reveals all of the scalar P–P couplings (Figure 4). In the following discussion phosphorus nuclei are numbered according to Figure 1.

At ambient temperature the 121.5-MHz spectrum (Figure 2) shows a broad unresolved downfield resonance at 190.52 ppm, a pair of doublets at 158.13 and 156.70 ppm, a pair of doublets at 155.23 and 154.58 ppm, and a pair of broad doublets at 149.74 and 148.31 ppm. Although at first sight it might be assumed that the low-field signal arises from the μ-PPh$_2$ group, variable-temperature studies show that this resonance broadens and collapses faster than the high-field doublet of doublets as the temperature is raised. This line broadening can be attributed to the quadrupolar effects of the ^{59}Co ($I = {}^7/_2$) nucleus. Moreover at low temperatures (Figure 3) additional fine structure is resolved in the high-field doublets, whereas the low-field signal remains as a doublet of doublets. We assign the low-field resonance to the phosphite bound to cobalt (P4) and the high-field resonances to P(1) of the phosphido group. Although the high-field resonance signal appears as a doublet of doublets (Figure 3), the COSY spectrum (Figure 4) indicates that the corresponding ^{31}P nucleus P(1) is coupled to three other phosphorus nuclei, P(2), P(3), and P(4). The COSY spectrum also shows that P(2) is coupled to three other phosphorus nuclei, P(2), P(3), and P(4), P(2) is coupled with P(1), P(3), and P(4), P(3) is coupled only to P(1) and P(2), and P(4) is coupled to P(1) and P(2). A complete analysis of shifts and coupling constants is given in Table IV.

There are several notable features of this assignment: (i) $^2J_{P(1)-P(3)}$ is large (177.4 Hz) as expected for two trans related ligands. Trans $^2J_{P-P(\mu\text{-}PPh_2)}$ values in **3** (L = PPh_3H)[13] and (L)$(CO)_2Ru(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}C\text{-}i\text{-}Pr)Ru(CO)_3$ (L = $Ph_2PC{\equiv}C\text{-}i\text{-}Pr$)[19] are 183 and 215 Hz, respectively; (ii) $^3J_{P(2)-P(4)}$ (80.6 Hz) is significantly larger than any of the cis couplings in this molecule, consistent with a significant interaction between P(2) and P(4) through the Ru–Co bond *trans* to both ligands; (iii) of the remaining $^2J_{P-P}$ values all of which are cis couplings, the largest is $^2J_{P(1)-P(4)}$ (39.7 Hz) between the cobalt coordinated phosphite and the bridging phosphorus nucleus and the smallest $^2J_{P(1)-P(2)}$ of 11.5 Hz. For the compounds of type **3** (L = phosphine) no cis coupling between the μ-PPh$_2$ group and equatorial phosphines was observable. These results are in agreement with the fact that P–P couplings to phosphite ligands are invariably larger than those to phosphines probably as a result of increased "s" character in the M–P (phosphite) bonds.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for operating grants (to A.J.C.) and for funds to support a 3-month visit of S.G. to Waterloo and the University of Rennes for a "Professeur Invitē" position (1 month) to A.J.C. Thanks are also due to C. Roger (Bruker Spectrospin Canada) for recording the ^{31}P spectrum of 4 at 121.5 MHz.

Registry No. 1, 82544-75-0; **2a**, 103533-71-7; **2b**, 103617-40-9; **3a**, 103533-72-8; 4, 103533-73-9; Co, 7440-48-4; Ru, 7440-18-8.

Supplementary Material Available: A table of thermal parameters (1 page); a listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Oxidative-Addition and Proton-Transfer Reactions of Fluorocarbon Acids. Structures of *trans*-$(Ph_3P)_2Pt(H_2O)(PhC{=}CHPh)^+HC(SO_2CF_3)_2^-$ and *trans*-$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$†

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Received February 6, 1986

Oxidative addition of $H_2C(SO_2CF_3)_2$ to $(Ph_3P)_2Pt(PhC{\equiv}CPh)$ yields the *trans*-diphenylvinyl compound *trans*-$(Ph_3P)_2Pt$(*trans*-$PhC{=}CHPh)[C\text{-}HC(SO_2CF_3)_2]$ in which restricted rotation about the $Pt\text{-}HC(SO_2CF_3)_2$ bond has been characterized by ^{31}P DNMR spectroscopy. Recrystallization in air from isopropyl alcohol affords *trans*-$(Ph_3P)_2Pt$(*trans*-$PhC{=}CHPh)(H_2O)^+HC(SO_2CF_3)_2^-$: $P2_1/n$, monoclinic, $a = 12.478$ (5) Å, $b = 18.935$ (5) Å, $c = 21.891$ (4) Å, $\beta = 100.43$ (2)°, $R = 0.053$. Oxidative addition of $H_2C(SO_2CF_3)_2$ to $(Ph_3P)_2Pt(C_2H_4)$ forms $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$: $P2_1/c$, monoclinic, $a = 17.555$ (2) Å, $b = 13.650$ (1) Å, $c = 17.880$ (3) Å, $\beta = 112.70$ (1)°, $R = 0.038$. Analysis of the structural data reveals $H_2C(SO_2CF_3)_2$ to be a large, highly hindered carbon acid, and it is probable that steric effects contribute to the tendency of $HC(SO_2CF_3)_2^-$ to exist as an anion rather than coordinate to electron-deficient metal centers following proton transfer.

Introduction

We have previously outlined the organometallic chemistry of fluorocarbon acids of the type $RHC(SO_2CF_3)_2$ (R = H, Ph).[1] These acids possess an unusual collection of properties in that they are strong, nonhygroscopic, nonoxidizing protic acids whose conjugate bases have been shown[2] to coordinate to transition metals, via the central,

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† The $C\text{-}HC(SO_2CF_3)_2$ formulation indicates that the $CH(SO_2CF_3)_2$ group is bonded to Pt via the methine carbon atom.

