−1701 (1)	1241 (1)	53.3 (3)
P	972.6 (7)	1265 (1)	971 (1)	33.0 (3)
F(1)	1368 (4)	5002 (4)	−2510 (5)	132 (2)
F(2)	331 (3)	4585 (5)	−1402 (5)	116 (2)
F(3)	1315 (4)	5521 (5)	−512 (5)	134 (2)
F(4)	2627 (2)	2134 (4)	−916 (4)	103 (1)
F(5)	2625 (2)	3759 (5)	−2101 (4)	116 (1)
F(6)	2632 (3)	3980 (7)	−13 (5)	165 (2)
O	1216 (2)	2400 (4)	−1942 (4)	70 (1)
C(1)	1108 (3)	2957 (5)	408 (5)	39 (1)
C(2)	1429 (3)	3271 (5)	−966 (5)	46 (1)
C(3)	1124 (4)	4585 (8)	−1373 (7)	94 (2)
C(4)	2346 (3)	3295 (7)	−1009 (6)	71 (2)
C(21)	610 (3)	1568 (4)	2624 (4)	34 (1)
C(22)	−67 (3)	2316 (5)	2772 (5)	46 (1)
C(23)	−370 (3)	2578 (6)	4000 (6)	56 (2)
C(24)	−4 (3)	2065 (7)	5082 (5)	65 (2)
C(25)	650 (4)	1282 (7)	4971 (5)	62 (2)
C(26)	954 (3)	1031 (5)	3724 (5)	45 (1)
C(31)	1960 (3)	611 (5)	1128 (5)	40 (1)
C(32)	2512 (3)	1184 (6)	1958 (5)	52 (1)
C(33)	3279 (3)	747 (7)	1987 (6)	67 (2)
C(34)	3499 (4)	−273 (6)	1197 (7)	77 (2)
C(35)	2959 (3)	−860 (6)	386 (6)	65 (2)
C(36)	2185 (3)	−427 (6)	341 (6)	52 (1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

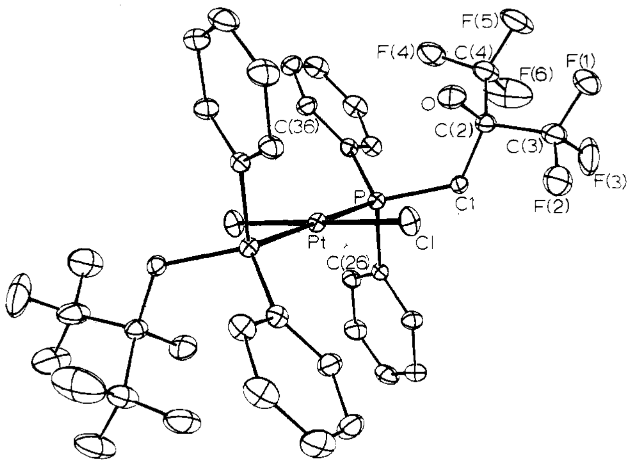

Figure 1. ORTEP diagram of the structure of *trans*-$[PtCl_2\{PPh_2CH_2C(CF_3)_2OH\}_2]$ (**5**).

of 0.87 (8) e Å^{-3}. At (0.500, 0.416, 0.500), 0.87 Å distant from the platinum atom, it was of no chemical significance. The final positional and thermal parameters for structure **5** are given in Table III.

Compound 2. The 57 non-hydrogen atoms of the complex and the molecule of chloroform solvate were readily located by the heavy-atom method. All 25 hydrogen atoms were observed in a difference Fourier synthesis, ranging in intensity from 0.7 (1) to 0.3 (1) e Å^{-3}. They were included in the structure factor calculations assuming idealized geometries. The final cycle of refinement included 313 variables (positional and anisotropic thermal parameters for Pt, Cl, O, P, and F atoms, positional and isotropic thermal parameters for C atoms, and an overall scale factor) and used 3030 reflections for which $F_o > 3\sigma(F_o)$ with a p value of 0.07. The model converged at agreement factors of $R_1 = 0.034$ and $R_2 = 0.045$. The estimated standard deviation on an observation of unit weight was 1.00 e. A statistical analysis of the data showed no unusual trends, and the largest peak in a final difference Fourier was 0.9 (1) e Å^{-3} at (0.203, 0.277, 0.215), 0.99 Å from the platinum atom and of no chemical significance. The final positional and thermal parameters for compound **2** are given in Table IV.

Structure amplitudes, hydrogen atom parameters, and anisotropic thermal parameters for both structures have been deposited.[10]

Table IV. Atomic Positional ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for Compound **2**

