Journal of Organometallic Chemistry, 382 (1990) 303–317
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20246

Preparation and properties of methylplatinum fluoroalkoxide and phenoxide complexes, $PtMe(OR)(PMe_3)_2$ and $PtMe(OR)(HOR)(PMe_3)_2$ ($R = CH(CF_3)_2, C_6H_5$) *

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(Received May 17th, 1989)

Abstract

Reactions of *cis*-$PtMe_2(PMe_3)_2$ with 1,1,1,3,3,3-hexafluoro-2-propanol in 1/1 and 1/2 ratios give *cis*-$PtMe(OCH(CF_3)_2)(PMe_3)_2$ (**1**) and its hydrogen-bonded alcohol adduct, *cis*-$PtMe(OCH(CF_3)_2)(HOCH(CF_3)_2)(PMe_3)_2$ (**2**), respectively. Complex **2** undergoes exchange of the fluoroalkoxide ligand on addition of phenol to give *cis*-$PtMe(OC_6H_5)(PMe_3)_2$ (**3**) or its phenol adduct, *cis*-$PtMe(OC_6H_5)(HOC_6H_5)(PMe_3)_2$ (**4**), depending on the ratio of added phenol to the complex. IR and NMR data of **2** and **4** indicate the presence of O–H ··· O hydrogen bonding between the alkoxide (or phenoxide) ligand and the associated alcohol (or phenol) both in the solid state and in solution. Thermodynamic parameters for the association of the $HOCH(CF_3)_2$ with **1** in toluene have been obtained by means of ^1H NMR spectroscopy as $\Delta H°$ -5.1 kcal mol^{-1}, $\Delta G°$ -2.6 kcal mol^{-1}, and $\Delta S°$ -9.1 e. u. at 273 K. Reaction of **1** with CO at room temperature gives *cis*-$PtMe(COOCH(CF_3)_2)(PMe_3)_2$ (**7a**) produced through CO insertion into the Pt–O bond as confirmed by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. The *cis* complex **7a** is isomerized into *trans*-$PtMe(COOCH(CF_3)_2)(PMe_3)_2$ (**7b**) under the reaction conditions. Reaction of the phenoxide complex **3** with CO does not cause insertion of CO into the Pt–O bond, and gives *trans*-$PtMe(OPh)(PMe_3)_2$.

Introduction

The chemistry of late transition metal alkoxides [1] is recently attracting growing attention partly because of their relevance to organic synthesis where late transition metal alkoxides are believed to be involved [2–11] and partly because of their

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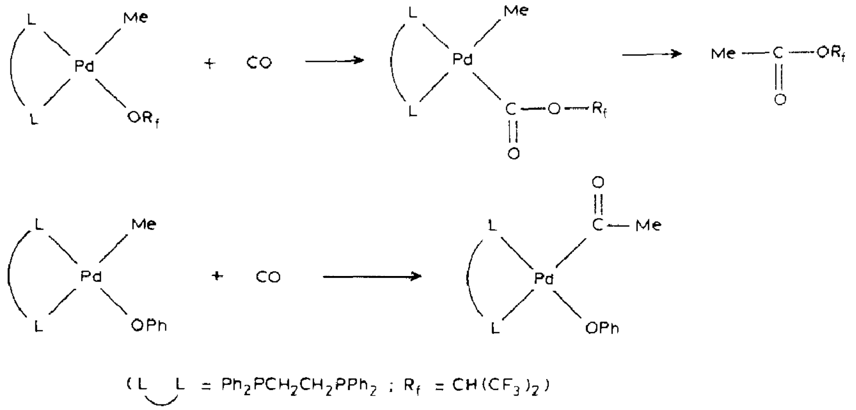
* Dedicated to Professor G. Wilke on the occasion of his 65th birthday.

0022-328X/90/\$03.50

recently discovered unique chemical reactivities such as CO insertion into metal–alkoxide bonds [12a,13,14a,14c,15b,16,17] and adduct formation with alcohols through strong hydrogen bonding [18,19,20b].

In the course of our study on the chemistry of methylpalladium alkoxides we have observed that methylpalladium fluoroalkoxide complexes undergo CO insertion into the Pd–O bond whereas methylpalladium phenoxide complexes do not undergo the CO insertion into the Pd–phenoxide bond but rather give the CO insertion product into the Pd–methyl bond (eq. 1, 2) [20a,21].

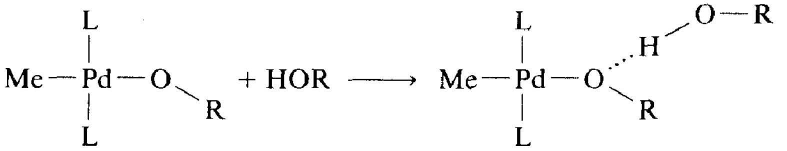


(1)

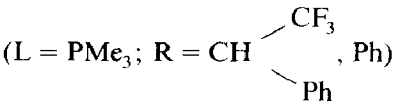
(2)

(L L = $Ph_2PCH_2CH_2PPh_2$; R_f = $CH(CF_3)_2$)

As another intriguing feature of the palladium alkoxide complexes strong hydrogen-bond formation has been observed between methylpalladium fluoroalkoxide or aryloxide complexes and acidic fluoroalcohol or phenol (eq. 3) [20b].



$$\mathrm{Me{-}\overset{\displaystyle L}{\underset{\displaystyle L}{Pd}}{-}O{\diagdown}R} + \mathrm{HOR} \longrightarrow \mathrm{Me{-}\overset{\displaystyle L}{\underset{\displaystyle L}{Pd}}{-}O(\cdots H{-}OR){\diagdown}R} \qquad (3)$$



$$(\mathrm{L = PMe_3;\ R = CH(CF_3)(Ph),\ Ph})$$

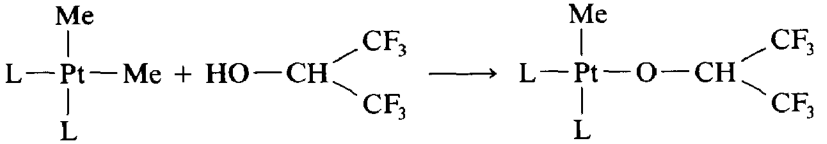
Similar behavior has been observed with their nickel analogs.