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0276-7333/86/2305-1969$01.50/0 © 1986 American Chemical Society

methine carbon atom, in only two cases. They are, in addition, soluble in nondonor solvents such as toluene and dichloromethane, which makes possible study of their chemistry with minimal interference from coordinating solvents.[3-5] As part of an effort to study protonation by $RHC(SO_2CF_3)_2$ of small molecules coordinated to platinum and other group VIII metals, we have examined the reactions of $H_2C(SO_2CF_3)_2$ with the $(Ph_3P)_2Pt$ complexes of CO_3^{2-}, ethylene, and diphenylacetylene, the topics of this paper. Also described is the structure of *trans*-$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ which leads to greatly increased understanding of the tendency of fluorocarbon acids to react by simple proton transfer rather than oxidative addition.

Results

Protonation of $(Ph_3P)_2PtCO_3$. This carbonate complex reacts with 1 equiv of $H_2C(SO_2CF_3)_2$ to form *cis*-$(Ph_3P)_2Pt(CO_3H)^+HC(SO_2CF_3)_2^-$ (1). It exhibits a sharp OH stretching band at 3556 cm^{-1} which shifts to 2634 cm^{-1} in the OD analogue. The ^{31}P NMR spectrum comprises a 7.7 ppm singlet at ≥−80 °C with $J_{PtP} = 3750$ Hz. This indicates that 1 contains a bidentate bicarbonate ligand coordinated to Pt(II) and that the OH group in it is not significantly hydrogen-bonded.[6]

Oxidative Addition to $(Ph_3P)_2Pt(Ph_2C_2)$. Reaction of this diphenylacetylene complex with $H_2C(SO_2CF_3)_2$ in toluene provides *trans*-$(Ph_3P)_2Pt$(*trans*-PhC=CHPh)$[C\text{-}HC(SO_2CF_3)_2]$ (2) in 71% yield. The compound contains a $HC(SO_2CF_3)_2$ group, bonded to platinum through the methine carbon atom, and a *trans*-1,2-diphenylvinyl moiety which is also attached to Pt. Its spectroscopic properties are similar to those of $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ (3), obtained[2] by addition of $H_2C(SO_2CF_3)_2$ to $(Ph_3P)_2Pt(C_2H_4)$. In this case, however, the acetyleneic ligand is retained and the product arises by 1,3-addition of $H_2C(SO_2CF_3)_2$ to the Pt—C≡C unit. The vinyl C=C stretching band occurs at 1635 cm^{-1}. The ^1H NMR spectrum of 2 in CD_2Cl_2 shows a singlet at 4.16 ppm due to the Pt-C*H*$(SO_2CF_3)_2$ proton and a singlet at 6.29 ppm due to the vinylic proton. In ionic compounds containing $HC(SO_2CF_3)_2^-$, the methine proton has a chemical shift of 3.7–3.9 ppm[3] and so coordination to platinum again leads to a downfield shift relative to the free ion. The ^{19}F NMR spectrum at ≤−60 °C comprises a singlet at δ −75.7, again demonstrating that fluorine in the $C\text{-}HC(SO_2CF_3)_2$ ligand is more shielded than in ionic $HC(SO_2CF_3)_2^-$ which has $\delta(^{19}F)$ −81. Importantly, the four-bond Pt-F coupling is 17 Hz, thus establishing that the $HC(SO_2CF_3)_2$ group is in fact covalently bonded to platinum and is not present as an anion. The ^{31}P NMR spectrum at −60 °C is an AB quartet with δ_A 23.9, δ_B 26.8, $J_{AB} = 382$ Hz, $J_{P_APt} = 3160$ Hz, and $J_{P_BPt} = 3122$ Hz. These resonances broaden on warming and coalesce at 2 °C in a manner typical of dynamic equilibria averaging two coupled, nonequivalent phosphorus nuclei, which is attributed here to restricted rotation about the Pt–C bond in the $Pt\text{-}HC(SO_2CF_3)_2$ moiety. Analysis of the ^{31}P DNMR spectra (cf. Experimental Section) reveals that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this process are 11.6 ± 0.7 kcal/mol and 1.5 ± 3 eu, respectively, in good agreement with the 14.6 kcal/mol $\Delta H_{act.}$ (at 22 °C) value obtained for the rotational barrier in 3. No reaction was observed between $H_2C(SO_2CF_3)_2$ and complexes of alkenes or alkynes bearing strongly electron-withdrawing substituents, e.g., $(Ph_3P)_2Pt(CF_3C{\equiv}CCF_3)$ and $(Et_3P)_2Pt[(CN)_2C{=}C(CN)_2]$.

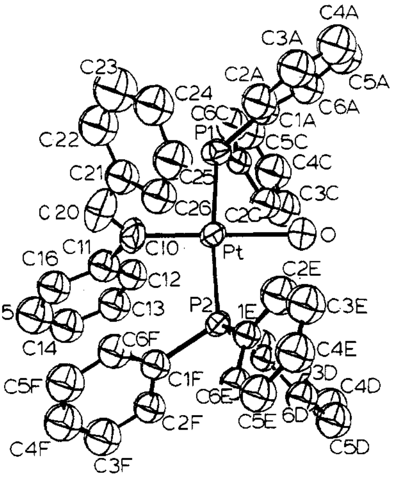

Figure 1. ORTEP drawing of the $(Ph_3P)_2Pt(H_2O)(Ph_2C_2H)^+$ cation in 4. Phenyl ring B has been omitted for clarity. Ellipsoids are drawn with 50% probability boundaries.

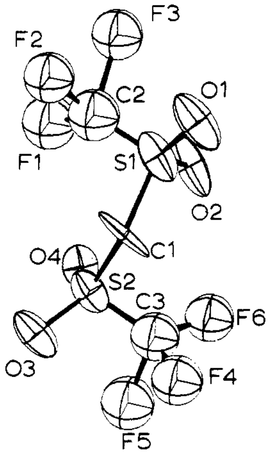

Figure 2. ORTEP drawing of the $HC(SO_2CF_3)_2^-$ anion in 4 with 50% probability boundaries.

It was earlier found that solvolysis of the Pt–C bond in $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ is facilitated by a kinetic trans effect of the hydride ligand. The diphenylvinyl ligand in 2 also has a high trans influence, and this compound also readily reacts with nucleophiles. On recrystallization in air from isopropyl alcohol, *trans*-$(Ph_3P)_2Pt(H_2O)(PhC{=}CHPh)^+HC(SO_2CF_3)_2^-$ (4) is obtained. The coordinated water presumably arises from adventitious moisture in the solvent or from the atmosphere. Its infrared spectrum demonstrates an OH stretching band at 3355 cm^{-1}; the vinyl C=C stretch occurs at 1625 and at 1605 cm^{-1} in the Raman spectrum. Retention of the trans stereochemistry is indicated by a singlet ^{31}P resonance at 23.5 ppm with $J_{P\text{-}Pt} = 3160$ Hz.

