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Displacement of norbornadiene (NBD) from the mixed alkyl compound, $Pt(CH_3)(CF_3)(NBD)$ by various ligands and the insertion of difluorocarbene into a $Pt–CH_3$ bond promoted by the addition of iodide ion to $Pt(CH_3)(CF_3)(NBD)$

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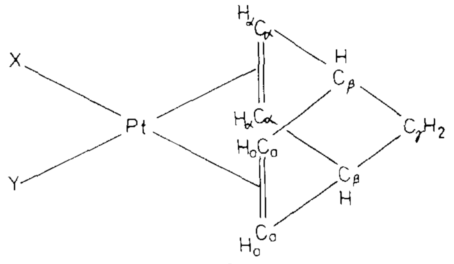
Abstract

$Pt(CH_3)(CF_3)(NBD)$ was found to react with neutral ligands L to give *cis*-$Pt(CH_3)(CF_3)L_2$ (L_2 = 1,2-bis(diphenylphosphino)ethane (dppe); 2,2′-dipyridyl (bipy); N,N,N′,N′-tetramethylethylenediamine (tmen); and L = pyridine (py); dimethylsulfoxide-*S* (DMSO). These reactions occurred less readily than with $Pt(CF_3)_2(NBD)$. With CH_3CN, *cis*-$Pt(CH_3)(CF_3)(NBD)$ gave *cis*-$Pt(CH_3)(CF_3)(CH_3CN)_2$ in equilibrium with starting materials. N,N-dimethylformamide (DMF) did not react. $Pt(CH_3)(CF_3)(NBD)$ reacted with iodide to give a mixture of $Pt(CH_3)I(NBD)$, $Pt(CF_3)I(NBD)$, and $Pt(–CF_2CH_3)I(NBD)$, the product of a formal insertion of a difluorocarbene moiety into a $Pt–CH_3$ bond. The products were characterized by multinuclear NMR spectroscopy then converted into dppe derivatives, which were separated and isolated.

1. Introduction

Displacement of 1,5-cyclooctadiene (COD) from dialkyl compounds $PtR_2(COD)$ by ligands L has long been used to prepare compounds *cis*-PtR_2L_2 [1–3]. We have more recently shown [4–6] that norbornadiene (NBD), with its smaller "bite" angle, is more readily displaced from $PtR_2(NBD)$ ($R = CH_3$, CF_3) than is COD from $PtR_2(COD)$. While $Pt(CH_3)_2(NBD)$ (**2**) undergoes diolefin displacement reactions with neutral ligands L = N/donor ligands and dimethylsulfoxide (DMSO) [4,5], $Pt(CF_3)_2(NBD)$ (**3**) reacts with an even wider range of ligands, L = N-donors, DMSO, R′CN, and N,N-dimethylformamide (DMF) to give *cis*-$Pt(CF_3)_2L_2$ [4,6]. With halide ions, X^-, **3** reacted as shown in Scheme 1. Neither the bis(trifluoromethyl) anionic complex **5** nor the presumed difluorocarbene complex **6** was detected, both being extremely sensitive to traces of moisture.



$X = CH_3$ $Y = CF_3$ **1**
$X = CF_3$ $Y = I$ **14**
$X = CH_3$ $Y = I$ **15**
$X = CF_2CH_3$ $Y = I$ **16**

We have recently described [7] the isolation of $Pt(CH_3)(CF_3)(NBD)$ (**1**) as a minor product from the reaction of $Pt(CH_3)_2(NBD)$ (**2**) with CF_3I (the major product being $Pt(CF_3)_2(NBD)$ [7,8]). Since there are significant differences between the reactions of **2** and **3** toward added ligands, we set out to examine the reactions of the mixed alkyl compound **1** with the same ligands.

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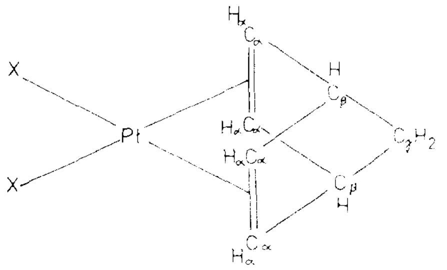


