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Comparison of σ-Alkyl and σ-Perfluoroalkyl Groups as Ligands. 2. Crystal and Molecular Structures of Dimethyl[(2-vinylphenyl)diphenylphosphine]platinum(II) and Bis(trifluoromethyl)[(2-vinylphenyl)diphenylphosphine]platinum(II)

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The crystal and molecular structures of the title compounds have been determined from three-dimensional X-ray diffractometer data. Both complexes are isostructural and crystallize in the monoclinic space group $P2_1/c$ (hereinafter SP is the ligand (2-vinylphenyl)diphenylphosphine). Cell parameters are as follows: $Pt(CH_3)_2(SP)$, **1**, a = 9.224 (4) Å, b = 18.521 (7) Å, c = 12.668 (5) Å, β = 119.19 (2)°, Z = 4; $Pt(CF_3)_2(SP)$, **2**, a = 9.3680 (5) Å, b = 19.3262 (6) Å, c = 12.6339 (9) Å, β = 117.35 (1)°, Z = 4. Block-diagonal and full-matrix least-squares refinement converged at R = 0.026 (**1**, 3827 unique reflections) and R = 0.030 (**2**, 3058 unique reflections). The structures have approximately square-planar geometry with the SP ligand chelating via phosphorus and a π-bonded vinyl group which is almost normal to the metal coordination plane. Nonplanarity of the vinyl group in **2** was established by location and refinement of its hydrogen atoms. Important bond lengths are: **1**, $Pt-CH_3$ (trans to P) = 2.166 (5) Å, $Pt-CH_3$ (trans to vinyl) = 2.052 (6) Å, Pt–P = 2.276 (1) Å, Pt–vinyl = 2.223 (5) and 2.201 (5) Å (terminal C); **2**, $Pt-CF_3$ (trans to P) = 2.082 (5) Å, $Pt-CF_3$ (trans to vinyl) = 2.032 (5) Å, Pt–P = 2.310 (1) Å, Pt–vinyl = 2.290 (5) and 2.245 (5) Å (terminal C). The $Pt-CF_3$ bonds in **2** are shorter than the analogous $Pt-CH_3$ bonds in **1** whereas the opposite is true of the Pt–P and Pt–vinyl bonds. Although these bond-length trends can be interpreted in terms of $Pt(d_\pi)-CF_3(\sigma^*)$ back-bonding, it seems more likely that the $Pt-CF_3$ bond contraction is primarily a consequence of the positive charge induced on the σ-carbon atom by the electronegative fluorine atoms. The trends in Pt–P and Pt–vinyl bond lengths probably reflect a combination of two effects: (1) approximately equal σ-donor abilities or trans influences for CH_3^- and CF_3^- and (2) a cis-bond-weakening influence of unknown origin for the fluoroalkyl ligand which is also manifest from the structural comparison of $PtClR(PMePh_2)_2$ ($R = CH_3$, **3**; $R = C_2F_5$, **4**).

Introduction

The nature of transition-metal–σ-fluoroalkyl bonding is controversial, particularly with regard to the extent of $d\pi-\sigma^*$ back-bonding.[1] There are also few structural determinations which allow direct comparison of the cis and trans influences of σ-alkyl and σ-fluoroalkyl ligands. We[1] have reported detailed structural analyses of the planar platinum(II) complexes *trans*-$PtClR(PMePh_2)_2$ [R = CH_3 (**3**), CF_3, C_2F_5 (**4**)] in which the alkyl or perfluoroalkyl groups are trans to chlorine. It was of obvious interest to determine the structures of closely comparable alkyl- and perfluoroalkyl–platinum(II) complexes in which these groups are trans to neutral ligands, especially potential π acceptors. We describe here the structures of the complexes $PtR_2(SP)$[2] (R = CH_3, **1**, or CF_3, **2**) and compare the results with those derived from structural studies of *cis*-$Pt(CF_3)_2[PMe_2(C_6F_5)]_2$ and $[Pt(CH_3)\{PMe_2(C_6F_5)\}_3]PF_6$, which were reported briefly by Manojlović-Muir et al.[3] after our work was complete.

Experimental Section

Preparations. Solvents were AR grade and were stored over sodium or 3A molecular sieves as appropriate. Spectroscopic and microanalytical data were obtained as described previously.[1] The complexes $Pt(CH_3)_2(SP)$, **1**,[4] and $Pt(CF_3)_2(COD)$[5] were prepared by literature procedures. We found that the reaction between $Pt(CH_3)_2(COD)$ and CF_3I to give $Pt(CF_3)_2(COD)$ was complete in 1–2 days rather than the 4 days specified.[5]

Bis(trifluoromethyl)[(2-vinylphenyl)diphenylphosphine]platinum(II), $Pt(CF_3)_2(SP)$, 2. (2-Vinylphenyl)diphenylphosphine (0.13 g, 0.45 mmol) was added to a solution of $Pt(CF_3)_2(COD)$ (0.20 g, 0.45 mmol) in 10 mL of benzene. After 3–5 min the product began to precipitate as colorless microcrystals. After 3 h of stirring the solid was filtered, washed successively with two 0.5-mL portions of benzene and and one 2-mL portion of *n*-hexane, and dried in vacuo; yield 0.23 g (91%), mp 230–245 °C (dec). Anal. Calcd for $C_{22}H_{17}F_6PPt$: C, 42.5; H, 2.7; M_r = 621. Found: C, 42.3; H, 2.9; M_r = 594 (vpo, CH_2Cl_2, 25 °C). IR (Nujol, cm^{-1}): 1505 (w, sh) [$\nu(C{=}C)$]. ^1H NMR ($CDCl_3$, δ): 7.48, 7.9 (br, mult, aromatic H), 6.50 (dd of ^{195}Pt 1:4:1 triplets, H_1), 5.50 (d of ^{195}Pt 1:4:1 triplets, H_2), 4.00 (dd of ^{195}Pt 1:4:1 triplets, H_3) (H_1, H_2, and H_3 are defined in Figure 1); $J_{H_1-H_2}$ = 8 Hz, $J_{H_1-H_3}$ = 14 Hz, $J_{H_2-H_3}$ < 1 Hz, J_{P-H_1}, J_{P-H_2} < 1 Hz, J_{P-H_3} = 4 Hz, J_{Pt-H_1} = 16 Hz, J_{Pt-H_2} = 26 Hz. The ^{195}Pt satellites of H_3 were obscured by signals arising from small amounts of impurity and by the high noise level necessitated by the low solubility of **2** in $CDCl_3$, but J_{Pt-H_3} is probably ca. 20 Hz.