Structure of *trans*-$(Ph_3P)_2Pt(H_2O)(PhC{=}CHPh)^+HC(SO_2CF_3)_2^-$ (4). Figure 1 shows an ORTEP drawing of the $(Ph_3P)_2Pt(H_2O)(Ph_2C_2H)^+$ cation and the cation labeling scheme; phenyl ring B has been deleted for clarity. Figure 2 depicts the $HC(SO_2CF_3)_2^-$ counterion. Important bond distances and angles are given in Table IV. The coordination about platinum is close to square

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Table I. Summary of Crystal Data and Intensity Collection for $[(Ph_3P)_2Pt(H_2O)(Ph_2C_2H)]HC(SO_2CF_3)_2$ (4) and $(Ph_3P)_2PtH[CHC(SO_2CF_3)_2]$ (3)

	4	3
	Crystal Parameters	
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
cryst dimens, mm^3	0.25 × 0.18 × 0.10	0.36 × 0.12 × 0.08
cell parameters (23 °C)		
a, Å	12.478 (5)	17.555 (2)
b, Å	18.935 (5)	13.650 (1)
c, Å	21.891 (4)	17.880 (3)
α, idealized, actual, deg	90, 89.98 (2)	90, 90.02 (1)
β, deg	100.43 (2)	112.70 (1)
γ, idealized, actual, deg	90, 90.05 (3)	90, 89.99 (1)
V, Å^3	5087 (5)	3952 (3)
Z	4	4
d(calcd), g cm^{-3}	1.56	1.68
abs coeff, cm^{-1}	29.9	38.3
max, min, av transmissn factors	1.00, 0.65, 0.91	1.00, 0.95, 0.98
formula	$C_{53}H_{44}PtF_6O_5P_2S_2$	$C_{39}H_{32}PtF_6O_4P_2S_2$
fw	1196.10	999.84
	Measurement of Intensity Data (23 °C)	
diffractometer	CAD 4	
radiatn	Mo K$\bar{\alpha}$ (λ = 0.71069 Å) graphite monochromatized	
scan type and range, 2θ, deg	ω–2θ, 0–44	ω–2θ, 0–50
ω scan width = $A + B \tan\theta$	A = 0.80, B = 0.35	A = 0.70, B = 0.35
unique reflctns measd (region)	6546 ($h,k,\pm l$)	6951 ($h,k,\pm l$)
obsd reflctns^a	3241 [$F_o^2 > 2.0\sigma(F_o^2)$]	4313 [$F_o^2 > 2.0\sigma(F_o^2)$]
refinement by full-matrix least squares		
no. of parameters	342	487
R^b	0.053	0.038
$R_w{}^b$	0.061	0.039
GOF^b	1.74	1.10
p^a	0.04	0.04

[a] The intensity data were processed as described in: *CAD4 and SDP-PLUS User's Manual*; B. A. Frenz & Assoc.: College Station, TX, 1982. The net intensity $I = [K/\mathrm{NPI})](C - 2B)$, where K = 20.1166 × attenuator factor, NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/\mathrm{NPI}))^2[C + 4B + (pI)^2]$ where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = 1/2[\sigma(I)/I]F_o$. [b] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = (||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight (GOF) is $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

planar. Displacement from the least-squares plane containing Pt, P1, P2, O, and C10 are 0.006 (1), −0.148 (5), −0.126 (4), 0.075 (12), and −0.016 (20) Å, respectively (cf. supplementary material). The cis bond angles around the platinum atom differ significantly from 90° reflecting displacement of the bulky triphenylphosphine ligands away from the large diphenylvinyl ligand toward the coordinated water molecule.

The Pt–C bond length, 1.99 (2) Å, is similar to the 2.02 (2) and 2.022 (8) Å distances found for the platinum–carbon single bonds in *trans*-$(PhPEt_2)_2PtCl(CH{=}CH_2)$[7] and *trans*-$(Ph_3P)_2PtBr(CH{=}CHPh)$,[8] respectively. Likewise unremarkable is the Pt–C10–C20 angle, 128 (2)°, but the C10–C20 distance, 1.24 (2) Å, is considerably shorter than the 1.347 (11) Å C=C bond length in the above styrylplatinum complex and the 1.31–1.35 Å range found[7] in metal σ-vinyl compounds. The least-squares plane containing C11, C10, C20, C21, and Pt is twisted 78° out of the P1, P2, O, C10, Pt platinum coordination plane, probably because of steric effects. The Pt–P1 and Pt–P2 separations, 2.322 (4) and 2.311 (4) Å, respectively, differ significantly but are comparable to the 2.310 (2) and 2.304 (2) Å bond lengths in $(Ph_3P)_2PtBr(CH{=}CHPh)$.[8] The Pt–O distance involving the coordinated water molecule, 2.21 (1) Å, is longer than that in the $[Pt_2(HPO_4)_4(H_2O)_2]^{2-}$ ion, 2.15 (1) Å,[9] presumably reflecting, in part, a structural trans effect of the *C*-diphenylvinyl ligand.

The phenyl rings attached to the vinylic carbon atoms C10 and C20 are seen to be trans to one another, and the dihedral angle between their respective least-squares planes is 103°.

The structure of the $HC(SO_2CF_3)_2^-$ anion in 4, shown in Figure 4, is similar to that found in the Rb^+ salt.[10] The S1–C1–S2 angle is 128 (1)°, reflecting sp^2 hybridization at the methine carbon atom C1. The S–O bond lengths range from 1.43 (1) to 1.48 (1) Å with $d(\text{S–O})_{av}$ = 1.45 (1) Å.

