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Contribution from the Istituto di Chimica Industriale and Centro di Chimica Metallorganica del CNR, Facoltà di Ingegneria, Università di Padova, 35100 Padova, Italy, Istituto di Chimica Farmaceutica, Università di Milano, 20131 Milano, Italy, Istituto di Chimica e Tecnologia dei Radioelementi, CNR, 35100 Padova, Italy, and Institut de Cristallographie, Batiment des Sciences Physiques, CH-1005 Lausanne, Switzerland

Electrophilic Cleavage of C–F Bonds in Hydrido Trifluoromethyl Complexes of Platinum(II) by Proton Acids. Synthesis of Hydrido Carbene and Hydrido Carbonyl Derivatives and X-ray Structures of *trans*-$PtH(CF_3)(PPh_3)_2$ (180 K) and *trans*-$[PtH(\overline{COCH_2CH_2O})(PPh_3)_2]BF_4$ (298 K)

Rino A. Michelin,*[1a] Renzo Ros,[1a] Giuseppe Guadalupi,[1b] Gabriella Bombieri,[1c] Franco Benetollo,[1d] and Gervais Chapuis[1e]

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The low-temperature (180 K) crystal and molecular structure of the hydridoplatinum(II) complex *trans*-$PtH(CF_3)(PPh_3)_2$ (**1**) has been determined by X-ray diffraction. The monoclinic crystal, space group $P2_1/n$, has lattice parameters $a = 11.839$ (4) Å, $b = 18.352$ (7) Å, $c = 14.465$ (3) Å, $\beta = 92.97$ (2)°, and $Z = 4$. The structure was refined to $R = 0.0294$ and $R_w = 0.0296$ for 3410 independent reflections. The coordination geometry around the Pt atom in **1** is distorted square planar and involves the trifluoromethyl ligand trans to the hydride, which was directly located. Important bond lengths in **1** are Pt–C = 2.009 (8) Å, Pt–H 1.72 (9) Å, Pt–P = 2.274 (2) and 2.273 (2) Å, and C–F(average) = 1.404 (9) Å. The lengthening of the C–F distance in **1** in comparison with fluorocarbon compounds is reflected in its reaction chemistry. It is observed that the C–F bond in **1** undergoes electrophilic cleavage by a proton acid such as ethereal HBF_4 in the presence of a protic nucleophile (MeOH, $HOCH_2CH_2OH$, $HSCH_2CH_2SH$) under mild conditions to give the hydrido carbene complexes *trans*-$[PtH(carbene)(PPh_3)_2]BF_4$ [carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$, $\overline{CSCH_2CH_2S}$]. When the reaction of **1** with HBF_4 is carried out in the presence of H_2O, the CF_3 group is converted to a CO group, giving *trans*-$[PtH(CO)(PPh_3)_2]BF_4$. These reactions have been shown to proceed through the initial formation of the highly reactive hydrido difluorocarbene *trans*-$[PtH(CF_2)(PPh_3)_2]BF_4$, which has been fully characterized by low-temperature ^1H, ^{19}F, and ^{31}P NMR spectra. The conversion of a CF_3 group to a carbene ligand in complexes *trans*-$PtH(CF_3)L_2$ (L = PPh_3, $PBzPh_2$, PBz_3, PCy_3) appears to be influenced by steric effects such as the bulk of the metal-coordinated phosphine ligands L and the entering protic nucleophile. The hydrido carbene complexes *trans*-$[PtH(carbene)L_2]BF_4$ (carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$) have been characterized by their IR, ^1H NMR, and ^{31}P NMR spectra. The structure of *trans*-$[PtH(\overline{COCH_2CH_2O})(PPh_3)_2]BF_4$ (**2**) was established by an X-ray diffraction study. Crystal data: monoclinic, space group $C2/c$, $a = 16.292$ (5) Å, $b = 14.689$ (3) Å, $c = 16.735$ (5) Å, $\beta = 114.13$ (3)°, $Z = 4$. The structural model was refined to $R = 0.047$ for 2543 independent reflections. The coordination geometry around Pt(II) is distorted square planar with the carbene ligand rotated with respect to the coordination plane by 61.3 (2)° and with the ligand trans to the located hydrido ligand. The molecule has a crystallographically imposed 2-fold axis passing through the hydrido ligand, the platinum, and the coordinated carbon of the dioxycarbene ligand. The Pt–C and Pt–P bond lengths are 2.01 (2) and 2.287 (2) Å, respectively, while the Pt–H bond length is 1.72 (8) Å. The five-membered cyclic dioxycarbene ligand is almost planar with $C(sp^2)$–O bond distances of 1.30 (1) Å, indicating significant π-bonding between the oxygens and the carbene carbon.

Introduction

It is known that σ-perfluoroalkyl complexes of the transition metals show a remarkably higher thermal stability as compared with their σ-alkyl counterparts[2] and that the perfluoroalkyl group is quite resistant to chemical attack, paralleling the known inertness of fluorocarbon compounds.[3] However, C–F bonds α to the transition metal are susceptible to electrophilic attack under mild conditions by proton and Lewis acids to give carbene and carbonyl complexes.[4] Such reactivity has been explained by a weakening of the C–F bonds α to the transition metal, which accounts for the reduced C–F stretching frequencies[5] and increased bond lengths[6] in comparison with those in aliphatic compounds. Trifluoromethyl complexes of platinum(II) are no exception. Recently we reported in a preliminary communication[7] that the CF_3 group in *trans*-$PtX(CF_3)L_2$ complexes (X = H, L = PPh_3; X = Cl, L = PMe_2Ph)[8] can be converted to a carbene ligand by reaction at room temperature with an ethereal solution of HBF_4 in dry Et_2O in the presence of a protic nucleophile according to eq 1.

$$trans\text{-}PtX(CF_3)L_2 \xrightarrow[Et_2O]{HBF_4} [trans\text{-}PtX(CF_2)L_2]^+ \xrightarrow{\text{protic nucleophile}} trans\text{-}[PtX(carbene)L_2]BF_4 \quad (1)$$

X = H, L = PPh_3; protic nucleophile = MeOH, $HOCH_2CH_2OH$, $HOCH_2CH_2CH_2OH$, $HSCH_2CH_2SH$; carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$, $\overline{COCH_2CH_2CH_2O}$, $\overline{CSCH_2CH_2S}$

X = Cl, L = PMe_2Ph; protic nucleophile = MeOH, $HOCH_2CH_2OH$; carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$

Similarly, the reactions of *trans*-$PtH(CF_3)L_2$ (L = PPh_3, PCy_3) with HBF_4 in the presence of H_2O lead to the conversion of CF_3 to a CO group[7] (eq 2).

$$trans\text{-}PtH(CF_3)L_2 \xrightarrow[Et_2O]{HBF_4} [trans\text{-}PtH(CF_2)L_2]^+ \xrightarrow{H_2O} trans\text{-}[PtH(CO)L_2]BF_4 \quad (2)$$

L = PPh_3, PCy_3

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(1) (a) Università di Padova. (b) Centro di Chimica Metallorganica del CNR. (c) Università di Milano. (d) Istituto di Chimica e Tecnologia dei Radioelementi, CNR. (e) Institut de Cristallographie, Batiment des Sciences Physiques.

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Both reactions have been suggested to proceed through a difluorocarbene intermediate, which was not isolated, reacting rapidly with the protic nucleophile to give the carbene or carbonyl products.

