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Formation of $Pt(CH_3)(CF_3)$ (diolefin) from $Pt(CH_3)_2$(diolefin) and CF_3I (diolefin = NBD, norbornadiene, or COD, 1,5-cyclooctadiene). The crystal structures of (η^4-norbornadiene)(methyl)(trifluoromethyl)-platinum(II) and (η^4-norbornadiene)bis(trifluoromethyl)platinum(II)

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Abstract

Reaction between $Pt(CH_3)_2$(diolefin) (diolefin = norbornadiene (NBD); 1,5-cyclooctadiene (COD)) and two mole equivalents of CF_3I produces, in addition to the previously reported products $Pt(CF_3)_2$(diolefin) (**2**) and $[Pt(CH_3)_3I]_4$, the mixed alkyl compound $Pt(CH_3)(CF_3)$(diolefin) (**1**). The crystal structure of $Pt(CH_3)(CF_3)$(NBD) (**1a**) has been determined, together with that of $Pt(CF_3)_2$(NBD) (**2a**) for comparison. The complexes are isomorphous and isostructural. The Pt–C (CH_3) and Pt–C (CF_3) bond distances in **1a** are similar {each 2.07(2) Å}, and are similar to the Pt–C distance in **2a**. The Pt–C (norbornadiene) distances likewise show only slight differences {means 2.23(2) (**1a**), 2.26(4) Å (**2a**)}.

1. Introduction

The only known preparative route to bis(trifluoromethyl)platinum(II) complexes involves the reaction of trifluoromethyl iodide with $Pt(CH_3)_2$(diolefin) (**3**) to give $Pt(CF_3)_2$(diolefin) (**2**). This reaction was first reported by Clark and Manzer for the 1,5-cyclooctadiene (COD) complex [1], and we recently used a similar method to prepare $Pt(CF_3)_2$(NBD) (**2a**) (NBD = norbornadiene) [2]. Although it has always been clear [1] that these reactions must proceed *via* a sequence of oxidative addition–reductive elimination reactions, with the mixed alkyl complex $Pt(CH_3)(CF_3)$(diolefin) (**1**) as an intermediate (Scheme 1), such compounds have not previously been detected. We describe below the isolation and characterization of the complex $Pt(CH_3)(CF_3)$(NBD) (**1a**) and the characterization in solution of $Pt(CH_3)(CF_3)$(COD) (**1b**). The crystal structure of the complex **1a** has been determined, together with, for comparison, the structure of $Pt(CF_3)_2$(NBD) (**2a**).

2. Experimental details

2.1. Starting materials

Trifluoromethyl iodide was supplied by Fluorochem Ltd. Published methods were used to prepare $Pt(CH_3)_2$(COD) [1], $Pt(CH_3)_2$(NBD) [3], and Pt $(CF_3)_2$(NBD) [2].

2.2. General

The 99.6 MHz ^1H, 94.2 MHz ^{19}F, 25.05 MHz ^{13}C, and 21.4 MHz ^{195}Pt NMR spectra were recorded on a

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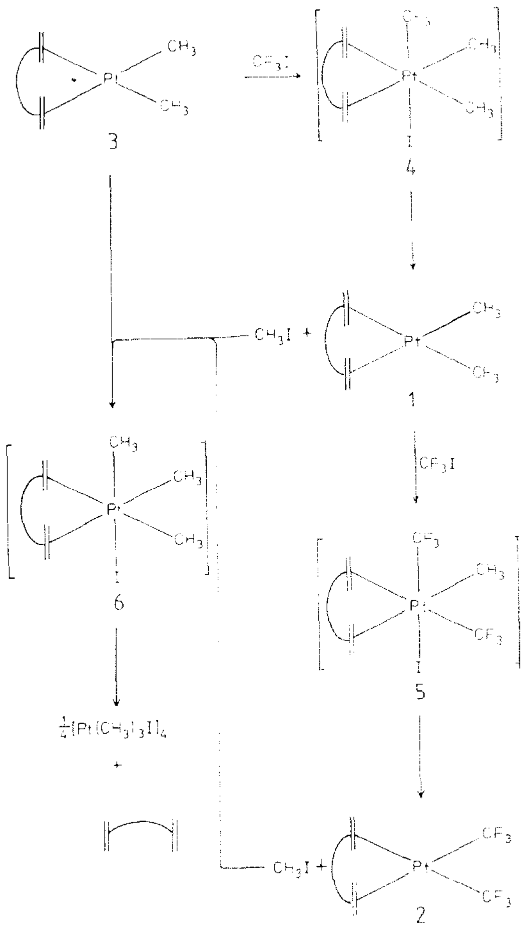
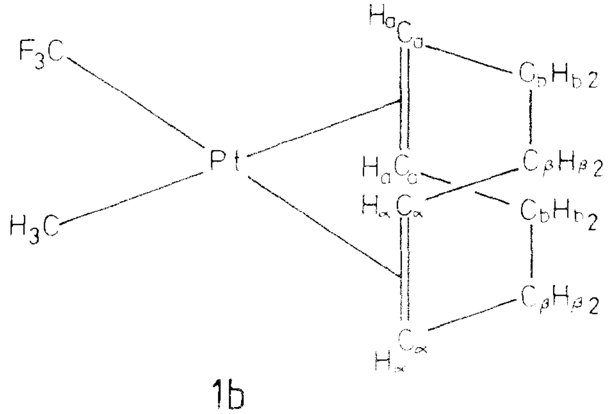


Scheme 1.