Structure of *trans*-$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ (3). The Pt–C bond in this compound is quite sensitive to nucleophilic attack by even such weak bases as alcohols. This leads to rearrangement to $(Ph_3P)_4Pt_2(\mu\text{-}PPh_2)(\mu\text{-}H)Ph^+HC(SO_2CF_3)_2^-$. Consequently, crystal growth experiments must employ nondonor solvents under anhydrous conditions. Crystals of 3 suitable for crystallographic work were, after some difficulty, obtained from methylene chloride–pentane. Figure 3 provides an ORTEP view of the structure and shows the labeling scheme employed. Selected bond distances and angles for the discreetly packed molecules are given in Table V. The coordination geometry about platinum closely approximates square planar with the metal atom being displaced only 0.04 Å from the

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Table III. Positional Parameters and Their Estimated Standard Deviations for $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Pt	0.24590 (2)	0.41952 (2)	0.16578 (2)	2.918 (5)	C13	0.0957 (6)	0.5412 (7)	–0.1753 (5)	5.5 (3)
S1	0.3640 (1)	0.5322 (2)	0.3247 (1)	4.82 (6)	C14	0.0847 (6)	0.4752 (7)	–0.1228 (6)	5.9 (3)
S2	0.1910 (1)	0.6113 (2)	0.2414 (1)	4.92 (6)	C15	0.1427 (5)	0.4674 (7)	–0.0445 (5)	4.7 (2)
P1	0.2919 (1)	0.5112 (2)	0.0835 (1)	3.13 (5)	C16	0.3362 (4)	0.6337 (6)	0.1054 (4)	3.3 (2)
P2	0.1992 (1)	0.2833 (2)	0.2095 (1)	3.25 (5)	C17	0.2854 (5)	0.7139 (6)	0.0983 (5)	4.6 (2)
F1	0.3453 (4)	0.6642 (4)	0.4233 (3)	7.4 (2)	C18	0.3167 (6)	0.8074 (6)	0.1106 (5)	5.3 (3)
F2	0.3486 (4)	0.5176 (5)	0.4638 (3)	10.2 (2)	C19	0.3999 (6)	0.8212 (7)	0.1290 (5)	5.5 (2)
F3	0.4593 (4)	0.5866 (5)	0.4683 (4)	8.3 (2)	C20	0.4498 (5)	0.7430 (7)	0.1379 (5)	5.0 (2)
F4	0.1015 (4)	0.5277 (5)	0.3094 (4)	10.1 (2)	C21	0.4194 (5)	0.6484 (6)	0.1257 (5)	4.3 (2)
F5	0.0768 (3)	0.6778 (5)	0.2858 (4)	8.6 (2)	C22	0.1008 (4)	0.2448 (6)	0.1344 (4)	3.5 (2)
F6	0.1832 (3)	0.6332 (6)	0.3834 (3)	10.3 (2)	C23	0.0479 (5)	0.3154 (7)	0.0864 (5)	5.1 (2)
O1	0.3955 (4)	0.6056 (6)	0.2900 (4)	7.1 (2)	C24	–0.0257 (5)	0.2889 (9)	0.0283 (6)	6.9 (3)
O2	0.4020 (4)	0.4363 (5)	0.3423 (4)	7.6 (2)	C25	–0.0498 (5)	0.1936 (8)	0.0151 (6)	7.3 (3)
O3	0.1276 (4)	0.5924 (6)	0.1662 (4)	8.0 (2)	C26	0.0014 (6)	0.1238 (8)	0.0624 (6)	7.0 (3)
O4	0.2327 (4)	0.7051 (4)	0.2524 (4)	7.3 (2)	C27	0.0752 (5)	0.1481 (7)	0.1206 (5)	5.3 (2)
C1	0.2576 (4)	0.5095 (6)	0.2726 (4)	3.4 (2)	C28	0.2682 (4)	0.1801 (6)	0.2235 (4)	3.6 (2)
C2	0.3791 (6)	0.5779 (8)	0.4277 (6)	6.3 (3)	C29	0.3264 (5)	0.1805 (6)	0.1902 (5)	4.3 (2)
C3	0.1363 (6)	0.6140 (7)	0.3113 (6)	5.8 (3)	C30	0.3802 (6)	0.1024 (7)	0.2011 (6)	6.1 (3)
C4	0.3723 (5)	0.4384 (6)	0.0694 (4)	3.7 (2)	C31	0.3738 (6)	0.0227 (7)	0.2447 (5)	6.0 (3)
C5	0.3799 (5)	0.4329 (7)	–0.0041 (5)	5.6 (2)	C32	0.3166 (6)	0.0201 (7)	0.2780 (5)	6.3 (3)
C6	0.4420 (6)	0.3777 (8)	–0.0121 (6)	7.5 (3)	C33	0.2641 (5)	0.0990 (6)	0.2680 (5)	5.2 (2)
C7	0.4965 (6)	0.3277 (8)	0.0510 (6)	7.1 (3)	C34	0.1820 (5)	0.2887 (6)	0.3035 (4)	3.9 (2)
C8	0.4897 (5)	0.3309 (7)	0.1263 (6)	5.8 (3)	C35	0.1049 (5)	0.2919 (6)	0.3061 (5)	5.2 (2)
C9	0.4279 (5)	0.3877 (6)	0.1356 (5)	4.5 (2)	C36	0.0964 (7)	0.3011 (8)	0.3793 (6)	8.4 (3)
C10	0.2128 (4)	0.5260 (6)	–0.0196 (4)	3.4 (2)	C37	0.1614 (7)	0.3077 (8)	0.4502 (6)	9.2 (3)
C11	0.2213 (5)	0.5928 (6)	–0.0739 (4)	4.4 (2)	C38	0.2385 (7)	0.3030 (8)	0.4492 (5)	7.6 (3)
C12	0.1639 (6)	0.5994 (7)	–0.1523 (5)	5.5 (3)	C39	0.2500 (6)	0.2945 (7)	0.3771 (5)	5.5 (3)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H1	0.342	0.467	–0.049	H16	0.064	0.382	0.094
H2	0.0448	0.375	–0.063	H17	–0.062	0.338	–0.004
H3	0.539	0.289	0.045	H18	–0.101	0.176	–0.027
H4	0.527	0.295	0.171	H19	–0.017	0.058	0.054
H5	0.423	0.391	0.186	H20	0.111	0.098	0.152
H6	0.267	0.636	–0.056	H21	0.329	0.235	0.158
H7	0.171	0.644	–0.190	H22	0.0422	0.104	0.180
H8	0.056	0.546	–0.229	H23	0.410	–0.032	0.252
H9	0.036	0.436	–0.141	H24	0.313	–0.036	0.308
H10	0.135	0.423	–0.007	H25	0.224	0.097	0.292
H11	0.228	0.703	0.085	H26	0.058	0.288	0.257
H12	0.282	0.862	0.107	H27	0.043	0.303	0.382
H13	0.422	0.886	0.135	H28	0.155	0.317	0.500
H14	0.507	0.754	0.154	H29	0.285	0.305	0.499
H15	0.455	0.594	0.131	H30	0.304	0.292	0.376