Table I. Crystal Data

	1	2
a, Å	9.224 (4)	9.3680 (5)
b, Å	18.521 (7)	19.3262 (6)
c, Å	12.668 (5)	12.6339 (9)
β, deg	119.19 (2)	117.35 (1)
formula wt	513.49	621.44
ρ_{obsd}, g cm^{-3}	1.79 (2)	1.9 (1)
ρ_{calcd}, g cm^{-3}	1.81	2.03
Z	4	4
unit cell volume, Å^3	1889.3	2031.7
space group	$P2_1/c$	$P2_1/c$
crystal dimensions, mm	0.21 × 0.14 × 0.28 mm	0.28 × 0.09 × 0.15 mm
absorption coefficient, cm^{-1}	78.94 (Mo Kα)	145.20 (Cu Kα)

Collection and Reduction of X-ray Intensity Data. Recrystallization of **1** from benzene–ethanol gave pale yellow tabular crystals, and **2** formed almost colorless crystals from dichloromethane–*n*-hexane.

Approximate unit cell dimensions for both complexes were obtained from preliminary Weissenberg (0*kl*, 1*kl*) and precession (*h*0*l*, *h*1*l*) photographs. Systematic absences of the types *h*0*l* ($l = 2n + 1$) and 0*k*0 ($k = 2n + 1$) observed in both cases uniquely define the centrosymmetric, monoclinic space group $P2_1/c$ (C_{2h}^5, No. 14). For Z = 4, neither molecule has any imposed crystal symmetry. Full details of the crystal data for both complexes are listed in Table I.

Reflection data for **1** and **2** were collected on a Picker FACS-1 fully automatic four-circle diffractometer. The crystals were mounted on quartz fibers and were aligned with a crystallographic unit cell axis and the instrumental ϕ axis approximately coincident (**1**, $c \parallel \phi$; **2**, $a \parallel \phi$). Accurate unit cell dimensions and crystal orientation matrices, together with their estimated standard errors, were obtained from the least-squares refinement of the 2θ, ω, χ, and ϕ values of 12 carefully centered high-angle reflections.[6]

Full details of the experimental conditions and data collection methods used are given in Table II. During data collection three "standard" reflections for each complex showed small isotropic decreases in intensity (**1**, 1.2%; **2**, 2.0%). These decreases were assumed to be independent of 2θ, and the reflection data were corrected accordingly.

Reflection intensities were reduced to values of $|F_o|$ and each was assigned an individual estimated standard deviation ($\sigma(F_o)$).[7] For these data sets the instrumental uncertainty factor (ρ)[8] was assigned a value of $0.002^{1/2}$. Reflection data were sorted, equivalent reflections

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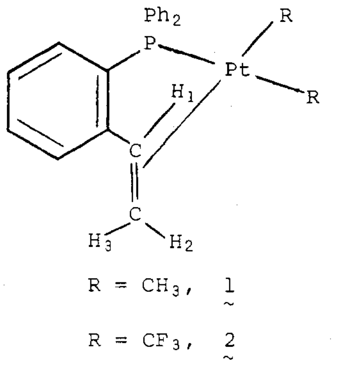

Figure 1. Schematic diagram for **1** and **2**.

Table II. Details of Data Collection[a]

	1	2
radiation	Mo Kα, λ 0.7107 Å	Cu Kα, λ 1.5418 Å
monochromator	graphite crystal	graphite crystal
takeoff angle, deg	3.0	3.0
scan method	θ–2θ scans	θ–2θ scans
scan speed, deg min^{-1}	2	2
scan width,[b] deg	2θ – 0.95 to 2θ + 0.95 + Δ	2θ – 0.95 to 2θ + 0.95 + Δ
total bkgd count time, s	20	20
"standard" reflections	3 every 97	3 every 97
"standard" indices	$(\bar{6}00)$, (2,13,0), (018)	(037), (600), (0,14,3)
2θ scan limit, deg	60	124
no. of data	5672	3788
no. of data with $I/\sigma(I) \geq 3.0$	3827	3058

[a] Data were collected at 20 ± 2° (**1**) and 23 ± 2° (**2**). [b] The scan range was asymmetric; the term Δ is the 2θ angular separation of the Kα_1 and Kα_2 components of the diffracted beam.

were averaged, and reflections with $I/\sigma(I) < 3.0$[7] were discarded as being unobserved. Reflections for which the individual background measurements differed by $\geq 4.0\sigma$ were also discarded. The statistical R factors (R_s)[7] for the terminal data sets were 0.022 (**1**, 3827 reflections) and 0.010 (**2**, 3058 reflections).