X = CH_3 **2**
X = CF_3 **3**
X = I **22**

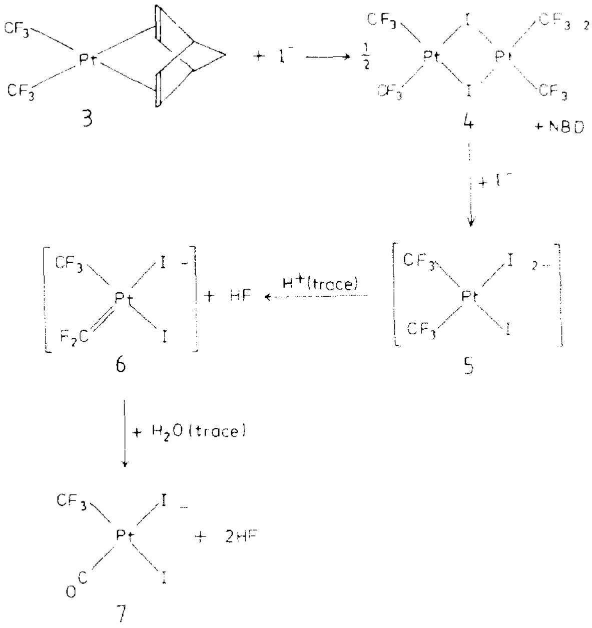
2. Experimental details

2.1. Instrumentation and general methods

The 100 MHz ^1H, 94.2 MHz ^{19}F, 40.3 MHz ^{31}P, 25.1 MHz ^{13}C, and 21.4 MHz ^{195}Pt NMR spectra were recorded on a JEOL JNM FX-100 spectrometer with a 10 mm broadband tunable probe. 400 MHz ^1H and 100.4 MHz ^{13}C spectra were obtained with a JEOL JNM GX-400 spectrometer having a 5 mm $^1H/^{13}C$ dual probe. Chemical shifts (positive to lower shielding) are relative to internal tetramethylsilane (TMS) for ^1H and ^{13}C, to internal $CFCl_3$ for ^{19}F, to 85% H_3PO_4 in a coaxial capillary for ^{31}P, and to a separate sample of Na_2PtCl_6 in H_2O for ^{195}Pt. All ^{13}C, ^{31}P, and ^{195}Pt spectra were ^1H-decoupled.

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

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



Scheme 1.

2.2. Starting materials

Trifluoromethyl iodide was provided by Fluorochem Ltd. Published methods were used to prepare $PtCl_2(NBD)$ [9], $PtI_2(NBD)$ [10], $Pt(CH_3)_2(NBD)$ (**2**) [5], $Pt(CF_3)_2(NBD)$ (**3**) [8], and $Pt(CF_3)I(NBD)$ (**14**) [6]. $Pt(CH_3)(CF_3)(NBD)$ (**1**) was isolated from the reaction of **2** with CF_3I [7]. Attempts to prepare **1** by reaction of $Pt(CF_3)I(NBD)$ with methyl-lithium were unsuccessful.

2.3. Preparation of $Pt(CH_3)I(NBD)$ (15)

This complex was previously prepared by a different route [11].

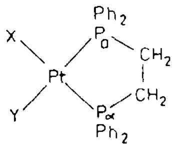
First $Pt(CH_3)Cl(NBD)$ was prepared by an adaptation of the method originally used to prepare $Pt(CH_3)Cl(COD)$ [2]. In this $Pt(CH_3)_2(NBD)$ (**1**) (0.50 g, 1.6 mmol) was dissolved in a mixture of 5 ml of dichloromethane and 4 ml of methanol, acetyl chloride (0.13 ml, 1.5 mmol) was added dropwise, and the solution stirred for 15 min. The volume was then decreased under reduced pressure to 1 ml. A white solid separated. The mixture was kept at 5°C for 2 h, and the solid then filtered off, washed with diethyl ether (2 × 1 ml), and dried under vacuum. The yield of $Pt(CH_3)Cl(NBD)$ was 0.27 g (50%).

To a solution of $Pt(CH_3)Cl(NBD)$ (0.27 g, 0.78 mmol) in 5 ml acetone was added a solution of sodium iodide (0.12 g, 0.80 mmol) in 2 ml of acetone. A precipitate of NaCl formed. The mixture was heated under reflux for 1 h to ensure complete reaction. The solid NaCl was then filtered off, and the filtrate concentrated under reduced pressure to 1 ml. n-Hexane (10 ml) was then added to precipitate $Pt(CH_3)I(NBD)$ as a white solid, which was filtered off, washed with hexane, and dried under vacuum. Yield was 0.08 g (24%).

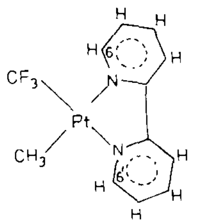
2.4. Isolation of solids from reactions of $Pt(CH_3)(CF_3)(NBD)$ (1) with neutral ligands

2.4.1. 1,2-bis(diphenylphosphino)ethane (dppe)

Solid dppe (0.040 g, 0.10 mmol) was slowly added to a solution of **1** (0.037 g, 0.10 mmol) in 1 ml of acetone, and the mixture stirred for 30 min. The dppe dissolved, and another white solid, $Pt(CH_3)(CF_3)(dppe)$ (**8**) separated out. The acetone was removed under reduced pressure. The residual solid was washed with 0.25 ml of acetone and dried under vacuum. Yield was 0.052 g (78%).