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal paramter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

C1,P1,P2 plane. Closure of the P1–Pt–P2 angle, 156.98 (7)°, from the idealized 180° value is associated with the small bulk of the hydride ligand. Likewise, small distortions are seen in the P1–Pt–C1 and P2–Pt–C1 angles, 108.2 (2)° and 94.7 (2)°, respectively. The Pt–P1 and Pt–P2 distances, 2.302 (2) and 2.288 (2) Å, respectively, appear unremarkable.

The $HC(SO_2CF_3)_2$ ligand is rotated with respect to the metal coordination plane, and the dihedral angle between the S1–C1–S2 and P1–Pt–P2 planes is 84.8°. Importantly, the bond between platinum and C1, the methine carbon atom in the strongly electronegative $C\text{-}HC(SO_2CF_3)_2$ ligand, is 2.212 (8) Å and is longer than expected. For perfluoroalkyl groups, Pt–C(sp^3) bonds are usually less than 2.08 Å, a generalization that has been explained in terms of bond ionicity.[11] In this case, however, the bis[(trifluoromethyl)sulfonyl]methyl group is trans to hydride, and elongation of the Pt–C bond may represent in part a structural trans effect. Indeed, a parallel kinetic effect is operative as well since solvolysis of 2 by tetrahydrofuran is considerably faster than for the cis isomer.[2]

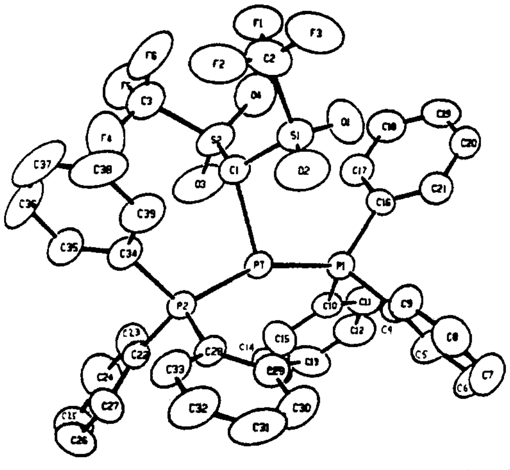

Figure 3. ORTEP drawing of $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ showing the labeling scheme. Ellipsoids are drawn with 33% probability boundaries.

Dimensions of the $C\text{-}HC(SO_2CF_3)_2$ ligand differ significantly from those in ionic $HC(SO_2CF_3)_2^-$ (vide supra), but both have a cis configuration. The S1–C1–S2 angle, 117.8 (4)°, is considerably reduced with respect to the 126 (1)° value in the ion, indicating a change in hybridization at

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[11] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon: New York, 1982; Vol. 6, p 532.

Table IV. Selected Bond Distances (Å) and Angles (deg) in [*trans*-$(Ph_3P)_2Pt(H_2O)$(*trans*-PhCHCPh)]$HC(SO_2CF_3)_2$ (4)

	Bond Distances		
Pt–P1	2.322 (4)	C10–C20	1.24 (2)
Pt–P2	2.311 (4)	C10–C11	1.59 (2)
Pt–C1	1.99 (2)	C20–C21	1.53 (3)
Pt–O	2.21 (1)	C11–C12	1.39 (2)
P1–C1A	1.79 (1)	C12–C13	1.39 (2)
P1–C1B	1.83 (1)	C13–C14	1.38 (2)
P1–C1C	1.81 (1)	C14–C15	1.36 (2)
P2–C1D	1.80 (1)	C15–C16	1.39 (2)
P2–C1E	1.83 (1)	C11–C16	1.37 (2)
P2–C1F	1.84 (1)	C21–C22	1.36 (2)
C1–S1	1.68 (2)	C22–C23	1.38 (2)
C1–S2	1.65 (2)	C23–C24	1.40 (2)
S1–O1	1.46 (1)	C24–C25	1.34 (2)
S1–O2	1.48 (1)	C25–C26	1.41 (2)
S2–O3	1.43 (1)	C26–C21	1.41 (2)
S2–O4	1.43 (1)	C2–F3	1.72 (4)
S1–C2	1.44 (4)	C3–F4	1.26 (4)
S2–C3	1.51 (4)	C3–F5	1.64 (4)
C2–F1	1.36 (4)	C3–F6	1.26 (4)
C2–F2	1.38 (4)		
	Bond Angles, deg		
P1–Pt–P2	171.2 (1)	Pt–C10–C2	128 (2)
P1–Pt–C10	93.0 (5)	Pt–C10–C11	120 (1)
P1–Pt–O	87.4 (3)	C1–C20–C21	119 (2)
P2–Pt–C10	92.1 (5)	C20–C10–C11	112 (2)
P2–Pt–O	87.6 (3)	Pt–P1–C1A	108.3 (5)

Table V. Selected Bond Distances (a) and Angles (deg) in *trans*-$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ (3)