JEOL JNM FX-100 spectrometer with a 10 mm tunable probe. A 5 mm tube was used with an adapted spinner for the ^{1}H and ^{19}F spectra. 100.4 MHz ^{13}C spectra were recorded on a JEOL JNM GX-400 spectrometer with a 5 mm dual ^{1}H/^{13}C dual probe, and 200 MHz ^{1}H NMR spectra on a Bruker 200ACF spectrometer. Chemical shifts (positive to lower field) are relative to internal tetramethylsilane (TMS) for ^{1}H and ^{13}C, to internal CFCl$_3$ for ^{19}F, and to a separate sample of Na$_2$PtCl$_6$/H$_2$O for ^{195}Pt. ^{13}C and ^{195}Pt spectra were ^{1}H-decoupled.



1b

The assignments of the olefinic protons were confirmed by measurement of nuclear Overhauser enhancement (see Results section), by both 1-D and 2-D NOESY [4] at 200-MHz.

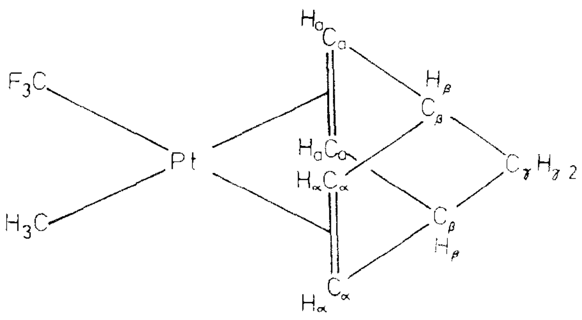
IR spectra were recorded as Nujol mulls on a Perkin-Elmer 283B spectrometer.

C and H microanalyses were carried out by the microanalytical service in this Department, or by the National Analytical Laboratory, Melbourne, which also carried out the F analyses.

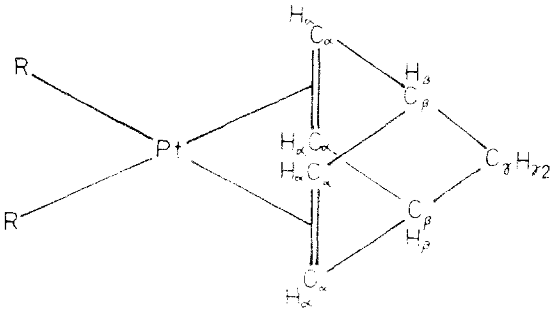
2.3. *Preparation of compounds*

2.3.1. *Pt(CF$_3$)$_2$(NBD) (2a)*

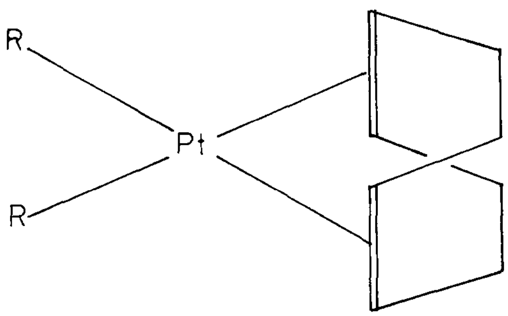
The preparation of Pt(CF$_3$)$_2$(NBD) (**2a**) by reaction of Pt(CH$_3$)$_2$(NBD) (**3a**) with excess CF$_3$I has been previously described [2]. It is analogous to the preparation of Pt(CF$_3$)$_2$(COD) (**2b**) [1]. Crystals of **2a** were grown by slow evaporation of dichloromethane from a solution in dichloromethane/n-hexane. ^{19}F, ^{13}C, and



1a



R = CF$_3$ 2a
R = CH$_3$ 3a



R = CF$_3$ **2b**
R = CH$_3$ **3b**

^{195}Pt NMR spectra have been previously described [5], but not the ^{1}H spectrum: (in CDCl$_3$) δ(H$_\alpha$) 6.13, J(Pt–H$_\alpha$) 43.7 Hz; δ(H$_\beta$) 4.31; δ(H$_\gamma$) 1.77.