The present investigation was designed to elucidate the following factors: first, whether the C–F bond weakening was essential in determining the reaction chemistry described in eq 1 and 2; second, whether the intermediacy of a difluorocarbene species observed for several transition metals[4a–c] could be proved also for Pt(II) systems. In this paper we report the low-temperature X-ray crystal structure of *trans*-$PtH(CF_3)(PPh_3)_2$, which was made necessary since the previously reported structural determination[9] did not give reliable information on Pt–CF_3 and C–F bond distances due to the large thermal motion of the atoms of the CF_3 group at room temperature. Furthermore, we provide direct NMR evidences on the formation of the hydrido difluorocarbene complex *trans*-$[PtH(CF_2)(PPh_3)_2]^+$ as a highly reactive intermediate in reactions 1 and 2 to afford hydrido carbene or hydrido carbonyl derivatives. In addition, we report the X-ray crystal structure of *trans*-$[PtH(\overline{COCH_2CH_2O})(PPh_3)_2]BF_4$, which represents the first structural characterization of a d^8 carbene complex containing the hydride ligand.[10]

Experimental Section

General Procedures, Apparatus, and Materials. All reactions were carried out under dry nitrogen or argon atmosphere. Diethyl ether was distilled under N_2 from sodium benzophenone ketyl. All other solvents were of reagent grade purity and were dried over molecular sieves without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. ^1H, ^{19}F, and ^{31}P NMR spectra were obtained on a Varian FT-80A spectrometer. Melting points were determined on a hot plate apparatus and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. The complexes *trans*-$PtH(CF_3)L_2$ (L = PPh_3, $PBzPh_2$, PBz_3, PCy_3) were prepared as previously reported.[8] HBF_4 (54% solution in Et_2O) was a commercially available product and was used as received.

Preparation of Hydrido Carbene Complexes. The complexes *trans*-$[PtH(carbene)(PPh_3)_2]BF_4$ (carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$, $\overline{COCH_2CH_2CH_2O}$, $\overline{CSCH_2CH_2S}$) were prepared by the same procedure that is described below for *trans*-$[PtH(\overline{COCH_2CH_2O})(PPh_3)_2]BF_4$. To a suspension of *trans*-$PtH(CF_3)(PPh_3)_2$ (1.20 g, 1.52 mmol) in Et_2O (80 mL) was added $HOCH_2CH_2OH$ (1 mL) and the mixture stirred at 0 °C for 15 min. Then HBF_4 (54% in Et_2O) (20 drops) was added and the reaction mixture stirred for 30 min at 0 °C and 40 min at room temperature to form a viscous solid material. MeOH (3 mL) was added and the mixture stirred at room temperature for an additional 20 min. The white solid was filtered off and washed with MeOH (3 mL) and Et_2O (10 mL). It was recrystallized from CH_2Cl_2–Et_2O. Yield: 0.95 g, 74%. The spectroscopic data for the aforementioned hydrido carbene complexes have been reported previously.[7] The following complexes are new.

***trans*-$\{PtH[C(OMe)_2](PBzPh_2)_2\}BF_4$.** To a suspension of *trans*-$PtH(CF_3)(PBzPh_2)_2$ (0.15 g, 0.18 mmol) in Et_2O (10 mL) were added a few drops of HBF_4 (54% in Et_2O) and MeOH (1 mL) at room temperature. After 1 h a white product was obtained, which was filtered and washed with Et_2O (3 × 5 mL) and dried under vacuum. Yield: 0.15 g, 95%. Mp: 210–211 °C. Anal. Calcd for $C_{41}H_{41}O_2BF_4P_2Pt$: C, 54.14; H, 4.54. Found: C, 53.91; H, 4.32. Spectroscopic data for this as well as for the other hydrido carbene complexes reported here are listed in Table I.

***trans*-$\{PtH[C(OMe)_2](PBz_3)_2\}BF_4$.** A suspension of *trans*-$PtH(CF_3)(PBz_3)_2$ (0.40 g, 0.50 mmol) in Et_2O (15 mL) was treated with a few drops of a 54% ethereal solution of HBF_4 and MeOH (15 mL) at room temperature. After 1 h a white product was obtained, which was filtered and washed with Et_2O (3 × 5 mL). IR and NMR (^1H and ^{31}P) data showed that the product contained a small amount (ca. 10% based on integration of the phosphorus resonances in the ^{31}P NMR spectrum) of *trans*-$[PtH(CO)(PBz_3)_2]BF_4$ (vide infra).

The solid mixture was recrystallized first from CH_2Cl_2–heptane and then twice from CH_2Cl_2–MeOH to give pure *trans*-$\{PtH[C(OMe)_2](PBz_3)_2\}BF_4$. Yield: 0.303 g, 60%. Mp: 217–218 °C. Anal. Calcd for

Table I. IR[a] and NMR[b] Data for the Hydrido Carbene and Hydrido Carbonyl Complexes of Pt(II)

compound	IR, cm^{-1}		^1H NMR					$^{31}P\{^1H\}$ NMR		
	ν(PtH)	ν(PtCO)	δ(H)	$^1J(PtH)$, Hz	$^2J(HP)$, Hz	$^3J(HF)$, Hz	δ(other)	δ(P)	$^1J(PtP)$, Hz	$^3J(PF)$, Hz
trans-$[PtH(CF_2)(PPh_3)_2]BF_4$[c]			−4.57 (tt)	596	12.4	52.4		23.3 (t)	2606	4.6
trans-$\{PtH[C(OMe)_2](PBzPh_2)_2\}BF_4$	2101 (w)		−7.89 (t)	641	12.3		3.99 (t),[d] 3.52 (br)[e]	24.1 (s)	2796	
trans-$\{PtH[C(OMe)_2](PBz_3)_2\}BF_4$	2134 (w)		−8.77 (t)	606	15.1		3.28 (t),[f] 3.27 (s, br)[e]	22.3 (s)	2778	
trans-$\{PtH[C(OMe)_2]PCy_3)_2\}BF_4$	2043 (w)		−8.48 (t)	624	15.5		1.10 (m),[g] 4.25 (br)[e]	40.6 (s)	2546	
trans-$[PtH(\overline{COCH_2CH_2O})(PCy_3)_2]BF_4$	2099 (m-w)		−7.99 (t)	682	14.6		1.62 (m),[g] 4.84 (s)[h]	40.4 (s)	2565	
trans-$[PtH(CO)(PPh_3)_2]BF_4$	2190 (m)[i]	2090 (s)[i]	−4.45 (t)	899	10.0			23.1 (s)	2545	
trans-$[PtH(CO)(PBz_3)_2]BF_4$	2187 (w)[j]	2073 (s)[j]	−6.04 (t)	844	10.2		3.32 (t)	32.4 (s)	2641	
trans-$[PtH(CO)(PCy_3)_2]BF_4$	2167 (m)[l]	2044 (s)[l]	−4.69 (t)	918	8.6		1.65 (m)[g]	46.3 (s)	2304	

[a] Nujol mull unless otherwise stated; w = weak, m = medium, and s = strong. [b] NMR spectra in CD_2Cl_2; s = singlet, t = triplet, br = broad, and m = multiplet. ^1H NMR spectra referenced to internal Me_4Si; ^{31}P NMR spectra referenced to external H_3PO_4 85%. Negative chemical shifts are upfield from the reference used. [c] NMR spectra at −75 °C. ^{19}F NMR (CD_2Cl_2, $CFCl_3$ internal reference): δ (CF_2) 159.5 (dt), $^2J(PtF)$ = 457 Hz, $^3J(HF)$ = 52.4 Hz, $^3J(FP)$ = 4.6 Hz. [d] P–CH_2Ph; $^2J(HP) + {}^4J(HP)$ = 8.2 Hz, $^3J(HPt)$ = 38.9 Hz. [e] OMe. [f] P–CH_2Ph; $^2J(HP) + {}^4J(HP)$ = 7.3 Hz, $^3J(HPt)$ = 34.6 Hz. [g] P–C_6H_{11}. [h] –CH_2CH_2–; $^4J(HPt)$ = 4.7 Hz. [i] IR (CH_2Cl_2): ν(PtH) = 2182 cm^{-1}; ν(PtCO) = 2083 cm^{-1}. See also ref 39. [j] IR (CH_2Cl_2): ν(PtH) = 2192 cm^{-1}; ν(PtCO) = 2077 cm^{-1}. [k] P–CH_2Ph; $^2J(HP) + {}^4J(HP)$ = 7.2 Hz, $^3J(HPt)$ = 34.1 Hz. [l] IR (CH_2Cl_2): ν(PtH) = 2163 cm^{-1}; ν(PtCO) = 2054 cm^{-1}. See also ref 28.