X = CF3 Y = CH3 8
X = I Y = CF3 17
X = I Y = CH3 18
X = I Y = CF2CH3 19



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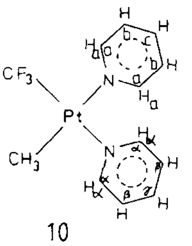
2.4.2. 2,2′-dipyridyl (bipy)

To a solution of **1** (0.050 g, 0.14 mmol) in 2 ml of acetone was added a solution of bipy (0.023 g, 0.15 mmol) in 1 ml of acetone. The solution was kept at room temperature for 1 h, during which yellow crystals deposited. The solid was filtered off, and washed with diethyl ether (3 × 1 ml). A second crop was obtained by evaporating the filtrate to dryness under reduced pressure and washing the resultant solid with diethyl ether (3 × 1 ml). Total yield of $Pt(CH_3)(CF_3)(bipy)$ (**9**) was 0.047 g (81%).

2.4.3. Pyridine (py)

Pyridine (75 μl, 0.93 mmol) was added to a solution of **1** (0.140 g, 0.38 mmol) in 3 ml of acetone, and the solution was stirred for 30 min. The solvent was removed under reduced pressure, and the white solid residue washed with diethyl ether (2 × 2 ml) and dried under vacuum. Yield of *cis*-$Pt(CH_3)(CF_3)py_2$ (**10**) was 0.158 g (96%). This solid decomposed over the course of several days if left exposed to the atmosphere. It was stable if stored in a sealed vial in the dark.



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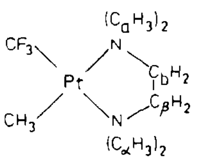

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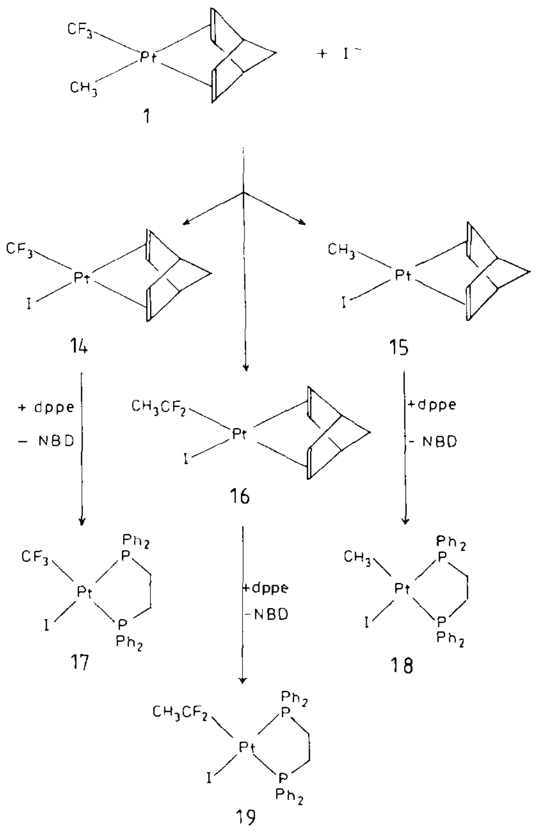
2.4.4. N,N,N′,N′-Tetramethylethylenediamine (tmen)

To a solution of **1** (0.020 g, 0.05 mmol) in 3 ml of acetone was added tmen (45 μl, 0.30 mmol). The solution was warmed to 45°C for 10 min, then concentrated to 1 ml with a rotary evaporator. n-Hexane (5 ml) was then added, to precipitate $Pt(CH_3)(CF_3)(tmen)$ (**11**) as a white solid, which was filtered off, washed with diethyl ether (2 × 1 ml), and dried under vacuum, to give 0.015 g (70% yield). This solid also decomposed unless stored in a sealed vial in the absence of light.



Scheme 2.