atom	x	y	z	U_{eq},[a] Å^2
Pt	2494.8 (2)	2186.8 (4)	−2459.8 (2)	29.05 (8)
Cl(1)	7597 (3)	6223 (5)	4595 (3)	139 (2)
Cl(2)	9027 (3)	5604 (8)	5034 (3)	189 (3)
Cl(3)	8007 (4)	3962 (5)	4037 (3)	185 (3)
P(1)	1715 (1)	560 (3)	−2698 (1)	34.8 (7)
P(2)	3512 (1)	1176 (3)	−2281 (1)	31.7 (7)
F(1)	970 (4)	4698 (8)	−1835 (4)	136 (3)
F(2)	458 (4)	2948 (9)	−1669 (4)	138 (3)
F(3)	1575 (5)	3019 (11)	−1328 (4)	141 (4)
F(4)	372 (5)	2914 (10)	−3807 (4)	137 (4)
F(5)	−235 (4)	3120 (10)	−3105 (6)	145 (4)
F(6)	412 (4)	4685 (8)	−3268 (6)	151 (4)
F(7)	4790 (3)	5089 (7)	−2111 (4)	85 (2)
F(8)	3894 (3)	4802 (7)	−3074 (3)	80 (2)
F(9)	3823 (4)	6150 (6)	−2253 (4)	85 (2)
F(10)	3713 (4)	5150 (7)	−1021 (3)	84 (2)
F(11)	4708 (4)	4229 (8)	−846 (4)	90 (3)
F(12)	3810 (4)	3083 (7)	−868 (3)	80 (2)
O(1)	1612 (3)	3320 (7)	−2678 (3)	49 (2)
O(2)	3073 (3)	3878 (6)	−2318 (3)	42 (2)
C(1)	952 (5)	1358 (11)	−2566 (5)	54 (3)
C(2)	1012 (5)	2872 (10)	−2570 (5)	40 (2)
C(3)	4146 (5)	2550 (10)	−2134 (5)	42 (3)
C(4)	3800 (5)	3860 (10)	−2007 (5)	39 (2)
C(5)	998 (7)	3400 (14)	−1847 (7)	84 (4)
C(6)	386 (7)	3407 (14)	−3184 (7)	87 (4)
C(7)	4081 (6)	4996 (11)	−2351 (5)	59 (3)
C(8)	4010 (6)	4083 (11)	−1174 (6)	60 (3)
C(9)	8246 (7)	5526 (14)	4312 (7)	91 (4)
C(21)	1883 (4)	−917 (9)	−2143 (4)	32 (2)
C(22)	2079 (5)	−2054 (10)	−2399 (5)	48 (3)
C(23)	2242 (6)	−3211 (12)	−1972 (6)	69 (3)
C(24)	2188 (6)	−3147 (12)	−1287 (6)	68 (3)
C(25)	2000 (6)	−2016 (12)	−1024 (6)	67 (3)
C(26)	1836 (5)	−896 (11)	−1445 (5)	54 (3)
C(31)	1414 (5)	−34 (10)	−3630 (5)	40 (2)
C(32)	1714 (5)	449 (11)	−4112 (5)	52 (3)
C(33)	1476 (6)	36 (12)	−4846 (6)	65 (3)
C(34)	941 (6)	−846 (13)	−5073 (6)	72 (4)
C(35)	625 (7)	−1333 (13)	−4607 (6)	80 (4)
C(36)	860 (5)	−926 (11)	−3867 (5)	56 (3)
C(41)	3566 (4)	315 (9)	−3073 (4)	35 (2)
C(42)	3572 (5)	1040 (11)	−3678 (5)	53 (3)
C(43)	3537 (6)	395 (12)	−4320 (6)	68 (3)
C(44)	3520 (6)	−929 (13)	−4335 (6)	71 (4)
C(45)	3515 (6)	−1664 (12)	−3759 (6)	67 (3)
C(46)	3528 (5)	−1059 (11)	−3127 (5)	52 (3)
C(51)	3872 (5)	65 (10)	−1513 (5)	39 (2)
C(52)	3547 (5)	12 (11)	−990 (5)	52 (3)
C(53)	3836 (6)	−788 (13)	−370 (6)	73 (4)
C(54)	4426 (7)	−1519 (14)	−317 (7)	84 (4)
C(55)	4762 (6)	−1472 (13)	−814 (6)	78 (4)
C(56)	4480 (6)	−636 (12)	−1414 (5)	61 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Structure Descriptions

Compound 5. The crystals are built up from independent molecules of the trans isomer, with a shortest Pt··Pt distance of 10.20 Å. The shortest intermolecular distance is 2.54 Å between the alcohol hydrogen atom and HC(25) at (x, y, $z - 1$). An ORTEP drawing appears in Figure 1, and selected bond lengths and angles are given in Table V. Additional dimensions have been deposited.[10]

The coordination geometry about the platinum is trans square planar, with the platinum atom lying on a center of symmetry. The only deviation from an ideal geometry comes from the two different P–Pt–Cl angles of 87.25 (5) and 92.75 (5)°.

The Pt–P bond length in **5** is 2.319 (1) Å, less than that in *trans*-$[Pt\{P(C_6H_{11})_3\}_2Cl_2]$ [2.337 (2) Å],[11] but greater than that in *trans*-$[Pt(PEt_3)_2Cl_2]$ [2.298 (18) Å],[12] consistent with our

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[10] See paragraph at end of paper regarding supplementary material available.

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[12] Messmer, G. G.; Amma, E. L. *Inorg. Chem.* **1966**, *5*, 1775.

Table V. Selected Intramolecular Dimensions[a]

		compound **2**	
	compound **5**	ligand 1	ligand 2
	Bond Lengths (Å)		
Pt-P	2.319 (1)	2.210 (3)	2.200 (3)
Pt-O		2.030 (6)	2.034 (6)
Pt-Cl	2.303 (1)		
P-C(1)	1.835 (5)	1.82 (1)	1.84 (1)
P-C(21)	1.824 (4)	1.812 (9)	1.811 (9)
P-C(31)	1.809 (5)	1.815 (9)	1.817 (9)
C(1)-C(2)	1.540 (7)	1.54 (1)	1.56 (1)
C(2)-O	1.388 (7)	1.36 (1)	1.38 (1)
C(2)-C(3)	1.508 (9)	1.52 (2)	1.53 (2)
C(2)-C(4)	1.555 (8)	1.51 (1)	1.55 (1)
C(3)-F(1)	1.306 (9)	1.32 (2)	1.34 (1)
C(3)-F(2)	1.344 (9)	1.32 (2)	1.35 (1)
C(3)-F(3)	1.343 (9)	1.31 (1)	1.32 (1)
C(4)-F(4)	1.292 (8)	1.31 (2)	1.32 (1)
C(4)-F(5)	1.303 (8)	1.34 (2)	1.34 (1)
C(4)-F(6)	1.328 (9)	1.31 (2)	1.31 (1)
	Bond Angles (deg)		
Cl-Pt-P	87.25 (5)		
P-Pt-Cl	92.75 (5)		
P(1)-Pt-P(2)		103.72 (9)	
P(1)-Pt-O(1)		82.7 (2)	
P(2)-Pt-O(2)		85.2 (2)	
O(1)-Pt-O(2)		88.2 (3)	
Pt-P-C(1)	119.1 (2)	101.9 (4)	103.1 (3)
Pt-P-C(21)	104.5 (2)	121.0 (3)	114.1 (3)
Pt-P-C(31)	118.8 (2)	115.6 (4)	120.6 (4)
C(1)-P-C(21)	99.7 (2)	106.1 (5)	105.5 (5)
C(1)-P-C(31)	105.2 (2)	106.1 (4)	106.2 (4)
C(21)-P-C(31)	107.3 (2)	104.9 (4)	106.5 (4)
P-C(1)-C(2)	121.7 (4)	111.8 (8)	110.4 (7)
O-C(2)-C(4)	104.2 (4)	108.7 (8)	106.7 (7)
O-C(2)-C(3)	107.4 (5)	107.3 (9)	113.8 (7)
O-C(2)-C(1)	115.2 (4)	114.0 (8)	113.8 (7)
C(1)-C(2)-C(4)	112.7 (4)	108.4 (8)	108.3 (7)
C(1)-C(2)-C(3)	108.5 (5)	108.7 (9)	108.8 (9)
C(3)-C(2)-C(4)	108.6 (5)	110 (1)	109.9 (8)
C(2)-O(1)-Pt		122.0 (6)	121.2 (5)