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Table II. Crystallographic Data for **1** and **2**

	1	**2**
chemical formula	$C_{37}H_{31}F_3P_2Pt$	$C_{39}H_{35}BO_2F_4P_2Pt$
fw	789.69	879.55
space group (No.)	$P2_1/n$ (No. 14)	C_2/c (No. 15)
a/Å	11.839 (4)	16.292 (5)
b/Å	18.352 (7)	14.689 (3)
c/Å	14.465 (3)	16.735 (5)
β/deg	92.97 (2)	114.13 (3)
V/Å^3	3138.58	3654.96
Z	4	4
T/°C	−93	25
ρ_{calcd}/g cm^{-3}	1.67	1.60
λ/Å	0.7107	0.7107
$R(F_o)$	0.029	0.047
$R_w(F_o)$	0.030	
μ(Mo Kα)/cm^{-1}	44.23	38.09
transmission coeff (rel)	80/100	63/100

$C_{45}H_{49}BF_4O_2P_2Pt$: C, 55.97; H, 5.11. Found: C, 55.54; H, 4.95.

trans**-[PtH($\overline{COCH_2CH_2O}$)(PCy$_3$)$_2$]BF$_4$.** A suspension of *trans*-PtH(CF$_3$)(PCy$_3$)$_2$ (0.25 g, 0.30 mmol) in Et$_2$O (10 mL) was treated with a few drops of a 54% ethereal solution of HBF$_4$ and ethylene glycol (1 mL) at room temperature. After 1 h a white product was obtained, which was filtered and dried under vacuum.

The white product was crystallized first from CH$_2$Cl$_2$–*n*-heptane and then from CH$_2$Cl$_2$–MeOH. Yield: 0.244 g, 81%. Anal. Calcd for $C_{39}H_{71}BF_4O_2P_2Pt$: C, 51.13; H, 7.81. Found: C, 50.82; H, 7.80.

trans**-{PtH[C(OMe)$_2$](PCy$_3$)$_2$}BF$_4$.** A suspension of *trans*-PtH(CF$_3$)(PCy$_3$)$_2$ (0.22 g, 0.274 mmol) in Et$_2$O (10 mL) was treated with a few drops of a 54% ethereal solution of HBF$_4$ and MeOH (1 mL) at room temperature. After 1 h a white product was obtained, which was filtered. On the basis of spectroscopic data (IR and NMR), the crude reaction product was revealed to be a mixture of *trans*-{PtH[C(OMe)$_2$](PCy$_3$)$_2$}BF$_4$ and *trans*-[PtH(CO)(PCy$_3$)$_2$]BF$_4$ (see below) in a 1:4 ratio (based on ^{31}P NMR integration). Attempts to separate by crystallization the hydrido carbene complex from the carbonyl compound were unsuccessful.

Preparation of Hydrido Carbonyl Complexes. *trans*-[PtH(CO)(PPh$_3$)$_2$]BF$_4$. To a suspension of *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ (0.10 g, 0.13 mmol) in Et$_2$O (10 mL) were added a few drops of HBF$_4$ (54% in Et$_2$O) and H$_2$O (one drop) at room temperature. After 1 h of stirring, a white product was obtained, which was filtered, washed with Et$_2$O (2 × 5 mL), and dried under vacuum. Yield: 0.090 g, 80%. Mp: 156 °C (decomposition with effervescence). Anal. Calcd for $C_{37}H_{31}BF_4OP_2Pt$: C, 53.19; H, 3.74. Found: C, 52.90; H, 3.58. IR and NMR data for the hydrido carbonyl derivatives are reported in Table I.

trans**-[PtH(CO)(PBz$_3$)$_2$]BF$_4$.** This complex was prepared as above, starting from *trans*-PtH(CF$_3$)(PBz$_3$)$_2$ (0.20 g, 0.23 mmol), ethereal HBF$_4$, and H$_2$O. Yield: 0.18 g, 84%. Mp: 203 °C. Anal. Calcd for $C_{43}H_{43}BF_4OP_2Pt$: C, 56.16; H, 4.71. Found: C, 55.90; H, 4.53.

trans**-[PtH(CO)(PCy$_3$)$_2$]BF$_4$.** This complex was prepared as above, starting from *trans*-PtH(CF$_3$)(PCy$_3$)$_2$ (0.20 g, 0.25 mmol), ethereal HBF$_4$, and H$_2$O. Yield: 0.21 g, 80%. Mp: 209 °C dec. Anal. Calcd for $C_{37}H_{67}BF_4OP_2Pt$: C, 50.97; H, 7.74. Found: C, 50.78; H, 7.60.

X-ray Measurements and Structure Determination for 1 and 2. The crystal data for **1** and **2** are summarized in Table II together with some experimental details. **1** crystallizes as white prisms from a benzene–hexane mixture, while **2** is in the form of white prisms obtained from a 1,2-dichloroethane–Et$_2$O solution. Crystals of both compounds were lodged in Lindemann glass capillaries. **1** was centered on an Enraf-Nonius CAD4 diffractometer equipped with a low-temperature apparatus, while **2** was centered on a four-circle Philips PW 1100 diffractometer, using Mo K$\bar{\alpha}$ graphite-monochromated radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections in the interval $12 < 2\vartheta < 20°$. For the determination of precise lattice parameters, 25 strong reflections with $20 < 2\vartheta < 28°$ were considered. Integrated intensities for hkl reflections with $h,k > 0$ for **1** and $k,l > 0$ for **2** were measured, and three standard reflections were monitored every 180 min. There was no significant fluctuation of intensities other than those expected from Poisson statistics.

The intensities data were corrected for Lorentz–polarization effects and for absorption, by using Gaussian integration for **1** and by following the method of North et al. for **2**;[11] no corrections were made for extinction.

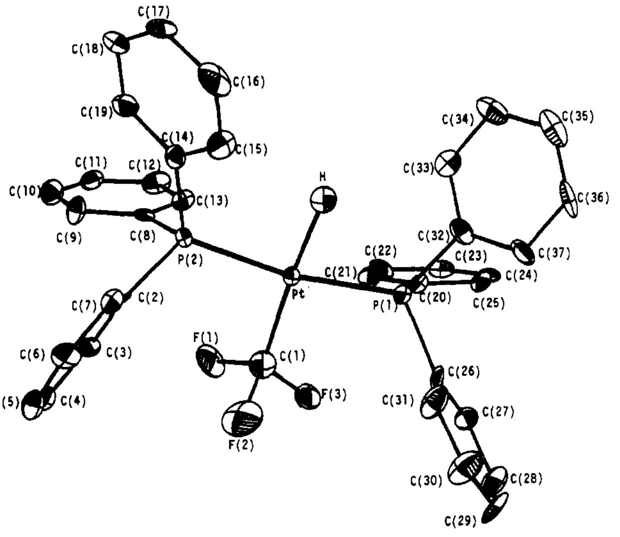

Figure 1. Perspective view of the complex *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ (**1**). The thermal ellipsoids are at 50% probability.

