Acknowledgment. A.F.H. and K.M. thank the Australian Government for Commonwealth Postgraduate Awards.

Registry No. Hg(pipdtc)$_2$, 21439-62-3; CH$_2$Cl$_2$, 75-09-2; Bu$_4$NClO$_4$, 1923-70-2; Hg, 7439-97-6; Hg$_2$(pipdtc)$_3$]ClO$_4$, 130882-78-9; Hg(NO$_3$)$_2$, 10045-94-0; Na(pipdtc), 873-57-4; Hg$_2$(ClO$_4$)$_2$, 7616-83-3.

Supplementary Material Available: Tables S-I-S-V, listing experimental crystallographic details, hydrogen coordinates, anisotropic themal parameters for Hg and S, isotropic thermal parameters for C, N, O, and Cl, and equations of least-squares planes (7 pages); a listing of structure factor data (11 pages). Ordering information is given on any current masthead page.

Contribution from the Research Laboratory of Resources Utilization and Department of Electronic Chemistry,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Association of a Methylplatinum Fluoroalkoxide Complex with a Fluoro Alcohol through O–H···O Hydrogen Bonding in the Solid State and in Solution

Kohtaro Osakada,*[,1a] Yong-Joo Kim,[1a] Masako Tanaka,[1a] Shin-ichi Ishiguro,[1b] and Akio Yamamoto*[,1a,c]

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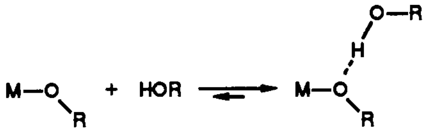
X-ray crystallography of *cis*-PtMe(OCH(CF$_3$)$_2$)(PMe$_3$)$_2$(HOCH(CF$_3$)$_2$ (**1**), which has been prepared by reaction of *cis*-PtMe(OCH(CF$_3$)$_2$(PMe$_3$)$_2$ (**2**) with 1,1,1,3,3,3-hexafluoro-2-propanol, reveals its molecular structure with square-planar coordination and association of the alkoxide ligand with the fluoro alcohol through O–H···O hydrogen bonding. Crystals of **1** are trigonal, space group $P3_1$, with $a = 9.347$ (6) Å, $c = 23.317$ (3) Å, and $Z = 3$. Structure calculation converged to $R = 0.089$ and $R_w = 0.111$ for 2397 reflections with $I \geq 3\sigma(I)$. The short distance between two oxygen atoms in the molecule (2.63 (5) Å) indicates the presence of O–H···O hydrogen bonding between the alkoxide ligand and the associated alcohol. Results of calorimetric titration of complex **2** with 1,1,1,3,3,3-hexafluoro-2-propanol in toluene solutions show formation of **1** as the exclusive adduct of **2** with the alcohol in the solution. Thermodynamic parameters for association, **2** + HOCH(CF$_3$)$_2$ $\rightleftarrows$ **1**, are obtained as $\Delta H° = -24.7$ kJ mol^{-1}, $\Delta S° = -46.0$ J mol^{-1} K^{-1}, and $\Delta G° = -10.9$ kJ mol^{-1} at 25 °C in toluene.

Introduction

Recent studies on alkoxide, aryloxide and hydroxide complexes of group 8–10 metals (Rh, Ru, Ni, Pd, and Pt) revealed their association with alcohols or water through O–H···O hydrogen bonding.[2-6]



(1)

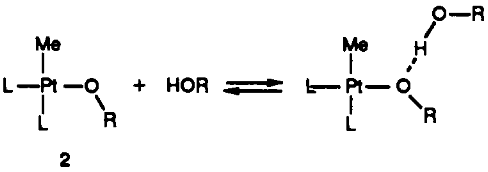
The above equilibrium in the solution is shifted to the right when R is an electron-withdrawing group such as aryl and fluorinated alkyl groups. Several complexes having the alcohol associated through O–H···O hydrogen bonding were isolated as crystals. Studies on chemical properties of these transition-metal alkoxides having hydrogen-bonded alcohol revealed that these compounds were involved as intermediates in associative exchange of the alkoxide group ligated to a late transition metal with alcohol in solution.[5b,7] Comparison of detailed features of the association through O–H···O hydrogen bonding is deemed worthwhile to understand the chemistry of the late-transition-metal alkoxides.