[a] Intramolecular dimensions have been tabulated so as to facilitate comparisons between compounds **5** and **2**. The atom-numbering scheme is the same for compound **5** and ligand 1 in compound **2**.

proposal that HL^1 is a bulky monodentate phosphine, more sterically demanding than PEt_3 but less so than $P(C_6H_{11})_3$.

The length of the C–O bond in **5** is 1.388 (7) Å. This appears to be the first report of a crystallographically determined C–OH bond length in a fluorinated alcohol; it is slightly longer than the values around 1.36 Å that we have found in fluorinated alkoxides[13] but significantly shorter than the C–O bond lengths of 1.41 Å found in unfluorinated metal alkoxides[14] and those of 1.42–1.45 Å found in unfluorinated alcohols.[15] The order of decreasing C–O bond length in these different types of compounds is consistent with the our previous suggestion that there is some π-character to the C–O bond in fluorinated alkoxides associated with the strong electron-withdrawing power of the CF_3 groups.[15] The slightly longer C–O bond length found in the free alcohol would be expected, since the electron density on the oxygen atom would be less when it is bonded to hydrogen rather than to an electropositive metal atom.

The possibility of the alcohol group in **5** being hydrogen bonded either intra- or intermolecularly was investigated, but there were no close approaches. The closest atom, F(4), lies 2.407 (4) Å removed from the hydrogen; the O–OH–F(4) angle is 91.9 (3)°. Thus the fluorinated alcohol appears to be dangling free, and the preferential formation of the trans isomer is due to steric factors rather than to stabilization by hydrogen bonding.

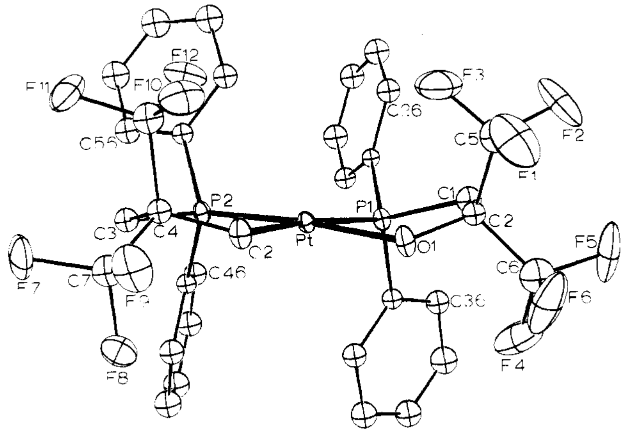

Figure 2. ORTEP diagram of the structure of *cis*-$[\overline{Pt\{PPh_2CH_2C(CF_3)_2O\}_2}]$ (**2**).

Compound 2. An ORTEP drawing of the cis isomer appears in Figure 2, and selected bond distances and angles are given in Table V.

The crystals are built up from independent molecules, with a shortest intermolecular distance of 2.504 (8) Å from F(2) to HC(36) at $(x, {}^1/_2 + y, -{}^1/_2 - z)$. The closest approach of the solvent molecule to the complex is 2.922 (5) Å between Cl(3) and HC(22) at $(1 - x, y, z)$.

The coordination geometry of **2** is slightly distorted square planar. Some weighted least-squares plane results are given in Table S-X.[10] The four angles around the platinum deviate from an ideal square-planar geometry, with the P(1)–Pt–P(2) angle (103.72 (9)°), considerably greater than the O(1)–Pt–O(2) angle (88.2 (3)°). Steric interactions between the phenyl groups are therefore more significant than those involving the CF_3 groups.

The two chelate rings differ in conformation; ring(1), containing P(1) and O(1), is in an asymmetric envelope conformation with both carbon atoms lying on one side of the plane, while ring(2) is in an asymmetric skew conformation, with the two carbons lying on opposite sides of the plane. That both of these conformations are found in a single molecule would suggest that the energy difference between them is small, and the favored conformation is likely determined by packing factors in the solid state, while rapid inversion occurs in solution. Torsional angles around each chelate ring are given in Table S-VIII.[10]

The weighted average of the two Pt–P bond lengths in **2** is 2.203 (3) Å; a shortening relative to **5** would be expected to result from the greater trans influence of the phosphino group over that of the fluorinated alkoxide.

A number of other structures of platinum(II) complexes with *cis*-P_2O_2 donor sets have been reported; they have Pt–P bond lengths slightly longer than that in **2**. For example, the Pt–P bond lengths in $[Pt(CO_3)(PR_3)_2]$ are 2.262 (7)[16] and 2.24 Å[17] for R = *i*-Pr and Ph, respectively. One previously reported structure very similar to **2** is that of $[\overline{Pt\{OC(CF_3)_2)OC(CF_3)_2O\}}(PPh_2Me)_2]$ (**11**), where the Pt–P bond length is 2.223 (9) Å,[18] indistinguishable from the value of 2.203 (3) Å in **2**.