The structure of **1** was refined by considering the previously published data[9] at room temperature (298 K). Anisotropic thermal parameters were assigned to all the non-hydrogen atoms during the least-squares full-matrix refinement. The hydrogen atoms of the phenyl rings were introduced at their idealized positions (d_{C-H} = 0.95 Å and U_{iso} = 0.04 Å^2) and were allowed to ride on associated carbon atoms during the refinement. At the last stages of the refinement a difference Fourier revealed the highest peak of electron density of about 0.8 e Å^{-3} in the usual position for a hydrogen atom bound to platinum (Pt–H = 1.7 Å). The contribution of the hydrido ligand was included in the last refinement cycles, and its position was refined with a fixed isotropic thermal parameter (U = 0.08 Å^2). The structure converged to the R value of 0.0294 (R_w = 0.0296), which was considered as final.

The structure of **2** was solved by using three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares techniques with anisotropic thermal parameters assigned to all the non-hydrogen atoms, except the fluorines of the BF$_4$ group, which were refined isotropically because of some degree of disordering of this group. Attempts to solve this partial disordering with reduced occupancy factors in two alternative positions were not successful.

Phenyl hydrogen atoms were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d_{C-H} = 0.95 Å and U_{iso} = 0.08 Å^2).

The hydrido ligand was identified as in **1** (the electron density residual was about 0.75 e Å^{-3}) and was refined with a fixed isotropic thermal factor (U = 0.10 Å^2). The structure reached convergency at R = 0.047.

The function minimized was $\sum w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$ in both references. The anomalous dispersion terms[12] for Pt were taken into account in the refinement. Atomic scattering factors were taken from ref 12. Data processing and computations were carried out by using the SELX 76 program package[13] and ORTEP[14] for drawings.

Results and Discussion

Description of the Structure of *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ (1). An ORTEP view of the molecule is given in Figure 1. The final structural parameters are listed in Table III. Selected bond lengths and bond angles are listed in Table IV. This low-temperature study, besides the improvement in the structural results, allowed the localization of the hydrido ligand at a Pt–H distance of 1.72 (9) Å, which is in the range of the observed Pt–H distances such as 1.78 Å in PtH(μ-SiMe$_2$)[P(C$_6$H$_{11}$)$_3$]$_2$,[15] 1.66 Å in PtH(SB$_9$H$_{10}$)(PEt$_3$)$_2$,[16] and 1.72 (8) Å in **2** (see below). (The high

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Table III. Atomic Coordinates (×10^4) for Non-Hydrogen Atoms and U_{eq}[a] (×10^3) with Esd's in Parentheses for **1**

	x/a	y/b	z/c	U_{eq}, Å^2
Pt	5692.4 (2)	4220.0 (1)	7716.8 (2)	15.2 (1)
H	6160 (74)	5106 (47)	7758 (58)	80[b]
P(1)	7542 (2)	3931 (1)	7567 (1)	16 (1)
P(2)	3935 (1)	4705 (1)	7809 (1)	15 (1)
F(1)	4192 (4)	3038 (2)	7031 (3)	47 (2)
F(2)	4852 (4)	2826 (2)	8410 (3)	55 (2)
F(3)	5876 (4)	2651 (2)	7250 (3)	45 (2)
C(1)	5160 (6)	3183 (5)	7612 (5)	35 (1)
C(2)	3020 (5)	4279 (3)	8632 (4)	16 (2)
C(3)	2377 (5)	3667 (3)	8376 (4)	17 (2)
C(4)	1736 (6)	3313 (4)	9015 (5)	25 (3)
C(5)	1727 (6)	3559 (4)	9905 (5)	27 (2)
C(6)	2378 (6)	4158 (4)	10178 (5)	27 (2)
C(7)	3008 (6)	4523 (4)	9542 (5)	22 (2)
C(8)	3124 (5)	4680 (3)	6712 (4)	14 (2)
C(9)	1942 (5)	4729 (4)	6654 (4)	20 (2)
C(10)	1356 (6)	4734 (4)	5812 (5)	21 (2)
C(11)	1922 (6)	4685 (4)	5010 (5)	23 (2)
C(12)	3091 (6)	4638 (4)	5040 (4)	24 (2)
C(13)	3680 (6)	4631 (3)	5896 (4)	20 (2)
C(14)	3895 (5)	5668 (3)	8139 (4)	17 (2)
C(15)	4714 (6)	5924 (4)	8794 (5)	26 (2)
C(16)	4681 (6)	6653 (4)	9083 (5)	35 (3)
C(17)	3864 (6)	7107 (4)	8707 (5)	32 (3)
C(18)	3057 (6)	6858 (4)	8051 (5)	28 (3)
C(19)	3083 (6)	6144 (4)	7784 (5)	23 (2)
C(20)	7850 (5)	3703 (3)	6380 (4)	15 (2)
C(21)	6966 (6)	3604 (3)	5722 (5)	22 (2)
C(22)	7192 (6)	3437 (4)	4818 (5)	26 (2)
C(23)	8302 (6)	3350 (4)	4571 (5)	23 (2)
C(24)	9174 (6)	3451 (3)	5214 (5)	22 (2)
C(25)	8958 (6)	3630 (3)	6117 (4)	18 (2)
C(26)	8099 (5)	3181 (4)	8273 (5)	20 (2)
C(27)	8020 (6)	3230 (4)	9233 (5)	32 (3)
C(28)	8492 (7)	2693 (4)	9798 (5)	39 (3)
C(29)	9014 (6)	2098 (4)	9431 (6)	36 (3)
C(30)	9050 (6)	2036 (4)	8486 (6)	35 (3)
C(31)	8605 (6)	2570 (4)	7904 (5)	24 (2)
C(32)	8538 (6)	4686 (4)	7844 (5)	19 (2)
C(33)	8314 (6)	5344 (4)	7414 (4)	22 (2)
C(34)	9035 (6)	5938 (4)	7566 (5)	30 (3)
C(35)	9963 (6)	5860 (4)	8180 (5)	35 (3)
C(36)	10185 (6)	5208 (4)	8626 (6)	34 (3)
C(37)	9479 (6)	4617 (4)	8438 (5)	27 (2)

[a] U_{eq} = one-third of the trace of the orthogonalized U_{ij} tensor. [b] Fixed isotropic thermal parameters.

Table IV. Relevant Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for **1**

(a) Bond Lengths

Pt–H	1.72 (9)	P(2)–C(2)	1.827 (7)
Pt–P(1)	2.274 (2)	P(2)–C(8)	1.813 (6)
Pt–P(2)	2.273 (2)	P(2)–C(14)	1.831 (6)
Pt–C(1)	2.009 (8)	F(1)–C(1)	1.410 (8)
P(1)–C(20)	1.823 (7)	F(2)–C(1)	1.391 (9)
P(1)–C(26)	1.816 (7)	F(3)–C(1)	1.411 (9)
P(1)–C(32)	1.850 (7)		