2.3.2. Pt(CH$_3$)(CF$_3$)(NBD) (1a)

The complex Pt(CH$_3$)$_2$(NBD) (**3a**) (2.00 g, 6.3 mmol) was dissolved in 10 ml CH$_2$Cl$_2$, and the solution was transferred to a thick-walled Carius tube of 30 ml capacity. The solution was degassed and frozen under vacuum. Trifluoromethyl iodide (12 mmol) was condensed into the tube, which was then sealed. The tube was immediately covered with aluminium foil to exclude light, and allowed to warm to room temperature. After 16 h at this temperature, during which some crystals of [Pt(CH$_3$)$_3$I]$_4$ separated, the tube was opened. The solution was taken to dryness under reduced pressure. The resultant solid, which contained unchanged Pt(CH$_3$)$_2$(NBD), Pt(CH$_3$)(CF$_3$)(NBD), Pt(CF$_3$)$_2$(NBD), and [Pt(CH$_3$)$_3$I]$_4$, was extracted with acetone (2 × 10 ml), to leave 0.62 g of [Pt(CH$_3$)$_3$I]$_4$. The combined acetone extracts were taken to dryness. A column (25 × 1 cm) of Florisil in dry, distilled n-hexane was prepared, and the solid transferred to the top of the column. Initial elution with n-hexane (120 ml) removed unreacted Pt(CH$_3$)$_2$(NBD) (0.44 g, after the eluted solution was taken to dryness). Dry, acid-free CH$_2$Cl$_2$/n-hexane (volume ratio 1 : 8, 140 ml) was then used to elute Pt(CH$_3$)(CF$_3$)(NBD) (0.30 g after the solution was taken to dryness). Finally, elution with neat CH$_2$Cl$_2$ (80 ml) gave Pt(CF$_3$)$_2$(NBD) (0.15 g, after removal of solvent). The crude Pt(CH$_3$)(CF$_3$)(NBD) was recrystallized by addition of n-hexane (10 ml) to a CH$_2$Cl$_2$ solution (2 ml), followed by slow evaporation of the solvent. The colourless crystals were filtered off on a sintered glass funnel (0.25 g, 11%).

Analysis: Found: C, 29.3; H, 2.9; F, 15.1. C$_9$H$_{11}$F$_3$Pt calcd.: C, 29.1; H, 3.0; F, 15.4%.

NMR (in (CD$_3$)$_2$)CO, ^{13}C values from 100.4 MHz spectra, ^{1}H values from 200 MHz spectra; norbornadiene atoms are labelled as in structure **1a**): ^{1}H δ(Pt–CH$_3$) 0.66, ^2J(Pt–CH$_3$) 89.2 Hz; δ(H$_a$) 5.54, J(Pt–H$_a$) 38.8 Hz; δ(H$_\alpha$) 5.85, J(Pt–H$_\alpha$) 45.0 Hz; δ(H$_\beta$) 4.24; H$_\gamma$, two non-equivalent protons, δ(H$_{\gamma1}$) 1.73, J(F–H$_{\gamma1}$) 0.64 Hz, δH$_{\gamma2}$ 1.66, J(F–H$_{\gamma2}$) 0.45 Hz, ^2J(H$_{\gamma1}$H$_{\gamma2}$ 8.6 Hz). ^{13}C δ(Pt–CH$_3$) 4.54 (quartet), ^1J(Pt–C) 788.1 Hz, J(F–C) 4.9 Hz; δ(Pt–CF$_3$) 130.20 (broad quartet), ^1J(C–F) 342.8; δ(C$_a$) 97.01, J(Pt–C$_a$) 41.0; δ(C$_\alpha$) 99.70, J(Pt–C$_\alpha$) 51.0; δ(C$_\beta$) 51.74, J(Pt–C$_\beta$) 38.1 Hz; δ(C$_\gamma$) 75.41, J(Pt–C$_\gamma$) 55.7. ^{19}F −34.02 ppm, ^2J(Pt–CF$_3$) 893.6 Hz. ^{195}Pt (quartet) −3869 ppm.

2.3.3. Reaction of Pt(CH$_3$)$_2$(COD) (3a) with CF$_3$I

An analogous reaction was carried out between Pt(CH$_3$)$_2$(COD) and CF$_3$I. After [Pt(CH$_3$)$_3$I]$_4$ was filtered off, the solution contained unchanged Pt(CH$_3$)$_2$(COD), Pt(CF$_3$)$_2$(COD) (previously characterized [1]), and Pt(CH$_3$)(CF$_3$)(COD) (**1b**). This last compound was not isolated, but was characterized in solution by NMR spectroscopy (in CDCl$_3$, with cyclooctadiene atoms labelled as in structure **1b**): ^{1}H (100 MHz) δ(Pt–CH$_3$) 0.78, ^2J(Pt–CH$_3$) 80.2 Hz; δ(H$_a$) 5.11, J(Pt–H$_a$) 37.5 Hz; δ(H$_\alpha$) 5.33, J(Pt–H$_\alpha$) 40.3 Hz; δ(H$_b$, H$_\beta$) 2.33. ^{13}C (100.4 MHz) δ(Pt–CH$_3$) 1.79, ^1J(Pt–C) 730.5 Hz, J(F–C) 5.9 Hz; δ(C$_a$) 103.90, J(Pt–C$_a$) 46.9 Hz; δ(C$_\alpha$) 104.84, J(Pt–C$_\alpha$) 66.4 Hz; δ(C$_b$, C$_\beta$) 29.04 (peaks from platinum coupling not resolved). ^{19}F −30.53 ppm, ^2J(Pt–CF$_3$) 810.6 Hz. ^{195}Pt (quartet) −3807 ppm.

2.3. Crystal data

1a: C$_9$H$_{11}$F$_3$Pt, $M_r = 371.3$, orthorhombic, space group $P2_12_12_1$, a = 8.040(3), b = 9.185(2), c = 13.041(5) Å, V = 963.5 Å^3, Z = 4, D_c = 2.560 g cm^{-3}, F(000) = 680, μ(Mo Kα) = 153.2 cm^{-1}, T = 297 K.

2a: C$_9$H$_8$F$_6$Pt, $M_r = 425.2$, orthorhombic, space group $P2_12_12_1$, a = 8.138(1), b = 9.450(2), c = 13.475(3) Å, V = 1036.3(4) Å^3, Z = 4, D_c = 2.724 g cm^{-3}, F(000) = 776, μ(Mo Kα) = 143.0 cm^{-1}, T = 293 K.