The Pt–O bond lengths in **2** could also be averaged to a value of 2.032 (4) Å. In **11**, the bond length is 2.024 (9) Å. In a structure where PPh_3 is substituted for PPh_2Me in **11**, the value is virtually identical with that of **2**, 2.032 (9) Å.[18] The C–O bond

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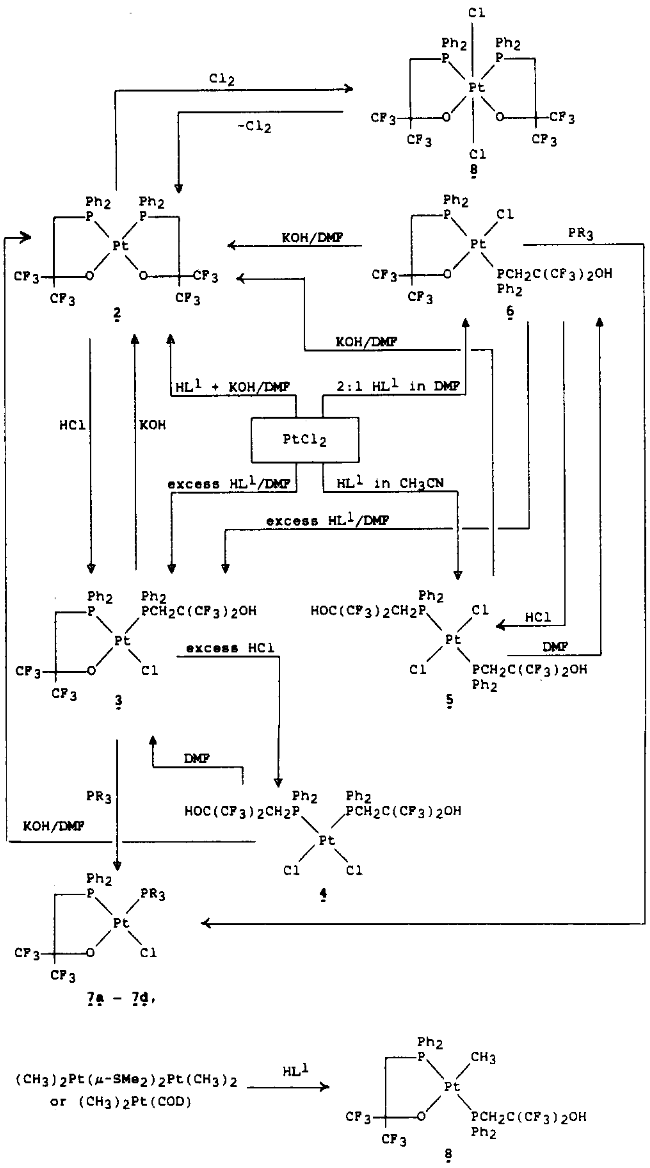
Scheme I. Synthesis of Platinum Complexes of $PPh_2CH_2C(CF_3)_2OH$ (HL^1)



lengths in **2** had an average value of 1.370 (7) Å, shorter than that expected for a C–O single bond and, as expected, shorter than the bond in **5**.

All other dimensions in the structure were unexceptional.

Results and Discussion

Synthesis. The range of complexes prepared in this study, together with their methods of synthesis and interconversion, is summarized in Scheme I.

Our general approach to the preparation of fluorinated alkoxides of platinum in previous work[19] has been to treat with KOH a nonaqueous solution containing the alcohol and a suitable complex of $PtCl_2$, causing the alcohol to coordinate in the ionized form, while at the same time precipitating KCl. Use of this approach with HL^1 and a solution of $PtCl_2$ in dimethylformamide (DMF) led to the expected neutral complex *cis*-$[Pt(L^1)_2]$ (**2**) in which both of the ligands are ionized and chelating. A cis geometry would be expected with this combination of hard alkoxide and soft phosphine ligands, due to Pearson's antisymbiotic effect.[20]

When $PtCl_2$ in DMF was treated with an excess of HL^1 in the absence of KOH, only one ligand was chelated, the second coordinating through phosphine only to give *cis*-$[PtCl(L^1)(HL^1)]$ (**3**). Treatment of this with KOH caused ring closure to give **2**, a reaction that could be reversed by cautious treatment with HCl. However, the reaction of excess HCl with **3** caused opening of the second chelate ring to give *cis*-$[PtCl_2(HL^1)_2]$ (**4**) in which both fluoro alcohol ligands are un-ionized; this also was reversible.

When the amount of ligand added to the solution of $PtCl_2$ in DMF was limited to the stoichiometric 2:1 ratio, the product was *trans*-$[PtCl(L^1)(HL^1)$ (**6**), which on treatment with excess HL^1 rearranged to the cis isomer **3**. Reaction of **6** with KOH caused ring closure with trans → cis isomerization to give *cis*-$[Pt(L^1)_2]$. Treatment of **6** with HCl caused ring cleavage to yield *trans*-$[PtCl_2(HL^1)_2]$ (**5**); the same product could be made directly by the reaction of $PtCl_2$ with free ligand in acetonitrile solution. Reaction of **5** with DMF caused ring closure without isomerization, regenerating **6**, while strong base led to ring closure with inversion, producing *cis*-$[Pt(L^1)_2]$. Phosphine-catalyzed equilibration of **4** and **5** could not be established; heating **4** with excess HL^1, even in a nonbasic solvent, caused ring closure to regenerate **3**.

The palladium(II) analogue of **5**, *trans*-$[PdCl_2(HL^1)_2]$ (**10**), was similarly prepared by reaction of HL^1 with $[PdCl_2(PhCN)_2]$ in a nonbasic solvent. In view of the more labile nature of palladium complexes, it is probable that cis–trans equilibration would be easier for this complex than for the platinum system, and it therefore appears that the trans isomer is the more stable form for $[MCl_2(HL^1)_2]$ complexes of both metals.

The reaction of either *cis*- or *trans*-$[PtCl(L^1)(HL^1)]$ (**3** or **6**) with other phosphines $PPh_{3-n}Me_n$ (n = 0–3) led to phosphine exchange and, in the case of **6**, inversion, giving *cis*-$[PtCl(L^1)(PR_3)]$ (**7a–d**).