(b) Bond Angles

P(2)–Pt–C(1)	95.2 (2)	F(1)–C(1)–F(2)	99.6 (5)
P(2)–Pt–H	85 (3)		
P(1)–Pt–H	85 (3)		
P(1)–Pt–C(1)	94.1 (2)	Pt–C(1)–F(3)	119.4 (5)
P(1)–Pt–P(2)	170.3 (1)	Pt–C(1)–F(2)	118.5 (5)
Pt–P(1)–C(32)	114.2 (2)	Pt–C(1)–F(1)	117.7 (5)
Pt–P(1)–C(26)	116.5 (2)	P(2)–C(2)–C(7)	120.9 (5)
Pt–P(1)–C(20)	112.6 (2)	P(2)–C(2)–C(3)	120.4 (5)
C(26)–P(1)–C(32)	103.7 (3)	P(2)–C(8)–C(13)	119.6 (5)
C(20)–P(1)–C(32)	102.7 (3)	P(2)–C(8)–C(9)	122.2 (5)
C(20)–P(1)–C(26)	105.7 (3)	P(2)–C(14)–C(19)	122.8 (5)
Pt–P(2)–C(14)	115.4 (2)	P(2)–C(14)–C(15)	118.3 (5)
Pt–P(2)–C(8)	112.6 (2)	P(1)–C(20)–C(25)	121.2 (5)
Pt–P(2)–C(2)	116.5 (2)	P(1)–C(20)–C(21)	119.7 (5)
C(8)–P(2)–C(14)	103.4 (3)	P(1)–C(26)–C(31)	123.1 (5)
C(2)–P(2)–C(14)	102.7 (3)	P(1)–C(26)–C(27)	118.0 (5)
C(2)–P(2)–C(8)	104.7 (3)	P(1)–C(32)–C(37)	123.5 (5)
F(2)–C(1)–F(3)	99.8 (5)	P(1)–C(32)–C(33)	117.0 (5)
F(1)–C(1)–F(3)	97.8 (5)		

esd's in the Pt–H distances quoted in the literature prevent a more accurate comparison.) The least-squares best mean plane through P(1), P(2), C(1), and H (deviations: P(1), 0.000 (2); P(2), 0.000 (2); C(1), 0.000 (7); H, −0.02 (8)) indicates coplanarity of these donor atoms while the Pt deviates from the plane by −0.0507 (3) Å.

The Pt–P distances (2.274 (2), 2.273 (2) Å) are equal, within experimental error, to those found in the hydrido cyanomethyl complex *trans*-PtH(CH_2CN)(PPh_3)$_2$ (Pt–P = 2.276 (4), 2.272 (4) Å).[17] The Pt–C(1) distance (2.009 (8) Å) is significantly shorter than that found in the aforementioned hydrido cyanomethyl complex *trans*-PtH(CH_2CN)(PPh_3)$_2$ [Pt–C = 2.16 (1) Å][17] and it is also shorter than the metal–carbon bond lengths found in some fluoroalkyl complexes such as CpMo(C_3F_7)(CO)$_3$ (Cp = η^5-C_5H_5; Mo–C(perfluoroalkyl) = 2.288 (9) Å),[6d] *cis*-PtF[CH(CF_3)$_2$](PPh_3)$_2$[18] (Pt–C = 2.07 (2) Å), *cis*-Pt(CF_3)$_2$[PMe$_2$(C_6F_5)]$_2$[19] (2.058 (4) Å), PtCl(CF_3)(Ph_2PCH=$CHPPh_2$)[20] (Pt–C = 2.188 (8) Å), and Pt(CF_3)$_2$(SP) (SP = (2-vinylphenyl)diphenylphosphine; Pt–C = 2.082 (5) and 2.032 (5) Å for CF_3 trans and cis to phosphorus, respectively).[21] However, the Pt–C distance is comparable to that found in *trans*-PtCl(C_2F_5)($PMePh_2$)$_2$ (2.002 (9) Å, averaged over two independent molecules),[22] where the pentafluoroethyl group is trans to chloride. A comparison with the Pt–CF_3 distance in *trans*-PtCl(CF_3)($PMePh_2$)$_2$ was not possible since its structural analysis did not give an accurate determination of Pt–Cl, Pt–C, and C–F bond lengths owing to inversion disorder of the Cl and CF_3 groups about the platinum atom.[22] Finally, the Pt–C distance is shorter than that observed in Ru(CF_3)($HgCF_3$)(CO)$_2$(PPh_3)$_2$ (Ru–CF_3 = 2.084 (13) Å) where trifluoromethyl is trans to a carbonyl group.[4b] It is worthwhile noting that the Pt–C distance in **1** is close to the Pt–C(carbene) distance in *trans*-[PtH($\overline{\mathrm{COCH_2CH_2O}}$)($PPh_3$)$_2$]$BF_4$ (**2**) (Pt–C = 2.01 (2) Å; see below) and comparable to the Pt–C(carbene) distances of several other carbene complexes, which are in the range 1.92–2.07 Å.[10]

It has been observed[22] that there are interesting similarities between CO and perfluoroalkyl groups in their platinum(II) complexes. For instance, the two ligands are similar to the extent that both are lower in the "Pt–Cl" (IR- and structural-based) trans-influence series than in the NMR-based series. The low structural trans influence of CO on Pt–Cl bonds has been attributed to an electrostatic effect caused by its π-back-bonding activity; the contraction of the Pt–C distances in the perfluoroalkyl complex *trans*-PtCl(C_2F_5)($PMePh_2$)$_2$[22] is attributed to the electrostatic effect of a positive charge induced on the ligating carbon atom by the electronegative fluorine atoms. A second similarity is that CO, like $C_2F_5^-$, appears to lengthen metal–phosphorus bonds cis to it.[22,23] The M–P bond lengthening appears to be associated with cis ligands having rather short metal–ligand distances. As noted earlier,[8b] this latter effect is not observed in the hydridoplatinum(II) complexes *trans*-PtH(R)(PPh_3)$_2$ (R = CF_3, CH_2CN), which both display equal Pt–P bond distances, albeit the Pt–CF_3 distance in **1** is significantly shorter than that

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found for Pt–CH$_2$CN (relative contraction ca. 0.15 Å). The Pt–P bond distance in **1** is also comparable with that found in the hydrido carbene derivative **2** (Pt–P = 2.288 (2) Å). It is possible that angle distortions and/or different steric effects may be responsible for the observed differences. We note that, for hydridoplatinum(II) complexes, CF_3^- has close similarities with the trans influence of carbene rather than that of CO groups on the basis of ν(PtH) and ^1J(PtH) data. Thus, *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ displays ν(PtH) at 2069 cm^{-1} (CH$_2$Cl$_2$) and ^1J(PtH) of 544 Hz (CD$_2$Cl$_2$).[8] The hydrido carbene complexes *trans*-[PtH(carbene)(PPh$_3$)$_2$]BF$_4$[7] display ν(PtH) in the range 2079–2088 cm^{-1} (CH$_2$Cl$_2$) and ^1J(PtH) in the range 650–699 Hz (CD$_2$Cl$_2$). In particular, the hydrido difluorocarbene complex *trans*-[PtH(CF$_2$)(PPh$_3$)$_2$]BF$_4$ (see below) has ^1J(PtH) of 596 Hz. The corresponding data for *trans*-[PtH(CO)(PPh$_3$)$_2$]BF$_4$ are as follows: ν(PtH), 2182 cm^{-1} (CH$_2$Cl$_2$); ^1J(PtH) 899 Hz (CD$_2$Cl$_2$) (see Table I). These data are supported also by structural evidence, which indicates that the trans influence of a perfluoroalkyl group such as $C_2F_5^-$ in *trans*-PtCl(C$_2$F$_5$)(PMePh$_2$)$_2$[22] is about the same as those of the carbene and triethylphosphine ligands in *cis*-PtCl$_2$[C(OEt)NHPh](PEt$_3$)[24] and *cis*-PtCl$_2$[CN(Ph)CH$_2$CH$_2$N(Ph)](PEt$_3$).[25]

The coordination to the metal ion of the CF_3^- moiety determines, as expected, an enlargement of the P(1)–Pt–C(1) and P(2)–Pt–C(1) angles to the values 94.1 (2) and 95.2 (2)°, respectively, with contraction of the P(1)–Pt–H and P(2)–Pt–H angles (their values being both 85 (3)° due to the lesser steric demand of the hydrido ligand).

