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THE PREPARATION AND CHARACTERIZATION OF A PLATINUM ETHER COMPLEX

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Summary

The reaction of $[Pt((F_3C)C{=}CH(CF_3))(P(C_2H_5)_3)_2CH_3OH]PF_6$ with allene in methanol affords a novel metallocyclic ethereal complex $[\overline{Pt((F_3C)CHC(CF_3){=}C(CH_3)CH_2O}CH_3)(P(C_2H_5)_3)_2]PF_6$, which has been characterized by ^1H, ^2H, ^{19}F and ^{31}P NMR spectroscopy. Its structure has also been determined by a single crystal X-ray analysis. The crystals are monoclinic, space group $P2_1/n$, with cell dimensions a 20.012(5), b 17.222(5), c 8.902(3) Å and β 91.54(5)°. The structure was refined by full matrix least-squares methods on F, using 3097 unique observations collected by automated four circle diffractometer. Refinement converged at $R = 0.066$. The Pt atom has a distorted square-planar coordination geometry, with *cis* P atoms, and Pt—P distances of 2.219(4) Å (*trans* to O) and 2.324(4) Å (*trans* to C). These results show the ethereal group is a weak ligand to platinum(II) but because of the chelating effect, its displacement by other ligands is thermodynamically not favorable. The mechanism of formation of the ethereal complex is also discussed.

Introduction

Although thioethers, selenoethers and telluroethers all form stable complexes with platinum(II), ethereal platinum complexes are as yet unknown [1]. Interaction of ethereal oxygen with platinum(II) has, however, been invoked in a mechanism proposed for the thermal isomerization of vinyl ethers [2]. This absence of stable platinum ether complexes is probably due to the "hard" [3] or "class a" [4] character of the oxygen atom and the small permanent dipole moment in the R_2O molecule, so that the Pt—O bonds in such complexes are therefore expected to be very weak. In the course of our study of the reactions of acetylenes with platinum(II) complexes [5], we have been able to isolate a stable ethereal platinum complex. We present here details of its crystal and

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molecular structures, and its physical and chemical properties, as well as a discussion of the mode of formation of the ether ligand.

Experimental

Infrared spectra were recorded using Nujol mulls between KBr plates on a Perkin—Elmer 621 or a Beckman IR 12 spectrophotometer. ^{1}H and ^{19}F NMR spectra were recorded on a Varian HA-100, ^{31}P on a Bruker WP-60 and ^{2}H on a Varian XL-100 spectrometer. The NMR data are summarized in Table 1. Melting points were recorded on a Thomas Hoover instrument. Micro-analyses were carried out by Midwest Microlab Ltd., Indianapolis, Indiana.

Preparation of $[Pt((F_3C)CHC(CF_3)=C(CH_3)CH_2OCH_3)(PEt_3)_2]PF_6$ *(I)*

Silver hexafluorophosphate (0.40 g) in methanol (3 ml) was added dropwise to a solution of 1.0 g of *cis*-$Pt(C_4F_6H)Cl(PEt_3)_2$ in 27 ml methanol. The white precipitate of AgCl was separated by centrifugation. The resulting colourless solution of $[Pt(C_4F_6H)(PEt_3)_2(MeOH)]PF_6$ was then saturated with allene and a slight positive pressure was maintained throughout the reaction. After 2 h, the reaction mixture was filtered and its volume reduced under vacuum to about 7 ml, at which point precipitation of white crystals of I commenced. Ether was then added and the mixture cooled in an ice bath to complete precipitation. The white crystals were then filtered and washed with ether. Yield: 1.04 g (81%).

Recrystallization from methanol/diethyl ether provided crystals suitable for X-ray analysis. Analysis: Found: C, 29.80; H, 4.91; F, 28.17. $C_{20}H_{39}F_{12}OP_3Pt$ calcd.: C, 29.60; H, 4.84; F, 28.09%. Decomposes at 125°C with gas evolution.

Preparation of $[Pt((F_3C)CDC(CF_3)=C(CH_3)CH_2OCH_3)(PEt_3)_2]PF_6$ *(Ib)*

The same procedure was employed as in the preparation of I, except for the use of *cis*-$Pt(C_4F_6D)Cl(PEt_3)_2$ as starting material. This was prepared by the reaction of $PtHCl(PEt_3)_2$ with hexafluorobut-2-yne, C_4F_6, in CH_3OD [6].

Preparation of $[Pt((F_3C)CHC(CF_3)=C(CH_2D)CH_2OCD_3)(PEt_3)_2]PF_6$ *(Ic)*

The same procedure as in I was employed except for the use of CD_3OD as reaction medium.

Preparation of $[Pt((F_3C)CHC(CF_3)=C(CH_3)CH_2OCH_3)(PEt_3)_2(CO)]PF_6$ *(II)*

I (80 mg) was dissolved in 0.5 ml of acetone which was then saturated with carbon monoxide gas. Addition of diethyl ether under a CO atmosphere afforded 55 mg of II as white crystalline material. M.p. 116—118°C (dec). Analysis: Found: C, 29.78, H, 4.78; F, 27.10. $C_{21}H_{39}F_{12}O_2P_3Pt$ calcd.: C, 30.04; H, 4.68; F, 27.16%.

Equilibrium study of I with CD_3CN

On addition of a measured quantity of CD_3CN to a solution of I in $CDCl_3$, the OCH_3 proton resonance was observed to shift upfield. The chemical shift of the OCH_3 resonance as a function of the CD_3CN concentration was monitored, and by extrapolation to infinite concentration of CD_3CN, the chemical shift of the OCH_3 group in $[Pt((CF_3)CHC(CF_3)=C(CH_3)CH_2OCH_3)(PEt_3)_2(CD_3CN)]PF_6$ (III) was determined. The equilibrium constant K in eq. 1 was then calculated based on the chemical shift of OCH_3 in III, I and the average position at a certain concentration of CD_3CN.

$$CD_3CN + [\overline{Pt((F_3C)CHC(CF_3)=C(CH_3)CH_2O}CH_3)(PEt_3)_2]^+ \overset{K}{\rightleftharpoons}$$

$$\underset{(III)}{[Pt((F_3C)CHC(CF_3)=C(CH_3)CH_2OCH_3)(PEt_3)_2(CD_3CN)]^+} \qquad (1)$$

The attempted isolation of III by addition of ether to an acetonitrile solution of I resulted only in the recovery of I.