	Bond Distances		
Pt–P1	2.302 (2)	S2–O4	1.451 (7)
Pt–P2	2.288 (2)	S2–C3	1.85 (1)
Pt–C1	2.212 (8)	C2–F1	1.31 (1)
C1–S1	1.763 (8)	C2–F2	1.28 (1)
C1–S2	1.763 (8)	C2–F3	1.32 (1)
S1–O1	1.399 (7)	C3–F4	1.32 (1)
S1–O2	1.446 (7)	C3–F5	1.30 (1)
S1–C2	1.86 (1)	C3–F6	1.26 (1)
S2–O3	1.400 (7)		
	Bond Angles		
P1–Pt–C1	108.2 (2)	S1–C1–S2	117.8 (4)
P2–Pt–C1	94.7 (2)	O1–S1–O2	121.2 (5)
Pt–C1–S1	106.3 (4)	O3–S2–O4	117.7 (5)
Pt–C1–S2	109.6 (4)		
C10–Pt–O	178.8 (7)	Pt–P1–C1B	120.2 (5)
S1–C1–S2	123 (1)	Pt–P1–C1C	110.7 (5)
O1–S1–O2	121 (1)	Pt–P2–C1D	106.5 (5)
C1–S1–C2	101 (2)	Pt–P2–C1E	115.8 (5)
C1–S2–C3	93 (2)	Pt–P2–C1F	118.5 (5)
O3–S2–O4	118 (1)		

Table VI. Calculated Nonbonded Distances Involving the Methine Hydrogen Atom in *trans*-$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$

atom	H atom dist, Å	atom	H atom dist, Å
F1	3.33	O3	3.01
F2	2.72	O4	3.25
F3	4.08	C34	2.76
F4	2.51	C35	3.45
F5	3.85	C36	4.01
F6	2.86	C37	3.45
O1	3.38	C38	3.45
O2	2.74	C39	2.75

C1 such that this carbon atom becomes more nearly tetrahedral. Also consistent with a tetrahedral C1 geometry are the Pt–C1–S1 and Pt–Cl–S2 angles of 106.3 (4) and 109.6 (4)°, respectively. The C1–S1 and C1–S2 bond lengths in the covalent compound are 1.76 (1) Å much larger than the 1.65 (2) Å $d(C–S)_{av}$ in the ion, indicating reduction in C–S multiple-bond character. In 3, there are two distinct sets of sulfur-oxygen contacts: S1–O1 and S2–O3 are 1.399 (7) and 1.400 (7) Å, respectively, while the S1–O4 and S2–O4 bond lengths are 1.446 (7) and 1.451 (7) Å, respectively. These values are alternately shorter and longer than the 1.45 (1) Å $d(S–O)_{av}$ in the $HC(SO_2CF_3)_2^-$ ion in 4. While this alternation in S–O bond lengths is interesting, we are reluctant to stress its importance as it is found as well in $(Ph_3P)_2RuH(CO)(CH_3CN)_2{}^+HC(SO_2CF_3)_2{}^-$[3] but not in $(Ph_3P)_4OsH_3{}^+HC(SO_2CF_3)_2{}^-$.[4] Detailed commentary is better reserved until a high precision structure of $HC(SO_2CF_3)_2^-$, preferably in a salt not containing heavy metal atoms, is completed.

Discussion

Brønsted acids such as hydrogen chloride react with $(Ph_3P)_2Pt$(acetylene) complexes to give, ultimately, *cis*-$(Ph_3P)_2PtCl_2$ and the corresponding olefin in a reaction considered to proceed through a σ-vinyl–Pt(II) intermediate which reacts with additional acid with cleavage of the Pt–C σ-bond. Proton NMR studies of such σ-vinyl species indicate that the proton adds cis with respect to the platinum.[12] The opposite obtains in addition of $H_2C(SO_2CF_3)_2$ to $(Ph_3P)_2Pt(Ph_2C_2)$ as the phenyl rings in the diphenylvinyl moiety of 4 are trans, an arrangement which reduces nonbonded repulsions between them. It is not clear whether the stereochemistry of 4 represents that of the initial product or whether cis addition occurs, followed by isomerization as occurs in *trans*-$(Ph_2PCH_3)_2PtCl[CCl{=}C(H)Cl]$.[13]

As noted above, the hydrogen atom on the methine carbon C1 in $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ was not located in the electron density maps. We have, as a heuristic device, added this hydrogen atom in an idealized position with atomic coordinates 0.2397, 0.4783, and 0.3105, and with $d(C–H) = 0.95$ Å so that the hydrogen atom projects onto the center of the Pt,S1,S2 plane. A stereo drawing of the structure thus generated is shown in Figure 4. Reference to this figure explains some initially puzzling features of the oxidative addition chemistry of $H_2C(SO_2CF_3)_2$.

Reaction of $HRC(SO_2CF_3)_2$ (R = H) with $(Ph_3P)_2Pt(C_2H_4)$ in toluene yields, as noted above, *trans*-$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ (3). In tetrahydrofuran, this compound undergoes formal reductive elimination, via the stable intermediate *trans*-$(Ph_3P)_2PtH(THF)^+HC(SO_2CF_3)_2^-$ with which it is in equilibrium, to form $(Ph_3P)_2Pt(THF)_n$. This in turn reacts with additional tetrahydrofuranate (or 3) to form the phosphide-bridged dimer $(Ph_3P)_3Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)Ph^+HC(SO_2CF_3)_2^-$. The same chemistry occurs in other weak bases such as methanol, but a base is required to generate this dimer at room temperature. When the same reaction is carried out in toluene with instead $PhHC(SO_2CF_3)_2$ or $CH_3HC(SO_2CF_3)_2$, none of the expected oxidative-addition product $(Ph_3P)_2PtH[C\text{-}RC(SO_2CF_3)_2]$ (R = Ph, CH_3) is obtained, and, instead, $RC(SO_2CF_3)_2^-$ salts of $(Ph_3P)_3Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)Ph^+$ are formed in quantitative yield by ^{31}P NMR analysis.[2] This was interpreted as meaning that the reductive elimination process is quite sensitive to steric effects, and the origin of such sensitivity is revealed in Figure 4.

The methine hydrogen atom can be seen to lie in a cavity comprised of three fluorine and two oxygen atoms. Table III gives a listing of calculated nonbonding distances be-

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[12] Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. Dalton Trans.* 1971, 2667.

[13] Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* 1977, *16*, 698.