The C(1)–F distances are 1.391 (9), 1.410 (8), and 1.411 (9) Å (average 1.404 (9) Å). They are comparable with the C$_\alpha$–F distances in *trans*-PtCl(C$_\alpha$F$_2$–C$_\beta$F$_3$)(PMePh$_2$)$_2$[22] (C$_\alpha$–F = 1.366 (14)–1.402 (14) Å; 1.387 Å average) but they are significantly longer than those found for C$_\beta$–F (range 1.302 (15)–1.363 (18) Å; 1.332 Å average). The average C$_\beta$–F distance is close to that observed in gaseous CF$_3$CF$_2$I (average 1.338 (4) Å)[26] by electron diffraction. The C(1)–F distance in **1** may be compared with the C–F bond distances found in Ru(CF$_3$)(HgCF$_3$)(CO)$_2$(PPh$_3$)$_2$.[4b] For this latter complex it is found that the C–F distance for the Ru–CF$_3$ group (C–F = 1.38 (1) Å average) is almost 0.1 Å longer than the average C–F distance for the Hg–CF$_3$ group (1.29 (1) Å). This bond weakening is reflected in the reactivity of C–F bonds α to ruthenium toward electrophiles such as aqueous HClO$_4$ and anhydrous HCl to give carbonyl and carbene derivatives. Similarly, in the compound CpMo(C$_3$F$_7$)(CO)$_3$[6d] the average α-carbon–fluorine bond length is 1.40 Å, whereas β-C–F and γ-C–F distances are ca. 1.33 (average) and 1.27 Å (average), respectively. As a consequence of the α-C–F bond lengthening, a fluoride ion could be abstracted from the carbon atoms of the perfluoroalkyl group in CpMo(C$_3$F$_7$)(CO)$_3$ and CpMo(CF$_3$)(CO)$_3$ by reaction with SbF$_5$ to yield the fluorocarbene complexes {CpMo[C(F)CF$_3$](CO)$_3$}SbF$_6$ and [CpMo(CF$_2$)(CO)$_3$]SbF$_6$.[4a] From these data, we may conclude that also for **1** the observed α-C–F bond lengthening (and hence weakening) is responsible for its susceptibility to react with electrophiles to give C–F bond cleavage.

Electrophilic Cleavage of C–F Bonds in *trans*-PtH(CF$_3$)L$_2$ Complexes by Proton Acids. The formation of the hydrido difluorocarbene complex *trans*-[PtH(CF$_2$)(PPh$_3$)$_2$]BF$_4$ by reaction of **1** with ethereal HBF$_4$ (eq 3) has been detected and fully characterized by low-temperature NMR spectroscopy (Table I).

$$\underset{\mathbf{1}}{trans\text{-}PtH(CF_3)(PPh_3)_2} \xrightarrow[-75\ °C]{CD_2Cl_2,HBF_4\cdot Et_2O} \underset{\mathbf{1^*}}{trans\text{-}[PtH(CF_2)(PPh_3)_2]BF_4} \xrightarrow[-75\ to\ +25\ °C]{H_2O} trans\text{-}[PtH(CO)(PPh_3)_2]BF_4 \quad (3)$$

The ^{1}H NMR spectrum at −75 °C of a CD$_2$Cl$_2$ solution of **1** and HBF$_4$ (1 drop of a 54% ethereal solution) shows a triplet of triplets (with ^{195}Pt satellites) at δ −4.57 of the hydride resonance due to coupling either with two equivalent fluorine and phosphorus atoms.

The values of δ(H) (−4.57 ppm) and ^1J(PtH) (596 Hz) are comparable with those found for *trans*-[PtH(carbene) (PPh$_3$)$_2$]BF$_4$ complexes (carbene = C(OMe)$_2$, COCH$_2$CH$_2$O, COCH$_2$CH$_2$CH$_2$O, CSCH$_2$CH$_2$S; δ(H) = −6.22 to −7.68; ^1J(PtH) = 650–699 Hz)[7] and *trans*-{PtH[CN(Me)CH$_2$CH$_2$N(Me)](PEt$_3$)$_2$}BF$_4$ (δ(H) = −6.9; ^1J(PtH) = 702 Hz).[27] The ^1J(PtH) value of **1*** is however larger than those found for *trans*-[PtH(carbene)(PCy$_3$)$_2$]PF$_6$ (carbene = C(OMe)$_2$, C(OMe)(CH$_2$Ph), COCH$_2$CH$_2$CH$_2$),[28] which are in the range 470–552 Hz. The values of ^2J(HP) (12.4 Hz) and ^3J(HF) (52.4 Hz) found in **1*** are respectively smaller and larger than those found in the starting complex **1** (18.5 and 28.0 Hz, respectively).[8] The ^{19}F NMR spectrum of **1*** shows the difluorocarbene resonance markedly downfield (δ(CF$_2$) + 159.5; doublet of triplets with ^{195}Pt satellites) with respect to that found for CF$_3$ in **1** (δ(CF$_3$) −16.8).[8b] A similar behavior has been reported for the difluorocarbene ligands in [CpMo(CF$_2$)(CO)$_3$]SbF$_6$ [δ(CF$_2$) + 242.47 vs external CF$_3$COOH corresponding to ca. δ +165 with respect to internal CFCl$_3$] and [CpMo(CF$_2$)(CO)$_2$(PPh$_3$)]SbF$_6$ (δ(CF$_2$) +239.04 vs CF$_3$COOH, corresponding to δ +162 with respect to internal CFCl$_3$).[4a] The value of ^2J(PtF) (457 Hz) of **1*** is similar to that found for **1** (448 Hz), whereas ^3J(FP) (4.6 Hz) is smaller than that for **1** (10.0 Hz).[8b] The ^{31}P{^{1}H} NMR spectrum of **1*** displays the expected triplet with ^{195}Pt satellites centered at δ 23.3. It is observed that slowly raising the temperature from −75 °C to room temperature leads to the progressive disappearance of the hydride resonance of **1*** in the ^{1}H NMR spectrum with the simultaneous formation of a triplet (with ^{195}Pt satellites) at δ −4.45 (^2J(HP) = 10.0 Hz, ^1J(PtH) = 899 Hz) due to the hydride resonance of *trans*-[PtH(CO)(PPh$_3$)$_2$]BF$_4$ (Table I). No other species were detected in the reaction mixture. The formation of the carbonyl derivative is presumably due to the hydrolysis of the CF$_2$ ligand by traces of H$_2$O present in the reaction mixture. The rapid hydrolysis of metal-bound CF$_2$ groups to CO has been reported to occur in certain complexes of Ru[4b] and Fe.[4c] Conversely, it is remarkable that in the zerovalent ruthenium complex Ru(CF$_2$)(CO)$_2$(PPh$_3$)$_2$ the CF$_2$ ligand is stable toward nucleophilic attack but not toward electrophilic attack.[29] Attempts to isolate the hydrido difluorocarbene species **1*** in the solid state were unsuccessful. The solid obtained by reaction of **1** with HBF$_4$ in Et$_2$O was found to be extremely moisture-sensitive, and the Nujol mull IR spectra always exhibit bands at 2190 and 2090 cm^{-1} diagnostic of Pt–H and Pt–CO stretchings, respectively, of *trans*-[PtH(CO)(PPh$_3$)$_2$]BF$_4$ (Table I). Thus, C–F stretchings in the range 1150–1230 cm^{-1}, which have been assigned to a transition-metal-coordinated CF$_2$ ligand,[4b,c] were not detected. Finally, it is noteworthy to mention that the formation of the hydrido carbonyls *trans*-[PtH(CO)(PR$_3$)$_2$]BF$_4$ and *trans*-[PtH(CO)(PR$_3$)$_2$]SiF$_5$ (PR$_3$ = PEt$_3$, PPh$_3$) have been reported to occur as byproducts in the reaction of *trans*-PtHCl(PR$_3$)$_2$ with C$_2$F$_4$ in Pyrex glass or silica tubes, presumably through BF$_3$- or SiF$_4$-catalyzed hydrolysis of fluorovinyl-Pt(II) intermediates.[30]

The C–F bond cleavage in *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ (**1**) occurs also with electrophiles EX such as HPF$_6$, NOBF$_4$, and *p*-toluenesulfonic acid. When the reactions are carried out in wet Et$_2$O, the corresponding carbonyl derivatives are isolated from

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the reaction mixtures (eq 4) and identified by comparison with

$$trans\text{-}[PtH(CF_3)(PPh_3)_2] + EX \xrightarrow[H_2O]{Et_2O} trans\text{-}[PtH(CO)(PPh_3)_2]X + EF + 2HF \quad (4)$$

$$EX = HPF_6,\ NOBF_4,\ p\text{-toluenesulfonic acid}$$

the data obtained for *trans*-[PtH(CO)$(PPh_3)_2$]BF_4 (Table I).