2.5. Reaction of 1 with iodide

A solution of **1** (0.208 g, 0.56 mmol) in 1 ml of acetone was added to solid sodium iodide (0.087 g, 0.58 mmol). The solution immediately became warm, and turned bright orange. Examination of the solution by multinuclear NMR spectroscopy (see Results section) showed that, in addition to some unchanged **1**, the solution contained $Pt(-CF_2CH_3)I(NBD)$ (**16**), $Pt(CH_3)I(NBD)$ (**14**), and $Pt(CF_3)I(NBD)$ (**15**). Some $Pt(CF_3)I(NBD)$ crystallized out after several minutes' standing. This solid was filtered off, and the filtrate added to solid dppe (0.227 g, 0.57 mmol). At this point, a small quantity of $Pt(-CF_2CH_3)I(dppe)$ (**19**) separated, and was immediately filtered off. The filtrate was allowed to stand at 5°C for 16 h, during which a white solid containing **19** and $Pt(CF_3)I(dppe)$ (**18**) was deposited. After this solid was filtered off, the filtrate was concentrated to half its original volume, and kept at 5°C for 16 h. The combined solid containing **19** and **18** was washed with diethyl ether (2 × 0.5 ml) and dried under vacuum. The solid was then extracted four times, each with 5 ml of benzene (more benzene than this caused the final product to be contaminated with **18**). The combined benzene extracts were concentrated with a rotary evaporator to 0.5 ml, and cyclohexane (3 ml) was added to precipitate **19**. Yield of pure product was 0.012 g (3% based on **1**).

2.6. Preparation of $Pt(CF_3)I(dppe)$ (18)

A solution of $Pt(CF_3)I(NBD)$ (**15**) (0.050 g, 0.10 mmol) in 3 ml of acetone was added to solid dppe (0.041 g, 0.10 mmol), and the mixture was stirred for 15 min. The acetone was then removed under reduced pressure to give a pale yellow solid, which was washed with benzene (2 × 0.5 ml) and dried under vacuum. Yield of **18** was 0.048 g (59%).

3. Results

Microanalytical data are given in Table 1, ^1H and ^{13}C NMR data in Table 2, and NMR data for other nuclei in Table 3. Atom labelling is as shown in the structural drawings.

3.1. Reactions of $Pt(CH_3)(CF_3)(NBD)$ (1) with neutral ligands, L

3.1.1. 1,2-bis(diphenylphosphino)ethane (dppe)

The chelating diphosphine dppe readily displaces COD from $PtR_2(COD)$ ($R = CH_3$, CF_3 [2]), so it is not surprising that it reacts readily with **1** at ambient temperature to give $Pt(CH_3)(CF_3)(dppe)$ (**8**). The ^{19}F NMR signals from the trifluoromethyl group, and the ^1H signals from the methyl group, each showed the expected doublet of doublets (from coupling with two non-equivalent ^{31}P nuclei) with "satellites" from coupling to ^{195}Pt ($I = \frac{1}{2}$, 34% abundance). The Pt–CH_3 coupling constant (68.1 Hz) corresponded to that expected for methyl *trans* to dppe phosphorus (*cf.* 71.0 Hz in $Pt(CH_3)_2(dppe)$ [12]). The Pt–CF_3 coupling constant (684.8 Hz) is relatively low, as expected for trifluoromethyl *trans* to a phosphine ligand [13]. The ^{13}C NMR spectrum of the methyl group showed, in addition to coupling to two non-equivalent ^{31}P nuclei and to ^{195}Pt, a small quartet coupling (6.4 Hz) to ^{19}F. The two ^{31}P–Pt–^{13}C coupling constants to the methyl carbon were quite different (84.2 and 6.4 Hz). Since two-bond coupling constants between ^{31}P and another nucleus bound to a metal are usually largest when the nuclei are mutually *trans* [14], the larger coupling constant is assigned to the ^{31}P nucleus *trans* to methyl, P_a. The ^{13}C spectrum of the trifluoromethyl carbon showed a doublet of doublets of quartets (coupling to two non-equivalent ^{31}P nuclei, and to three ^{19}F nuclei). Satellite peaks from coupling with ^{195}Pt were too weak to be observed. The larger ^{31}P–Pt–^{13}C coupling constant is again assigned as the coupling with the ^{31}P nucleus *trans*, P_α (Table 2). The ^{31}P NMR spectrum showed two quartets (from coupling with three ^{19}F), each with satellites from coupling with ^{195}Pt (^1J(Pt–P) 1787, 2060 Hz). Comparison of the Pt–P coupling constants with those for $Pt(CH_3)_2(dppe)$ (1794 Hz [12]) and $Pt(CF_3)_2(dppe)$ (1984 Hz [12]) allowed the signal from **8** with the smaller Pt–P coupling constant to be assigned to a P_a *trans* to methyl, and the other quartet to P_α *trans* to trifluoromethyl. With this assignment, the *trans* F_3C–Pt–P_α coupling constant (54.9 Hz) is larger in magnitude than the *cis* F_3C–Pt–P_a coupling constant (15.9 Hz), as expected [15].