2.4. Data collection, structure determination, and refinement

X-ray diffraction data were collected on Nicolet R3m diffractometers using graphite crystal monochromatized Mo Kα radiation from crystals measuring 0.38 × 0.35 × 0.31 mm (**1a**) and 0.30 × 0.26 × 0.15 mm (**2a**). 1002 and 855 unique reflections were collected for **1a** and **2a** up to $2\theta_{max} = 50°$ and of these 909 [$I > 2.5\sigma(I)$] and 769 [$I > \sigma(I)$] respectively were considered observed and used in structure refinement. Data were corrected for absorption. Although complex **1a** turned black during the data collection, the maximum decrease of 1% in the intensities of two standards monitored during this time indicated negligible crystal decay. With complex **2a**, this problem was more acute, necessitating scaling of the data to allow for decrease in diffraction intensity. This also accounts for the paucity of observed data, and is reflected in the disorder observed, particularly in the trifluoromethyl groups. The structures were solved by Patterson methods of SHELX-86 [6] and refined by full-matrix least-squares refinement (SHELX-76 [7]) to residuals R $\{= \sum \| F_o | - | F_c \| / \sum | F_o |\}$ and R_w $\{= (\sum w \| F_o | - | F_c \|^2 / \sum w | F_o |^2)^{\frac{1}{2}}\}$ of 0.042, 0.045 (**1a**) and 0.062, 0.067 (**2a**). No hydrogen atoms were included in the refinements. Neutral atom scattering factors were used [8] with the data corrected for the effects of anomalous dispersion [8]. The disorder in one of the trifluoromethyl groups in **2a** was allowed for by including the fluorine atoms with partial site occupancies. Final atomic coordinates are given in Table 1 while bond distances and angles are listed in Table 2. Anisotropic thermal parameters, observed and calculated structure factors, and bond distances and angles within the norbornadiene ligand are available from the authors.

3. Results

3.1. *The reactions between $Pt(CH_3)_2(diolefin)$ (3) and CF_3I*

When $Pt(CH_3)_2$(diolefin) (**3**) reacts with a large excess of CF_3I, $Pt(CF_3)_2$(diolefin) (**2**) is always the major product [1,2]. The optimum molar ratio of CF_3I to **3** for maximizing the formation of the mixed-alkyl compounds $Pt(CH_3)(CF_3)$(diolefin) (**1**) in dichloromethane was approximately 2 : 1, and even then the yield of **1** was always low (up to 20% in the reaction mixture in solution). Addition of hydroquinone (0.03 M) as a radical scavenger had no significant effect on the distribution of products from the reaction.

3.2. *The crystal and molecular structures of 1a and 2a*

Complexes **1a** and **2a** are isostructural and isomorphous. Although there is considerable disorder in the trifluoromethyl groups, particularly in **2a**, the basic structural features of the two compounds are comparable, and similar. Figure 1 shows the molecular configuration for **1a**. The coordination about Pt is 'square', as expected with the C–Pt–C bond angle associated with the alkyl groups close to 90° [89.5(9)°, (**1a**); 91(1)°, (**2a**)]. The Pt–C distances are also equal within experimental error for the methyl and trifluoromethyl groups. With the exception of one value [2.36(4) Å in **2a**], all of the Pt–C (NBD) distances in both compounds are also similar, and close to the mean value of 2.23 Å. The distances between the Pt atom and the midpoints of the C=C bonds are also all similar [2.12, 2.15(2) Å in **1a** and 2.12, 2.21(3) Å in **2a**]. The single anomalous Pt–C value in **2a** is probably caused by poor data resulting from crystal instability. The "bite" angle of the chelating NBD ligand is 67(1)° in **1a**, and 68(1)° in **2a**, which may be compared with 70.4° in Pt(2-ethoxynaphth-1-yl)$_2$(NBD) [9], and 68.7° in Pt(2-ethoxynaphth-1-yl)Cl(NBD) [10].

TABLE 1. Atom coordinates (× 10^4) for **1a** and **2a**, with equivalent isotropic (**1a**) or isotropic thermal parameters (**2a**) $U_{eq} = (U_{11} + U_{22} + U_{33})/3$