Collection and reduction of X-ray data

A preliminary photographic examination indicated the monoclinic system. Systematic absences of $h0l$ for $h+l$ odd and $0k0$ for k odd are consistent only with space group $P2_1/n$, $\pm(x, y, z)$, $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ [7]. The crystal density was determined by flotation in a mixture of CCl_4 and CH_2BrCH_2Br, and showed that there are four formula units per cell. The crystals are elongated along [001], with prismatic faces of the form {110}. Crystal data are summarised in Table 2.

Intensity data were collected using a Picker FACS-1 four circle diffractometer. The sensitivity of the crystals to X-ray damage required that data be collected from two crystals. Cell constants and an orientation matrix were determined * at 18°C from the setting angles of 24 reflections for which $31 < 2\theta < 53°$. Cu radiation prefiltered with 0.015 mm of Ni foil was used, $\lambda(\text{Cu-}K_{\alpha_1})$ 1.54056 Å. ω-scans of intense, low-angle reflections were recorded to examine crystal mosaicity, and an average width of 0.12° at half-height was observed. Many crystals with macroscopic twinning were examined before any of suitable quality were obtained. The first was of approximate dimensions 0.35 mm × 0.10 mm × 0.09 mm, and was mounted with [001] offset by some 5° from coincidence with the spindle axis. A take-off angle of 2° was chosen for the tube, with a 5 mm × 5 mm counter aperture 32 cm from the crystal. The $\theta - 2\theta$ scan technique was used, at a scan rate of 1° min^{-1}. Background estimations were made for 10 s at the limits of a 1.4° scan, corrected for dispersion. Standard reflections 400, 020, 002, $0\bar{2}0$ and 210 were monitored every 200 observations, and showed a pronounced decrease after 2929 measurements had been made out to a 2θ maximum of 90°. Decomposition ranged from 1 to 16%, with two of the standards first appreciating, presumably as a result of an increased crystal mosaicity. Since this variation was neither isotropic, nor linear with exposure time, no decay correction was applied.

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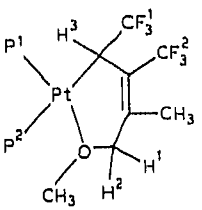
* Computing was performed on the DEC PDP-10 and the CDC Cyber 73/14 at the University of Western Ontario. Local versions of the following programs were used: cell refinement and orientation matrix, PICKTT; Fourier syntheses, FORDAP, by A. Zalkin; full-matrix least-squares refinement, WOCLS, a version of J.A. Ibers' NUCLS; function and errors, ORFFE, by W.R. Busing, H.A. Levy and K.O. Martin; and ORTEP for molecular illustrations, by C.K. Johnson.

TABLE 1

NMR DATA FOR



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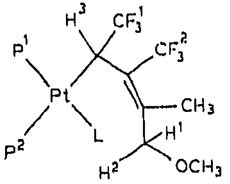

Complex	L	^{1}H NMR δ (ppm)				^{19}F NMR [c] δ (ppm)		^{31}P NMR [d] δ (ppm)	
		OCH_3	H^1	H^2	H^3	CF_3^1	CF_3^2	P^1	P^2
I		3.86 t [a] ^3J(PtH) 12.5 [b]	4.46 dt(br) ^3J(PtH) 18.5 ^2J(HH) 16.5	3.61 d(br)	~3.2	−53.61 tt ^3J(PtF) 89.8 ^4J(PF) 12.4 ^3J(HF) 12.4	−59.09 s(br)	5.84 J(PtP) 4529.9 J(PP) 17.8	13.34 J(PF) 11.8 J(PtP) 2230.7
II [e]	CO	3.41 s(br)	4.36 d(br) ^2J(HH) 11.9	3.78 d(br)		−58.16 [f] ^3J(PtF) 98	53.67 ^4J(PtF) ~30	4.48m [f] ^1J(PtP) 2994	4.40 J(PtP) 1698 J(PP) 28.9
III	CH_3CN	3.48 s(br)	4.36 d(br) ^2J(HH) 13	3.94 d(br)		−54.63 t(br) ^3J(PtF) 74	−52.95 s(br)	−2.08 J(PtP) 3897 J(PP) 23.8	6.38 J(PtP) 1941 J(PF) 10.6

[a] (br) broad; d, doublet; s, singlet; t, triplet; m, multiplet. [b] The coupling constants are in Hz, δ (ppm). [c] Reference $CFCl_3$. [d] Reference 85% H_3PO_4. [e] CD_3CN as solvent for ^{1}H NMR, CH_3CN as solvent for ^{19}F and ^{31}P NMR spectra. [f] Temperature at −40°C.

TABLE 2

CRYSTAL DATA

$C_{20}H_{39}F_{12}OP_3Pt$	F.w. 811.53
a 20.012(5) Å	β 91.54(5)°
b 17.222(5) Å	Cell volume 3066.9 Å^3
c 8.902(3) Å	Density (obs.) 1.75(2) g cm^{-3}
	Density (calc.) 1.76 g cm^{-3}

A second crystal of approximate dimensions 0.23 mm × 0.10 mm × 0.10 mm was therefore used to collect intensity data from the $90 < 2\theta < 110°$ shell, beyond which there was little significant intensity. A scan width of 1.2° was used, at a scan rate of 2° min^{-1}. Background counts were made at the scan limits for 20 s. Other experimental parameters were unchanged. Standard reflections 400, 020 and 002 were monitored as before, and again showed a marked decrease over the 44 h during which data were recorded. When 1497 measurements had been made, collection was terminated. After the standard reflections had been removed, a total of 4310 reflections was available. These were corrected for Lorentz, polarisation and background, and assigned σ values as described previously [8]. The value for p was 0.04 [9]. 3097 reflections with $F^2 > 3\sigma(F^2)$ were used in the solution and refinement of the structure. Since pronounced crystal decomposition had occurred, no attempt was made to apply an absorption correction, μ 55.9 cm^{-1}.