TABLE 1. Analytical data

Compound	Colour	Analysis (found/(calc.) %)			
		C	H	N [a]	F [b]
$Pt(CH_3)(CF_3)(dppe)$ (**8**)	White	49.6 (49.6)	4.1 (4.0)		8.3 (8.4)
$Pt(CH_3)(CF_3)(bipy)$ (**9**)	Yellow	32.9 (33.1)	2.5 (2.6)	6.2 (6.4)	
Cis-$Pt(CH_3)(CF_3)py_2$ (**10**)	White	32.9 (33.0)	3.1 (3.0)	6.3 (6.4)	13.4 (13.0)
$Pt(CH_3)(CF_3)(tmen)$ (**11**)	White	24.4 (24.3)	4.7 (4.8)	7.0 (7.1)	
$Pt(CH_3)I(NBD)$ (**15**)	White	22.3 (22.4)	2.5 (2.6)		
$PtI_2(NBD)$	Dark Yellow	15.2 (15.5)	1.4 (1.5)		
$Pt(CF_3)I(dppe)$ (**17**)	Pale Yellow	41.0 (41.1)	3.2 (3.1)		
$Pt(CF_2CH_3)I(dppe)$ (**19**)	White	42.8 (42.8)	3.5 (3.5)		5.1 (4.8)

[a] For nitrogen-containing complexes. [b] Where measured.

3.1.2. 2,2′-Dipyridyl (bipy)

NBD was displaced rapidly from **1** at ambient temperature by bipy to give $Pt(CH_3)(CF_3)(bipy)$ (**9**). ^1H and ^{13}C NMR spectra each displayed two sets of resonances (a total of ten ^{13}C resonances and eight ^1H multiplets were observed—data for some selected resonances are given in Table 2). The ^{13}C resonance for C_6 appeared as a quartet owing to "through space" coupling with the ^{19}F nuclei of the trifluoromethyl group, as previously observed for $Pt(CF_3)_2(bpy)$ and a number of platinum(**IV**) complexes $Pt(CF_3)_2XY(bpy)$ [8].

3.1.3. Pyridine (py)

Pyridine readily displaced NBD from **1** at ambient temperature. The *cis* geometry of the product **10**, was assigned on the basis of the observation of two sets of pyridine peaks in ^{13}C and ^1H spectra (*i.e.* six ^{13}C peaks and six ^1H multiplets; data for selected resonances are given in Table 2). This geometry is also consistent with the similarity of Pt–CH_3 and Pt–CF_3 coupling con-

TABLE 2. Selected ^{1}H and ^{13}C NMR data

Compound [a]	Solvent	$Pt-CH_3$ or $C-CH_3$		$Pt-CF_3$ or $Pt-CF_2$ $\delta_c[^{1}J(C-F)]$	Other parameters
		$\delta_H(^{1}J(Pt-CH_3)$	$\delta_c(^{1}J(Pt-C))$		
$Pt(CH_3)(CF_3)(dppe)$ **(8)**	CD_2Cl_2	0.62(68.1)	−3.24(573.1)	143.67[349.1]	$^{3}J(P_aCH_3)$ 6.7 $^{3}J(P_\alpha CH_3)$ 6.7 $^{2}J(P_aCH_3)$ 84.2 $^{2}J(P_\alpha CH_3)$ 6.4 $^{2}J(P_\alpha CF_3)$ 192.3 $^{2}J(P_aCF_3)$ 9.8 $^{3}J(F_3C-Pt-CH_3)$ 6.4
$Pt(CH_3)(CF_3)(bipy)$ **(9)**	$(CD_3)_2CO$	0.99(86.8)	[b]	[b]	C_6 151.45 [c] $C_{6'}$ 148.49 $J(Pt-C_{6'})$ 35.6
Cis-$Pt(CH_3)(CF_3)py_2$ **(10)**	CD_2Cl_2	0.66(86.1)	−20.57(797.6)	118.28[331.1]	$^{4}J(F_3C-Pt-CH_3)$ 0.6 $^{3}J(F_3C-Pt-CH_3)$ 4.3 $^{1}J(Pt-CF_3)$ 1956.2 H_a 8.72 $J(Pt-H_a)$ 18.6 H_α 8.56 $J(Pt-H_\alpha)$ 24.4 C_a 151.56 $J(Pt-C_a)$ 12.8 C_α 151.37 $J(Pt-C_\alpha)$ 17.1
$Pt(CH_3)(CF_3)(tmen)$ **(11)**	$(CD_3)_2CO$	0.39(88.2)	−19.79(841.0)	118.57(335.0)	$N-CH_3$: H_a 2.78 $^{3}J(Pt-H_a)$ 19.8 H_α 2.62 $^{3}J(Pt-H_\alpha)$ 25.6 δ_c 50.16, 49.20
Cis-$Pt(CH_3)(CF_3)$-$(DMSO$-*S*$)_2$ **(12)**	C_6D_6	1.41(78.4)	[d]	[d]	$S-CH_3$: H_a 2.62 $^{3}J(Pt-H_a)$ 14.6 H_α 2.66 $^{3}J(Pt-H_\alpha)$ 18.2
$Pt(CF_3)I(NBD)$ **(14)**	$(CD_3)_2CO$				H_a 6.13 $J(Pt-H_a)$ 37.2 H_α 5.68 $J(Pt-H_\alpha)$ 73.8
$Pt(CH_3)I(NBD)$ [e] **(15)**	$(CD_3)_2CO$	0.83(85.2)	3.44(680.5)		H_a 5.61 $J(Pt-H_a)$ 34.2 H_α 5.06 $J(Pt-H_\alpha)$ 76.6 C_a 100.37 $J(Pt-C_a)$ 27.3 C_α 74.95 $J(Pt-C_\alpha)$ 166.0 C_β 50.00 $J(Pt-C_\beta)$ 48.8 C_γ 72.69 $J(Pt-C_\gamma)$ 93.8
$PtI_2(NBD)$ **(22)**	$(CD_3)_2CO$				H_α 5.73 $J(Pt-H_\alpha)$ 66.8 C_α 77.94 $J(Pt-C_\alpha)$ 85.9 C_β 50.02 $J(Pt-C_\beta)$ 79.1 C_γ 72.32 $J(Pt-C_\gamma)$ 108.4