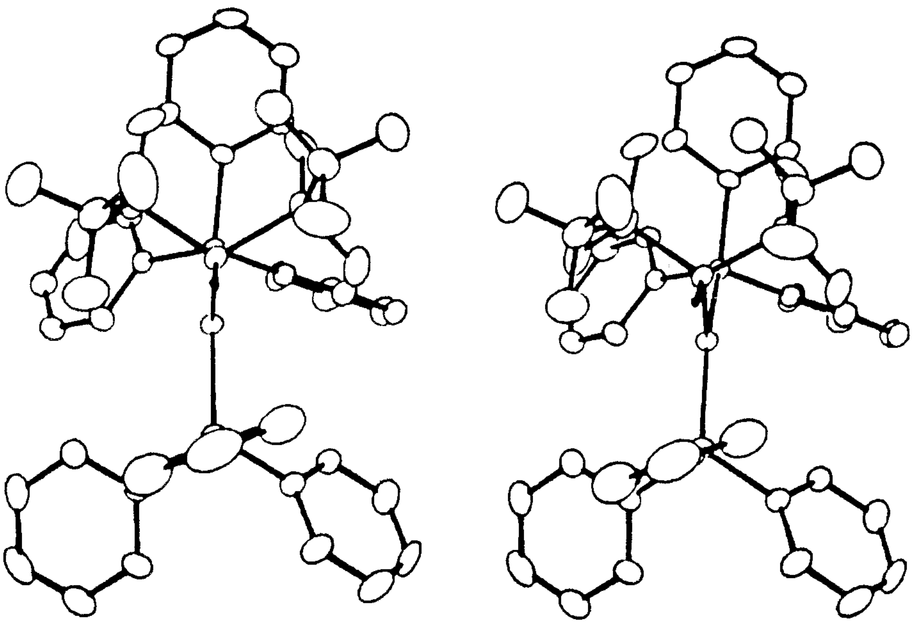

Figure 4. Stereoview of $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ with the methine hydrogen atom in an idealized position.

tween this hydrogen and surrounding atoms. Of the latter, F2, F4, F6, O2, and O3 are all ≤3.01 Å away. The phenyl ring comprised of C34–C39 forms a "lid" on the cavity, and the calculated distance between the ring centroid and methine hydrogen atom is 2.8 Å. A group larger than H, i.e., CH_3 or C_6H_5, will not fit into this cavity. Attempts to force a fit logically lead to severe nonbonded repulsive interactions, the result of which should be to lengthen the already long Pt–C bond and to make the ground state of *trans*-$(Ph_3P)_2PtH[C\text{-}RC(SO_2CF_3)_2]$ energetically closer to the transition state leading to Pt–C bond cleavage and subsequent reductive elimination.

The importance of steric effects in $H_2C(SO_2CF_3)_2$ chemistry can be further assessed in a *qualitative* way by calculation, based on unit cell dimensions of $Rb^+HC(SO_2CF_3)_2^-$ [8] and using a compression factor of 0.7 and a value of 1.56 Å for the ionic radius of Rb^+, of the atomic volume of $HC(SO_2CF_3)_2^-$. It is 175 Å^3 which may be compared with the volume of the di-*tert*-butylmethyl group, estimated by using the group volume increments of Kitaigorodskii,[14] of 155 Å^3. Although some errors may attend thsese volume estimates, it is nevertheless clear that $H_2C(SO_2CF_3)_2$ is a highly sterically hindered carbon acid and that steric effects account in part for the tendency for the $HC(SO_2CF_3)_2$ group to exist as an anion after proton transfer rather than to coordinate to metals, particularly to metals bearing other bulky groups such as triphenylphosphine. We surmise that, for this reason, as well as because charge in $HC(SO_2CF_3)_2^-$ is delocalized, $(Ph_3P)_3Rh^+HC(SO_2CF_3)_2^-$ adopts a saltlike composition rather than the covalent alternative $(Ph_3P)_3Rh[C\text{-}HC(SO_2CF_3)_2]$ even though in it, Rh(I) has a 14-electron configuration.[1]

Experimental Section

Reactions were carried out under a nitrogen atmosphere unless otherwise noted. Toluene was distilled from Na–K alloy and CD_2Cl_2 used as an NMR solvent was stored over CaH_2 on a vacuum line. NMR spectra were obtained on a Varian XL-200 instrument; positive chemical shifts are downfield of internal $(CH_3)_4Si$ or $CFCl_3$ or external 85% H_3PO_4. Raman spectra were obtained by using 5145-Å laser excitation; infrared spectra were recorded on Nujol mulls. The fluorocarbon acids were prepared by the method of Koshar and Mitsch[15] and were the generous gift of Robert Koshar, 3M Industrial and Consumer Sector Research Laboratory.

$(Ph_3P)_2Pt(CO_3H)^+HC(SO_2CF_3)_2^-$ (1). A solution of 0.07 g (0.25 mmol) of $H_2C(SO_2CF_3)_2$ in 3 mL of toluene was added with vigorous stirring to 0.21 g (0.25 mmol) of $(Ph_3P)_2PtCO_3{\cdot}C_6H_6$ in 5 mL of toluene. After 2 h, the white, microcrystalline product was collected on a filter, washed with fresh solvent, and vacuum dried. The yield was 0.30 g (94%). Anal. Calcd for $C_{40}H_{32}F_6O_7P_2PtS_2$: C, 45.3; H, 3.0; P, 5.9; Pt, 18.4; S, 6.0. Found: C, 44.9; H, 3.1; P, 6.0; Pt, 18.8; S, 5.9.

***trans*-$(Ph_3P)_2Pt(PhC{=}CHPh)[C\text{-}HC(SO_2CF_3)_2]$ (2).** Into a flame-dried flask were loaded under nitrogen 0.3 g (0.33 mmol) of $(Ph_3P)_2Pt(PhC{\equiv}CPh)$ and 0.093 g (0.33 mmol) of $H_2C(SO_2CF_3)_2$. The flask was attached to a high vacuum line, cooled (to prevent volatilization of the $H_2C(SO_2CF_3)_2$), and then evacuated. Toluene, 4 mL, was added by vacuum transfer. The reaction mixture was stirred at room temperature for 24 h and then heated at 60 °C for 5 min. Solvent was removed by distillation and the residue then recrystallized in drybox by rapid concentration using a rotary evaporator of a solution in CH_2Cl_2–hexane. The yield of yellow powder was 0.3 g (71%). Anal. Calcd for $C_{53}H_{41}F_6O_4P_2PtS_2$: C, 54.1; H, 3.5. Found: C, 53.9; H, 3.6. It is, with benefit of hindsight, very moisture-sensitive.