Table I. Crystal Data and Details of Refinement

formula	C$_{13}$H$_{24}$F$_{12}$O$_2$P$_2$Pt$_1$	T, °C	25
mw	697.35	λ, Å	0.710 69
cryst size, mm	0.3 × 0.4 × 0.4	d_{calcd}, g cm^{-1}	1.967
cryst syst	trigonal	μ, cm^{-1}	62.49
space group	$P3_1$[a]	R	0.089
a, Å	9.347 (6)	R_w[b]	0.111
c, Å	23.317 (3)	no. of variables	220
V, Å^3	1767 (2)	no. of observns ($I > 3\sigma(I)$)	2397
Z	3		

[a] See Experimental Section for the determination of the space group.
[b] $\omega = [\sigma(F_o)]^{-2}$.

Previously we reported that *cis*-PtMe(OCH(CF$_3$)$_2$)(PMe$_3$)$_2$ (**2**) reacted with 1,1,1,3,3,3-hexafluoro-2-propanol to give a complex formulated as *cis*-PtMe(OCH(CF$_3$)$_2$)(PMe$_3$)$_2$(HOCH(CF$_3$)$_2$) (**1**).[5a] The IR spectrum of complex **1** (KBr disk) shows a broad peak due to ν(OH) at ca. 2800 cm^{-1}, suggesting formation of hydrogen bonding of the OH group in the associated alcohol with the ligated oxygen atom in the alkoxide ligand. The ^{1}H NMR spectrum of **1** at −40 °C in CD$_2$Cl$_2$ shows a signal at 8.2 ppm due to the OH hydrogen in the alcohol moiety. The exceptionally high chemical shift of the OH proton is also observed in the ^{1}H NMR spectra of the other transition-metal fluoroalkoxides having a hydrogen-bonded fluoro alcohol[3-5] and suggests that the equilibrium shown below is shifted toward the right in the solution.



(2)

2

L = PMe$_3$; R = CH(CF$_3$)$_2$

^{1}H NMR spectra of toluene-d_8 solutions of mixtures of **2** and 1,1,1,3,3,3-hexafluoro-2-propanol in various ratios were measured

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(1) (a) Research Laboratory of Resources Utilization. (b) Department of Electronic Chemistry. (c) Present address: Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ohkubo, Shinjyuku-ku, Tokyo 109, Japan.

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Table II. Fractional Coordinates and Temperature Factors[a]

atom	x	y	z	B_{eq} (or B_{iso}),[b] Å^2
Pt	0.8120 (1)	−0.0407 (1)	0	2.79
P1	0.728 (1)	0.026 (1)	−0.0852 (3)	3.60
P2	0.980 (1)	−0.114 (1)	−0.0389 (4)	4.34
O1	0.655 (3)	0.020 (3)	0.0433 (9)	4.0
O2	0.373 (5)	−0.261 (5)	0.046 (2)	8.5
C1	0.869 (4)	−0.094 (4)	0.080 (1)	4.0
C2	1.105 (6)	0.020 (6)	−0.094 (2)	5.4
C3	0.858 (6)	−0.321 (6)	−0.075 (4)	11.1
C4	1.138 (7)	−0.113 (10)	0.003 (2)	9.9
C5	0.685 (3)	−0.115 (5)	−0.148 (2)	5.4
C6	0.867 (5)	0.233 (5)	−0.114 (1)	4.5
C7	0.545 (4)	0.041 (7)	−0.076 (2)	6.4
C8	0.601 (6)	0.086 (8)	0.132 (2)	8.6
C9	0.709 (4)	0.141 (5)	0.083 (2)	4.7
C10	0.735 (6)	0.290 (5)	0.057 (2)	5.5
C11	0.408 (5)	−0.402 (5)	0.050 (2)	5.0
C12	0.339 (7)	−0.497 (6)	−0.007 (3)	6.8
C13	0.328 (10)	−0.487 (10)	0.108 (4)	11.9
F1	0.639 (5)	0.210 (4)	0.174 (1)	11.2
F2	0.440 (3)	0.060 (4)	0.114 (1)	8.4
F3	0.569 (6)	−0.037 (6)	0.156 (2)	12.9
F4	0.807 (5)	0.412 (4)	0.098 (2)	10.6
F5	0.860 (3)	0.343 (3)	0.016 (1)	6.5
F6	0.628 (5)	0.307 (5)	0.035 (2)	10.9
F7	0.364 (8)	−0.611 (8)	0.108 (3)	16.0
F8	0.161 (6)	−0.573 (6)	0.102 (2)	11.8
F9	0.415 (8)	−0.391 (8)	0.149 (3)	14.8
F10	0.392 (6)	−0.603 (6)	−0.004 (2)	11.1
F11	0.174 (7)	−0.567 (7)	−0.013 (2)	13.7
F12	0.389 (7)	−0.422 (8)	−0.051 (3)	14.7
H20	0.527	−0.358	0.048	5.5

[a] Standard deviations are in parentheses. [b] B_{iso} for C10–C13, F7–F12, and H20.