TABLE 2 (continued)

Compound	Solvent	Pt–CH$_3$ or C–CH$_3$		Pt–CF$_3$ or Pt–CF$_2$ $\delta_c[^1J(C–F)]$	Other parameters
		$\delta_H(^1J(Pt–CH_3)$	$\delta_c(^1J(Pt–C))$		
Pt(CF$_2$CH$_3$)I(NBD) **(16)**	(CD$_3$)$_2$CO	1.86(26.4)	33.16(81.3)	118.85(284.0)	$^3J(H_3C–CF_2)$ 21.5 $^2J(F_2C–CH_3)$ 23.2 H$_a$ 5.98 $J(Pt–H_a)$ 32.1 H$_\alpha$ 5.43 $J(Pt–H_\alpha)$ 80.0 C$_a$ 106.9 $J(Pt–C_a)$ 23.5 C$_\alpha$ 81.5 $J(Pt–C_\alpha)$ 176.1 C$_\beta$ 50.5 $J(Pt–C_\beta)$ 47.1 C$_\gamma$ 73.6 $J(Pt–C_\gamma)$ 100.2
Pt(CF$_2$CH$_3$)I(dppe) **(19)**	CD$_2$Cl$_2$	1.67(17.9)	33.66(65.0)	[b]	$^3J(H_3C–CF_2)$ 23.7 $^2J(F_2C–CH_3)$ 21.7 $^3J(P_a–CH_3)$ 3.7 $^4J(P_a–CH_3)$ 7.7

[a] Atoms labelled as in structural drawings. Chemical shifts in ppm, coupling constants in Hz. [b] Peaks not detected. [c] Peak broadened by coupling with ^{19}F. [d] ^{13}C NMR spectrum not recorded. [e] ^{1}H NMR spectrum in CDCl$_3$ has been previously reported [11].

TABLE 3. ^{19}F, ^{31}P, and ^{195}Pt NMR data [a]