It is the purpose of the present study to prepare methylplatinum fluoroalkoxide and phenoxide analogs to provide a complete alkoxide set of the nickel, palladium and platinum triad and to compare their properties with those of the known platinum methoxide which has been studied into some details [12–15,22,23].

Results and Discussion

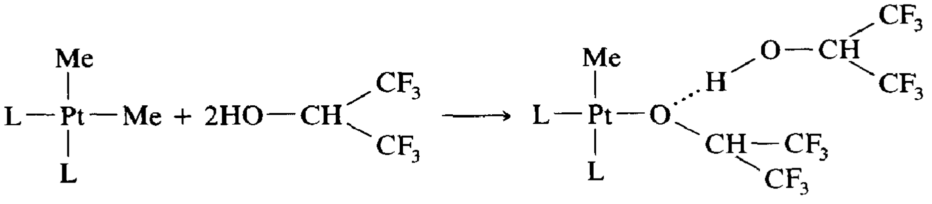
Preparation and characterization of the methylplatinum alkoxide and phenoxide complexes

cis-$PtMe_2(PMe_3)_2$ reacts with an equimolar amount of $(CF_3)_2CHOH$ at room temperature to give *cis*-$PtMe(OCH(CF_3)_2)(PMe_3)_2$ (**1**) which has been characterized by elemental analysis, IR and NMR spectroscopy, and X-ray crystallography (eq. 4). Reaction of *cis*-$PtMe_2(PMe_3)_2$ with two equivalents of the alcohol gives *cis*-$PtMe(OCH(CF_3)_2)(HOCH(CF_3)_2)(PMe_3)_2$ (**2**) in which associated alcohol is linked with the alkoxide ligand through an O–H ··· O hydrogen bonding (eq. 5).



(4)

(1)



(5)

(2)

(L = PMe$_3$)

Previously *trans*-$PtH_2(PMe_3)_2$ was reported to react with a large excess of methanol to give $[Pt(PMe_3)_2(\mu\text{-}H)_2Pt(PMe_3)_2H]OCH_3$ through an intermediary methoxide platinum complex, $HPt(OMe)(PMe_3)_2$ [23]. In the above reaction (eq. 4) $(CF_3)_2CHOH$, being more acidic than methanol, reacts readily with *cis*-$PtMe_2(PMe_3)_2$ to give the methylplatinum alkoxide complex even when only an equimolar amount of the alcohol was used. However, reaction of *cis*-$PtMe_2(PMe_3)_2$ with two equivalents of less acidic $HOCH(CF_3)Ph$ was so slow that it did not give platinum complexes with 2,2,2-trifluoro-1-phenylethoxide ligand.

Tables 1, 2, and 3 summarize elemental analyses and NMR data (^1H, ^{31}P, and ^{13}C) of **1** and **2**. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** show two doublets with Pt satellites in agreement with the proposed cis configurations having two nonequivalent PMe_3 ligands in the complexes. The low-field doublet signals of **1** and **2** flanked with Pt satellite signals with $J(^{195}Pt-^{31}P)$ values of 1899 and 1811 Hz,

Table 1

Melting points and analytical data of methylplatinum alkoxide complexes 1–6

Complex	M.p. (°C) [a]	Analysis (Found (calcd.) (%))	
		C	H
cis-$PtMe(OCH(CF_3)_2)(PMe_3)_2$ (1)	141–145	22.2 (22.4)	3.6 (3.5)
cis-$PtMe(OCH(CF_3)_2)(HOCH(CF_3)_2)(PMe_3)_2$ (2)	112–123	22.8 (22.7)	4.6 (4.2)
cis-$PtMe(OC_6H_5)(PMe_3)_2$ (3)	167–171	33.4 (34.3)	5.9 (5.8)
cis-$PtMe(OC_6H_5)(HOC_6H_5)(PMe_3)_2$ (4)	151–156	41.0 (41.5)	6.1 (5.9)
trans-$PtMe(OC_6H_5)(HOC_6H_5)(PMe_3)_2$ (5)	162–167	41.2 (41.5)	5.9 (5.9)
cis-$PtMe(OC_6H_4\text{-}OMe)(HOC_6H_4\text{-}OMe)(PMe_3)_2$ (6)	126–132	40.5 (41.4)	6.0 (6.0)

[a] Decomposed.

Table 2

^{1}H NMR data of complexes **1**–**6** [a]

Complex	Pt–CH_3	P–CH_3		OH	Others
1	0.16(dd) J(PH) 7 and 3 Hz J(PtH) 50 Hz	1.27(d) J(PH) 9 Hz J(PtH) 16 Hz	1.45(d) J(PH) 11 Hz J(PtH) 42 Hz		4.50(m) [b]
2	0.27(dd) J(PH) 7 and 3 Hz J(PtH) 50 Hz	1.30(d) J(PH) 9 Hz J(PtH) 17 Hz	1.50(d) J(PH) 11 Hz J(PtH) 46 Hz	8.16(s)	4.38(m) [b] 4.91(m) [c]
3	0.39(dd) J(PH) 8 and 4 Hz J(PtH) 55 Hz	1.34(d) J(PH) 9 Hz J(PtH) 17 Hz	1.56(d) J(PH) 11 Hz J(PtH) 42 Hz		
4	0.43(dd) J(PH) 10 and 4 Hz J(PtH) 53 Hz	1.32(d) J(PH) 9 Hz J(PtH) 17 Hz	1.57(d) J(PH) 11 Hz J(PtH) 44 Hz	11.32(s)	
5	0.32(t) J(PH) 7 Hz J(PtH) 81 Hz	1.25 [d] J(PtH) 30 Hz		10.54(s)	
6	0.42(dd) J(PH) 8 and 3 Hz J(PtH) 53 Hz	1.32(d) J(PH) 9 Hz J(PtH) 17 Hz	1.56(d) J(PH) 11 Hz J(PtH) 45 Hz	11.03(s)	3.67(s) [e] 3.64(s)

[a] 100 MHz at $-40\,^\circ$C in CD_2Cl_2. Abbreviations: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. [b] CH hydrogen of the alkoxide ligand. [c] CH hydrogen of the associated alcohol. [d] Observed as a triplet due to virtual coupling. Apparent splitting is 4 Hz. [e] OMe hydrogens.