The action of HL^1 on the bridged, dinuclear complex $[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$ gave ring closure (presumably with methane elimination), and the product was *trans*-$[PtMe(L^1)(HL^1)]$ (**8**). We were not able to isolate $[PtMe_2(HL^1)_2]$.

The complex *cis*-$[Pt(L^1)_2]$ (**2**) was rapidly oxidized by gaseous chlorine to the platinum(IV) derivative $[PtCl_2(L^1)_2]$ (**9**); this was of limited stability and slowly reverted to **2** in solution. Other potential oxidizing agents (Br_2, CH_3I) did not react with **2**. NMR data alone do not allow an unambiguous structural assignment to be made for **9**. The single ^{31}P signal indicates equivalent phosphines, and its $^1J(Pt,P)$ value of over 2200 Hz shows that these phosphines are trans to ligands of weak trans influence and consequently mutually cis. This is consistent with two possible arrangements, the chloride ligands being either cis or trans. The former arrangement makes the species chiral, and we therefore ran the ^{31}P spectrum in chiral solvent (ethyl L-(+)-lactate); no splitting of the signal was observed, indicating that the Cl^- ions were trans to each other. When the complex was allowed to react with ethanolic $AgNO_3$, precipitation of AgCl took place over several hours. It has previously been observed that Cl^- trans to phosphine in platinum(IV) complexes is sufficiently labilized to precipitate immediately, while Cl^- cis to phosphine and trans to Cl^- precipitates slowly.[21] On the basis of these two consistent pieces of evidence, we assign a configuration with trans Cl^- to **9**.

NMR Studies. Principal features of the ^1H and ^{19}F NMR spectra are given in Table VI; ^{31}P data are given in Table VII.

The spectra are consistent with the assigned structures; in particular, they establish whether the two phosphines are cis or trans disposed on platinum. The methylene group of L^1 couples to ^{31}P with ^2J = 11–12 Hz in each Pt^{2+} complex except **5**, where the two equivalent, strongly coupled trans phosphines give rise to the usual $X_2AA'X'_2$ pseudotriplet pattern.

In going from **2** to **3** and the four type **7** complexes, the ligand trans to P_A (phosphine in chelate ring) changes from $RC(CF_3)_2O^-$ to Cl^- and $^1J(Pt,P)$ increases from 3517 to 3800–3850 Hz, consistent with our conclusion that fluorinated alkoxide has a stronger trans influence than Cl^-.[19] A comparison of coupling constants with precedent[22] shows that **3** is the cis and **6** is the trans isomer of $[PtCl(L^1)(HL^1)]$. Values of $^1J(Pt,P)$ are 30–40% greater in

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Table VI. ^1H and ^{19}F NMR Data on Complexes

			^1H (CH_2 and CH_3–P)			^{19}F (CF_3)		
compd	solvent[a]		δ	^2J(P,H), Hz	^3J(Pt,H), Hz	δ	^4J(P,F), Hz	^4J(Pt,F), Hz
cis-$Pt(L^1)_2$ (**2**)	C	*b*	3.33	12	14	−76.3	...	11
cis-$PtCl(L^1)(HL^1)$ (**3**)	A	*b*	3.79	11.3	20.9	−76.4	2.3	~11
	A	*c*	3.15	11.3	18.0	−76.7	...	...
cis-$PtCl_2(HL^1)_2$ (**4**)	C	*c*	3.25	12.1	27	−76.3	...	...
trans-$PtCl_2(HL^1)_2$ (**5**)	A	*c*	3.31	4.3[d]	12.8	−76.0	...	...
trans-$PtCl(L^1)(HL^1)$ (**6**)	A	*b*	3.42	12.4[e]	21	−76.2		
	A	*c*	3.14	11.9	...	−75.2	...	...
cis-$PtCl(L^1)(PPh_3)$ (**7a**)	D	*b*	3.07	11.2	19.6	−77.1	1.3	5.4
cis-$PtCl(L^1)(PPh_2Me)$ (**7b**)	D	*b*	3.09	11.7	18.8	−77.2	1.8	...
	D	*f*	1.88	11.0[g]	35.2			
cis-$PtCl(L^1)(PPhMe_2)$ (**7c**)	D	*b*	3.11	11.5	17.6	−77.3	6.1	...
	D	*f*	1.63	11.1	34.3			
cis-$PtCl(L^1)(PMe_3)$ (**7d**)	D	*b*	3.05	11.9	23.6	−77.2	3.1	...
	D	*f*	1.26	11.5	33.5			
trans-$PtMe(L^1)(HL^1)$[h] (**8**)	C	*b*	3.19	11.1[i]	40.0	−77.3	...	...
	C	*c*	2.79	11.1	27.6	−76.6	...	...
$PtCl_2(L^1)_2$ (**9**)	D	*b*	3.98	13.7	10	−74.7	...	...
$PdCl_2(HL^1)_2$ (**10**)	C	*c*	3.53	4.3[d]	...	−75.8	...	...

[a] A = $(CD_3)_2CO$; C = $CDCl_3$; D = CD_2Cl_2. [b] Chelated L^1 ligand. [c] Nonchelated HL^1 ligand. [d] Apparent *J* value in triplet; see text. [e] $^4J(P_B,H)$ = 3.2 Hz. [f] CH_3–P signal. [g] $^4J(P_B,H)$ = 0.66 Hz. [h] CH_3 group: δ = 0.11; ^2J(Pt,H) = 88 Hz; ^3J(P,H) = 7.3 and 5.7 Hz. [i] $^4J(P_B,H)$ = 3.1 Hz.