Solution and Refinement of the Structures. The structures were readily solved by conventional Patterson and Fourier syntheses and were initially refined by block-diagonal least-squares methods. Atomic scattering factors and anomalous scattering factors for the nonhydrogen atoms were taken from ref 9. The data for **1** were corrected for absorption by the numerical analysis method (grid size, 8 × 6 × 14 points), while for **2** an analytical absorption correction was applied.[10] For both complexes fixed phenyl-hydrogen atom contributions were included in the scattering model (C–H = 0.95 Å,[11] $B_H = B_C$). These hydrogen-atom coordinates and temperature factors were recalculated after each cycle of refinement. For **1**, neither the vinyl nor the methyl protons were readily located and no attempt was made to include these in the scattering model. For **2**, the three vinyl protons were well defined and refined reasonably with isotropic temperature factors. An examination of $|F_o|$ and $|F_c|$ indicated no evidence of serious secondary extinction effects for **1**, but for **2** a secondary extinction correction was applied. A final cycle of full-matrix least-squares refinement on each complex with all nonhydrogen atoms anisotropic gave R values of 0.026 (**1**) and 0.030 (**2**) (R_w = 0.038 (**1**), R_w = 0.041 (**2**)). No individual parameter shift was greater than 0.1 of the estimated parameter standard deviation. The standard deviations of observations of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ (where m is the number of observations and n is the number of parameters varied), were 1.68 (**1**) and 1.69 (**2**). Weighting-scheme analyses showed no serious dependence of $w[|F_o| - |F_c|]^2$ on either $|F_o|$ or $\lambda^{-1} \sin \theta$. The final electron density difference Fourier maps showed no unusual features, the highest residual peaks being 0.7 e/Å^3 (**1**) and 1.4 e/Å (**2**).

Final atomic positional and thermal parameters are listed in Table III. Final tables of structure factors are available as supplementary material.

Computer Programs. The data reduction (SETUP), sorting (SORTER), Fourier (ANUFOR), least-squares (SFLS), and absorption correction (ACACA, TOMPAB) programs have been described elsewhere.[12] The figures were produced using ORTEP.[13] All calculations were carried out on the Univac-1108 computer of the Australian National University Computer Centre.

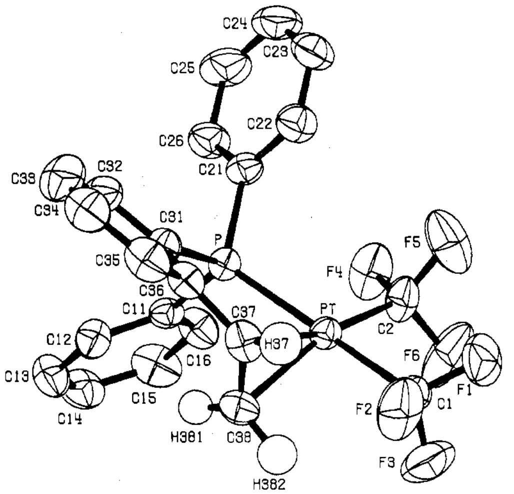

Figure 2. Stereochemistry and atom numbering scheme for **2**.

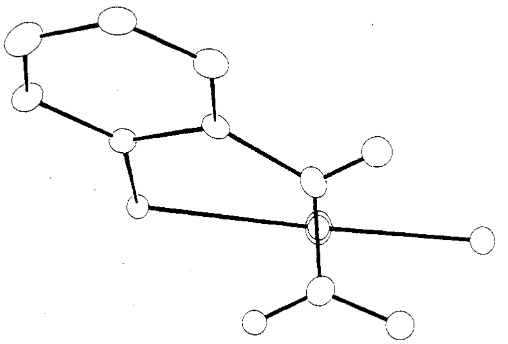

Figure 3. View of **2** down the Pt–C(2) axis.

Results

Description of the Structures. The complexes are isostructural. Both have discrete monomeric molecular units and there are no unusually short intermolecular contacts. A labeled perspective view of **2** and a projection of its inner coordination sphere are shown in Figures 2 and 3. The thermal ellipsoids have been drawn to include 50% of the probability distribution, and for clarity phenyl-hydrogen atoms have been omitted. No view of **1** is provided since it is visually indistinguishable from **2**. Hydrogen-atom nomenclature follows that of the parent carbon atoms. Bond-length and -angle data are in Table IV, and the results of the mean-plane and torsion-angle calculations are in Table V.

As expected, **1** and **2** have essentially square-planar geometry with the methyl or trifluoromethyl groups occupying cis-coordination sites and the SP ligands functioning in an established mode[4,14] as cis-bidentate donors. The maximum deviations of Pt, P, C(1), and C(2) from their respective coordination planes are small, being slightly greater for **2** than for **1** (see Table V). Equivalent interbond angles at Pt in **1** and **2** differ by less than 2°, and there are small (<5°), largely in-plane, deviations from ideal square-planar geometry which reflect the steric requirements of the coordinating groups. In particular, the P–Pt–MPV (MPV is the midpoint of the vinyl C=C bond) chelate bite angles are 85.5° (**1**) and 84.9° (**2**). As is usual for planar platinum(II)–olefin complexes,[15] the coordinated vinyl groups of **1** and **2** are approximately normal to the metal coordination plane. The ligand conformation is similar to that observed for chelate SP in Fe(CO)$_2$(SP)$_2$[16] and for the chelated arsenic analogue in PtCl$_2$(o-CH$_2$=