	x	y	z	$U_{iso}(10^3$ Å$^2)$
1a				
Pt	9099.5(9)	9406.0(10)	1286.7(6)	53.3(4)
C(1)	11838(31)	9163(34)	979(29)	62(20)
C(2)	11124(37)	8217(33)	467(24)	74(18)
C(3)	10698(38)	8823(35)	−594(21)	77(15)
C(4)	9389(32)	9936(32)	−374(18)	63(14)
C(5)	10158(33)	10989(27)	177(21)	66(15)
C(6)	11996(37)	10607(31)	340(20)	84(15)
C(7)	12303(45)	9825(24)	−705(19)	96(17)
C(10)	8885(38)	8196(37)	2622(24)	104(21)
C(20)	6835(31)	10388(19)	1607(13)	60(12)
F(21)	5680(17)	9489(20)	1920(17)	114(12)
F(22)	6933(23)	11418(24)	2277(19)	128(14)
F(23)	6235(32)	10976(37)	735(23)	196(28)
2a				
Pt	8972(1)	9424(1)	1248(1)	34.3(7)
C(1)	11781(81)	9169(55)	869(38)	53(16)
C(2)	10896(45)	8183(36)	440(23)	46(8)
C(3)	10671(51)	8721(41)	−576(27)	64(1)
C(4)	9281(53)	9940(45)	−362(29)	58(10)
C(5)	9953(54)	10988(42)	181(29)	54(10)
C(6)	11849(53)	10604(41)	377(27)	61(9)
C(7)	12169(64)	9780(46)	−708(31)	69(9)
C(10)	8671(49)	8327(43)	2521(29)	55(10)
C(20)	6817(52)	10523(39)	1502(25)	55(10)
F(21) *	5504(79)	9558(66)	1834(45)	117(20)
F(21) *	6704(51)	11132(41)	2305(27)	67(10)
F(22) *	6644(44)	11629(39)	895(23)	59(9)
F(24) *	6063(81)	10843(66)	574(45)	121(19)
F(25) *	5521(69)	9781(62)	951(36)	105(16)
F(11)	9049(33)	9005(27)	3351(18)	80(7)
F(12)	7322(42)	7693(33)	2732(23)	108(10)
F(13)	9806(51)	7213(43)	2537(29)	123(11)

* Site occupancy 0.6.

The packing of the complex molecules in the unit cell (Fig. 2) shows discrete complex units with no significant intermolecular associations.

3.3. *NMR spectra*

Chemical shifts and selected coupling constants are given in the experimental section. For each of the compounds $Pt(CH_3)(CF_3)$(diolefin) (**1a**, **1b**), there was one singlet with satellites in the ^{19}F spectrum, and the

TABLE 2. Bond distances (Å) and angles (°) about the coordination sphere

	1a	2a
Distances		
Pt-C(10)	2.07(2)	2.02(4)
Pt-C(20)	2.07(2)	2.07(4)
Pt-C(1)	2.25(2)	2.36(4)
Pt-C(2)	2.23(2)	2.24(4)
Pt-C(4)	2.23(2)	2.24(3)
Pt-C(5)	2.22(2)	2.21(4)
Angles		
C(10)-Pt-C(20)	89.5(9)	91(1)
C(10)-Pt-C(1)	100.2(10)	104(1)
C(10)-Pt-C(2)	101.6(10)	103(1)
C(10)-Pt-C(4)	160.2(11)	162(1)
C(10)-Pt-C(5)	158.5(9)	160(1)
C(20)-Pt-C(1)	159.8(7)	156(1)
C(20)-Pt-C(2)	161.6(8)	160(1)
C(20)-Pt-C(4)	101.1(7)	98(1)
C(20)-Pt-C(5)	100.5(7)	95(1)
C(1)-Pt-C(2)	32.0(10)	33(1)
C(1)-Pt-C(4)	75.3(9)	73(1)
C(1)-Pt-C(5)	64.8(8)	65(1)
C(2)-Pt-C(4)	64.3(8)	64(1)
C(2)-Pt-C(5)	74.3(7)	77(2)
C(4)-Pt-C(5)	35.4(8)	35(1)

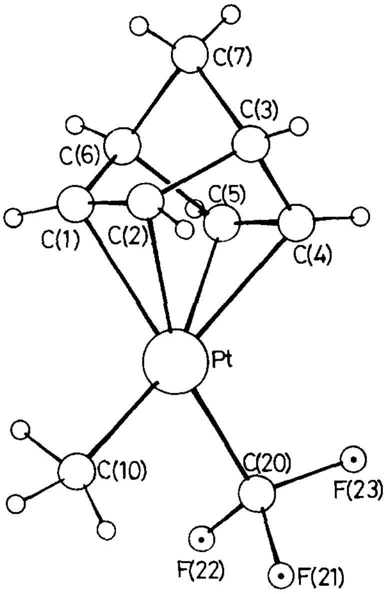


Fig. 1. Molecular configuration and atom naming scheme for **1a**. Complex **2a** is isomorphous with **1a**. Hydrogen atoms are included at calculated positions.

^1H-decoupled ^{195}Pt NMR spectrum showed a 1:3:3:1 quartet from coupling with the ^{19}F nuclei of a single trifluoromethyl group. The ^1H-decoupled 100.4 MHz ^{13}C spectra showed a quartet (with satellites) from the methyl carbon nucleus, with a small $^{19}F_3C-Pt-^{13}C$ coupling. Analogous couplings have previously been observed in some mixed alkyl platinum(IV) complexes [2]. The central quartet from the trifluoromethyl carbon was also observed in the ^{13}C spectrum from **1a**. Each separate carbon atom in the diolefin part of each molecule gave a singlet with satellites from coupling to ^{195}Pt, except for the signals for C_b and C_β in the COD complex **1b**, which were coincident, and which showed no resolvable coupling to platinum.