Table VII. ^{31}P NMR Data on Complexes

		P_A[b]			P_B			
compd	solvent[a]	δ	$\Delta\delta$[c]	^1J(Pt,P), Hz	δ	$\Delta\delta$	^1J(Pt,P), Hz	$^2J(P_A,P_B)$, Hz
cis-$Pt(L^1)_2$ (**2**)	C	17.3	+50.9	3517	...	...	...	...
cis-$PtCl(L^1)(HL^1)$ (**3**)	A	30.4	64.0	3819	−6.3	27.3	3410	14.4
cis-$PtCl_2(HL^1)_2$ (**4**)		...	...	...	2.0	35.6	3755	
trans-$PtCl_2(HL^1)_2$ (**5**)	C	...	...	...	3.2	36.8	2574	...
	A	...	...	...	3.0	36.6	2610	...
trans-$PtCl(L^1)(HL^1)$ (**6**)	C	28.9	62.5	2707	7.1	40.7	2580	463
	A	29.0	62.6	2854	6.7	40.3	2720	459
cis-$PtCl(L^1)(PPh_3)$ (**7a**)	D	29.7	63.3	3808	−1.9	4.1	3423	14.3
cis-$PtCl(L^1)(PPh_2Me)$ (**7b**)	D	32.2	65.8	3805	−14.4	13.6	3326	15.6
cis-$PtCl(L^1)(PPhMe_2)$ (**7c**)	D	31.5	65.1	3818	−28.5	18.5	3242	16.7
cis-$PtCl(L^1)(PMe_3)$ (**7d**)	D	32.2	65.8	3852	−35.4	26.6	3157	16.8
trans-$PtMe(L^1)(HL^1)$ (**8**)	C	37.0	70.6	3263	16.7	50.3	3125	444
$PtCl_2(L^1)_2$ (**9**)	A	2.4	36.0	2206	...	...	...	...
	D	3.8	37.4	2226	...	...	...	...
$PdCl_2(HL^1)_2$ (**10**)	C	...	...	...	6.4	40.0	...	

[a] A = $(CD_3)_2CO$; C = $CDCl_3$; D = CD_2Cl_2. [b] P_A is the phosphorus atom in the chelate ring throughout. [c] The coordination shift: $\Delta\delta = \delta_{coord} - \delta_{free}$.

the former, while $^2J(P_A,P_B)$ = 14.4 Hz in **3** but 459 Hz in **6**. In the four complexes *cis*-[$PtCl(L^1)(PR_3)$], **7a–d**, the coordination shift values for PR_3 increase steadily from PPh_3 to PMe_3, in accordance with the usual trend.[22]

The complexes *trans*-[$PtCl(L^1)(HL^1)$] (**6**) and *trans*-[$PtMe(L^1)(HL^1)$] (**8**) differ only in the substitution of methyl for chloride trans to the alkoxide and cis to the phosphines. For both the chelated and the monodentate phosphine in **8**, values of ^1J are 21% *greater* than in **6**, and there are similar increases in $\Delta\delta$. This is consistent with previous studies, notably those of Bennett and co-workers,[23] showing that the introduction of a group with a high trans influence has the effect of *strengthening* bonding to groups in cis positions and increasing ^1J(Pt,P).

NMR results for [$PtCl_2(L^1)_2$] (**9**), the only platinum(IV) complex characterized in this study, have been discussed above.

Reaction Mechanisms. The formation and interconversion of the complexes included in this study are consistent with substitution at platinum occurring through 5-coordinate, TBP intermediates, the groups that are mutually axial being trans in the related square-planar complexes.[24]

Reaction of HL^1 with solvated $PtCl_2$ in acetonitrile gives sterically-favored *trans*-[$PtCl_2(HL^1)_2$] (**5**). In basic dimethylformamide, deprotonation of one fluorinated alcohol is followed by coordination of the alkoxide and elimination of Cl^-, giving *trans*-[$PtCl(L^1)(HL^1)$] (**6**). Reaction of strong base then yields the stable cis form of [$Pt(L^1)_2$], **2**.

In the ring-opening reaction of **2** in acid, the postulated first step is protonation of one alkoxide followed immediately by coordination of Cl^-. The un-ionized alcohol rapidly dissociates to give *cis*-[$PtCl(L^1)(HL^1)$] (**3**), and the sequence may be repeated by further reaction with HCl, yielding the thermodynamically *disfavored cis*-[$PtCl_2(HL^1)_2$] (**4**).

In the reaction of [$Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2$] with HL^1, ring closure to give *trans*-[$PtMe(L^1)(HL^1)$] (**8**) probably occurs by an addition–elimination mechanism involving the six-coordinate platinum(IV) intermediate [$Me_2PtH(L^1)(HL^1)$], a mechanism believed to operate in the reaction of methyl–platinum compounds with HCl.[25]

The reactions of these complexes with phosphines are of two types: trans → cis isomerization of [$PtCl(L^1)(HL^1)$] (**6**), catalyzed by free HL^1, or conversion of either *cis*- or *trans*-[$PtCl(L^1)(HL^1)$] into *cis*-[$PtCl(L^1)(PR_3)$] (**7**) by reaction with other phosphines. Previous work[26] has demonstrated that isomerization of complexes [$PtCl_2(PR_3)_2$] may be catalyzed by phosphines, suggesting five-coordinate intermediates. However, the use of a different phosphine PR'_3 as catalyst leads to isomerization *without* phos-

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(26) Reference 24, p 313.

phine exchange, showing that the fifth ligand occupies a unique position in the intermediate.[27] In our system, we were unable to induce trans → cis isomerization of **6** by adding PR_3 without displacing HL^1.

Our failure to induce rearrangement of *cis*-$[PtCl_2(HL^1)_2]$ (**4**) to the presumed more stable trans isomer **5**, by treatment with excess free ligand HL^1, is clearly the result of destabilization of the 5-coordinate intermediate $[PtCl_2(HL^1)_3]$ by the bulk of the unidentate ligand.

These platinum complexes of HL^1 may be compared with those of other hybrid ligands chelating through phosphorus and oxygen. (Diphenylphosphino)acetic acid, HDPA, gives three types of complex, monodentate P-bonded $[PtX_2(HDPA)_2]$ (X = Cl, Br, I, SCN), readily undergoing ring closure with HX elimination to give intermediate [PtX(DPA)(HDPA)] and bidentate P-O-bonded $[Pt(DPA)_2]$.[28] The phosphines are cis disposed in all cases, whereas the palladium analogues have trans phosphines, showing that Ph_2PCH_2COOH is lower in its steric demands than HL^1 and electronic effects therefore dominate in determining the geometry of its platinum complexes.