respectively, are assigned to those of PMe_3 ligands which are situated at the position trans to the methyl ligand by comparison of the J values with those of other alkyl platinum complexes. The $J(^{195}Pt-^{31}P)$ values of 3867 and 3891 Hz for **1** and **2** of the PMe_3 ligand *trans* to the alkoxide ligand are similar to the corresponding J values of PtMe(OMe)(dpe) and related compounds [12b]. The difference in $J(^{195}Pt-^{31}P)$ values between two kinds of PMe_3 ligands in **1** and **2** is attributed to the larger trans influence of the methyl ligand than that of the fluoroalkoxide ligand. The ^{1}H NMR spectra of complexes **1** and **2** (Table 2) show signals due to Pt–CH_3 hydrogens at 0.1–0.3 ppm as doublets of doublets which are flanked with ^{195}Pt satellite signals. The signals arising from $P(CH_3)_3$ hydrogens appear as two doublets with satellites, indicating the presence of two nonequivalent PMe_3 ligands. Of the two signals in both complexes the doublet at 1.27 ppm in **1** and at 1.30 ppm in **2**, respectively, show smaller $J(^{195}Pt-^{1}H)$ values than the other doublets, and are assigned to PMe_3 ligands at a trans position to the methyl ligand. Signals due to Pt–CH_3 and $P(CH_3)_3$ carbons in $^{13}C\{^1H\}$ NMR spectra (Table 3) show chemical shifts and coupling constants which are consistent with the proposed structures of the complexes.

The ^{1}H NMR spectrum of **2** at $-40\,^\circ$C shows two signals due to OCH hydrogens at 4.38 and 4.91 ppm, respectively. The former signal is assigned to that of the fluoroalkoxide ligand by comparison with the chemical shift of the corresponding signal of **1**. A signal due to the OH hydrogen of **2** appears at 8.16 ppm, which is at considerably lower field than that of free $(CF_3)_2CHOH$ (3.3 ppm in CD_2Cl_2). A similar large shift of the OH hydrogen of the associated alcohols to the lower field has been observed also in Rh, Ni, and Pd complexes with fluoroalcohol

Table 3

^{31}P and ^{13}C NMR data of complexes **1**–**7b**

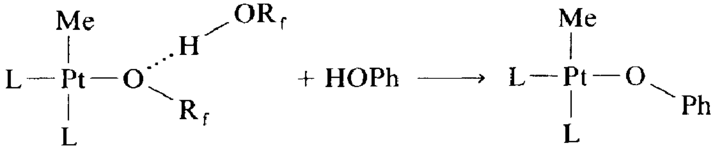
Complex	^{31}P{^{1}H} [a]		^{13}C{^{1}H} [b]				
			Pt–CH$_3$	P–CH$_3$		Others	
1	1.0 *J*(PP) 14 Hz *J*(PtP) 1889 Hz	−25.6 *J*(PtP) 3867 Hz	5.86(dd) *J*(PC) 95, 8 Hz *J*(PtC) 551 Hz	13.96(d) *J*(PC) 29 Hz *J*(PtC) 22 Hz	16.53(dd) *J*(PC) 30, 2 Hz *J*(PtC) 56 Hz	73.19(sep) [c] *J*(CF) 30 Hz	124.20(q) [d] *J*(CF) 288 Hz
2	−0.4 *J*(PP) 14 Hz *J*(PtP) 1811 Hz	−25.1 *J*(PtP) 3891 Hz	6.67(dd) *J*(PC) 93, 8 Hz *J*(PtC) 551 Hz	13.76(d) *J*(PC) 29 Hz *J*(PtC) 22 Hz	15.60(dd) *J*(PC) 45, 3 Hz *J*(PtC) 56 Hz	75.30(sep) [c] *J*(CF) 30 Hz 67.30(sep) [e] *J*(CF) 32 Hz	122.40(q) [d] *J*(CF) 288 Hz 122.10(q) [f] *J*(CF) 281 Hz
3	2.0 *J*(PP) 12 Hz *J*(PtP) 1703 Hz	−28.1 *J*(PtP) 3887 Hz					
4	−1.5 *J*(PP) 12 Hz *J*(PtP) 1727 Hz	−26.6 *J*(Ptp) 3887 Hz					
5	−1.0(s) *J*(PtP) 2813 Hz						
6	−0.1(d) *J*(PP) 12 Hz *J*(PtP) 1728 Hz	−25.1(d) *J*(PtP) 3859 Hz					
7a [g]	17.1(d) *J*(PP) 22 Hz *J*(PtP) 1779 Hz	−20.4(d) *J*(PtP) 2252 Hz	−8.50(dd) *J*(PC) 78, 8 Hz *J*(PtC) 498 Hz	14.73(dd) *J*(PC) 34, 2 Hz *J*(PtC) 90 Hz	17.10(dd) *J*(PC) 31, 2 Hz *J*(PtC) 31 Hz	61.29(m) [h]	196.20(dd) [i] *J*(PC) 177, 12 Hz *J*(PtC) 1313 Hz
7b [g]	−11.0(s) *J*(PtP) 2566 Hz		−12.3(br) [j]	13.82(t) *J*(PC) 19 Hz *J*(PtC) 80 Hz		61.1(br) [j]	

[a] 40 MHz in CD$_2$Cl$_2$ at −40 °C; ppm downfield positive to external PPh$_3$. [b] 68.5 MHz or 25 MHz in CD$_2$Cl$_2$ at −40 °C. [c] OCH carbon of the alkoxide ligand. [d] CF$_3$ carbon of the alkoxide ligand. [e] OCH carbon of the associated alcohol. [f] CF$_3$ carbon of the associated alcohol. [g] Spectra of a mixture of **7a** and **7b** were observed in the reaction mixture of 1 with CO (and ^{13}CO). See text. [h] Coupling constant was not obtained due to overlapping with signal of **7b**. [i] Pt–COOR$_f$ carbon. [j] Precise chemical shifts and coupling constants were not obtained due to broadening.

(or phenol) moiety associated with the alkoxide (phenoxide) ligand through strong O–H · · · O hydrogen bonding [18,19,20b].