$(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ (3) was prepared as previously described.[2] Crystals used for X-ray diffraction work were obtained in a drybox by diffusion of pentane into a CH_2Cl_2 solution of the compound.

$(Ph_3P)_2Pt(PhC{=}CHPh)(H_2O)^+HC(SO_2CF_3)_2^-$ (4). In air, a 0.2-g quantity of **2** was dissolved in 3 mL of warm isopropyl alcohol. On slow cooling, there separated 0.2 g of yellow needles of **4**. Anal. Calcd for $C_{53}H_{43}F_6O_5P_2PtS_2$: C, 53.2; H, 3.7; P, 5.2; Pt, 16.3. Found: C, 53.0; H, 3.6; P, 5.2; Pt, 16.0. The crystals were used as obtained for X-ray diffraction work.

^{31}P DNMR spectra were obtained in solutions of **2** in CD_2Cl_2 which were prepared on a high vacuum line. The spectrometer probe thermistor was calibrated by using a neat methanol sample according to the method of van Geet.[16] The chemical shift difference between the two types of ^{31}P nuclei was obtained by linear extrapolation of the observed chemical shift difference in the low-temperature spectra. The correlation coefficient for the linear fit of the chemical shift with temperature from −80 to −14 °C was 0.984. Free energies of activation were calculated by fitting the observed line widths or the valley between the intense inner lines using the equations of Kaplan[17] for the AB spin system. The

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(14) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961; pp 14–15.

(15) Koshar, R. J.; Mitsch R. A. *J. Org. Chem.* **1973**, *38*, 3358.

(16) van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

exchange rate at low temperatures was first estimated from the line widths of the outside peaks of the AB quartet. Then, the intrinsic linewidth, i.e., that in the absence of exchange, was varied to fit the observed width of the inside peaks. An accurate exchange rate was then calculated from observed line widths of the outside peaks. The small increase of $\Delta G^{\ddagger}$ with temperature indicates the entropy change is small. A least-squares linear fit of $\Delta G^{\ddagger}$ vs. temperature gives $\Delta H^{\ddagger} = 11.6 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = 1.5 \pm 3$ eu. Errors were calculated assuming a ±2° systematic error as described previously.[18] The experimental error is large because of the relatively narrow temperature range, −51 to +17 °C, over which the dynamic process perturbs the high resolution spectra.

X-ray Structure Determinations. Collection and Reduction of X-ray Data. A summary of crystal and intensity data for $[(Ph_3P)_2Pt(H_2O)(Ph_2C_2H)]HC(SO_2CF_3)_2$ and $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ is presented in Table I. The crystal classes and space groups were unambiguously determined by the Enraf-Nonius CAD4-SDP-PLUS peak search, centering, and indexing programs,[19] by the presence of systematic absences observed during data collection, and by successful solution and refinement. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure time. No decay was observed for $[(Ph_3P)_2Pt(H_2O)(Ph_2C_2H)]HC(SO_2CF_3)_2$, and a linear correction from 1.000 to 1.050 on I was applied for $(Ph_3P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ with use of program DECAY.[19] Empirical absorption corrections were applied for both compounds by use of ψ-scan data and programs PSI and EAC.[19] The scan parameters are show in Table I, and there was no evidence for peak overlap during data collection.

Solution and Refinement of the Structures. The structures were solved by conventional heavy-atom techniques. The Pt atoms were located by Patterson syntheses, and full-matrix least-squares refinement and difference-Fourier calculations were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation,[20] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values of $\Delta f'$ and $\Delta f''$.[21] Hydrogen atom positions were calculated for the Ph_3P, Ph_2C_2H, and $HC(SO_2CF_3)_2$ ligands and were included in the structure factor calculations but were not refined. Only some atoms in **4** were refined with anisotropic thermal parameters because of lack of significant data and the presence of some disorder in the $HC(SO_2CF_3)_2$ anion. The final difference Fourier maps did not reveal any chemically significant peaks. The largest peak observed for $[(Ph_3P)_2Pt(H_2O)(Ph_2C_2H)]HC(SO_2CF_3)_2$ was 0.95 e Å^{-3} located near C2 and F1. The largest peak observed for $(Ph_2P)_2PtH[C\text{-}HC(SO_2CF_3)_2]$ was 1.18 e Å^{-3} and was located near Pt (0.82 Å). The $HC(SO_2CF_3)_2$ anion in **4** is disordered which accounts for the large thermal parameters; however, the geometry of this anion is consistent with its established structure.

The final positional and thermal parameters of the refined and calculated atoms are given in Tables II (supplementary material) and III. ORTEP drawings of the molecules and ions including labeling schemes are shown in Figures 1–3.

Acknowledgment. The authors are grateful to the staff of the 3M Analytical and Properties Research Laboratory for the spectroscopic and analytical data. L.H.P. acknowledges support by the National Science Foundation for his contribution to this work.

Registry No. **1**, 103712-01-2; **2**, 103712-02-3; **3**, 99797-59-8; **4**, 103712-04-5; $H_2C(SO_2CF_3)_2$, 428-76-2; $(Ph_3P)_2Pt(CO_3)$, 17030-86-3; $(Ph_3P)_2Pt(PhC{=}CPh)$, 15308-61-9.

Supplementary Material Available: Tables of positional and thermal parameters, general temperature factor expressions, and weighted least-squares planes and Figure S1 (ORTEP drawing of the cation in **3** showing the labeling scheme) (19 pages); a listing of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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[17] Kaplan, J. I. *J. Chem. Phys.* **1958**, *28*, 278.

[18] Siedle, A. R.; Newmark, R. A.; Kruger, A. A.; Pignolet, L. H. *Inorg. Chem.* **1981**, *20*, 3399.

[19] All calculations were carried out on PDP 8A and 11/34 computers with use of the Enraf-Nonius CAD 4-SDP-PLUS programs. This crystallographic computing package is described by B. A. Frenz in *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University: Delft, Holland, 1978; pp 64–71. Frenz, B. A. In *Structure Determination Package and SDP-PLUS User's Guide*; B. A. Frenz and Associates: College Station, TX, 1982.

[20] D. T. Cromer and Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. *Ibid.*, Table 2.3.1.

[21] D. T. Cromer and J. A. Ibers in ref 20.