(2-Hydroxyphenyl)diphenylphosphine, $Ph_2PC_6H_4OH$, behaves like HL^1, giving the P-bonded adduct *trans*-$[PtCl_2(PPh_2C_6H_4OH)_2]$, which readily loses HCl to give *cis*-$[Pt(PPh_2C_6H_4O)_2]$.[29] When the bulk of the phosphine is increased by incorporating *tert*-butyl groups, ring closure is more difficult, isomerization does not occur, and the product is *trans*-$[Pt(P\text{-}t\text{-}Bu_2C_6H_4O)_2]$.[29]

Similarly, the very bulky β-ketophosphines *t*-$Bu_2PCH_2C(O)R$ (R = Ph, or *t*-Bu) give trans P-bonded complexes with both $PtCl_2$ and $PdCl_2$; reaction with strong base leads to deprotonation and the formation of *trans*-$[M\{P\text{-}t\text{-}Bu_2CH{=}C(O)R\}_2]$ in each case.[30]

A recent study[31] on platinum complexes of the neutral phosphinomethoxy ligand $Ph_2PCH_2CH_2OCH_3$ (L^2) shows that it forms *cis*-$[PtCl_2(L^2)_2]$, suggesting that, as would be expected, L^2 is less bulky than the fluorinated ligand HL^1. Loss of Cl^- gives successively *cis*-$[PtCl(PPh_2CH_2CH_2OCH_3)(L^2)]^+$ and finally the bis-chelated *cis*-$[Pt(PPh_2CH_2CH_2OCH_3)_2]^{2+}$. Interestingly, the substitution of carbonyl for chloride causes a change in geometry, presumably because of the introduction of an additional ligand of strong trans influence, and the complex found is *trans*-$[PtCl(CO)(L^2)_2]$.

All of this work is entirely consistent with our current studies, but our results on HL^1 complexes are unusual in that, for the key complexes $[PtCl_2(HL^1)_2]$ and $[PtCl(L^1)(HL^1)]$, we have been able to isolate both cis and trans isomers.

Steric Properties of Monodentate HL^1 and Bidentate L^1. In view of the importance of steric effects in determining the geometry and stability of various platinum(II) complexes of the ligand $Ph_2PCH_2C(CF_3)_2OH$, it was of interest to attempt to evaluate its steric demands in both the monodentate and bidentate forms. From the crystal structures of *trans*-$[PtCl_2(HL^1)_2]$ (**5**) and *cis*-$[Pt(HL^1)_2]$ (**2**), the ligand profile in each case was determined by using the program PROFILE.[32] This approach calculates ligand profiles from crystallographic coordinates and van der Waals radii. Cross sections of the ligand are taken perpendicular to the metal-ligand bond, and half-cone angles are calculated at convenient intervals (θ) around the slice. In the case of both HL^1, in **5**, and $(L^1)^-$, in **2**, cross sections of the ligand were taken at intervals of 0.2 Å at distances from 0.2 to 3.0 Å from the metal atom and a value of 10° was used for θ.

A profile of the monodentate ligand HL^1 is shown in Figure 3, where the maximum half-cone angle is shown as a function of θ. The maximum half-cone angles at positions corresponding to each of the three substituent groups on phosphorus are found to be 80.3° for $-CH_2C(CF_3)_2OH$ (at 0.60 Å, θ = 120°), 76.7° for phenyl(2) (at 0.80 Å, θ = 260°), and 82.0° for phenyl(3) (at 0.40 Å, θ = 60°). Averaging of these three maximum values then gives a mean cone angle for the ligand HL^1 of 159°.

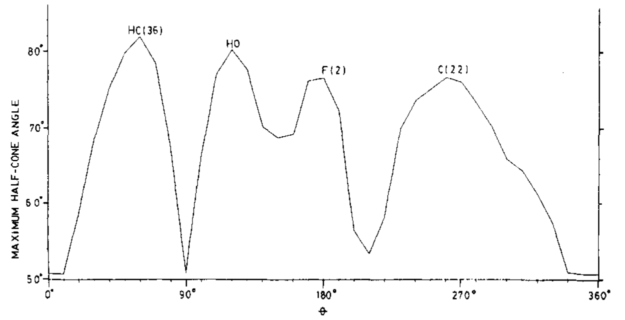

Figure 3. Maximum half-cone angle of HL^1 as a function of rotational angle, θ.

Profiles of numerous other tertiary phosphines have been calculated by similar methods, and tabulations are given by Tolman[33] and by Ferguson.[34] From these figures, the average cone angle of HL^1 is greater than that of PPh_3 (145°) and comparable to those of PPh_2-*t*-Bu (157°) and $PPh_2C_6F_5$ (158°); in other words, the $-CH_2C(CF_3)_2OH$ substituent is similar in its steric influence to *tert*-butyl or pentafluorophenyl.

We therefore suggest that the formation of trans isomer of $[PtCl_2(HL^1)_2]$ by the reaction of HL^1 with $PtCl_2$ is the result of dominance by steric factors in the stabilization of the complex. Consistent with this, only trans complexes of $PtCl_2$ are formed with both PPh_2-*t*-Bu[35] and $PPh_2C_6F_5$.[36]

For the chelating, bidentate ligand $Ph_2PCH_2C(CF_3)_2O^-$ ($(L^1)^-$) a cone angle calculation is less significant than for the monodentate ligand HL^1, since the steric interactions must inevitably be reduced by the formation of the chelate ring. Ligand profiles for $[Pt(L^1)_2]$ were examined to see how the two ligands fit together in a cis geometry, but there was no evidence that the two ligands are "meshed", in the sense of phenyl groups on one phosphino group fitting in between those on the adjacent ligand. Rather, the two phenyl groups on each ligand form relatively smooth surfaces. Absence of interleaving of phenyl groups is not surprising, since the rotation of the phosphine about the Pt-P bond is restricted by the incorporation of the Ph_2P group into a chelate ring.