The 200 MHz ^1H NMR spectrum of a degassed solution of $Pt(CH_3)(CF_3)(NBD)$ (**1a**) in $(CD_3)_2CO$ was examined in some detail. The methyl group showed a 1:3:3:1 quartet (with satellites), from a small (0.52 Hz) coupling with the fluorine nuclei. This may be compared with the value of 0.7 Hz for $^4J(^{19}F_3C-Pt-C^1H_3)$ in $Pt(CF_3)_2(CH_3)Ipy_2$ [2]. The protons of the coordinated norbornadiene gave, as expected, a second-order pattern, which was not analysed in detail. The "bridgehead" protons H_β gave a complex multiplet, and the olefinic protons two "complex triplets" with satellites (Fig. 3). Irradiation of the H_β multiplet caused considerable simplification of the spectrum, with the signals from the olefinic protons now singlets with satellites. In this spectrum with coupling to H_β removed, the protons attached to C_γ gave an AB pattern, with each peak showing quartet splitting from a small long-range coupling with the ^{19}F nuclei. The presence of this coupling is remarkable in view of the absence of resolved coupling to ^{19}F for the olefin protons, which are much closer, both in number of bonds and through space, to the trifluoromethyl group.

The olefinic protons *trans* to trifluoromethyl (H_α) would be expected to be related by nuclear Overhauser enhancement (nOe) to the protons of the methyl group which is *cis* to it. Difference spectra showed that only the resonance from the olefin protons at 5.85 ppm increased in intensity when the methyl protons were irradiated, and a 2-D NOESY spectrum showed a strong corresponding cross-peak. There was no mea-

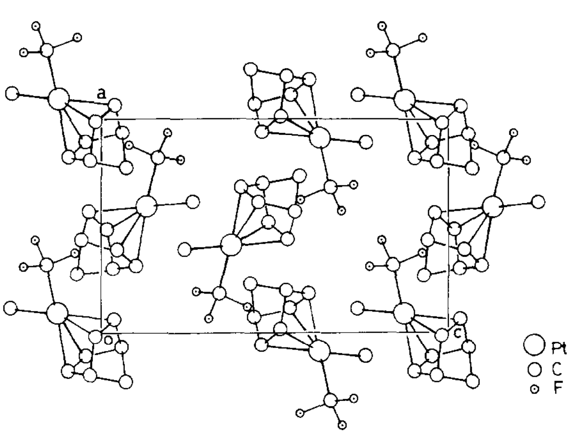


Fig. 2. Packing of **1a** in the unit cell viewed down *b*.

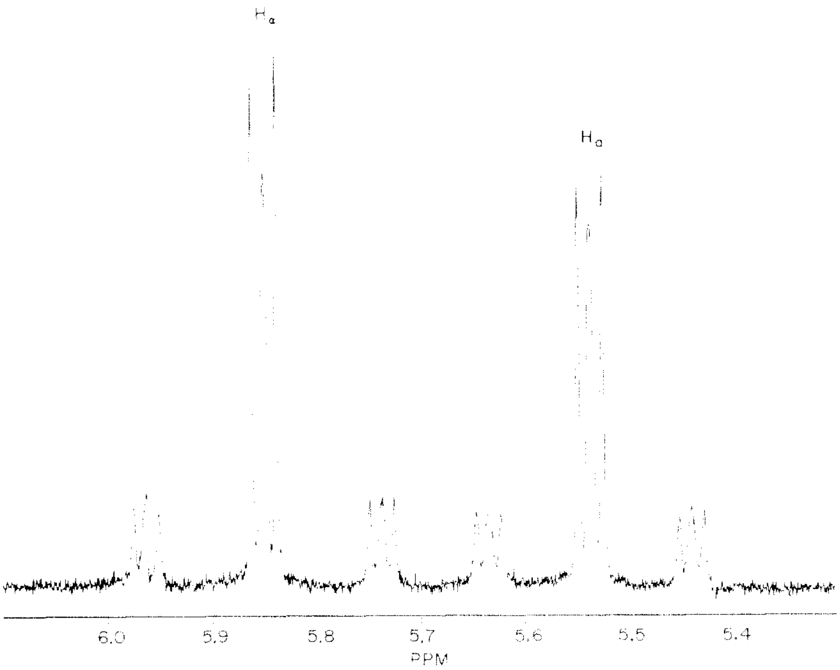


Fig. 3. The olefinic proton region of the 200 MHz ^1H NMR spectrum of $Pt(CH_3)(CF_3)(NBD)$ (**1a**). The labels H_a and H_α correspond to those in structure **1a**.

surable nOe interaction between the other olefinic protons (resonance at 5.54 ppm) and the methyl protons. This allowed the resonance at 5.85 ppm (with the larger coupling constant to ^{195}Pt) to be assigned to H_α. Assignments of olefinic ^{13}C resonances in **1a** and **1b**, and the olefinic ^1H resonances in **1b** were then made on the basis that the coupling constants to ^{195}Pt were larger *trans* to CF_3 than *trans* to methyl.