Table III. Selected Bond Distances and Angles[a]

Distances (Å)			
Pt–C1	2.06 (3)	Pt–O1	2.07 (3)
Pt–P1	2.334 (8)	Pt–P2	2.199 (8)
P1–C5	1.88 (5)	P1–C6	1.83 (4)
P1–C7	1.80 (4)	P2–C2	1.76 (5)
P2–C3	1.89 (5)	P2–C4	1.76 (3)
O1–C9	1.34 (5)	C9–C8	1.45 (6)
C9–C10	1.42 (6)	C8–F1	1.43 (6)
C8–F2	1.45 (7)	C8–F3	1.19 (8)
C10–F4	1.37 (5)	C10–F5	1.40 (5)
C10–F6	1.21 (5)	O1–O2	2.63 (5)
O2–C12	1.51 (6)	C11–C12	1.57 (10)
C11–F7	1.37 (9)	C11–F8	1.35 (10)
C11–F9	1.29 (10)	C13–F10	1.31 (7)
C13–F11	1.35 (7)	C13–F12	1.20 (8)
Pt–C11	3.78 (4)	Pt–H20	3.0
Angles (deg)			
C1–Pt–O1	86 (1)	C1–Pt–P2	89 (1)
C1–Pt–P1	174 (1)	O1–Pt–P2	175.0 (7)
O1–Pt–P1	88.0 (7)	P2–Pt–P1	96.9 (3)
Pt–P1–C7	112 (1)	Pt–P1–C6	116 (1)
Pt–P1–C5	117 (1)	C5–P1–C6	104 (2)
C6–P1–C7	99 (2)	C5–P1–C7	106 (2)
C2–P2–C3	105 (3)	C3–P2–C4	109 (4)
C2–P2–C4	98 (2)	Pt–P2–C2	114 (1)
Pt–P2–C3	110 (1)	Pt–P2–C4	120 (2)
Pt–O1–C9	123 (2)	O1–C9–C10	111 (4)
O1–C9–C8	110 (4)	C8–C9–C10	115 (4)
O2–C11–C13	104 (4)	O2–C11–C12	103 (5)
C12–C11–C13	120 (5)		

[a] Standard deviations are in parentheses.

to obtain equilibrium constants for eq 2. Dependence of the chemical shift of the OH hydrogen on the concentration of the complex agreed with the Scatchard equation.[8a] The ΔH° value for the association was obtained as −21 kJ mol^{-1} at 300 K from the temperature dependence of the equilibrium constants. However, a more accurate value of the enthalpy is expected to be obtained by direct calorimetric measurement.

In this paper, we describe the molecular structure of the alcohol-bonded alkoxide in the solid state and compare the results with its behavior in solution. We discuss further these results in relation to other alcohol-bonded alkoxide complexes.

Experimental Section

All the manipulations of the complexes were carried out under argon. Toluene was dried by Na–benzophenone and distilled under argon prior to use. The other solvents were dried, distilled, and stored under argon. 1,1,1,3,3,3-Hexafluoro-2-propanol was purchased from Tokyo Kasei Co. Complexes **1** and **2** were prepared according to the previously reported procedure.[5a]

X-ray Crystallography. Crystals of **1** suitable for X-ray crystallography were grown in Et_2O containing 1,1,1,3,3,3-hexafluoro-2-propanol (ca. 5% vol/vol) at −20 °C. Crystal data and the details of the structure refinement are summarized in Table I. Systematic absence of diffractions with $l = 3n$ was observed for $(00l)$ diffractions, indicating the space group $P3_1$ (No. 144) or its enantiomorph $P3_2$ (No. 145) for the crystals. Since a large influence due to absorption of the crystals on F_o prevented us from choosing the proper space group among them by comparison of the R values, the $P3_1$ space group was postulated in the structure calculations.