Compound [b]	Solvent	δ_F	$^2J(Pt–F)$	δ_P	$^1J(Pt–P)$	$^3J(PF)$	δ_{Pt} [c]
Pt(CH$_3$)(CF$_3$)(dppe) **(8)**	(CD$_3$)$_2$CO	−20.56 (dd)	684.8	P$_a$ 47.23 (q) P$_\alpha$ 43.57 (q)	1787.1 2060.5	15.9 54.9	
	CD$_2$Cl$_2$						−4819 (ddq)
Pt(CH$_3$)(CF$_3$)(bipy) **(9)**	(CD$_3$)$_2$CO	−21.62	808.7				
Cis-Pt(CH$_3$)(CF$_3$)py$_2$ **(10)**	(CD$_3$)$_2$CO	−22.24	861.2				−3711 (q)
Pt(CH$_3$)(CF$_3$)(tmen) **(11)**	(CD$_3$)$_2$CO	−21.32	840.5				
Cis-Pt(CH$_3$)(CF$_3$)-(DMSO-S)$_2$ **(12)**	C$_6$D$_6$ (CD$_3$)$_2$SO	−22.50 −21.86	806.9 807.5				
Cis-Pt(CH$_3$)(CF$_3$)-(NCCH$_3$)$_2$ **(13)**	CH$_3$CN	−22.53	905.8				
Pt(CF$_2$CH$_3$)I(NBD) **(16)**	(CD$_3$)$_2$CO	−56.80 (q)	466.9				
Pt(CF$_3$)I(dppe) **(17)**	(CD$_3$)$_2$CO	−14.64 (dd)	589.6	P$_a$ 38.09 (q) P$_\alpha$ 42.10 (q)	1784.3 3763.9	57.4 14.7	
	CD$_2$Cl$_2$						−4950 (ddq)
Pt(CH$_3$)I(dppe) **(18)**	CD$_2$Cl$_2$						−4967 (dd)
Pt(CF$_2$CH$_3$)I(dppe) **(19)**	(CD$_3$)$_2$CO	−46.92 (ddq)	433.4	P$_a$ 36.89 (t) P$_\alpha$ 41.81 (t)	1472.2 4141.9	42.7 31.7	
	CD$_2$Cl$_2$	−47.98	433.4				−4833 (ddt)

[a] Chemical shifts in ppm, coupling constants in Hz; d = doublet, t = triplet, q = quartet. [b] Atoms labelled as in structural diagrams. [c] Where measured.

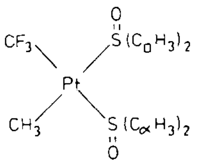
stants to those observed for $Pt(CH_3)(CF_3)(bipy)$ (**9**) (Tables 2 and 3).

3.1.4. N,N,N′,N′-Tetramethylethylenediamine (tmen)

Slight warming only was necessary for tmen to displace NBD from **1** in acetone, to give $Pt(CH_3)(CF_3)(tmen)$ (**11**). Two N-methyl peaks were observed in ^1H and ^{13}C NMR spectra.

3.1.5. Dimethylsulfoxide (DMSO)

Addition of two mole equivalents of DMSO to a benzene solution of **1** caused only slight reaction, but with 20 mole equivalents of DMSO in benzene, or in neat DMSO, NMR spectra showed that there was complete conversion into a new compound. Attempts to isolate a solid by removal of DMSO, or by chromatography on Florisil caused decomposition. We showed previously that *cis*-$Pt(CH_3)_2(DMSO)_2$ (^2J(Pt–CH_3) 78 Hz) exists only as the isomer with both DMSO ligands S-bound [5], while *cis*-$Pt(CF_3)_2(DMSO)_2$ exists predominantly as *cis*-$Pt(CF_3)_2$(DMSO-*S*)(DMSO-*O*)(^2J(Pt–CF_3) 788.6 Hz *trans* to DMSO-*S*; 881.4 Hz *trans* to DMSO-*O*) in equilibrium with a small amount of *cis*-$Pt(CF_3)_2$(DMSO-*S*)$_2$(^2J(Pt–CF_3) 710.5 Hz) [6]. For $Pt(CH_3)(CF_3)(DMSO)_2$, $^2J(Pt–CH_3) = 78.4$ Hz, and $^2J(Pt–CF_3) = 807.5$ Hz. These values indicate that the complex is *cis*, since mutually *trans* methyl and trifluoromethyl groups would be expected to give low Pt–CH_3 and Pt–CF_3 coupling constants [16], and are consistent with both DMSO ligands being S-bound, as in **12**. This formulation is also consistent with the observation of two singlets with satellites from Pt–S–CH_3 coupling in the ^1H NMR spectrum run in C_6D_6 (Table 2) [17] *.



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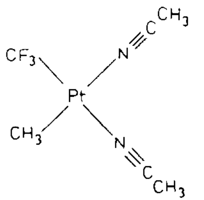

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3.1.6. Other potential ligands

When **1** was dissolved in neat acetonitrile, and the solution was kept at room temperature for one week, the ^{19}F NMR spectrum showed, as well as the peaks from **1**, a new singlet with satellites, corresponding to approximately 15% of the total intensity. The Pt–CF_3 coupling constant, 905.8 Hz, was large in magnitude, corresponding to the presence of a ligand of low trans influence *trans* to the trifluoromethyl group. The new complex was therefore formulated as *cis*-$Pt(CH_3)(CF_3)(NCCH_3)_2$ (**13**). No attempt was made to isolate this complex.