Structure solution and refinement

The structure was solved by the heavy atom method, and refined by full matrix least-squares techniques on F. The function $\Sigma\omega(|F_0| - |F_c|)^2$ was minimized, with weights $\omega = 4F_0^2/\sigma(F_0^2)$. Scattering factors for non-H atoms were taken from Cromer and Waber [10], and those for H from Stewart, Davidson and Simpson [11]. Corrections for anomalous dispersion were made to the scattering factors for Pt and P, as calculated by Cromer and Liberman [12]. With all non-H atoms included in the model, the six F atoms constrained as a rigid group of O_h symmetry [13], and anisotropic thermal parameters assigned to the Pt, phosphine P and CF_3 F atoms, agreement factors $R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.094$ and $R_2 = (\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2)^{1/2} = 0.128$ were achieved. A difference Fourier synthesis showed that there was residual electron density in the region of the PF_6 ion, so a disorder model was formulated. A second rigid F_6 group was included, the appropriate constraints were applied to the derivatives, and a multiplicity parameter was refined [14]. A P—F bond length of 1.58 Å was used [15]. Agreement parameters of $R_1 = 0.074$ and $R_2 = 0.091$ were the result, a significant improvement.

There are 39 H atoms in the cation, and evidence for all of these was found in a difference Fourier synthesis. The contributions of these atoms were therefore included, assuming idealised geometries and a C—H bond length of 0.95 Å. Isotropic thermal parameters 1.0 Å^2 greater than that of the atom to which the H atom is attached were used. Several cycles of refinement, with recalculated H

TABLE 3

ATOMIC POSITIONAL ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$)

Atom	x	y	z	U_{11} [a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	3652.5(3) [b]	2387.1(3)	2636(1)	58(1)	60(1)	70(1)	1.5(3)	11.3(3)	4.5(3)
P(1)	4218(2)	3474(2)	2256(4)	63(2)	72(2)	79(3)	−6(2)	16(2)	10(2)
P(2)	2593(2)	2905(2)	2959(4)	58(2)	68(2)	85(3)	3(2)	14(2)	7(2)
P(3)	−3202(3)	4380(3)	2586(6)	98(4)	122(4)	104(4)	14(3)	13(3)	−17(3)
F(1)	4435(7)	533(7)	1617(14)	170(12)	114(9)	159(11)	19(8)	52(9)	−35(8)
F(2)	4634(10)	1486(8)	240(15)	354(23)	143(11)	101(10)	92(13)	24(12)	9(8)
F(3)	5390(6)	1029(8)	1668(15)	128(11)	178(12)	199(13)	62(9)	55(9)	−19(9)
F(4)	5422(6)	906(7)	5837(15)	131(10)	154(11)	185(12)	37(8)	−57(9)	26(9)
F(5)	5525(7)	2011(10)	4951(18)	134(12)	218(16)	210(16)	−64(11)	−77(11)	90(13)
F(6)	4883(8)	1854(11)	6732(18)	178(15)	252(19)	156(13)	0(13)	−20(11)	−64(13)
O	3260(5)	1230(5)	2728(12)	100(8)	56(6)	110(8)	−13(5)	−6(6)	8(5)
C(1)	4571(7)	1792(8)	2869(18)	48(9)	88(10)	103(12)	27(7)	−2(8)	15(8)
C(2)	4715(12)	1218(12)	1651(23)	143(19)	101(14)	103(16)	32(13)	21(13)	−1(11)
C(3)	4524(10)	1389(9)	4373(19)	106(14)	84(11)	80(11)	12(9)	10(10)	6(8)
C(4)	5083(11)	1511(16)	5404(28)	86(16)	176(22)	119(18)	35(15)	−11(13)	50(16)
C(5)	4021(10)	933(10)	4855(20)	91(13)	91(11)	110(14)	18(9)	4(11)	20(9)
C(6)	3985(10)	529(12)	6367(24)	118(16)	140(17)	139(17)	38(13)	25(13)	34(14)
C(7)	3424(9)	718(10)	3880(23)	92(13)	94(12)	136(16)	1(9)	2(11)	24(11)
C(8)	2928(10)	881(11)	1474(24)	119(16)	107(14)	143(18)	−8(11)	−21(14)	−9(12)
C(9)	3757(8)	4374(8)	1969(20)	89(12)	64(9)	131(14)	−1(7)	35(10)	8(9)
C(10)	4172(10)	5099(10)	1768(23)	117(15)	79(11)	171(19)	−14(10)	13(13)	25(11)
C(11)	4707(10)	3398(11)	565(23)	94(14)	115(14)	111(15)	10(10)	31(11)	17(11)
C(12)	4301(11)	3268(13)	−838(21)	138(18)	173(21)	77(13)	23(14)	42(12)	40(12)
C(13)	4825(8)	3710(9)	3753(21)	83(12)	87(11)	115(14)	−28(8)	0(10)	7(9)
C(14)	4543(14)	3835(13)	5246(23)	200(26)	150(19)	91(15)	−50(17)	−4(16)	−30(13)
C(15)	2202(7)	3503(10)	1496(23)	51(10)	125(14)	131(15)	10(8)	14(9)	34(11)
C(16)	2214(11)	3137(16)	−37(24)	131(19)	228(28)	101(16)	64(18)	14(14)	42(16)
C(17)	1962(8)	2148(10)	3229(21)	78(11)	95(11)	125(15)	−13(9)	13(10)	15(10)
C(18)	1308(10)	2401(10)	3788(31)	73(12)	113(15)	189(23)	−14(9)	21(13)	34(12)
C(19)	2547(8)	3488(9)	4652(20)	95(13)	94(12)	105(13)	−15(9)	41(10)	−16(9)
C(20)	2748(10)	2983(15)	6032(22)	116(16)	190(21)	90(14)	8(15)	44(12)	−6(14)

[a] The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ Å^2. [b] Estimated standard deviations in this and other tables are given in parentheses, and refer to the least significant digit(s).

atom positions, lead to convergence at $R_1 = 0.066$ and $R_2 = 0.083$ (290 variables and 3097 unique reflections with $F^2 > 3\sigma(F^2)$). In the final cycle the maximum, non-group atom parameter shift was 0.06 esd. There was some residual electron density in the region of the Pt atom in a difference Fourier synthesis, but no peaks of any chemical significance. The disorder parameter of the anion refined to 0.40(2). A statistical analysis of the structure factors showed no abnormal trends, and there was no sign of secondary extinction. Final atomic parameters are given in Table 3, with group atom details given in Table 4. The tables of hydrogen atom parameters and structure factor amplitudes have been deposited *.