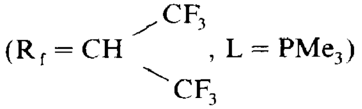
The IR spectrum of complex **2** in the solid state (KBr disk) shows a broad band due to ν(OH) vibration at 3070 cm^{-1}, while **1** shows no peak in the region. The peak is at a similar wavenumber to the peak of ν(OH) vibration of aliphatic alcohol which has O–H · · · O hydrogen bonding with each other, and higher than the corresponding peak of *trans*-PdMe(OR)(HOR)(PMe$_3$)$_2$ (R = CH(CF$_3$)Ph, Ph, C$_6$H$_4$-*p*-Me) (2300–2700 cm^{-1}). All these results suggest that complex **2** has O–H · · · O hydrogen bonding in the solid state and in solution.

Complex **2** reacts with an equimolar amount of phenol to give *cis*-PtMe(OPh)(PMe$_3$)$_2$ (**3**), which is produced through exchange of the alkoxide ligand with phenoxide group, as a crystalline product in a 41% yield.



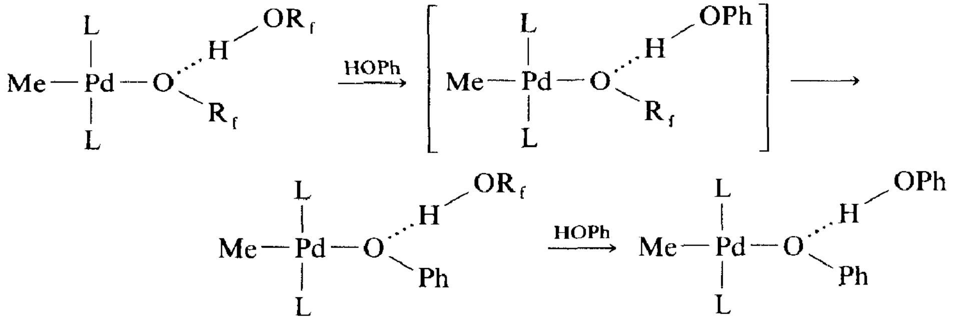
(6)

(**2**) (**3**)



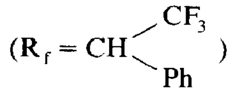
$$(\mathrm{R_f} = \mathrm{CH}\begin{smallmatrix}\mathrm{CF_3}\\ \\ \mathrm{CF_3}\end{smallmatrix}, \ \mathrm{L} = \mathrm{PMe_3})$$

Previously we observed that the fluoroalkoxide ligand in the methylpalladium fluoroalkoxide having hydrogen-bonded alcohol was readily replaced by the phenoxide ligand on treatment of the palladium complex with phenol. The displacement reaction proceeded stepwisely to give the intermediate alcohol-bonded palladium phenoxide and further to phenol-bonded palladium phenoxide depending on the amount of phenol added to the system [20b].



(7)

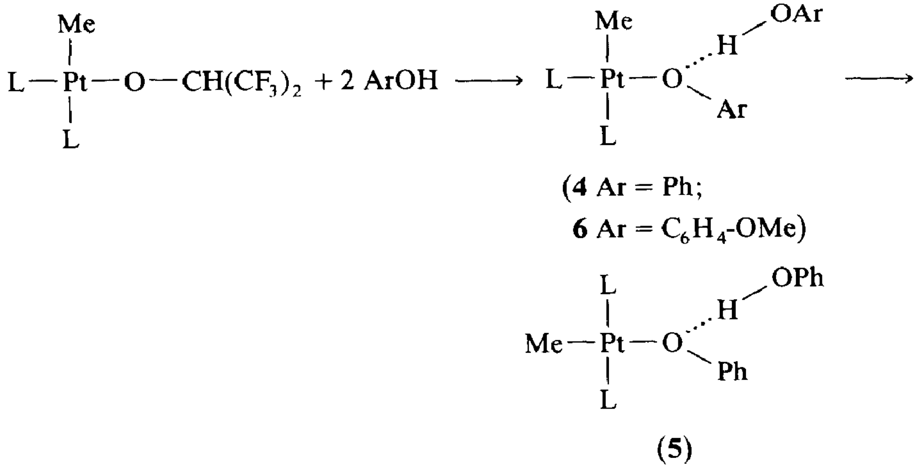
(isolable) (isolable)



$$(\mathrm{R_f} = \mathrm{CH}\begin{smallmatrix}\mathrm{CF_3}\\ \\ \mathrm{Ph}\end{smallmatrix})$$

The low isolated yield of the non-associated methylplatinum phenoxide suggested involvement of other species as we observed in the reaction of the palladium analog and led us to examine the reaction mixture of **2** with phenol with ^{1}H NMR spectroscopy. The study revealed the presence of some alcohol-bonded species rapidly exchanging in the solution. Isolation of the alcohol-free methylplatinum phenoxide **3** as the sole product in eq. 6 may be due to its low solubility in the reaction solution.

Reaction of **1** with two equivalents of phenol gives *cis*-PtMe(OPh)(HOPh)$(PMe_3)_2$ (**4**), which has been characterized by NMR and IR spectra as well as elemental analyses. Prolonged reaction causes partial isomerization of **4** to *trans*-PtMe(OPh)(HOPh)$(PMe_3)_2$ (**5**). Heating a toluene solution of isolated **4** at 80 °C for 6 h causes complete transformation of **4** to **5**.



(**4** Ar = Ph;
6 Ar = C_6H_4-OMe)

(**5**)

(8)

cis-PtMe$(OC_6H_4OMe)(HOC_6H_4OMe)(PMe_3)_2$ (**6**) is obtained similarly from the reaction of **1** with two equivalents of anisole. These complexes **4**, **5**, and **6** have O–H···O hydrogen bonding in their molecules as revealed by NMR (δ(OH) 10.5–11.3 ppm) and IR spectra (ν(OH) 2400–2600 cm^{-1}).