Cell constants were refined by least-squares calculation of setting angles of 20 reflections with $25° < 2\theta < 35°$. Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer at 25 °C. Empirical absorption correction was applied by measuring ψ scans at intervals of 10° around the diffraction vectors of reflections (013), (017), and (027), after all the non-hydrogen atoms were located (transmission range 38–100%). Structure calculations were carried out by using the program TEXSAN[9] on a DEC Micro VAX II. Atomic scattering factors were taken from the literature.[10]

The structure was solved by a combination of Patterson functions and Fourier techniques. Full-matrix least-squares calculations were applied by using isotropic temperature factors for the atoms in the associated alcohol and anisotropic temperature factors for the other non-hydrogen atoms. The hydrogen atom H20 was located at an idealized position with an isotropic temperature factor, and the parameters were not refined.

Calorimetric Titration. Calorimetric measurements were carried out by using a fully automatic on-line calorimetry system, in a room thermostated at 25 ± 0.2 °C.[11] Toluene solutions of **2** were titrated with 0.102 and 0.182 mM 1,1,1,3,3,3-hexafluoro-2-propanol solutions. A solution (40 mL) containing **2** was placed in a stainless-steel vessel, the inside of which was coated with Teflon. The vessel filled with argon gas was inserted in an aluminum block thermostated at 25.0 ± 0.0001 °C in an air bath. Portions of the 1,1,1,3,3,3-hexafluoro-2-propanol solution were added to this solution from an autoburet (APB-118, Kyoto Electronics). Heats of association at each titration point were measured with a certainty of ±0.02 J and corrected for heat of dilution of the titrant. The heat of dilution had been determined in advance by separate experiments and was found to be very small.

Data Analysis. Formation of **1** through association of **2** and 1,1,1,3,3,3-hexafluoro-2-propanol can be defined as in eq 3. The heat

$$\mathbf{2} + \mathrm{HOR} \rightleftharpoons \mathbf{1} \qquad (3)$$

$$K = [\mathbf{1}]/[\mathrm{HOR}][\mathbf{2}] \qquad (4)$$

$$\mathrm{HOR} = 1,1,1,3,3,3\text{-hexafluoro-2-propanol}$$

q_i measured at the ith titration point is expressed by formation constant K and enthalpy ΔH° where V_i denotes the volume of the test solution (eq 5). The concentrations of **2** and unassociated alcohol are related to the

$$q_i = -K\Delta H^\circ(V_i[\mathbf{2}]_i[\mathrm{HOR}]_i - V_{i-1}[\mathbf{2}]_{i-1}[\mathrm{HOR}]_{i-1}) \qquad (5)$$

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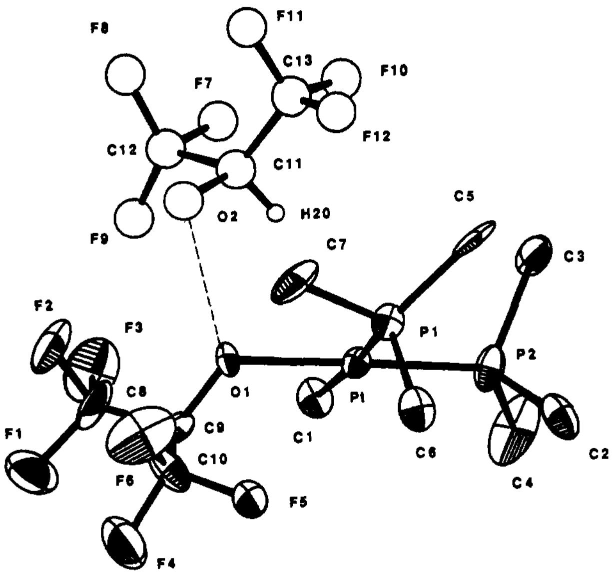

Figure 1. Molecular structure of **1** showing the atom labeling. Atoms of the methylplatinum alkoxide entity are shown as 30% probability thermal motion ellipsoids. Isotropic temperature factors are applied for the atoms in the hydrogen-bonded alcohol. See text.