Table III. Fractional Atomic Positional and Thermal Parameters for 1 and 2

atom	x/a	y/b	z/c	B, Å²	atom	x/a	y/b	z/c	B, Å²
Refined Positional Parameters for **1**									
Pt	0.08506 (2)	0.13013 (1)	0.28333 (1)		C(25)	0.5966 (7)	0.0790 (4)	0.7838 (5)	
P	0.32280 (13)	0.16896 (6)	0.44661 (10)		C(26)	0.5543 (6)	0.1092 (3)	0.6733 (5)	
C(11)	0.5052 (5)	0.1708 (2)	0.4278 (4)		C(31)	0.2759 (5)	0.2619 (2)	0.4638 (4)	
C(12)	0.5791 (6)	0.2339 (3)	0.4194 (5)		C(32)	0.3730 (7)	0.3044 (3)	0.5654 (5)	
C(13)	0.7127 (6)	0.2316 (3)	0.3977 (5)		C(33)	0.3164 (10)	0.3722 (3)	0.5758 (6)	
C(14)	0.7746 (6)	0.1676 (4)	0.3868 (5)		C(34)	0.1672 (9)	0.3969 (3)	0.4873 (6)	
C(15)	0.7026 (7)	0.1039 (3)	0.3938 (6)		C(35)	0.0708 (7)	0.3553 (3)	0.3870 (6)	
C(16)	0.5679 (6)	0.1050 (3)	0.4136 (5)		C(36)	0.1248 (5)	0.2883 (2)	0.3732 (4)	
C(21)	0.3919 (6)	0.1285 (2)	0.5951 (4)		C(37)	0.0262 (6)	0.2474 (3)	0.2583 (4)	
C(22)	0.2722 (7)	0.1158 (3)	0.6290 (5)		C(38)	0.0963 (7)	0.2268 (3)	0.1864 (5)	
C(23)	0.3197 (8)	0.0868 (3)	0.7423 (6)		C(1)	−0.1476 (6)	0.0964 (3)	0.1304 (5)	
C(24)	0.4799 (8)	0.0686 (3)	0.8174 (5)		C(2)	0.1107 (7)	0.0247 (3)	0.3394 (6)	
Refined Positional Parameters for **2**									
Pt	0.09394 (2)	0.13338 (1)	0.27738 (1)		C(32)	0.3857 (8)	0.2997 (3)	0.5535 (5)	
P	0.32878 (14)	0.17069 (6)	0.43638 (10)		C(33)	0.3389 (12)	0.3652 (3)	0.5683 (7)	
C(11)	0.5073 (5)	0.1699 (2)	0.4146 (4)		C(34)	0.1878 (9)	0.3899 (3)	0.4861 (6)	
C(12)	0.5756 (6)	0.2302 (3)	0.3997 (4)		C(35)	0.0900 (8)	0.3514 (3)	0.3893 (6)	
C(13)	0.7115 (7)	0.2269 (3)	0.3837 (5)		C(36)	0.1380 (6)	0.2861 (2)	0.3698 (4)	
C(14)	0.7762 (7)	0.1651 (3)	0.3791 (5)		C(37)	0.0408 (7)	0.2497 (3)	0.2584 (5)	
C(15)	0.7066 (8)	0.1039 (3)	0.3904 (6)		C(38)	0.0974 (8)	0.2299 (3)	0.1798 (5)	
C(16)	0.5731 (7)	0.1058 (3)	0.4078 (5)		C(1)	−0.1248 (6)	0.1059 (3)	0.1347 (4)	
C(21)	0.3860 (7)	0.1316 (2)	0.5814 (4)		F(1)	−0.2119 (4)	0.0582 (2)	0.1566 (3)	
C(22)	0.2654 (7)	0.1173 (3)	0.6133 (5)		F(2)	−0.2265 (5)	0.1589 (2)	0.0900 (4)	
C(23)	0.3038 (9)	0.0885 (3)	0.7226 (5)		F(3)	−0.1104 (5)	0.0786 (3)	0.0424 (3)	
C(24)	0.4596 (9)	0.0745 (3)	0.8018 (5)		C(2)	0.1243 (7)	0.0324 (3)	0.3276 (5)	
C(25)	0.5785 (8)	0.0884 (4)	0.7712 (5)		F(4)	0.2771 (4)	0.0147 (2)	0.4051 (3)	
C(26)	0.5436 (7)	0.1167 (3)	0.6616 (5)		F(5)	0.0388 (5)	0.0125 (2)	0.3839 (4)	
C(31)	0.2863 (6)	0.2598 (2)	0.4551 (4)		F(6)	0.0876 (5)	−0.0123 (2)	0.2380 (4)	
Calculated Hydrogen Atom Coordinates and Fixed Isotropic Thermal Parameters for 1									
H(14)	0.868	0.166	0.374	4.4	H(22)	0.159	0.127	0.575	3.8
H(15)	0.746	0.059	0.385	4.8	H(23)	0.239	0.080	0.767	4.6
H(16)	0.518	0.061	0.418	3.8	H(24)	0.510	0.048	0.894	4.5
H(32)	0.477	0.287	0.627	4.0	H(25)	0.708	0.065	0.837	4.9
H(33)	0.382	0.401	0.645	4.9	H(26)	0.637	0.117	0.651	4.0
H(34)	0.129	0.443	0.495	5.0	H(12)	0.538	0.279	0.429	3.4
H(35)	−0.034	0.373	0.327	4.3	H(13)	0.761	0.275	0.391	4.1
Calculated Hydrogen Atom Coordinates and Fixed Isotropic Thermal Parameters for 2									
H(13)	0.760	0.268	0.376	4.4	H(382)[a]	0.008 (7)	0.215 (3)	0.090 (5)	4.0 (12)
H(14)	0.870	0.164	0.368	4.5	H(37)[a]	−0.065 (7)	0.246 (4)	0.227 (5)	4.6 (16)
H(15)	0.752	0.061	0.386	4.6	H(22)	0.157	0.127	0.560	4.0
H(16)	0.525	0.064	0.415	3.8	H(23)	0.221	0.078	0.743	4.7
H(32)	0.486	0.282	0.611	4.1	H(24)	0.485	0.055	0.878	5.2
H(33)	0.408	0.393	0.633	5.9	H(25)	0.687	0.079	0.826	5.4
H(34)	0.153	0.434	0.498	4.9	H(26)	0.628	0.126	0.641	3.9
H(35)	−0.012	0.369	0.334	4.4	H(12)	0.529	0.274	0.400	3.5
H(381)[a]	0.206 (6)	0.242 (3)	0.209 (4)	2.9 (10)					

[a] Refined anisotropically.