X-ray crystallography of complexes 1 and 3

Figures 1 and 2 show molecular structures of complexes **1** and **3** as determined by X-ray crystallography. Crystal data and bond distances and angles are summarized in Tables 4 and 5. Complexes **1** and **3** have distorted square planar coordination

(*continued on p. 312*)

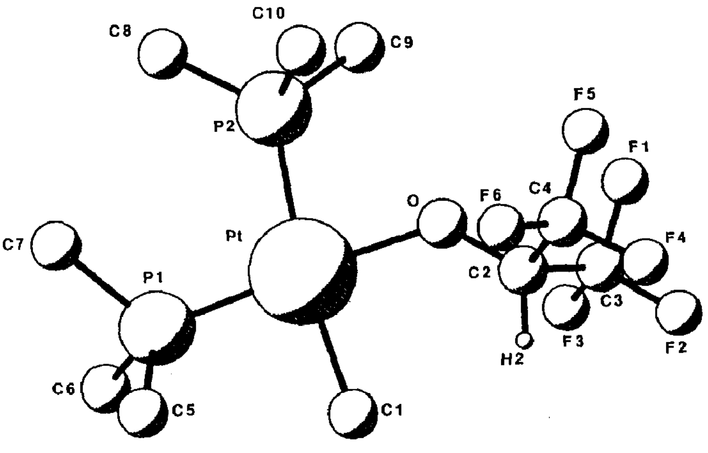


Fig. 1. PLUTO drawing of *cis*-PtMe$(OCH(CF_3)_2)(PMe_3)_2$ (**1**).

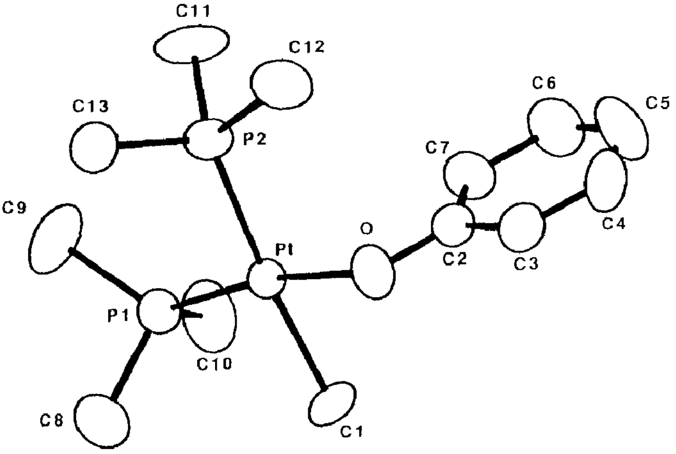


Fig. 2. ORTEP drawing of *cis*-PtMe(OPh)(PMe$_3$)$_2$ (**3**), showing 50% probability thermal motion ellipsoid.

Table 4

Crystal data, details of intensity measurements and structure refinement for complexes **1** and **3**

	1	**3**
Formula	$C_{10}H_{22}OP_2F_6Pt$	$C_{13}H_{26}OP_2Pt$
Mw	529.33	455.39
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1$
a (Å)	12.056(3)	9.0881(9)
b (Å)	16.938(3)	11.557(1)
c (Å)	9.156(3)	8.107(1)
β (deg)	104.91(2)	100.66(1)
V (Å^3)	1806.7(8)	836.8(2)
Z	4	2
$F(000)$	1008	440
μ (cm^{-1})	80.68	86.46
d_{cal} (g cm^{-3})	1.947	1.808
d_{obs} (g cm^{-3}) [a]	1.91	1.80
Crystal size (mm × mm × mm)	0.12 × 0.40 × 0.58	0.15 × 0.28 × 0.30
2θ range (deg)	3.0–45.0	3.0–60.0
Scan rate (deg min^{-1})	4	4
h, k, l range	$-12 < h < 12$ $0 < k < 18$ $0 < l < 9$	$-12 < h < 12$ $0 < k < 16$ $0 < l < 11$
Unique reflections	2362	2523
Used reflections ($F_o > 3\sigma(F_o)$)	1824	2320
R	0.044	0.037
R_w	0.044	0.036
Weighting scheme $\left[\text{parameters } q \text{ in } w = [\sigma^2(F_o) + q^2F_o^2]^{-1}\right]$	0.021	0.002

[a] By flotation in CH_2BrCH_2Br-hexane mixtures.

Table 5

Bond distances and angles for **1** and **3** [a]

1		**3**	
Bond distances (Å)			
Pt-C1	2.13(2)	Pt-C1	2.08(1)
Pt-P1	2.181(4)	Pt-P1	2.128(4)
Pt-P2	2.317(4)	Pt-P2	2.362(4)
Pt-O	2.07(1)	Pt-O	2.153(9)
P1-C5	1.80(2)	P1-C8	1.80(2)
P1-C6	1.79(2)	P1-C9	1.83(2)
P1-C7	1.87(2)	P1-C10	1.82(2)
P2-C8	1.80(2)	P2-C11	1.83(2)
P2-C9	1.84(2)	P2-C12	1.83(2)
P2-C10	1.80(3)	P2-C13	1.86(2)
O-C2	1.38(2)	O-C2	1.36(2)
C2-C3	1.53(3)	C2-C3	1.42(2)
C2-C4	1.55(3)	C2-C7	1.42(3)
C3-F1	1.29(3)	C3-C4	1.38(2)
C3-F2	1.31(3)	C4-C5	1.41(3)
C3-F3	1.32(4)	C5-C6	1.33(3)
C4-F4	1.33(3)	C6-C7	1.42(2)
C4-F5	1.22(3)		
C4-F6	1.25(3)		
C2-H2	1.01		
Bond angles (deg)			
C1-Pt-P1	88.3(5)	C1-Pt-P1	89.1(4)
C1-Pt-P2	169.7(5)	C1)-Pt-P2	168.7(4)
O-Pt-P1	177.6(3)	O-Pt-P1	169.5(3)
O-Pt-P2	80.6(3)	O-Pt-P2	86.3(3)
P1-Pt-P2	101.6(1)	P1-Pt-P2	101.4(1)
C1-Pt-O	89.6(5)	C1-Pt-O	82.8(5)
Pt-P1-C5	115.5(9)	Pt-P1-C8	113.9(7)
Pt-P1-C6	115.8(8)	Pt-P1-C9	122.0(8)
Pt-P1-C7	119.6(8)	Pt-P1-C10	109.8(6)
C5-P1-C6	103(1)	C8-P1-C9	99(1)
C6-P1-C7	100(1)	C9-P1-C10	104(1)
C5-P1-C7	100(1)	C8-P1-C10	107(1)
Pt-P2-C8	125.6(8)	Pt-P2-C11	115.1(5)
Pt-P2-C9	111.9(7)	Pt-P2-C12	116.2(6)
Pt-P2-C10	111.0(9)	Pt-P2-C13	116.3(6)
C8-P2-C9	100(1)	C11-P2-C12	102.0(8)
C9-P2-C10	101(1)	C12-P2-C13	100.8(8)
C8-P2-C10	105(1)	C11-P2-C13	104.4(8)
Pt-O-C2	125.3(9)	Pt-O-C2	119.9(8)
O-C2-C3	109(2)	O-C2-C3	116(1)
O-C2-C4	110(2)	O-C2-C7	123(1)
C3-C2-C4	110(2)	C2-C3-C4	120(2)
C2-C3-F1	114(2)	C3-C4-C5	120(2)
C2-C3-F2	114(2)	C4-C5-C6	119(2)
C2-C3-F3	109(2)	C5-C6-C7	126(2)
F1-C3-F2	108(2)	C6-C7-C2	115(2)
F2-C3-F3	106(2)	C3-C2-C7	121(1)
F1-C3-F3	105(2)		
C2-C4-F4	110(2)		
C2-C4-F5	110(2)		
C2-C4-F6	110(2)		