4. Discussion

4.1. The reactions between $Pt(CH_3)_2$(diolefin) (3) and CF_3I

The characterization of $Pt(CH_3)(CF_3)$(diolefin) (**1**) as a reaction product when CF_3I is in small excess makes it very likely that this mixed alkyl compound is an intermediate in the formation of the bis(trifluoromethyl) complex, as shown in Scheme 1. The initial product of oxidative addition of CF_3I to $Pt(CH_3)_2$(diolefin) would be the platinum(IV) diolefin complex $Pt(CH_3)_2(CF_3)I$(diolefin) (**4**). Platinum(IV) olefin complexes are not usually stable, presumably because of insufficient availability of metal π-electrons. There is only one example so far known of a stable complex, in which the olefin is part of a tridentate chelating ligand [11]. In general, a platinum(IV) diolefin complex $Pt(CH_3)_2(X)(Y)$(diolefin) may be transformed to a more stable complex in one of two ways. It may lose the diolefin ligand to form a stable platinum(IV) complex. This occurs when bromine reacts with $Pt(CH_3)_2(COD)$, to give $[Pt(CH_3)_2Br_2]_n$ [1] (*i.e.* X = Y = Br). Alternatively, a reductive elimination reaction may occur, to form a stable platinum(II) diolefin complex. In the reaction where $X = CF_3$ and Y = I, CH_3I is eliminated, to give $Pt(CH_3)(CF_3)$(diolefin) (**1**). Stable platinum(IV) compounds, $Pt(CH_3)_2(CF_3)IL_2$, with L a non-olefinic ligand, are known [12–14]. When heated, these compounds usually lose ethane, to give $Pt(CF_3)IL_2$ [12–14]. Similarly, trimethylplatinum(IV) complexes, $Pt(CH_3)_3IL_2$, usually lose ethane rather than methyl iodide [15–18]. One exception is the sterically crowded complex with $L = PPh_3$, which loses CH_3I [18]. The compounds (**4**) are therefore unusual, in losing methyl iodide, rather than ethane. The electron-donor property of the methyl ligands in $Pt(CH_3)_2$(diolefin) appears to enhance the metal–olefin bond strength [1,3,5,19], and if this also holds for the platinum(IV) intermediate (**4**), the elimination of both methyl groups as ethane may be inhibited.

Reaction of $Pt(CH_3)(CF_3)$(diolefin) with CF_3I gives a new platinum(IV) intermediate, $Pt(CH_3)(CF_3)_2I$(diolefin) (**5**), which produces the final product, $Pt(CF_3)_2$(diolefin) (**2**) by elimination of CH_3I. The CH_3I eliminated in the two reductive elimination reactions competes with CF_3I to react with the initial $Pt(CH_3)_2$(diolefin) (**3**), to give (as expected [1]) $[Pt(CH_3)_3(\mu\text{-}I)]_4$, presumably *via* loss of diolefin from the platinum(IV) intermediate $Pt(CH_3)_3I$(diolefin) (**6**).

Mechanistic studies of the oxidative addition of alkyl halides to dialkylplatinum(II) compounds, by kinetics and isotopic labelling studies, have usually been interpreted in terms of S_N2 attack by the metal centre on the carbon atom of the alkyl halide [14,20,21]. Results of mechanistic studies of reductive eliminations from organoplatinum(IV) complexes have been interpreted as indicating that there is a concerted elimination of two groups originally bound to the same metal atom (rather than an intermolecular reaction) [14,17,20]. For the reactions under consideration in this paper, kinetic studies would be difficult because a number of competing and sequential reactions lead to the final product. From the absence of any effect on the reaction product distribution when hydroquinone was introduced as a radical scavenger, it was unlikely that any important reaction in these reaction sequences proceeded by a radical chain mechanism.

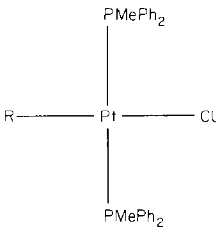
4.2. Comparison of properties of methyl and trifluoromethyl groups as ligands

The NMR *trans* influence of the trifluoromethyl ligands, as measured by platinum couplings to nuclei in *trans* ligands, has long been recognized as being slightly lower than that of methyl [13,14,22]. These comparisons involved analogous, separate, methyl and trifluoromethyl complexes. Coupling constants between ^{195}Pt and olefinic protons provide a sensitive measure of NMR trans influence, which correlates well with other coupling constants (*e.g.*, $^2J(Pt-CH_3)$ *trans* to the same ligands [23]. Some Pt–H(olefin) coupling constants for NBD and COD complexes are listed in Table 3. For compounds PtR_2(diolefin) the Pt–H coupling constant is larger in magnitude when $R = CF_3$ than when $R = CH_3$. The compounds described here are the first in which both methyl and trifluoromethyl groups are present in the one compound *trans* to coordinated olefin groups, and, consistently with the results presented in Table 3, the Pt–H(olefin) coupling constant in **1a** was larger than that *trans* to methyl. The behaviour of the one-bond $^{195}Pt-^{13}C$ coupling constants for the olefinic carbon atoms paralleled that of the Pt–H(olefin) couplings.

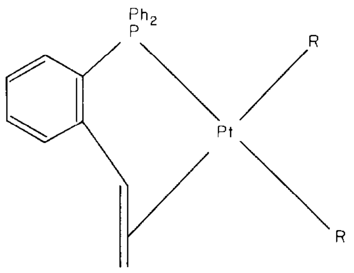
TABLE 3. Coupling constants between ^{195}Pt and olefinic protons for selected compounds

Compound	J(Pt–H) (Hz)	Ligand *trans* to olefin	Ref.
$Pt(CH_3)_2(COD)$ (**3b**)	40	CH_3	1
$Pt(CH_3)Cl(COD)$	35	CH_3	1
	78	Cl	
$Pt(CF_3)_2(COD)$ (**2b**)	42	CF_3	1
$Pt(CH_3)(CF_3)(COD)$	37.5	CH_3	a
1b	40.3	CF_3	
$Pt(CH_3)_2(NBD)$ (**3a**)	39.6	CH_3	3
$Pt(CF_3)_2(NBD)$ (**2a**)	43.7	CF_3	a
$Pt(CH_3)(CF_3)(NBD)$	36.3	CH_3	a
1a	45.4	CF_3	

[a] This work.