Results and discussion

It had been found previously that the reaction of $[Pt(CF_3C{=}CHCF_3)(PEt_3)_2S]$-$PF_6$ (S = acetone) with allene in acetone lead to the insertion of allene into the σ-Pt—C bond (eq. 2) [5]

(2)

When the same reaction was conducted in methanol, however, I was isolated in 80% yield. The ^1H and ^{19}F NMR spectra of I exhibit resonances completely different from those of the π-allylic complex previously identified [5] (Table 1, see below for more detailed discussion of the NMR spectra). In particular, the presence of the resonance at δ 3.86 ppm with ^{195}Pt satellites indicates that methoxide attack has taken place. This is further supported by the presence of a band in the IR spectrum of I at 1072 cm^{-1} for the C—O—C group. Elemental analysis of I agrees with an empirical formula of $Pt(PEt_3)_2(C_4F_6H \cdot MeOH \cdot C_3H_4)PF_6$. Since the complete structure of I could not be deduced from its spectroscopic data, its crystal structure was determined.

Description of the structure

The crystals are built up from well separated cations and anions, for the closest distance of approach is 2.39 Å between H2C(17) and F(9). The absence of closer contacts is probably responsible for the 60/40 disorder observed in the anion. A stereoview of the cation, with H atoms omitted, is shown in Fig. 1, while the chelate ring is depicted in Fig. 2. Selected intraionic distances are listed in Table 5 for the cation; the anions were constrained to O_h symmetry, P—F 1.58 Å [15].

The Pt atom has a distorted, square-planar coordination geometry, with *cis* P

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* The tables of hydrogen atom parameters, and of structure amplitudes (X10 in electrons) have been deposited as NAPS Document No. 03459 (9 pages). Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only \$ 5.00 for photocopies or \$ 3.00 for microfiche. Outside the U.S. and Canada add postage of \$ 3.00 for photocopy and \$ 1.00 for microfiche.

TABLE 4

GROUP AND GROUP ATOM DERIVED PARAMETERS

Group	x_g[a]	y_g	z_g	δ	ϵ	η	B (Å^2)	mult.
PF_6	−3202(3)[b]	4380(3)	2586(6)	−0.32(1)	2.90(1)	1.83(1)	11.9(6)	0.40(2)
PF_6'	−3202(3)	4380(3)	2586(6)	−2.294(8)	−3.076(8)	−2.046(9)	12.0(4)	0.60(2)

Atom	x	y	z	Atom	x	y	z
F(7)	−2960(8)	5225(4)	2178(23)	F(7')	−2611(4)	3774(5)	2738(14)
F(8)	−3942(3)	4607(10)	2102(18)	F(8')	−3649(5)	3750(6)	1749(14)
F(9)	−3069(9)	4105(11)	928(7)	F(9')	−3475(5)	4100(8)	4145(7)
F(10)	−3336(9)	4654(11)	4245(7)	F(10')	−2929(5)	4659(8)	1028(7)
F(11)	−2462(3)	4152(10)	3071(18)	F(11')	−2755(5)	5009(6)	3424(14)
F(12)	−3444(8)	3534(4)	2995(23)	F(12')	−3793(4)	4986(5)	2435(14)

[a] Group parameters are defined in ref. 13. [b] Positional parameters X10^4.

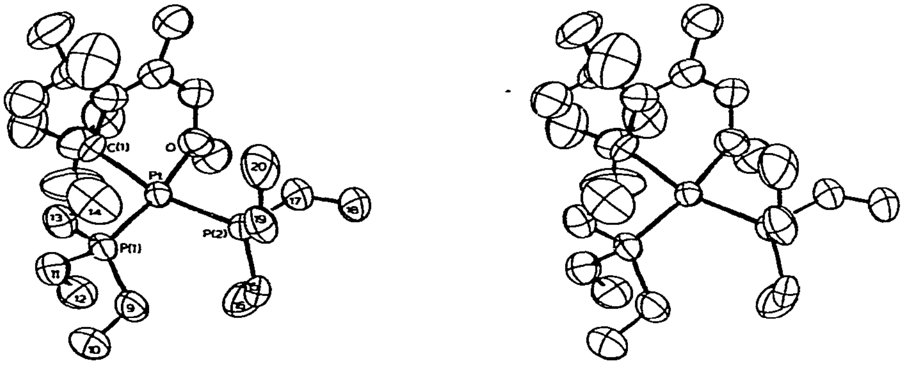


Fig. 1. A stereoview of the cation, with hydrogen atoms omitted. Atoms are drawn as 42% probability thermal ellipsoids.

atoms, Table 5. The σ-bonded C atom, C(1), has a much greater *trans*-influence than the ethereal O atom, for Pt—P(2) is some 21σ longer than Pt—P(1). The Pt—P(1) distance of 2.219(4) Å is one of the shortest ever observed, and close to that of 2.218(7) Å found in *cis*-[PtF(CH(CF$_3$)$_2$)(P(C$_6$H$_5$)$_3$)$_2$], where the triphenylphosphine ligand is *trans* to a F atom [16]. A value of 2.215(4) Å was found for a triethylphosphine ligand in [N(C$_2$H$_5$)$_4$][PtCl$_3$P(C$_2$H$_5$)$_3$], where the phosphine is *trans* to a Cl atom. Although the Pt—P bond length was short, there