As noted earlier for the HBF_4 reactions, it is suggested that also in reaction 4 a difluorocarbene intermediate is formed by attack of the electrophile on the C–F bond which is then rapidly hydrolyzed by H_2O to a CO group.

The reactions of *trans*-PtH$(CF_3)(PPh_3)_2$ (**1**) with protic nucleophiles such as alcohols and thiols in the presence of ethereal HBF_4 to give carbene derivatives are often accompanied by the formation of various amounts of carbonyl products (see also below) due to the presence of traces of H_2O in the solvent and/or in the reacting species. In most cases the carbonyl complexes could be conveniently extracted by taking advantage of their greater solubility in MeOH solvent.

It is observed that reactions 1 and 2 are influenced by either the nature of the entering protic nucleophile or the bulk of the metal-coordinated phosphines L. Thus, reaction of **1** with excess *t*-BuOH in the presence of ethereal HBF_4 (eq 5) does not lead

$$\mathbf{1} \xrightarrow[\text{RT, 12 h}]{HBF_4\cdot Et_2O,\ t\text{-BuOH}} trans\text{-}[PtH(CO)(PPh_3)_2]BF_4 \quad (5)$$

to the formation of the carbene Pt=C(OBu-*t*)$_2$ complex, the carbonyl derivative *trans*-[PtH(CO)$(PPh_3)_2$]BF_4 being isolated as the only reaction product. Analogous reactions of *trans*-PtH$(CF_3)L_2$ complexes (L = $PBzPh_2$, PBz_3, PCy_3) with excess MeOH and ethereal HBF_4 (eq 6) gave different amounts of the corre-

$$trans\text{-}PtH(CF_3)L_2 \xrightarrow[\text{room temperature}]{HBF_4\cdot Et_2O,\ MeOH} trans\text{-}\{PtH[C(OMe)_2]L_2\}BF_4 \quad (6)$$

$$L = PBzPh_2,\ PBz_3,\ PCy_3$$

sponding carbene complexes *trans*-{PtH[C(OMe)$_2$]L_2}BF_4 (Table I) depending on the nature of the phosphines L.

As for L = $PBzPh_2$, the complex *trans*-{PtH[C(OMe)$_2$]$(PBzPh_2)_2$}BF_4 was isolated in 95% yield, whereas for L = PBz_3 the parent dimethoxycarbene complex was isolated in 60% yield after separation from the carbonyl derivative by recrystallization from CH_2Cl_2–MeOH. As for the reaction of the PCy_3 derivative, the compounds *trans*-{PtH[C(OMe)$_2$]$(PCy_3)_2$}BF_4 and *trans*-[PtH(CO)$(PCy_3)_2$]BF_4 could not be separated by crystallization. However, on the basis of a ^{31}P NMR analysis, the amount of the carbene derivative present in the reaction products was estimated to be ca. 25%. It is noteworthy that the reaction of *trans*-PtH$(CF_3)(PCy_3)_2$ with $HOCH_2CH_2OH$ and HBF_4 in Et_2O gave *trans*-[PtH($\overline{COCH_2CH_2O}$)$(PCy_3)_2$]BF_4 in 81% isolated yield. Spectroscopic properties of the hydrido carbene and hydrido carbonyl complexes prepared in this work are reported in Table I.

There appear to be only a few hydrido–transition metal carbene complexes in the literature,[27,28,31,32] and these mostly have platinum as the central metal. These metal species were obtained by interaction of a metal substrate with an electron-rich olefin[31] or by nucleophilic attack of amines or alcohols on a metal-coordinated isocyanide[32] or acetylene[28] ligand, respectively.

In order to conclusively characterize the hydrido carbene complexes derived from hydrido trifluoromethyl compounds, the X-ray structure of the carbene complex *trans*-[PtH($\overline{COCH_2CH_2O}$)$(PPh_3)_2$]BF_4 (**2**) has been undertaken.

Description of the Structure of *trans*-[PtH($\overline{COCH_2CH_2O}$)$(PPh_3)_2$]BF_4 (2). The structure consists of well-separated

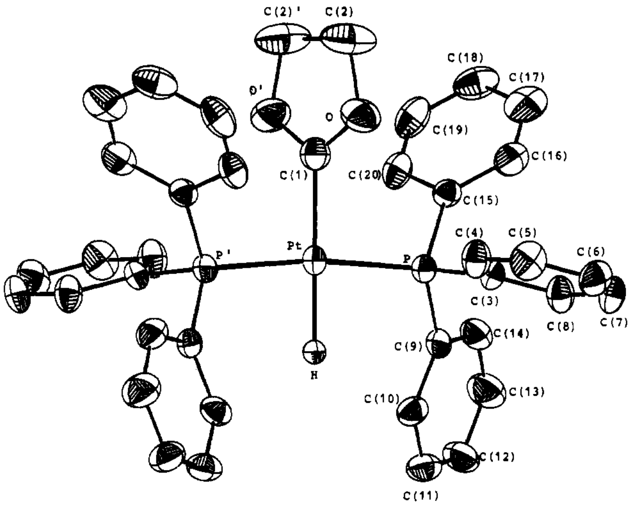

Figure 2. Perspective view of the complex *trans*-[PtH($\overline{COCH_2CH_2O}$)$(PPh_3)_2$]BF_4 (**2**). The thermal ellipsoids are at 40% probability.

Table V. Atomic Coordinates (×10^4) for Non-Hydrogen Atoms and U_{eq} (×10^3) with Esd's in Parentheses for **2**

	x/a	y/b	z/c	U_{eq}, Å^2
Pt	0	4663.4 (4)	2500	53.1 (2)
H	0	3495 (65)	2500	100[a]
P	1283 (1)	4559 (2)	2262 (1)	48.7 (9)
C(3)	2282 (5)	4473 (6)	3273 (6)	52 (3)
C(4)	2217 (6)	4677 (8)	4062 (6)	66 (4)
C(5)	2978 (7)	4660 (8)	4844 (6)	76 (4)
C(6)	3794 (7)	4442 (7)	4845 (7)	76 (5)
C(7)	3863 (6)	4232 (8)	4088 (7)	75 (5)
C(8)	3102 (6)	4239 (7)	3273 (6)	65 (4)
C(9)	1348 (5)	3604 (6)	1576 (6)	51 (4)
C(10)	1046 (6)	2749 (6)	1679 (6)	60 (4)
C(11)	1104 (7)	2025 (7)	1171 (7)	71 (5)
C(12)	1447 (8)	2170 (8)	538 (8)	84 (6)
C(13)	1734 (8)	3014 (8)	427 (9)	94 (7)
C(14)	1699 (7)	3717 (7)	964 (8)	75 (6)
C(15)	1454 (6)	5530 (6)	1672 (5)	50 (4)
C(16)	2269 (7)	5977 (7)	1895 (7)	77 (5)
C(17)	2359 (9)	6669 (8)	1382 (7)	95 (6)
C(18)	1632 (9)	6935 (8)	642 (7)	88 (6)
C(19)	820 (8)	6495 (9)	413 (7)	87 (6)
C(20)	730 (6)	5824 (7)	928 (6)	69 (4)
C(1)	0	6033 (11)	2500	69 (8)
O	639 (5)	6527 (5)	3061 (5)	95 (4)
C(2)	461 (11)	7504 (9)	2876 (11)	144 (12)
B	10000	112 (22)	2500	112 (13)
F(1)	9612 (7)	545 (8)	2916 (7)	173 (4)[b]
F(2)	10644 (8)	−489 (8)	3108 (8)	180 (4)[b]