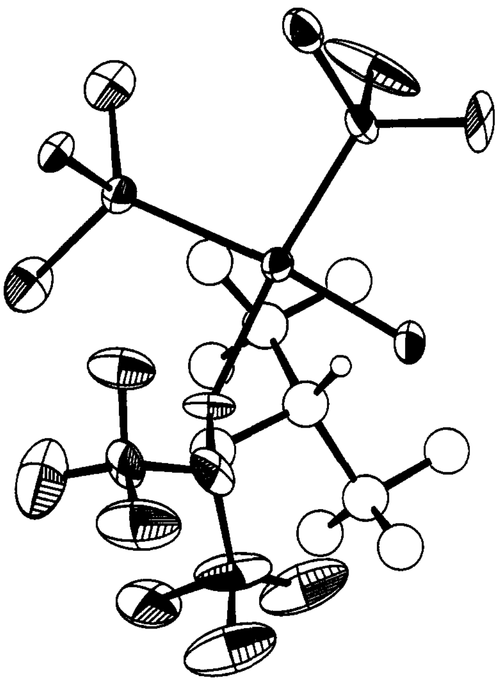

Figure 2. Structure of **1** viewed vertically to the coordination plane.

total concentrations, $C_{\mathrm{Pt},i}$, and $C_{\mathrm{HOR},i}$, respectively, according to the mass balance equations

$$C_{\mathrm{Pt},i} = [\mathbf{2}]_i + K[\mathbf{2}]_i[\mathrm{HOR}]_i \tag{6}$$

$$C_{\mathrm{HOR},i} = [\mathrm{HOR}]_i + K[\mathbf{2}]_i[\mathrm{HOR}]_i \tag{7}$$

Formation constants and enthalpies were determined simultaneously by minimizing $U = \sum(q_{i,\mathrm{obsd}} - q_{i,\mathrm{calcd}})^2$, and a nonlinear least-squares program according to an algorithm proposed by Marquardt was used.[12]

Results and Discussion

Structural Characterization of Complex 1. Figures 1 and 2 show the molecular structure of complex **1** revealed by X-ray crystallography. The molecule has a distorted square-planar coordination around the platinum center. The Pt–O bond distance (2.07 (3) Å) in **1** is similar to that of the already reported complex **2** without the associated alcohol (2.07 (1) Å).[5a] The Pt–C bond (2.06 (3) Å) in **1** is shorter than that in **2** (2.13 (2) Å. The O–C bond in **1** is 1.34 (5) Å, which is shorter than the C–O single-bond distances observed in organic compounds. Similar short distances of the C–O bonds in the alkoxide ligand have been reported in the crystal structures of Pt(Me)(OMe)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane), Pt(OMe)$_2$(dppe),[7] and **2**.[5a] The Pt–O–C angle of **1** is 123 (2)° and seems to be somewhat smaller than the corresopnding angle in **2** (125.3 (9)°).[5a] Previously we reported that *trans*-PdMe(OPh)(PMe$_3$)$_2$(HOPh) showed a considerably smaller Pd–O–C angle (121.4 (3)°) in the phenoxide ligand than the corresponding angle of *trans*-PdMe(OPh)(PMe$_3$)$_2$ (127.1 (3)°).

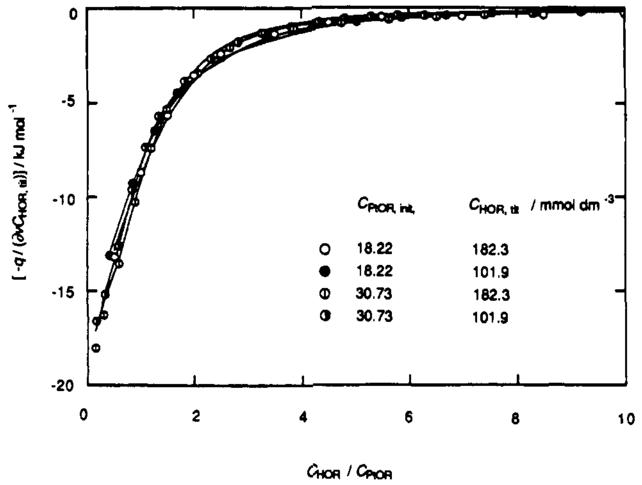

Figure 3. Calorimetric titration curves for the **2**-HOCH(CF$_3$)$_2$ system obtained in toluene at 25 °C. Concentrations of **2** and HOCH(CF$_3$)$_2$ in initial test solutions, $C_{\mathrm{PtOR,init}}$/mmol dm^{-3} and $C_{\mathrm{HOR,init}}$/mmol dm^{-3}, are given. The solid lines are calculated by using constants in Table IV.