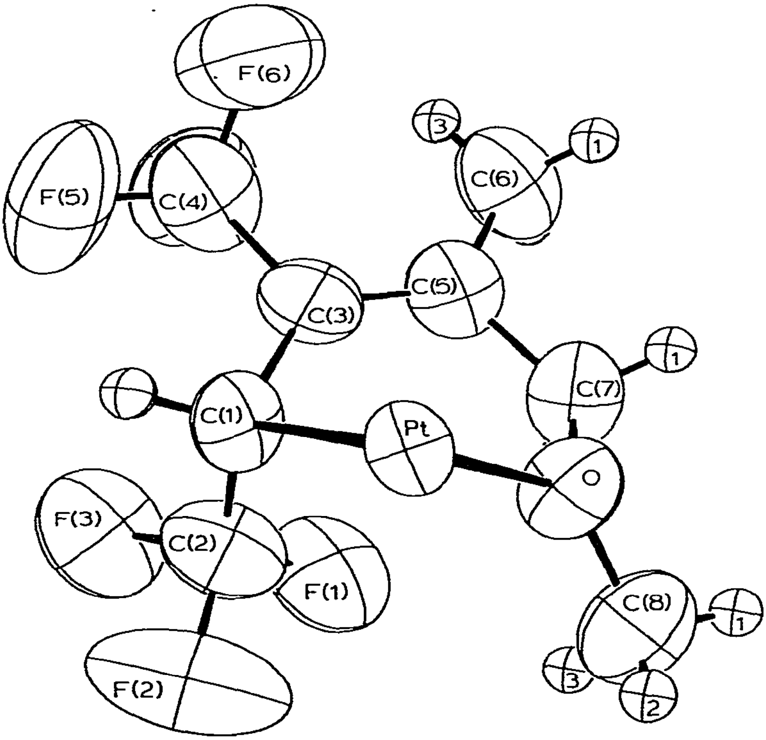


Fig. 2. The six-membered metallocyclic ligand, showing the atom numbering scheme.

TABLE 5

SELECTED INTRACATIONIC DIMENSIONS

Bond distances (Å)			
Pt—P(1)	2.219(4)	C(3)—C(4)	1.44(3)
Pt—P(2)	2.324(4)	C(3)—C(5)	1.36(2)
Pt—C(1)	2.109(12)	C(5)—C(6)	1.52(2)
Pt—O	2.144(9)	C(5)—C(7)	1.50(2)
C(1)—C(2)	1.50(2)	O—C(7)	1.39(2)
C(1)—C(3)	1.51(2)	O—C(8)	1.42(2)
Weighted mean distances (Å) [a]			
P—CH_2	1.823(7)	C—F	1.336(9)
		CH_2—CH_3	1.50(1)
Bond angles (Deg)			
P(1)—Pt—C(1)	88.8(4)	C(7)—C(5)—C(6)	110(2)
P(1)—Pt—P(2)	99.6(1)	C(7)—C(5)—C(3)	123(2)
P(2)—Pt—O	90.9(3)	C(6)—C(5)—C(3)	127(2)
C(1)—Pt—O	82.2(5)	C(1)—C(3)—C(4)	116(2)
Pt—O—C(8)	122(1)	C(1)—C(3)—C(5)	128(2)
Pt—O—C(7)	123(1)	C(4)—C(3)—C(5)	117(2)
C(7)—O—C(8)	114(1)	Pt—C(1)—C(2)	116(1)
O—C(7)—C(5)	116(1)	Pt—C(1)—C(3)	104(1)
C(2)—C(1)—C(3)	111(1)		
Weighted mean angles (Deg)			
Pt—P—CH_2	115.1(2)	C—C—F	114.9(7)
P—C—C	114.2(5)	F—C—F	103.0(8)
CH_2—P—CH_2	103.6(3)		

[a] Weighted means were computed from $\Sigma_i(x_i/\sigma_i^2)/\Sigma(1/\sigma_i^2)$.

was no noticeable lengthening of the trans Pt—Cl bond, a result attributed to steric strain [17]. Only where CF_3 substituents are present on the P atom has a shorter Pt—P distance been observed, as in *cis*-[$PtCl_2(CF_3)_2PCH_2CH_2P(C_6H_5)_2$]. In this case the value of 2.168(3) Å was *trans* to a Pt—Cl distance of 2.317(3) Å, and the authors adduced a Pt—P π interaction as being partly responsible for the short bond [18].

The chelate ring formed by reaction of allene and methanol with the vinyl ligand is bonded to the Pt atom through a sp^3 hybridised C atom and an ethereal O atom. This is the first example of a Pt ether complex, to the best of our knowledge. Whereas the Pt—C(1) bond distance is unexceptional, the Pt—O distance of 2.144(9) Å is rather long. In some acetylacetonate (acac) complexes of Pt, values for a Pt—O bond length have been measured. For example, in K[$Ptacac_2Cl$] a value of 1.968(14) Å was found, *trans* to a Cl atom, whereas the distance was 2.072(14) Å *trans* to a σ-bonded C atom. The relative *trans* influences of Cl and C are responsible [19]. In the dimeric complex [$Pt(C_3H_5)acac$]$_2$, the Pt—O distances were 2.07(2) and 2.07(2) Å, trans to a σ-bonded allyl ligand, and 1.98(2) and 1.99(2) Å, *trans* to a π-bonded allyl ligand [20]. Thus it is clear that the ethereal oxygen atom is acting as a Lewis donor, only forms a weak bond with the Pt atom, and has a very small *trans* influence.