$R = CH_3$ 7a
$R = CF_3$ 7b
$R = C_2F_5$ 7c



$R = CH_3$ 8a
$R = CF_3$ 8b

In a comparative study of the properties of alkyl and perfluoroalkyl ligands bound to platinum(II), Bennett and co-workers determined the crystal structures of *trans*-$PtCl(R)(PMePh_2)_2$ ($R = -CH_3$ (**7a**), $-CF_3$ (**7b**), and $-C_2F_5$ (**7c**)) [24], and $PtR_2(SP)$ ($R = -CH_3$ (**8a**), $-CF_3$ (**8b**), SP = (2-vinylphenyl)diphenylphosphine) [25]. Because of crystallographic disorder, bond distances for *trans*-$PtCl(CF_3)(PMePh_2)_2$ (**7b**) could not be used for comparisons, but no such disorder was observed for **7a** or **7c**. The Pt–Cl bond length *trans* to methyl in **7a** (2.412(2) Å) is significantly longer than that *trans* to pentafluoroethyl in **7c** (2.363(2) Å). On the other hand, the Pt–P bond length (2.276(1) Å) and the Pt–C (olefin) distances (2.223(5), 2.201(5) Å) in **8a** *trans* to methyl are all slightly shorter than the corresponding distances *trans* to trifluoromethyl in **8b** (Pt–P 2.310(1), Pt–C (olefin) 2.290(5), 2.245(5) Å).

Bennett and co-workers [24,25] discussed these observations in the light of the model of metal–fluoroolefin bonding developed by Hall and Fenske [26]. In this model, the trifluoromethyl ligand forms a strong covalent bond with the metal, but the electron-withdrawing fluorine atoms produce a high positive charge on the fluoroalkyl carbon atom, which, in turn, stabilizes (and contracts) the metal orbitals. The Pt–Cl bond of **7c** is then shortened relative to that in **7a** owing to this electrostatic interaction. For the Pt–olefin bond of **8b** relative to **8a**, however, the slightly lower σ-trans influence of CF_3 (which would tend to shorten *trans* bond lengths) is balanced by the lesser availability of metal d_π electrons (due to the orbital contraction mentioned above) which would tend to weaken and lengthen the metal–olefin bond. This produces the small net lengthening observed for **8b** relative to **8a**.

When a methyl and a trifluoromethyl ligand are bound to the one metal atom, as in **1a**, the "electrostatic" effect of the positive charge on the fluoroalkyl carbon atom would be expected to have both an isotropic component, involving all metal orbitals, and an anisotropic component, dependent on the effect on orbitals close to the fluoroalkyl group. Because of the isotropic component, the difference between the metal–carbon distances *trans* to methyl and trifluoromethyl in **1a** would be expected to be less than that between such distances in **8a** and **8b**. In keeping with this expectation, there is no significant difference between the two metal–olefin distances in **1a**.

Metal–carbon(fluoroalkyl) bond lengths are usually shorter than metal–alkyl bond lengths in analogous complexes. For example, the Mo–C (ethyl) bond length in $(\eta^5\text{-}C_5H_5)_2Mo(CO)_3(\text{-}C_2H_5)$ is 2.397 ± 0.019 Å [27], and the Mo–C (fluoroalkyl) bond length in $(\eta^5\text{-}C_5H_5)_2Mo(CO)_3(n\text{-}C_3F_7)$ is 2.288(13) Å [28]. Churchill and Fennessey [28] explained this decrease in terms of metal $d_\pi \rightarrow$ fluoroalkyl σ^* back donation. Bennett *et al.* [24] reported the smaller decrease in **7c** (2.002(8) Å) compared with **7a** (2.081(6) Å), and explained it in terms of the Hall and Fenske model [26], rather than metal–fluoroalkyl π-bonding. In this model, the orbital used by the trifluoromethyl ligand in its bond with the metal has more C 2s character than that used by the carbon atom in methyl. This would cause some bond shortening, but Bennett *et al.* [24], ascribed the major effect to contraction of the metal orbitals due to the electrostatic effect of the charge on the fluoroalkyl carbon. In **8b**, the Pt–C (CF$_3$) bond lengths (2.082(5) Å *trans* to P, 2.032(5) Å *trans* to olefin) were also shorter than the Pt–C (CH$_3$) bond lengths in **8a** (2.166(5) Å *trans* to P, 2.052(6) Å *trans* to olefin) [25]. The difference between the two bond lengths *trans* to olefin is quite small, and barely significant.

In **1a**, with the methyl and trifluoromethyl groups bound to the same metal atom, any isotropic electrostatic effect on metal orbitals will again have a common effect on both Pt–C bonds, so that the difference between the Pt–C(CF$_3$) and Pt–C(CH$_3$) bond lengths might be expected to be even smaller than the difference *trans* to olefin between those in **8a** and **8b**. The two Pt–C distances in **1a** are the same within experimental error, and close to those *trans* to olefin in **8a** and **8b**.

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