$CHC_6H_4AsPh_2$)[17] but differs from that found[18] for the closely related ligand (2-(*cis*-1-propenyl)phenyl)diphenylphosphine in the octahedral chelate complex $Mo(CO)_4$(*cis*-*o*-$CH_3CH{=}CHC_6H_4PPh_2$), the coordinated double bond of which lies in the Mo–P coordination plane.

The dihedral angles between the three-membered metal–olefin rings and the platinum coordination planes are 84° (**1**) and 81° (**2**), the terminal carbon atoms C(38) being tilted away from the phosphine ligand. Tilt angles of about 80° have been reported for a variety of platinum(II)–olefin complexes,[19-21] including Zeise's salt.[22,23]

The terminal Pt–C(38) distances [2.201 (5) Å, **1**; 2.245 (5) Å, **2**] are shorter (0.022 Å, **1**; 0.045 Å, **2**) than the Pt–C (37) distances (2.223 (5) Å, **1**; 2.290 (5) Å, **2**), and the positions at which the Pt–P–C(1)–C(2) coordination planes intersect the vinyl C=C bonds are displaced from the midpoint away from the terminal CH_2 group (Figure 3). Similar shortenings of terminal Pt(II)–vinyl bond lengths have been noted in the complexes *trans*-$PtCl_2$(*p*-$YC_6H_4CH{=}CH_2$)(NC_5H_4X) (X = Me, Y = NMe_2; X = Me, Y = H; X = Cl, Y = NO_2).[21] In this series, there is a correlation between the appropriate $^{195}Pt-^{13}C$ coupling constants, Pt–C bond lengths, and the electron-donating ability of Y.[24] However, in these complexes, the intersection of the platinum coordination plane and the C=C bond is displaced toward the terminal CH_2 group, in contrast with the situation in **1** and **2**, which presumably reflects steric constraints of coordinated SP.

The Pt–C(37) and Pt–C(38) metal–vinyl distances in **2** are longer than the corresponding distances in **1** and, correspondingly, the magnitudes of $J_{^{195}Pt-^1H}$ for the vinyl protons are smaller for **2** than for **1**. The metal–vinyl Pt–C distances for both **1** and **2** are longer than observed in planar platinum(II) complexes having olefin trans to chlorine [2.10 (2)–2.18 (2) Å],[17,22,23,25-27] a trend which is as expected in the case of **1** on the basis of the relative trans influences of Cl and CH_3.[28] The vinyl C=C distances in **1** [1.403 (7) Å; cf. $K[PtCl_3(C_2H_4)]H_2O$, 1.375 (4) Å][23] and in **2** [1.378 (8) Å] are significantly longer than the corresponding distance for the uncoordinated vinyl group in $Fe(CO)_2(SP)_2$.[16]

The dihedral angle between the planes Pt–C(37)–C(38) and C(36)–C(37)–C(38) can be used to describe the degree of bending back of the (*o*-diphenylphosphino)phenyl substituent

Table IV

(a) Important Bond Lengths (Å) and Angles (deg) in **1** and **2**

distance	**1**	**2**	distance	**1**	**2**
Pt-P	2.276 (1)	2.310 (1)	C(37)-C(38)	1.403 (7)	1.378 (8)
Pt-C(1)	2.166 (5)	2.082 (5)	C(37)-H(37)		0.89 (6)
Pt-C(2)	2.052 (6)	2.032 (5)	C(38)-H(381)		0.94 (5)
Pt-C(37)	2.223 (5)	2.290 (5)	C(38)-H(382)		1.09 (5)
Pt-C(38)	2.201 (5)	2.245 (5)	range of C-F		1.334 (7)-1.355 (7)
C(36)-C(37)	1.492 (7)	1.459 (8)	av C-F		1.343

angle	**1**	**2**	angle	**1**	**2**
P-Pt-C(1)	177.4 (2)	176.2 (2)	C(31)-C(36)-C(37)	121.0 (4)	121.6 (4)
P-Pt-C(2)	95.1 (2)	95.0 (2)	C(36)-C(37)-C(38)	121.1 (5)	123.6 (6)
P-Pt-C(37)	83.2 (1)	81.9 (2)	C(36)-C(37)-H(37)		123 (4)
P-Pt-C(38)	87.9 (1)	88.3 (2)	H(37)-C(37)-C(38)		112 (4)
C(1)-Pt-C(2)	86.1 (2)	88.1 (2)	H(381)-C(38)-C(37)		111 (3)
C(1)-Pt-C(37)	95.0 (2)	94.5 (2)	H(382)-C(38)-C(37)		117 (3)
C(1)-Pt-C(38)	91.8 (2)	89.6 (2)	H(381)-C(38)-H(382)		131 (4)
C(2)-Pt-C(37)	163.3 (3)	165.4 (2)	range of Pt-C-F		113.5 (4)-116.6 (3)
C(2)-Pt-C(38)	159.7 (3)	159.2 (2)	av of Pt-C-F		114.4
C(37)-Pt-C(38)	37.0 (2)	35.3 (2)	range of F-C-F		102.8 (5)-106.2 (5)
Pt-P-C(31)	103.2 (1)	103.4 (2)	av F-C-F		104.1
P-C(31)-C(36)	115.8 (3)	116.4 (4)			

(b) Bond Lengths (Å) and Angles (deg) within the Phenyl and Phenylene Rings and at Phosphorus