[a] Fixed isotropic thermal parameter. [b] *U* isotropic.

trans-[PtH($\overline{COCH_2CH_2O}$)$(PPh_3)_2$]$^+$ cation and BF_4^- anion units. The molecule has a crystallographically imposed C_2 symmetry. The 2-fold axis of rotation lies along the Pt–C(1) (of the dioxycarbene ligand) vector, which includes the boron of the BF_4 anion. The asymmetric units are then half cation and half anion. The coordination geometry around Pt(II) is distorted square planar where the dioxycarbene ligand is trans to hydride: the coordination is completed by the two phosphorus atoms from the triphenylphosphines. An ORTEP view of the complex cation showing its conformation and the atom-numbering scheme is in Figure 2. The final structural parameters are reported in Table V. Table VI reports significant bond lengths and angles. The Pt, P, C(1), H atoms are coplanar for sake of symmetry and the angles P–Pt–C(1) = 93.8 (1)° and P–Pt–H = 86 (3)° are comparable to those found in compound **1**, indicating that the steric requirements of the cyclic carbene ligand are not too different from those of the CF_3 moiety. The Pt–H, Pt–P, and Pt–C(1) bond distances are comparable to those found in **1**, indicating that the electronic factors are also of the same order.

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Table VI. Relevant Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for **2**

(a) Bond Lengths			
Pt–P	2.287 (2)	C(1)–O	1.30 (1)
Pt–H	1.72 (8)	O–C(2)	1.47 (2)
Pt–C(1)	2.01 (2)	C(2)–C(2)′	1.51 (2)
P–C(3)	1.811 (7)	B–F(1)	1.28 (2)
P–C(9)	1.842 (10)	B–F(2)	1.43 (2)
P–C(15)	1.819 (9)		
(b) Bond Angles			
P′–Pt–C(1)	93.8 (1)	P–C(3)–C(4)	118.7 (7)
P–Pt–H	86 (3)	P–C(9)–C(14)	121.4 (7)
P–Pt–P′	172.3 (1)	P–C(9)–C(10)	120.0 (7)
Pt–P–C(15)	113.3 (3)	P–C(15)–C(20)	117.9 (7)
Pt–P–C(9)	116.7 (3)	P–C(15)–C(16)	124.5 (7)
Pt–P–C(3)	112.2 (3)	Pt–C(1)–O	123.9 (4)
C(9)–P–C(15)	101.5 (4)	O–C(1)–O′	112.2 (5)
C(3)–P–C(15)	106.4 (4)	C(1)–O–C(2)	111.2 (9)
C(3)–P–C(9)	105.6 (4)	O–C(2)–C(21)	103 (1)
P–C(3)–C(8)	121.3 (7)	F(1)–B–F(2)	107.5 (7)

In addition the Pt–carbene bond, with a length of 2.01 (2) Å, may be compared with the Pt–C(carbene) bond distance of 2.002 (2) Å found in the carbene complex *trans*-$[PtCH_3(\overline{COCH_2CH_2CH_2})(PMePh_2)_2]PF_6$[33] in which a methyl group is trans to the carbene. On the other hand the Pt–C(1) distance of **2** is slightly longer than that reported for *trans*-$\{(PPh_3)_2Pt[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}]Br\}BF_4$ (Pt–C = 1.98 (1) Å) where the carbenoid ligand is trans to bromide.[34] The higher trans influence of hydride compared to halide[35] may account for the observed bond lengthening of the Pt–C(carbene) distance in **2**.

The cyclic carbene ligand approaches planarity; the oxygens and the carbons are slightly twisted with respect to the best mean plane calculated through them. The deviations are as follows: C(1), 0.000 (1) Å; O(1), –0.007 (9) Å; C(2), 0.037 (18) Å; C(2)′, –0.037 (18) Å; O(1)′, 0.007 (9) Å. The plane of the carbene intersects the platinum square plane at an angle of 61.3 (2)°.

The C(1)–O bond distance (1.30 (1) Å) is shorter than the C(2)–O distance (1.47 (2) Å), thus suggesting that there is considerable π-interaction between the carbene carbon and its neighboring oxygens. The C(2)–O bond distance is typical of single carbon–oxygen bonds.[36] The C(sp^2)–O distance may be compared with that found in $MnCl(\overline{COCH_2CH_2O})(CO)_4$ (1.31 (2) Å),[37] *cis*-$ReBr(\overline{COCH_2CH_2O})(CO)_4$ (1.303 (16), 1.247 (16) Å)[38] and *trans*-$[PtMe(\overline{COCH_2CH_2CH_2})(PMePh_2)_2]PF_6$ (1.26 (2) Å).[33] In *trans*-$\{PtCl[\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}](PPh_3)_2\}BF_4$, where both oxygen and nitrogen atoms stabilize the carbene carbon, the C(carbene)–O distance is 1.33 (1) Å.[34] Finally, the C(2)–C(2)′ distance of 1.51 (2) Å is comparable to that found in the above-mentioned 2-oxacyclopentylidene Pt(II) complex (1.56 (1) Å), as well as that found in the Mn–cyclic dioxycarbene derivative (1.53 (4) Å)[38] and in the Re–cyclic dioxycarbene complex[38] (1.480 (28) Å).

Registry No. **1**, 64933-37-5; **1***, 117984-73-3; **2**, 95614-97-4; $HOCH_2CH_2OH$, 107-21-1; *trans*-$[PtH(C(OMe)_2)(PPh_3)_2]BF_4$, 95614-95-2; CH_3OH, 67-56-1; *trans*-$[PtH(\overline{COCH_2CH_2CH_2O})(PPh_3)_2]BF_4$, 95614-99-6; $HO(CH_2)_3OH$, 504-63-2; *trans*-$[PtH(\overline{CSCH_2CH_2S})(PPh_3)_2]BF_4$, 95615-01-3; $HSCH_2CH_2SH$, 540-63-6; *trans*-$\{PtH[C(OMe)_2](PBzPh_2)_2\}BF_4$, 117984-62-0; *trans*-$PtH(CF_3)(PBzPh_2)_2$, 117984-63-1; *trans*-$\{PtH[C(OMe)_2](PBz_3)_2\}BF_4$, 117984-65-3; *trans*-$PtH(CF_3)(PBz_3)_2$, 117984-66-4; *trans*-$[PtH(\overline{COCH_2CH_2O})(PCy_3)_2]BF_4$, 117984-68-6; *trans*-$PtH(CF_3)(PCy_3)_2$, 95614-90-7; *trans*-$[PtH[C(OMe)_2](PCy_3)_2]BF_4$, 117984-70-0; *trans*-$[PtH(CO)(PCy_3)_2]BF_4$, 95614-89-4; *trans*-$[PtH(CO)(PPh_3)_2]BF_4$, 33915-37-6; *trans*-$[PtH(CO)(PBz_3)_2]BF_4$, 117984-71-1.

Supplementary Material Available: For **1** and **2**, tables of crystal data, anisotropic thermal parameters for non-hydrogen atoms, and calculated hydrogen positions (5 pages); tables of structure factors (23 pages). Ordering information is given on any current masthead page.

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