The Pt–P1 bond between the platinum center and the PMe$_3$ ligand trans to the methyl ligand (2.334 (8) Å) is considerably longer than the Pt–P2 bond between the platinum and the PMe$_3$ ligand cis to the methyl group (2.199 (8) Å), reflecting the larger trans influence of the methyl ligand than that of the alkoxide. The P–Pt–P angle is larger than 90° probably due to larger steric repulsion between the two PMe$_3$ ligands than that between the PMe$_3$ ligand and the methyl or the alkoxide ligand.

The distance between two oxygen atoms in the molecule is 2.63 (5) Å which is reasonable as a O···O distance with the O–H···O hydrogen bonding by comparison with the corresonding O···O distances reported in organic molecules having the hydrogen bonding.[8b] Thus, although the OH hydrogen of the associated alcohol is not located from the difference Fourier map, there remains little doubt regarding the presence of the O–H···O hydrogen bonding between the alkoxide ligand and the alcohol in the solid state. The above O···O distance is quite similar to those reported recently in the other transition-metal phenoxide complexes having phenol associated through O–H···O hydrogen bonding such as *trans*-PdH(OPh)(PCy$_3$)$_2$(HOPh) (PCy$_3$ = tricyclohexylphosphine), Rh(OC$_6$H$_4$-*p*-Me)(PMe$_3$)$_3$(HOC$_6$H$_4$-*p*-Me), *trans*-NiMe(OPh)(PMe$_3$)$_2$(HOPh), and *trans*-PdMe(OPh)(PMe$_3$)$_2$(HOPh) (2.59–2.62 Å).[2-4]

Molecule of **1** shows 3.78 (4) Å of Pt···C11 distance between the CH carbon atom of the associated alcohol and the metal center. The position of the hydrogen calculated on the basis of ideal geometry (d(C–H) = 0.95 Å) is 3.0 Å from the platinum center. These d(Pt···C) and d(Pt···H) distances are almost equal to the sum of the van der Waals radii of these atoms.[13] As shown in Figure 2 the C–H bond is oriented toward the middle of the Pt–C1 bond. From these results, there seems to be very little interaction between the CH group and the platinum atom in the molecule.

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[12] Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

[13] Van der Waals radii of Pd and Pt were estimated as 1.6 and 1.8 Å, respectively. See: (a) Huheey, J. E. *Inorganic Chemistry*; Harper & Row Pub. Inc.: New York, 1983; p 323. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table IV. Least-Squares Refinement of Formation Constant log *K* and Thermodynamic Parameters of the **2**–$HOCH(CF_3)_2$ System in Toluene at 25 °C

log K	1.93 (0.04)[a]	U[b]	0.130
$\Delta H°$, kJ mol^{-1}	-24.7 (0.2)	R[c]	0.048
$\Delta G°$, kJ mol^{-1}	-10.9	N[d]	59
$\Delta S°$, J mol^{-1} K^{-1}	-46.0		

[a] Values in parentheses refer to 3 standard deviations. [b] Error-square sum. [c] The Hamilton *R* factor. [d] The number of calorimetric data points.

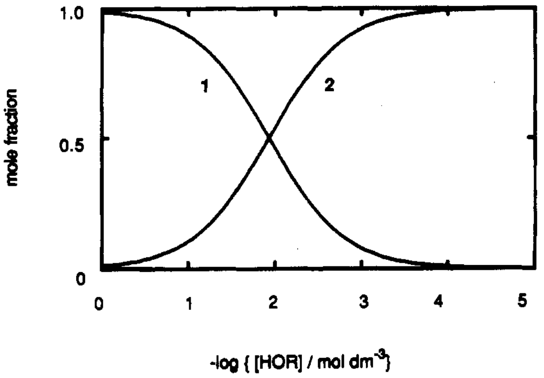

Figure 4. Distribution of complexes in the **2**–$HOCH(CF_3)_2$ system in toluene at 25 °C.

A more obvious attractive interaction of CH and NH hydrogens with d^8 metal centers of the complexes having square planar coordinations has been reported in the crystal structures of *trans*-$PdBr(CR{=}CRCR{=}CHR)(PPh_3)_2$ (R = COOMe) (d(Pd···H) = 2.3 Å)[14] and *trans*-$PtH(NHPh)(PEt_3)_2$ (d(Pt···H) = 2.96 Å).[15]