	1			**2**		
distance	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$
P-C(n1)	1.811 (4)	1.827 (5)	1.815 (4)	1.816 (5)	1.820 (5)	1.807 (5)
C(n1)-C(n2)	1.383 (6)	1.386 (7)	1.397 (7)	1.383 (7)	1.390 (8)	1.394 (7)
C(n2)-C(n3)	1.388 (7)	1.388 (8)	1.391 (7)	1.379 (8)	1.375 (8)	1.382 (8)
C(n3)-C(n4)	1.352 (8)	1.353 (8)	1.362 (9)	1.353 (9)	1.364 (9)	1.399 (11)
C(n4)-C(n5)	1.377 (9)	1.351 (8)	1.378 (9)	1.388 (9)	1.362 (9)	1.363 (9)
C(n5)-C(n6)	1.382 (8)	1.375 (7)	1.380 (7)	1.367 (8)	1.381 (8)	1.398 (7)
C(n6)-C(n1)	1.397 (7)	1.381 (6)	1.392 (6)	1.403 (7)	1.384 (7)	1.405 (7)

	1			**2**		
angle	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$
P-C(n1)-C(n2)	123.3 (3)	117.3 (4)	124.2 (4)	122.0 (4)	118.1 (4)	123.1 (4)
P-C(n1)-C(n6)	118.1 (4)	123.8 (4)	115.8 (3)	118.5 (4)	123.1 (4)	116.4 (4)
C(n6)-C(n1)-C(n2)	118.5 (4)	118.9 (5)	119.8 (4)	119.4 (5)	118.8 (5)	120.3 (4)
C(n1)-C(n2)-C(n3)	120.5 (5)	119.3 (5)	119.6 (5)	119.8 (5)	119.9 (6)	120.3 (6)
C(n2)-C(n3)-C(n4)	120.5 (5)	120.6 (5)	120.1 (5)	120.6 (5)	121.0 (6)	119.2 (6)
C(n3)-C(n4)-C(n5)	120.2 (5)	120.6 (5)	120.7 (5)	120.4 (5)	119.4 (5)	120.9 (5)
C(n4)-C(n5)-C(n6)	120.2 (5)	120.3 (5)	120.6 (5)	120.1 (6)	120.9 (6)	120.8 (6)
C(n5)-C(n6)-C(n1)	121.1 (5)	120.4 (5)	119.3 (5)	119.6 (5)	119.9 (6)	118.4 (5)
C(n5)-C(n6)-C(n7)						119.8 (5)
C(n1)-C(n6)-C(n7)						121.6 (4)
Pt-P-C(n1)	115.6 (1)	120.2 (1)	103.2 (1)	116.2 (1)	117.9 (2)	103.4 (2)
C(1n)-P-C(2n)	105.3 (2)			106.4 (2)		
C(2n)-P-C(3n)	104.4 (2)			104.2 (2)		
C(3n)-P-C(1n)	106.9 (2)			107.5 (2)		

on the double bond. The values of this angle for **1** (104.0°) and **2** (103.2°) are comparable with similarly defined angles in the complexes *trans*-$PtCl_2(p\text{-}YC_6H_4CH{=}CH_2)(NC_5H_4X)$, viz. 106.5° (X = Me, Y = NMe_2), 108.4° (X = Me, Y = H), and 107.0° (X = Cl, Y = NO_2).[21]

In **2** the vinylic hydrogen atoms were located, albeit with necessarily large errors in their positional and thermal parameters. The observed ranges of the R–$\hat{C}$–R interbond angles [112 (4)–130 (4)°, R = H or C] and C–H distances [0.89 (6)–1.09 (5) Å] are similar to those found for coordinated ethylene in $Rh(C_5H_5)(C_2H_4)(C_2F_4)$ by X-ray diffraction [H–$\hat{C}$–R = 112 (5)–124 (4)°, C–H = 0.92 (8)–1.00 (6) Å][29] and in $K[PtCl_3(C_2H_4)]H_2O$ by neutron diffraction [H–$\hat{C}$–R = 114.6 (6)–121.2 (5)°, C–H = 1.086 (8)–1.096 (7) Å].[23] The substituents on the vinyl group in **2** are bent back asymmetrically from the central metal atom. The angle α between the normals to the three-atom planes defined[15] by the olefinic carbon atoms and their substituents is 26°, and the angles β and β' between the olefinic bond and the plane are 75 and 79°, respectively (Figure 4). These angles compare favorably with those found in $Rh(C_5H_5)(C_2H_4)(C_2F_4)$ (α = 42.4°, β = 69.1°)[29] and in $K[PtCl_3(C_2H_4)]H_2O$ (α = 32.5°, β = 72.7°).[23]

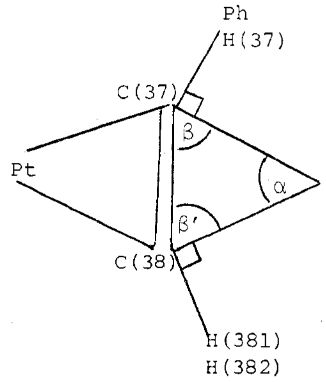

Figure 4. Diagram showing definition of bend-back angles.

The Pt–P distance trans to CF_3 [2.310 (1) Å] is 0.034 Å longer than the Pt–P distance trans to CH_3 [2.276 (1) Å]. Comparison with other Pt(II)–P distances may be vitiated by the potential contraction in Pt–P bond lengths due to chelation.

Table V. Unweighted Mean Planes and Dihedral Angles[a]

Planes

Molecule **1**: Orthogonal Coordinates, $X = 9.224x - 6.179z$, $Y = 18.521y$, $Z = 11.059z$

Plane 1: $0.8435X - 0.1914Y - 0.5018Z + 2.879 = 0$			
Pt	0.0303 (2)	C(2)	−0.000 (8)
P	−0.015 (1)	C(37)[b]	−0.574 (6)
C(1)	−0.015 (6)	C(38)[b]	0.818 (6)
Plane 2: $-0.6228X - 0.2074Y - 0.7544Z + 2.262 = 0$			
Pt	0.0000 (2)	C(38)	0.000 (6)
C(37)	0.000 (6)		
Plane 3: $-0.0655X + 0.8615Y - 0.5036Z - 2.597 = 0$			
C(36)	0.000 (5)	C(38)	0.000 (5)
C(37)	0.000 (5)		