Within the chelate ring, C(3) is an asymmetric C atom, and the crystals contain pairs of enantiomeric cations. The presence of a formal double bond

TABLE 6

SELECTED WEIGHTED LEAST-SQUARES PLANES [a]

Plane 1: $3.128x + 1.261y + 8.727z = 3.745$			
Pt	−0.0005(6)	O	−0.189(11)
P(1)	−0.018(4)	C(1)	0.415(16)
P(2)	0.016(4)		
Plane 2: $9.695x - 13.72y - 3.328z = 1.023$			
C(1)	−0.005(14)	C(5)	−0.02(2)
C(3)	0.002(16)	C(6)	0.00(2)
C(4)	0.03(3)	C(7)	0.02(2)

[a] Distances given are displacements from the plane in Å.

between C(3) and C(5) is indicated, both from the bond length of 1.36(2) Å, close to the average value of 1.337(6) Å quoted for a number of such bonds [21], and from the planarity of the atoms C(1), C(3), C(4), C(5), C(6) and C(7), (Table 6). The geometry at the ethereal O atom is other than that expected for sp^3 hybridization, for the angles are 122(1), 123(1) and 114(1)°. The four atoms O, Pt, C(7) and C(8) are not coplanar, as would be required for sp^2 hybridization, for the methyl substituent C(8) is 0.28(4) Å from the plane formed by Pt, O and C(7). Thus the O atom is apparently intermediate between sp^2 and sp^3 hybridization, which renders it, too, effectively asymmetric. We conclude that the ligand is therefore 1,2-bis(trifluoromethyl)-3-methyl-4-methoxybut-2-enyl-O,C^4.

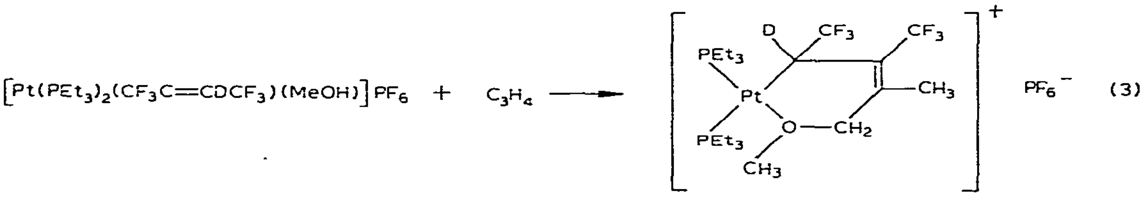
NMR spectra of I

On the basis of the crystallographic information, the NMR data can now be analyzed in greater detail. In the ^{19}F NMR spectrum of I, there are two broad resonances for the two CF_3 groups. The low field one at δ −53.61 ppm is a 1/2/1 triplet with ^{195}Pt satellites. The triplet arises from coupling with the *trans* P nuclei and the vicinal H atom. The two coupling constants $^3J(PF)$ and $^2J(FH)$ are accidentally identical, resulting in a symmetrical triplet. The high field CF_3 resonance at δ −59.09 ppm is a broad singlet, with the mutual coupling of the two CF_3 groups not resolved since they are no longer joined by a C=C bond.

In the ^1H NMR spectrum the PCH_2CH_3 protons exhibit the characteristic 1/2/2/2/1 quintet pattern for a *cis* arrangement of the two phosphines [22]. The coordination of the OCH_3 group to Pt is evidenced from the large Pt—H coupling (12.5 Hz). Therefore, the solid state structure also persists in solution. The two methylene protons are nonequivalent (δ 4.46 and 3.61 ppm) and appear as doublets, with the low field one exhibiting ^{195}Pt satellites. A sample double resonance experiment shows that they are coupled to each other (J(HH) 16.5 Hz). Since they are attached to a 6-membered metallocyclic ring, they are at different distances from the Pt atom (Fig. 2, Pt—H1C(7) 3.61 Å, Pt—H2C(7) (occluded) 3.80 Å). Apparently, due to this difference, only H1C(7) is coupled with ^{195}Pt, presumably via through-space coupling. The methine proton resonates at ~δ 3.2 ppm and is partially obscured by the high field methylene proton signal. Moreover, the various couplings to several different nuclei make it even more difficult to observe. While the vinylic methyl group is also obscured, in this case by the PEt_3 signal, both methine and methyl groups can be detected readily in the ^2H NMR spectra of Ib and Ic (see below).

In the ^{31}P NMR spectrum of I, besides the PF_6^- resonance, there are two mutually coupled signals with ^{195}Pt satellites. In addition, the resonance at low field is further split into a quartet due to P—F coupling. Hence, this resonance is assigned to the phosphine ligand *trans* to the Pt—C bond of the chelate ring. The unusually short Pt—P bond (2.219(4) Å) of the other phosphine ligand is reflected in the exceptionally large value of 4529.9 Hz for its Pt—P coupling constant. Recently, Bennett et al. prepared a range of planar platinum(II) complexes with *cis* disposition of phosphine ligands and used the *J*(PtP) value to assess the *trans*-influence of various ligands [23]. The large *J*(PtP) value thus places the ethereal ligand as the group with the weakest *trans*-influence. Not surprisingly, both the Pt—P bond distance and the *J*(PtP) value lie on the extremity of Pidcock's correlation curve for the longest bond length and largest *J*(PtP) [24].

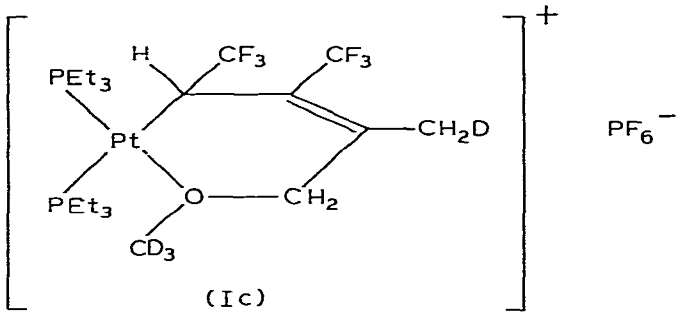
When a deuterium labelled vinylic complex, $[Pt(PEt_3)_2(CF_3C{=}CDCF_3)(MeOH)]PF_6$, was allowed to react with allene in methanol, complex Ib was obtained. In its ^1H NMR spectrum, the methine resonance at δ ~3.2 ppm is absent. The low field resonance in its ^{19}F NMR spectrum is a doublet instead of the triplet observed for I. The ^2H NMR spectrum exhibits one broad resonance at —4.40 ppm upfield from $CDCl_3$. Thus, there is no exchange of the vinylic proton in the reaction, and the deuterium is in the methine position in Ib:



(3)

(Ib)

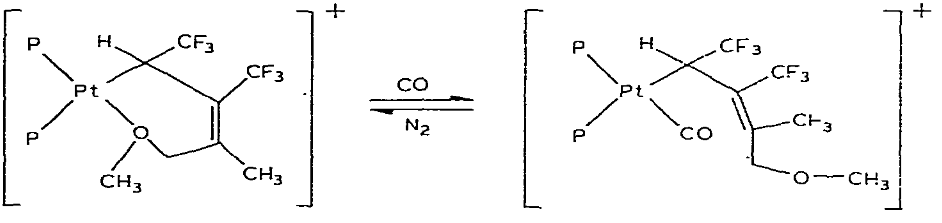
When reaction 3 is conducted in CD_3OD and a non-deuterium labelled vinylic platinum complex is used, Ic is obtained. Its ^2H NMR spectrum exhibits two resonances at —3.84 and —5.86 ppm (relative intensities 3/1) corresponding to the methoxy methyl and the vinylic methyl resonances respectively. Ic therefore has the structure,



(Ic)

Substitution reactions

Carbon monoxide reacts with I readily by displacing the ethereal end of the chelate to form II. The reaction is, however, reversible and I can be regenerated



(4)

(I) (II)

by passing N_2 into a solution of II. Therefore, the NMR spectra of II had to be recorded under a CO atmosphere. The ^{31}P NMR spectrum shows that the two phosphines are *cis* ($J(PP)$ 28.9 Hz) with respect to each other with the low field resonance displaying P—F coupling. In the ^1H NMR spectrum of II, the resonance for the methoxyl-methyl group is shifted to higher field (δ 3.41 ppm) compared with that of I, and the ^{195}Pt satellites are no longer observable. The two methylene protons remain non-equivalent owing to the asymmetric α C atom. The two CF_3 groups appear as two broad resonances in the ^{19}F NMR with one resonance exhibiting ^{195}Pt satellites (thus the Pt—C bond still remains intact).

CH_3CN reacts with I in a similar fashion. The displacement of the ethereal end of the metallocycle again causes an upfield shift of the OCH_3 signal, the magnitude of which depends on the concentration of CD_3CN. Thus, the equilibrium 5 is fast on the NMR time scale at 30° C. (The ^{31}P NMR signals are

$$I + CH_3CN \overset{K}{\rightleftharpoons} III \tag{5}$$

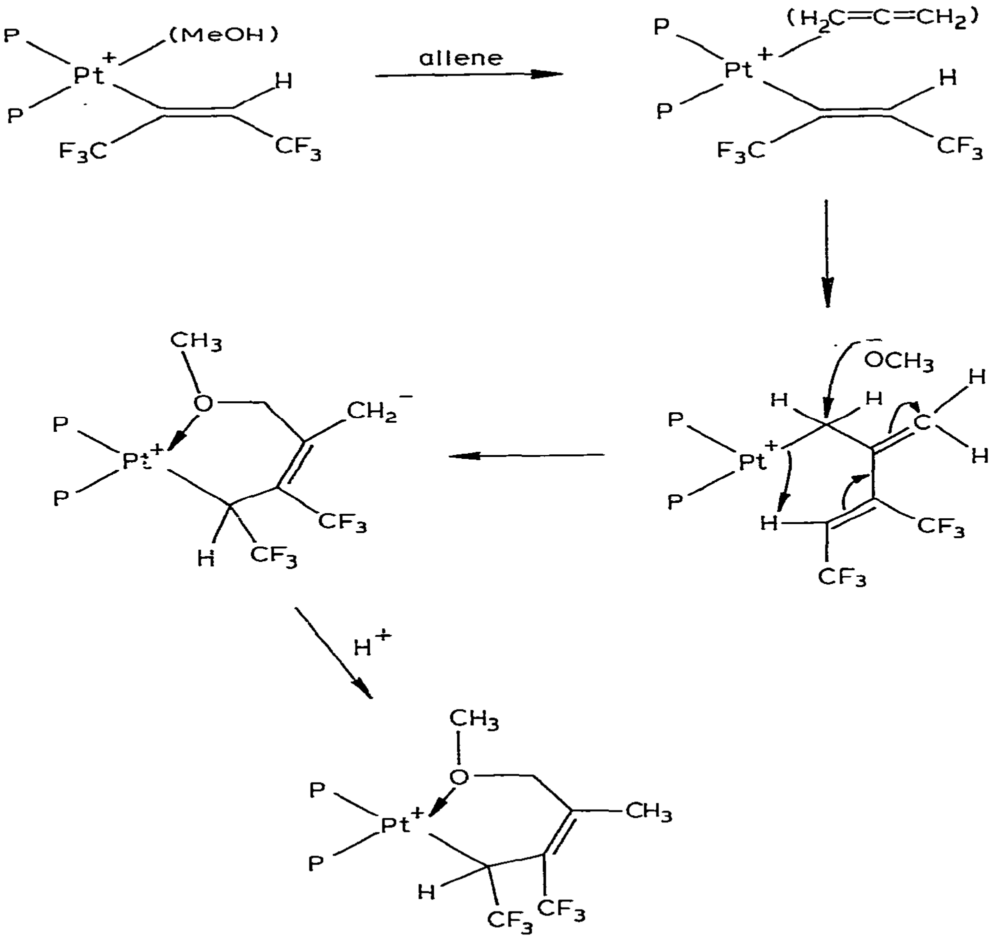
broad at 30° C and have to be measured at −40° C). From the average position of the OCH_3 resonance and the concentration of CD_3CN, K was determined to be 0.16 ± 0.01 l mol^{-1}. The attempted isolation of III by addition of ether to an acetonitrile solution of I resulted only in the recovery of I.