Calorimetric Measurement of the Association of the Alcohol with 2. The calorimetric titration curves obtained with the mixtures of **2** and 1,1,1,3,3,3-hexafluoro-2-propanol are shown in Figure 3. The heat of reaction, q_i, measured at each titration point is normalized with the volume of the titrant added, δv_i, and the concentration of the alcohol in the titrant, $C_{HOR,tit}$. The term $-q_i[(\delta v_i)C_{HOR,tit}]^{-1}$ is plotted against $C_{HOR,i}/C_{Pt,i}$ where $C_{HOR,i}$ and $C_{Pt,i}$ denote the total concentrations of the alcohol and the complex, respectively, in solution. The titration curves are well explained in terms of the formation of **1**. The formation constant of **1**, *K*, and the enthalpy obtained are summarized in Table IV. The solid lines in Figure 3, calculated by using the constants in Table IV, well reproduce the experimental points. Figure 4 shows the species distribution of **1** and **2**, calculated from the obtained equilibrium constant, as a functional logarithm of free alcohol concentration. Further association of **1** with the alcohol to give $PtMe(OCH(CF_3)_2)(PMe_3)_2(HOCH(CF_3)_2)_2$ in the solution may be virtually negligible under the experimental conditions examined as the introduction of the species with least-squares calculations did not significantly reduce the *R* factor.

The above thermodynamic parameters were obtained for concentrations of the initial solutions of **2** of 30.7 and 18.2 mM. However, the experimental points obtained for lower concentrations of the complexes (5.1 and 10.2 mM) slightly deviated from the curves calculated by using the constants (Table IV), suggesting that some unexpected reactions occur in the system at low concentrations of the complexes (<10 mM). Although we do not have sufficient evidence, dissociation of the alkoxide or PMe_3 ligand to some extent might be responsible for the behavior.

Previously, we have estimated the enthalpy of reaction 2 in toluene-d_8 as -21 kJ mol^{-1} based on the ^1H NMR measurement of the equilibrated mixtures.[5a] This value is comparable to the value obtained in the present study (-24.7 kJ mol^{-1}). The difference between these two values is considered to be mainly due to experimental errors in the NMR study because it involves inevitable errors in determination of the chemical shift of the broad OH hydrogen signals and in measurement of the temperature of the NMR sample solution.[16] We have obtained the enthalpies of association of *trans*-$PdMe(OPh)(PMe_3)_2$ and PdMe(OPh)(dmpe) (dmpe = 1,2-bis(dimethylphosphino)ethane) with phenol as -23 and -17 kJ mol^{-1}, respectively, at 300 K in CD_2Cl_2 by NMR spectroscopy.[5b] Poor solubility of these palladium complexes in hydrocarbons prevented us from obtaining thermodynamic parameters for the association in hydrocarbons in which more negative enthalpy values are expected. The enthalpy values obtained with palladium and platinum complexes having fluoroalkoxide and phenoxide complexes are in the range of those with intermolecular O–H···O hydrogen bonding of aliphatic alcohols (-12 to -25 kJ mol^{-1}). Previously Bergman and his co-workers reported the association enthalpy of $Rh(OC_6H_4\text{-}p\text{-}Me)(PMe_3)_3$ with *p*-cresol in cyclohexane as -58.6 kJ mol^{-1}, which is comparable to that of alkoxide anion with alcohol.[3]

Conclusion

The crystallographic study of **1** unambiguously established its molecular structure as having an O–H···O hydrogen bonding in the solid state. The O···O distance is 2.63 Å, which is quite similar to those of the rhodium and palladium aryloxide complexes having associated phenols already reported. Results of calorimetric titration of **2** with $HOCH(CF_3)_2$ confirmed formation of **1** as an exclusive adduct of **2** and the alcohol. Thermodynamic parameters obtained agreed with the values obtained in the previous study by means of NMR spectroscopy. Enthalpies of association of the similar transition-metal alkoxide complexes with alcohols vary in a wide range depending on the kind of the metal center and the alcohol as well as on the structures of the complexes.

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Supplementary Material Available: Table S1 (anisotropic thermal factors) and Table S2 (bond distances and angles) (3 pages); Table S3 (observed and calculated structure factors) (17 pages). Ordering information is given on any current masthead page.

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(16) NMR studies in ref 5a were carried out with concentrations of the complexes at 90–250 mM that are much higher than the concentration range below 10 mM where anomalies in the thermodynamic parameters were obtained in the calorimetric measurement. The thermodynamic parameters obtained by the NMR spectroscopy are free from serious errors observed in the results of calorimetric measurements that are carried out with low concentrations of the complexes (5.1 and 10.2 mM).