Angles (deg) between Planes

1–2	83.8	1–3	88.1	2–3	104.0

Planes

Molecule 2: Orthogonal Coordinates, $X = 9.368x - 5.804z$, $Y = 19.326y$, $Z = 11.222z$

Plane 1: $0.8212X - 0.1474Y - 0.5512Z + 2.723 = 0$			
Pt	0.0280 (2)	C(2)	−0.001 (7)
P	−0.013 (1)	C(37)[b]	−0.504 (7)
C(1)	−0.014 (6)	C(38)[b]	0.849 (7)
Plane 2: $-0.6939X - 0.1856Y - 0.6957Z + 2.138 = 0$			
Pt	0.0000 (2)	C(38)	0.000 (7)
C(37)	0.000 (7)		
Plane 3: $-0.0867X + 0.8755Y - 0.4754Z - 2.942 = 0$			
C(36)	0.000 (5)	C(38)	0.000 (5)
C(37)	0.000 (5)		
Plane 4: $0.1406X + 0.8494Y - 0.5086Z - 2.466 = 0$			
C(36)	0.000 (5)	H(37)	0.00 (7)
C(37)	0.000 (5)		
Plane 5: $-0.1757X + 0.9610Y - 0.2137Z - 3.862 = 0$			
C(38)	0.000 (6)	H(382)	0.00 (5)
H(381)	0.00 (5)		
Plane 6: $-0.0043X + 0.9146Y - 0.4043Z - 3.319 = 0$			
C(36)	0.064 (5)	H(37)	0.00 (7)
C(37)	−0.074 (5)	H(381)	0.00 (5)
C(38)	−0.071 (5)	H(382)	0.08 (5)

Angles (deg) between Planes

1–2	80.8	2–3	103.2
1–3	86.5	4–5	26

[a] Distances of atoms from planes are given in Å with standard deviations in parentheses. [b] These atoms were not used to define the plane.

This may be a significant effect since in the trigonal-bipyramidal complex $Fe(CO)_2(SP)_2$, which has equivalent axial P donors and where one SP ligand is chelating and the other is a monodentate P donor, the chelated Fe–P distance is ca. 0.035 Å shorter than the nonchelated Fe–P distance.[17] Nevertheless, the Pt–P distance trans to CF_3 in **2** agrees well with that trans to the fluoroalkyl group in *cis*-$PtF[CH(CF_3)_2](PPh_3)_2$ [2.310 (7) Å][30] and in *cis*-$Pt(CF_3)_2[PMe_2(C_6F_5)]_2$ [2.326 (1) Å].[3] Likewise, the Pt–P distance trans to CH_3 in **1** compares well with previously observed values, e.g., (±)-*cis*-$Pt[CH_2C_6H_4P$-*t*-$Bu(o\text{-}tol)_2]_2$ [2.295 (6) Å],[31] *cis*-$Pt(CH_2CH_2CH_2CH_2)(PPh_3)_2$ [2.279 (5), 2.285 (6) Å],[32] *cis*-$Pt[C({=}CH_2)(CMe_2)OCO](PPh_3)_2$ [2.341 (4), 2.334 (4) Å],[33] and $[Pt(CH_3)\{PMe_2(C_6F_5)\}_3]PF_6$ [2.327 (1) Å].[3]

The Pt–CF_3 distances in **2** [Pt–C(1) = 2.082 (5) Å, Pt–C(2) = 2.032 (5) Å] are shorter than the corresponding distances in **1** [Pt–C(1) = 2.166 (5) Å, Pt–C(2) = 2.052 (5) Å], the relative difference being greater for the bonds trans to phosphorus (0.084 Å) than for those trans to the vinyl group (0.030 Å). For comparison, the Pt–CF_3 bonds in *cis*-$Pt(CF_3)_2[PMe_2(C_6F_5)]_2$ are 0.040 Å shorter than the Pt–CH_3 bond in $[Pt(CH_3)\{PMe_2(C_6F_5)\}_3]PF_6$.[3] In both **1** and **2** the Pt–C bond trans to phosphorus is longer than that trans to vinyl [0.114 Å (**1**), 0.050 Å (**2**), which is consistent with the relative trans influences of these two ligands.[28] The Pt–CH_3 bond lengths in **1** correlate inversely with the magnitudes of $^2J_{Pt-CH_3}$, viz., 67 Hz (trans to P) and 86.5 Hz (trans to vinyl),[4] and are in the range 2.08–2.12 Å generally found for neutral platinum(II) complexes.[1] The Pt–CF_3 distances in **2** can be compared with the few reported platinum(II)–fluoroalkyl bond lengths, i.e., *trans*-$PtCl(C_2F_5)(PMePh_2)_2$ [2.002 (17) Å],[1] *cis*-$PtF[CH(CF_3)_2](PPh_3)_2$ [2.07 (2) Å],[30] $[Pt(CF_3)(\eta^4\text{-}C_4Me_4)(PMe_2Ph)_2]SbF_6$ [2.103 (16) Å],[34] and $[Pt(CF_3)\{PMe_2(C_6F_5)\}_3]PF_6$ [2.058 (4) Å].[3]

Bond distances and angles at phosphorus and within the phenyl rings are normal. The angles at P, C(21), and C(36) in the chelate rings of **1** and **2** show some deviations from the expected values of 115, 120, and 120° which reflect some ring strain. Larger, although qualitatively similar distortions have previously been noted for the bidentate SP ligand in the complex $Fe(CO)_2(SP)_2$.[16] Structural parameters for the CF_3 groups in **1** are comparable with those reported[34] for the complex $[Pt(CF_3)(\eta^4\text{-}C_4Me_4)(PMe_2Ph)_2]SbF_6$.