Addition of acetone or styrene to a solution of I in chloroform caused scarcely any change in the ^1H NMR spectrum, except for a very small upfield shift of the OCH_3 signal. The equilibrium thus lies far to the side of the ethereal complex. All these results indicate that although the ethereal group is a weak ligand to Pt, because of the chelating effect, its displacement by other ligands is thermodynamically not favourable. This is consistent with the fact that the closing of a six-membered ring is only slightly less favourable than that of a five-membered ring [25], and presumably in this case the presence of a double bond decreases the ligand bite and further increases the tendency for ring closure.

Mechanism

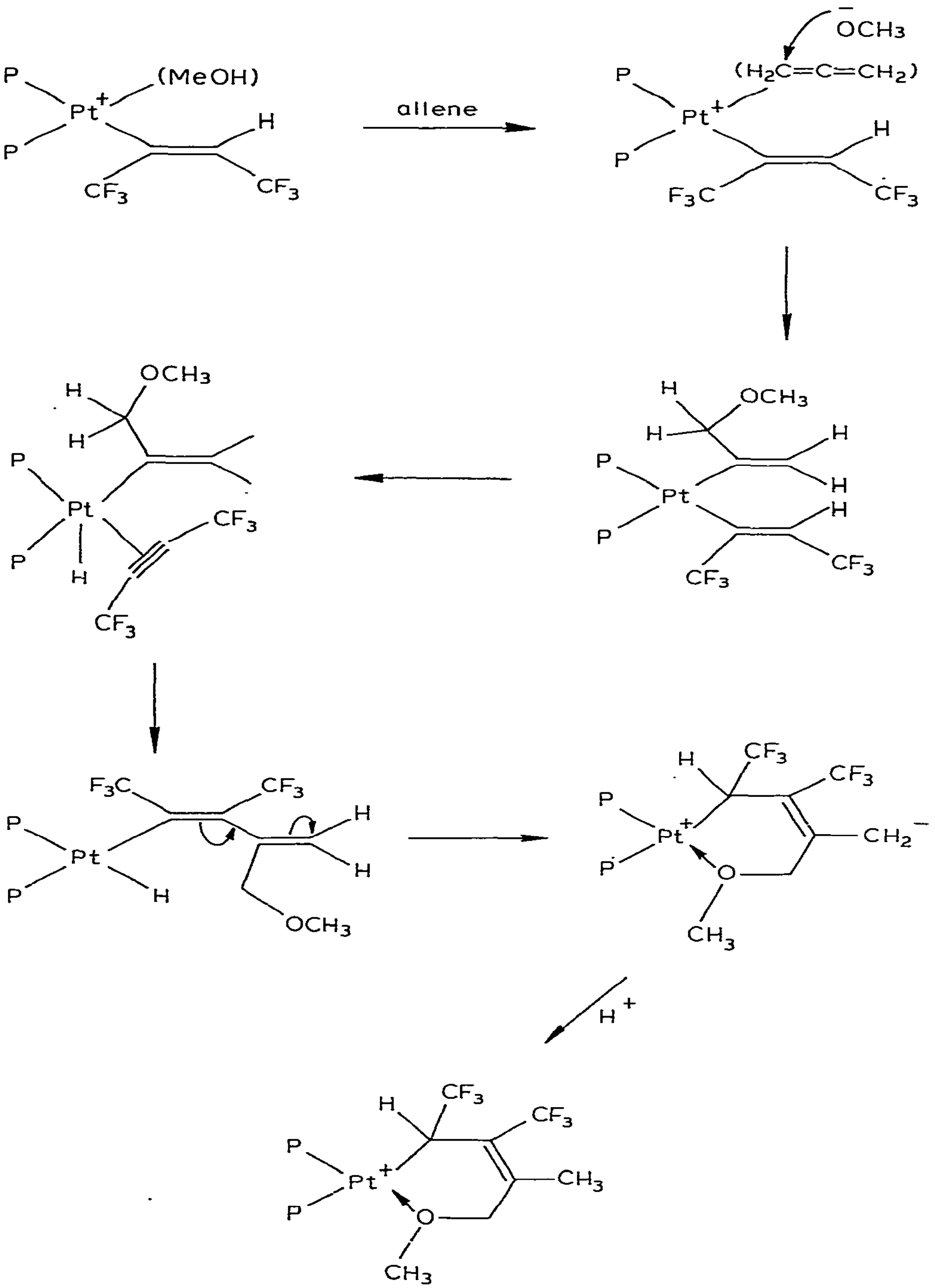
The mechanism of the formation of I is a matter for speculation although some indirect information is available. From the ^2H labelling experiments, the vinylic proton does not exchange with solvent and is incorporated into the methine position of the product. It seems that there are two possible routes depending on whether nucleophilic attack by OCH_3 occurs after or before the rupture of the Pt—vinylic bond (Schemes 1 and 2). In Scheme 1, an insertion

SCHEME 1



reaction occurs involving the vinylic group and allene of the type previously observed in other solvents [5]. Nucleophilic attack on the α carbon by the OCH_3 followed by reaction with H^+ would generate the ethereal complex. In Scheme 2 an initial methoxide attack on the coordinated allene occurs. This type of reaction is well known in Pd [26,27] and Pt [28,29] chemistry and is particularly favourable when electron-withdrawing groups are present in the complex [30]. (The methyl analog of the vinylic complex, $[Pt(PEt_3)_2(CH_3C{=}CHCH_3)(MeOH)]PF_6$, reacts with allene in methanol to afford only the π-allylic complex). The incorporation of the vinylic ligand might require a β-elimination of the C—H bond to form an acetylene hydrido-platinum complex, the acetylene then undergoing insertion into the alkyl bond. This is followed by α addition of the Pt—H bond, and a final recombination of H^+ gives the ethereal complex. However further work will be required to demonstrate the validity of either of these mechanisms.

SCHEME 2


P
P
Pt+
(MeOH)
H
CF3
CF3
allene
OCH3
(H2C=C=CH2)
Pt+
F3C
CF3
OCH3
H
Pt
CF3
CF3
OCH3
F3C
CF3
H
H
Pt
H
OCH3
CF3
CF3
CH2−
O
CH3
H+
CF3
CF3
Pt+
CH3
O
CH3

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