Instead of interleaving, the steric strain is relieved by the opening up of the P-Pt-P angle to 103.72 (9)° and by rotation about $P-C_6H_5$ bonds, leading to angles between the planes of the phenyl rings of 39.6° between rings 2 and 5 on one side of the coordination plane and 46.6° between rings 3 and 4 on the other side. The CF_3 groups on the two cis alkoxide ligands are so far apart that there is no significant interaction between them, and the O-Pt-O angle closes down to 88.2 (3)°; the chelate ring bite angles are also less than 90°.

As a result of this change in ligand bulk, steric effects become increasing subordinate to electronic factors in determining complex geometry when one or both of the phosphinoalkoxide ligands is bidentate. Both isomers may be isolated for $[PtCl(L^1)(HL^1)]$, with the cis form favored, while for $[Pt(L^1)_2]$ only the cis isomer could be prepared.

In cases where both cis and trans isomers of a complex $[PtX_2(ER_3)_2]$ may be prepared, it is generally found that the cis isomer is the more stable. In compounds where the trans isomer is stabilized through the bulky nature of ER_3, there is usually no synthetic route available to the disfavored cis form. Our success

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in isolating the unstable *cis*-[$PtCl_2(HL^1)_2$] is clearly the result of the unusual synthetic approaches provided by the ready protonation–deprotonation equilibrium associated with the presence of the fluorinated alcohol function in the molecule.

Conclusions. This study has significantly extended the range of known platinum(II) complexes of P–O hybrid ligands to include a phosphino alcohol in both monodentate and bidentate modes of coordination. We have shown the value of a soft phosphine ligand in stabilizing the Pt–O bond, and we have again demonstrated that steric, electronic, and kinetic factors may all be significant in determining the geometry of a platinum(II) complex formed in any particular situation.

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Supplementary Material Available: For the structure determinations of compounds **2** and **5**, tables of hydrogen atom positional parameters (Table S-I), anisotropic thermal parameters (Tables S-II and S-III), supplementary bond distances and angles (Tables S-VI and S-VII), and weighted least-squares planes (Tables S-IX and S-X), and for **2**, a table of selected torsion angles (Table S-VIII) (10 pages); tables of calculated and observed structure factors (Tables S-IV and S-V) (51 pages). Ordering information is given on any current masthead page.

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Nucleophilic Activation of Carbon Monoxide. 4. Dihydrogen Reduction of the Methoxycarbonyl Adduct $Ru_3(CO)_{11}(CO_2CH_3)^-$

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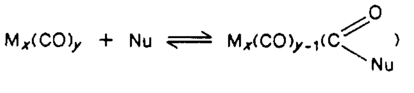
The anionic triruthenium cluster $Ru_3(CO)_{11}(CO_2CH_3)^-$ reacts with dihydrogen in dry THF to give methyl formate plus the hydride cluster $HRu_3(CO)_{11}^-$. Use of D_2 instead leads to the formation of DCO_2CH_3 plus $DRu_3(CO)_{11}^-$ as shown by ^2H NMR. The rate of the hydrogenation is demonstrated to be first order in [H_2] but inhibited by CO. These observations are interpreted in terms of a mechanism by which the principal pathway for reduction of the cluster involves the reversible dissociation of coordinated CO followed by rate-limiting H_2 addition to the unsaturated intermediate. Details of the synthesis and spectroscopic properties of the $Ru_3(CO)_{11}(CO_2CH_3)^-$ anion are also described.

Introduction

Investigations in this laboratory have been concerned with the activation of coordinated carbon monoxide by oxygen nucleophiles such as hydroxide or methoxide ion.[3,4] Such reactions with OH^- are key to CO activation in mechanisms for homogeneous catalysis of the water gas shift reaction in alkaline solution,[5-8] while CH_3O^- activation is involved in certain methoxide cocatalyzed processes such as the carbonylation of methanol[9] and the reductive carbonylation of nitroarenes.[10] Methoxycarbonyl adducts, such as $M_x(CO)_{y-1}(CO_2CH_3)^-$, are likely intermediates in the latter catalysis cycles, while other adducts (e.g., eq 1) are proposed to be the labilized species in nucleophile-catalyzed CO exchange and other substitution reactions of metal carbonyl complexes.[11] However, few such adducts have been subjected to direct kinetics investigation.



$$M_x(CO)_y + Nu \rightleftharpoons M_x(CO)_{y-1}(C(=O)Nu) \quad (1)$$

In this context, we have undertaken a quantitative investigation of certain reactions of the triruthenium methoxycarbonyl anion $Ru_3(CO)_{11}(CO_2CH_3)^-$ (I), which can be prepared via the reaction of methoxide salts with the neutral cluster $Ru_3(CO)_{12}$.[3,4a] In previous reports[3] from this laboratory, it was shown that I is dramatically activated toward ligand substitution reactions relative to $Ru_3(CO)_{12}$ and that this enhanced lability apparently also leads to a markedly greater reactivity toward dihydrogen:[3]

$$Ru_3(CO)_{11}(CO_2CH_3)^- + P(OCH_3)_3 \rightarrow Ru_3(CO)_{10}(CO_2CH_3)(P(OCH_3)_3)^- + CO \quad (2)$$

$$Ru_3(CO)_{11}(CO_2CH_3)^- + H_2 \rightarrow HRu_3(CO)_{11}^- + HCO_2CH_3 \quad (3)$$

A similar reaction of the mononuclear (ethoxycarbonyl)cobalt carbonyl species $Co(CO)_4(CO_2C_2H_5)$ (to give ethyl formate plus $Co_2(CO)_8$) has also been reported and investigated mechanistically by Ungváry and Markó.[12] In that case the parent carbonyl would be the unstable cation $Co(CO)_5^+$.

Described here is a kinetics investigation of the reaction of $Ru_3(CO)_{11}(CO_2CH_3)^-$ with dihydrogen. Also summarized are the details of the synthesis procedure and spectroscopic properties of this anionic cluster, parts of which have been described earlier.

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