(continued)

Table 5 (continued)

1		3
Bond angles (deg)		
F4–C4–F5	104(2)	
F5–C4–F6	110(2)	
F4–C4–F6	112(2)	
O–C2–H2	123	
C3–C2–H2	97	
C4–C2–H2	106	

[a] Standard deviations are in parentheses.

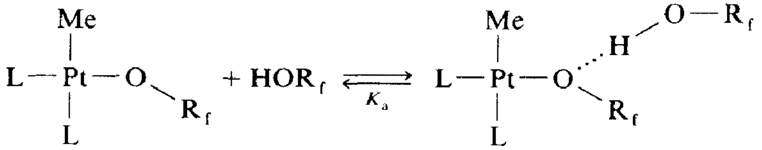
around the platinum center. The P–Pt–P angles (101.6(1)° for **1** and 101.4(1)° for **3**) are considerably larger than 90° probably due to large steric repulsion between two PMe_3 ligands. The Pt–O bond lengths in **1** (2.07(1) Å) and **3** (2.153(9) Å) are significantly longer than those in PtMe(OMe)(dpe) and $Pt(OMe)_2(dpe)$ (1.99 and 2.04 Å) [14d]. The O–C bond lengths in complexes **1** (1.38(2) Å) and **3** (1.36(2) Å) are shorter than those in organic compounds, as have been observed in the previously determined structures of alkoxides of palladium, platinum, and iridium [1].

A difference Fourier map of complex **1** shows the β-hydrogen of the fluoroalkoxide ligand at a proper distance from the bonding carbon. The distance between the hydrogen and the platinum center indicates the absence of Pt · · · H interaction.

The Pt–P bond lengths between the platinum center and the PMe_3 ligand *trans* to the methyl group in **1** and **3** (2.317(4) and 2.362(4) Å, respectively) are considerably larger than the Pt–P1 bond lengths between the platinum center and the PMe_3 ligand *cis* to the methyl group in **1** and **3** (2.181(4) and 2.128(4) Å, respectively) reflecting the larger *trans* influence of the methyl ligand than that of the alkoxide or phenoxide. The larger *trans* influence of the methyl group fully supports the NMR assignments.

Association of $(CF_3)_2CHOH$ with complex 1

The formation of complexes **1** and **2** in the reaction of $PtMe_2(PMe_3)_2$ with one and two equivalents of $HOCH(CF_3)_2$ (eq. 4 and 5) suggests the presence of an equilibrium shown below (eq. 9) in the solution.



$$\mathrm{L{-}\overset{\overset{\textstyle Me}{|}}{\underset{\underset{\textstyle L}{|}}{Pt}}{-}O{-}R_f} + \mathrm{HOR_f} \underset{K_a}{\rightleftharpoons} \mathrm{L{-}\overset{\overset{\textstyle Me}{|}}{\underset{\underset{\textstyle L}{|}}{Pt}}{-}O(R_f)\cdots H{-}O{-}R_f} \qquad (9)$$

(1) (2) ($R_f = CH(CF_3)_2$)

The association constants are obtained from Scatchard plots [24] by using ^1H NMR spectroscopy. These procedures have been already used for estimation of equilibrium constants for the association of phenols with Rh and Pd phenoxides [18,20b]. The association constants K_a for eq. 9 are obtained at several temperatures by a calculation procedure which is modified to minimize empirical error as shown in our previous paper (See Experimental) [20b].

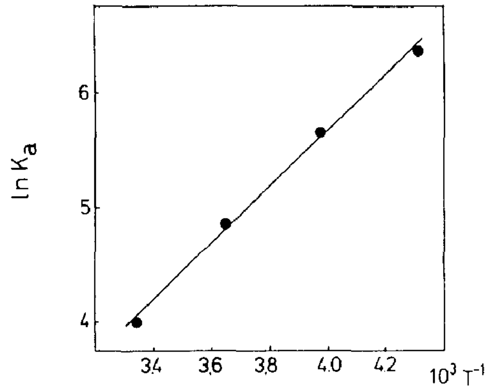


Fig. 3. Temperature dependence of equilibrium constants for $1 + HOCH(CF_3)_2 \rightleftarrows 2$.

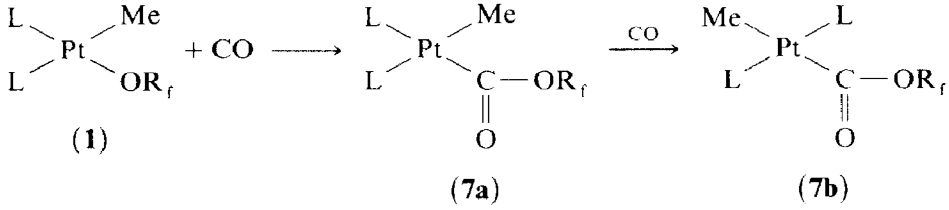
Figure 3 shows temperature dependence of the association constant K_a. Thermodynamic parameters for this association are obtained as $\Delta H°$ -5.1 kcal mol^{-1}, $\Delta G°$ -2.6 kcal mol^{-1}, and $\Delta S°$ -9.1 e.u. at 273 K. The enthalpy value of 5.1 kcal mol^{-1} to break the hydrogen bond in the fluoroalcohol-bonded complex **2** is smaller than the values of 14.0 kcal mol^{-1} (in cyclohexane) and 11.4 kcal mol^{-1} (in benzene) for the hydrogen bond in *p*-cresol-bonded rhodium *p*-methylphenoxide reported by Bergman [18].