Discussion

The structural comparison of **1** and **2** confirms that transition-metal–fluoroalkyl bonds are shorter than transition-metal–alkyl bonds, in agreement with other work on platinum(II) complexes[1,3] and π-$C_5H_5Mo(CO)_3R$ (R = C_2H_5, *n*-C_3F_7).[35] As noted above, the Pt–P and Pt–vinyl bonds trans to the Pt–C σ bonds are significantly longer in the fluoroalkyl **2** than in the alkyl **1**. In contrast, the Pt–Cl bond trans to the Pt–C σ bond is shorter in the fluoroalkyl **4** than in the alkyl **3**, and the Pt–P bond trans to Pt–C in *cis*-$Pt(CF_3)_2[PMe_2(C_6F_5)]_2$ and $[Pt(CH_3)\{PMe_2(C_6F_5)\}_3]PF_6$ are equal within experimental error.[3] The trend in our complexes obviously could be explained by assuming that the Pt–CF_3 bonds in **2** can compete with the Pt–P and Pt–vinyl bonds for metal π-electron density and that they do this more effectively than the Pt–CH_3 bonds in **1**. Since Cl^- is not considered to be a good π-acceptor ligand, we do not expect the Pt–Cl bond to be longer in **4** than in **3**, and the observed shortening in this case must arise from some other effect. However, the notion of $M(d\pi)$–$CF_3(\sigma^*)$ back-bonding finds no support in the MO calculations of Hall and Fenske[36] on $Mn(CO)_5R$ (R = CH_3, CF_3). These authors suggest that the σ-bonding orbital used by carbon for bonding to the metal in fluoroalkyls probably has more s character than the corresponding orbital in the alkyls and also that the electronegative fluorine atoms induce a positive charge on the carbon atom which lowers the energies of the metal orbitals used for bonding to that carbon atom and to the other ligands. For reasons discussed previously,[1] we believe the second of these effects to be the most important, particularly as NMR data suggest that the trans influences, and hence the σ-donor abilities, of CH_3^- and CF_3^- do not greatly differ. We can reasonably expect that the more ionic Pt–Cl bond trans to Pt–C_2F_5 in **4** will be contracted by the positive charge on carbon, whereas the more covalent Pt–P and Pt–vinyl bonds trans to Pt–CF_3 in **2** will be more responsive to σ-donor ability of the trans-carbon atoms. On this basis, we would expect the Pt–P and Pt–vinyl bond lengths in **1** and **2** to be approximately equal. The observed lengthening of these bonds in **2** relative to **1** may be a manifestation of the cis-bond-weakening effect of σ-fluoroalkyl ligands which was evident from comparison of the structures of **3** and **4**,[1] but it is not clear why the effect is not observed in the structural comparison of *cis*-$Pt(CF_3)_2[PMe_2(C_6F_5)]_2$ and $[Pt(CH_3)\{PMe_2(C_6F_5)\}_3]PF_6$.[3]

As noted above, the bend-back angles α and β of the substituents on the coordinated vinyl group in **2** are within experimental error of those found for the ethylenic hydrogen atoms in the more accurate neutron diffraction study of $K[PtCl_3(C_2H_4)]H_2O$.[23] Further, the C=C bond lengths of the coordinated double bonds of **1** and **2** are close to that found in Zeise's salt[23] and are significantly shorter than those observed for low-valent metal complexes containing electron-withdrawing olefins such as $C_2(CN)_4$ or C_2F_4.[15] Since the bend-back angles and the length of the coordinated double bond have been correlated with π back-bonding[15] and since the most recent calculations[37] indicate π back-bonding in Zeise's salt to be far less significant than σ bonding, we suggest that π back-bonding to the vinyl group in **2** is relatively weak. The just significantly ($\sim 2.4\sigma$) longer vinyl C=C bond length in **1** would be consistent with slightly stronger π back-bonding to the olefin in this case. Nevertheless, the structural parameters for the vinyl groups in **1** and **2** support the contention that the differences in metal–ligand bond lengths in **1** and **2** result from changes in the σ-bonding framework and are not primarily due to π bonding.

Registry No. **1**, 39530-95-5; **2**, 68900-24-3; $Pt(CF_3)_2(COD)$, 37035-32-8.

Supplementary Material Available: Table VI, listing anisotropic thermal parameters for **1** and **2**, and Table VII, listing observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. A. Bennett, H.-K. Chee, and G. B. Robertson, *Inorg. Chem.*, preceding paper in this issue, and references cited therein.
(2) Abbreviations: SP = (2-vinylphenyl)diphenylphosphine [*o*-styryldiphenylphosphine], $o\text{-}CH_2{=}CHC_6H_4PPh_2$; COD = 1,5-cyclooctadiene; Me = methyl; *t*-Bu = *tert*-butyl; Ph = phenyl; *o*-tol = *o*-tolyl.
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(6) The programs contained in the Picker Corp. FACS-1 disk operating system (1972) were used for all phases of diffractometer control and data collection.
(7) The formulas used for data reduction are as follows: Lp (Lorentz–polarization factor) = $(\cos^2 2\theta + \cos^2 2\theta_m)/2 \sin 2\theta$, where θ and θ_m are the reflection and monochromator Bragg angles, respectively; I (net peak intensity) = $[CT - (t_p/t_b)(B_1 + B_2)]$, where CT is the total peak count in t_p s and where B_1 and B_2 are the individual background counts in $t_b/2$ s; $\sigma(I)$ (reflection significance) = $[CT + (t_p/t_b)^2 (B_1 + B_2)]^{1/2}$; $\sigma(F_o)$ (the reflection esd) = $\{[\sigma(I)/Lp]^2 + (\rho|F_o|^2)^2\}^{1/2}/2|F_o|$; $\sigma_s(F_o)$ (the reflection esd from counting statistics alone) = $\sigma(I)/2Lp|F_o|$; R_s (the statistical R factor) = $\sum\sigma_s(F_o)/\sum|F_o|$.
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