Reactions of complexes 1 and 3 with CO

Platinum methoxide complexes such as PtMe(OMe)(dpe) and $Pt(OMe)_2$(dpe) undergo facile CO insertion into the Pt–O bond to give the platinum complexes with methoxycarbonyl ligands. Previously we observed CO insertion into Pd–O bond in the palladium fluoroalkoxide $PdMe(OCH(CF_3)_2)$(dpe) to give $PdMe(COOCH(CF_3)_2)$(dpe) which released the corresponding ester on reductive elimination at -20 °C in the presence of excess CO [20a].

Reaction of complex **1** with CO (1 atm) was examined and the reaction products were characterized in situ by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. The reaction mixture initially (1 h from the start of the reaction) contains *cis*-$PtMe(COOCH(CF_3)_2)(PMe_3)_2$ (**7a**) produced through CO insertion into the Pt–O bond in addition to the starting complex **1** (eq. 10). The $^{13}C\{^1H\}$ NMR spectrum shows clearly the signals due to PtCH$_3$, P(CH$_3$)$_3$, OCH, CF$_3$, and CO carbons of **7a** with reasonable ^{195}Pt–^{13}C and ^{31}P–^{13}C coupling constants (Table 3). The chemical shifts of signals due to the $COOCH(CF_3)_2$ ligand are similar to those of $PdMe(COOCH(CF_3)_2)$(dpe) [20a]. The $^{31}P\{^1H\}$ NMR spectrum of the mixture shows two doublets due to **7a** with two nonequivalent PMe_3 ligands. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of **1** with ^{13}CO shows splitting due to ^{13}C–^{31}P coupling, the J values of which agree with those obtained in the corresponding $^{13}C\{^1H\}$ NMR spectrum. Thus obtained coupling constants, $J(^{195}Pt-^{13}C)$, and $J(^{31}P-^{13}C)$ of the $COOCH(CF_3)_2$ ligand and $J(^{195}Pt-^{31}P)$ values in **7a**, are similar to those of already reported PtMe(COOMe)(dpb) (dpb = 1,2-bis(diphenylphosphino)butane) and $Pt(COOMe)_2$(dpe) [12c,14c].

Prolonged carbonylation causes formation of *trans*-$PtMe(COOCH(CF_3)_2)(PMe_3)_2$ (**7b**) and decrease in the amount of **7a** initially formed. Monitoring this reaction by $^{31}P\{^1H\}$ NMR spectroscopy shows exclusive formation of **7a** at the initial stage of the reaction followed by a gradual increase in the amount of **7b** at the expense of **7a** indicating the isomerization of **7a** to **7b** under the reaction conditions. Signals due to *trans*-$PtMe(OCH(CF_3)_2)(PMe_3)_2$, isomerization product of **1**, are not observed in $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR spectra throughout the reaction.



(10)

The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of complex **7b** are compatible with the *trans* configuration although broadening of the signals precluded determination of some of the coupling constants. The reason for the line broadening of the spectra is not clear at present. Some platinum alkoxycarbonyl complexes were reported to undergo decarbonylation to generate the corresponding platinum alkoxide complexes in the absence of CO [1]. On the other hand, association of CO with square planar platinum(II) complexes to give five-coordinated complex was also reported [14a]. In the present case there may be a fast equilibrium between **7b** and the decarbonylation product *trans*-$PtMe(OCH(CF_3)_2)(PMe_3)_2$ or the five-coordinated CO adducts $PtMe(CO)(COOCH(CF_3)_2)(PMe_3)_2$ under these conditions, although the presence of these complexes was not confirmed by the NMR spectroscopy.

Reaction of the *cis*-methylplatinum phenoxide complex **3** with CO under similar conditions was also monitored by NMR spectroscopy to compare the reactivity of the Pt–OPh complex with those of the Pt–$OCH(CF_3)_2$ and Pt–OMe complexes. The NMR spectra of the reaction mixture show isomerization of **3** to *trans*-$PtMe(OPh)(PMe_3)_2$ but no other signals than those of the two complexes are observed in $^{31}P\{^1H\}$ NMR spectra during the reaction for 6 h. The peak positions and coupling constants in the $^{31}P\{^1H\}$ NMR and the $^{13}C\{^1H\}$ NMR spectra (Pt–CH_3 and $P(CH_3)_3$ region) are similar to those of the phenol-bonded phenoxide complex **5**, which has the same *trans* geometry as *trans*-$PtMe(OPh)(PMe_3)_2$. The $^{31}P\{^1H\}$ NMR signals of the reaction mixture of **3** using ^{13}C enriched CO do not show splitting due to ^{13}C–^{31}P coupling, indicating no incorporation of CO into the complex. These results indicate that CO promotes isomerization of the *cis* complex **3** to its *trans* isomer but CO is not inserted into the Pt–OPh bond nor into the Pt–CH_3 bond under these conditions.

trans-$PdMe(OPh)(PEt_3)_2$ was reported to undergo CO insertion into the Pd–C bond (10 atm at room temperature) although CO insertion into the Pd–O bond was not observed [21]. On the other hand $PdMe(OCH(CF_3)_2)(dpe)$ reacts with CO even at −60 °C to give $PdMe(COOCH(CF_3)_2)(dpe)$ [21a]. The present study shows that CO insertion into the Pt–$OCH(CF_3)_2$ bond of **1** occurs at room temperature but is not observed at −40 °C whereas the methylplatinum phenoxide complex does not undergo insertion of CO into the Pt–OPh bond nor into the Pt–C bond. These differences in reactivities of the alkoxide and phenoxide complexes for CO insertion are intriguing.

Experimental

All manipulations of the complexes were carried out under nitrogen or argon atmosphere. 1,1,1,3,3,3-Hexafluoro-2-propanol was purchased from Tokyo Kasei Co. Ltd. ^{13}CO (99% isotopic purity) was purchased from CEA (Commissariat à l'energie atomique). *cis*-$PtMe_2(PMe_3)_2$ was prepared according to the literature [25].

Elemental analyses were carried out by Dr. M. Tanaka of our laboratory by using Yanagimoto CHN Autocorder Type MT-2. NMR spectra were recorded on a JEOL FX-100 spectrometer by Dr. Y. Nakamura. IR spectra were recorded on a JASCO IR-810 spectrophotometer.

Preparation of *cis*-$PtMe(OCH(CF_3)_2)(PMe_3)_2$ (1)

To an Et_2O (8 ml) solution of *cis*-$PtMe_2(PMe_3)_2$ (600 mg, 1.6 mmol) was added $(CF_3)_2CHOH$ (270 mg, 1.6 mmol) at room temperature. After stirring the reaction mixture for 12 h the solvent was removed under reduced pressure to give **1** as a white solid, which was filtered, and recrystallized from Et_2O (450 mg, 53%).

Preparation of *cis*-$PtMe(OCH(CF_3)_2)(HOCH(CF_3)_2)(PMe_3)_2$ (2)

1,1,1,3,3,3-Hexafluoro-2-propanol (320 mg, 1.9 mmol) was added to an Et_2O (6 ml) solution of *cis*-$PtMe_2(PMe_3)_2$ (340 mg, 0.91 mmol) at room temperature. After stirring the solution for 3 h the solvent was removed under reduced pressure to give **2** as a white solid, which was recrystallized from Et_2O containing added $(CF_3)_2CHOH$ (ca. 0.2 *M*) (330 mg, 53%).

Recrystallization of **2** from Et_2O without added $(CF_3)_2CHOH$ sometimes gave crystals of **1**.

Preparation of *cis*-$PtMe(OC_6H_5)(PMe_3)_2$ (3)

Phenol (50 mg, 0.53 mmol) was added to an Et_2O (6 ml) solution of **2** (370 mg, 0.53 mmol) at room temperature. Stirring for 4 h at this temperature caused precipitation of **3** as a white solid, which was filtered and dried in vacuo (99 mg, 41%).

Preparation of *cis*-$PtMe(OC_6H_5)(HOC_6H_5)(PMe_3)_2$ (4)

Phenol (120 mg, 1.3 mmol) was added to an Et_2O (6 ml) solution of **2** (410 mg, 0.59 mmol) at room temperature. After stirring for 1 h the solvent was removed under reduced pressure to give **4** as a white solid, which was recrystallized from a CH_2Cl_2/Et_2O (1/1) mixture (216 mg, 67%).

Preparation of *trans*-$PtMe(OC_6H_5)(HOC_6H_5)(PMe_3)_2$ (5)

A toluene (10 ml) solution of a mixture of *cis*-$PtMe_2(PMe_3)_2$ (300 mg, 0.79 mmol) and phenol (150 mg, 1.6 mmol) was stirred for 12 h at 80 ° C. The solvent was removed filtered and washed with Et_2O (150 mg, 35%).

Preparation of *cis*-$PtMe(OC_6H_4\text{-}p\text{-}OMe)(HOC_6H_4\text{-}p\text{-}OMe)(PMe_3)_2$ (6)

Anisole (150 mg, 1.2 mmol) was added slowly to an Et_2O (6 ml) solution of **2** (410 mg, 0.59 mmol). Stirring the mixture for 2 h at room temperature caused precipitation of **6** as a white solid, which was filtered, washed with Et_2O and hexane (290 mg, 82%).

X-ray crystallography

Crystals suitable for X-ray crystallography were grown in Et_2O at −20 °C. Intensities were collected on a Rigaku AFC-5 four-cycle diffractometer by using Mo-K_α radiation (λ 0.71068 Å). Detailed conditions of data collection are summarized in Table 4. The standard reflections, monitored after every 200 reflections in data collection of **1**, showed an approximate 5% decrease in the intensity during the measurement (47 h). Empirical absorption correction was applied for **1** [26]. Absorption correction by Gaussian integration ($8 \times 8 \times 8$) was applied for complex **3** [27].

Calculations were carried out with the program systems SAPI85 on a FACOM A-70. Each structure was solved by common Fourier methods. A full-matrix least-squares refinement procedure was used with anisotropic temperature factors assigned to all non-hydrogen atoms. The hydrogen atom of the 1,1,1,3,3,3-hexafluoro-2-propoxide ligand was extracted from a difference Fourier map, and included in the least-squares calculations without further refinement of its parameters.

Tables of fractional coordinates, anisotropic thermal factors, and observed and calculated structure factors are available from the authors.

Determination of the association constants

Five NMR samples containing a mixture of **1** (0.090–0.250 *M*) and 1,1,1,3,3,3-hexafluoro-2-propanol (0.066 *M*) in toluene-d_8 were prepared. ^1H NMR spectra of the samples were measured at four fixed temperatures. The chemical shift of the OH hydrogen was referred to the center of the methyl signal of ^1H impurity of the solvent (2.09 ppm) as an internal standard. Association constants K_a for eq. 8 were calculated from the Scatchard equation [24]. Detailed calculation procedures were shown in the previous paper [20b].

The K_a values of 5.8×10^2 (232 K), 2.8×10^2 (253 K), 1.3×10^2 (273 K), and 5.5×10 (295 K), respectively, were obtained.

Reaction of complexes 1 and 3 with CO

An NMR tube containing a CD_2Cl_2 solution of **1** was sealed with a serum cap under argon atmosphere. After removing argon in the tube by a syringe, carbon monoxide (1 atm) is introduced by cooling the solution at −80 °C. The reaction was carried out by keeping the solution at 25 °C. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of the reaction mixture was measured at −40 °C. For the initial hour of reaction formation of complex **7a** was observed, and the yield was 78% after 1 h. After the first hour the formation of **7b** was also observed with gradual decrease in the amount of **7a**. Shaking the mixture after introduction of CO caused formation of a mixture of **7a** and **7b** from the beginning of the reaction.

Acknowledgement

This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 63470079).

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