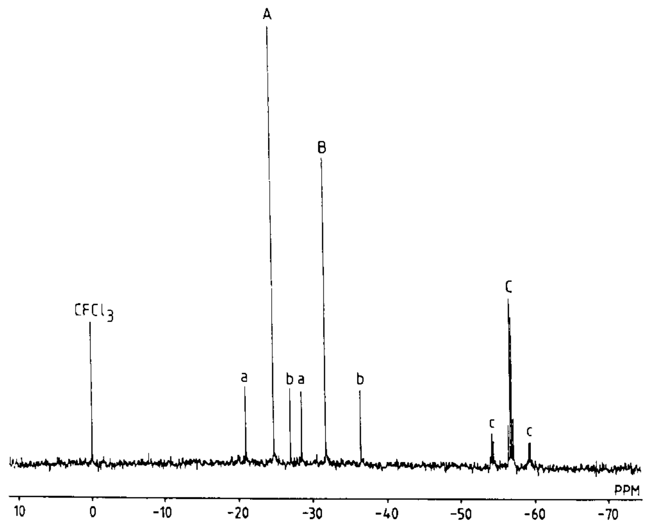

Fig. 1. ^1H-coupled ^{19}F NMR spectrum of the solution obtained by addition of NaI (one mole equivalent) to a solution of $Pt(CH_3)(CF_3)(NBD)$ (**1**) in $(CD_3)_2CO$. Peaks are labelled as follows: Aa $Pt(CF_3)I(NBD)$ (**14**); Bb $Pt(CH_3)(CF_3)(NBD)$ (**1**); Cc $Pt(CF_2CH_3)I(NBD)$ (**16**).

There was no observable reaction of **1** with N,N-dimethylformamide (DMF) on prolonged standing in DMF. Heating a solution under reflux caused decomposition.

3.2. Reaction of Pt(CH$_3$)(CF$_3$)(NBD) (1) with iodide

The addition of an equimolar quantity of sodium iodide to an acetone solution of **1**, in contrast with the corresponding reaction of *cis*-$Pt(CF_3)_2(NBD)$ (**3**) (Scheme 1), did not give a single product. The ^{19}F NMR spectrum of the reaction mixture recorded immediately after mixing is shown in Fig. 1. Peaks due to some unchanged **1** were still present (peaks labelled B,b). One singlet with satellites (A,a) (δ −24.6, ^2J(Pt–CF_3) 709.2 Hz) corresponded to $Pt(CF_3)I(NBD)$ (**14**), which we previously characterized [6]. The remaining peaks in the spectrum (C,c) were a quartet with satellites at −56.8 ppm. ^2J(Pt–CF_3) 466.9 Hz. This shift is larger than that for any signals ever previously observed for trifluoromethyl groups bound to platinum, and is closer to that characteristic of the α-fluorine atoms of a bound pentafluoroethyl group [18–21].

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* We previously reported [6] platinum coupling for the methyl protons of both DMSO ligands of *cis*-$Pt(CF_3)_2$(DMSO-*S*)(DMSO-*O*), but, on re-examination of the spectra, have concluded that only the S-bound ligand shows such coupling.

When the reaction was carried out in $(CD_3)_2CO$, the ^1H NMR spectrum of the solution showed, in addition to peaks from **1** and **14**, a set of peaks corresponding to $Pt(CH_3)I(NBD)$ (**15**), assigned by comparison with the spectrum of an authentic sample prepared independently. There was also an additional set of resonances from coordinated NBD (olefinic protons: 5.98 ppm, $J(Pt–H)$ 32.1 Hz; 5.43 ppm, $J(Pt–H)$ 80.0 Hz), and a triplet with satellites (1.86 ppm, $^3J(Pt–H)$ 26.4 Hz, triplet coupling 21.5 Hz). This triplet coupling matched the quartet splitting observed for resonance C in the ^{19}F NMR spectrum. These data allowed formulation of the new compound as $Pt(–CF_2CH_3)I(NBD)$ (**16**). The ^{13}C NMR spectrum (Table 2) was also consistent with this formulation. There remained, however, a small possibility that the observed spectrum was due to a mixture of equimolar quantities of $Pt(–CF_2CH_3)_2(NBD)$ and $PtI_2(NBD)$, rather than to **16**. The ^1H NMR spectrum of an authentic sample of $PtI_2(NBD)$ was therefore obtained (Table 2). The peaks did not correspond to any of those mentioned above.

Addition of sodium iodide in proportions greater than equimolar caused a larger proportion of **1** to be converted into **14**, **15**, and **16**. With a 1.75/1 proportion of NaI to **1**, all of the starting complex, **1**, was consumed. When larger proportions of NaI were added, some $PtI_2(NBD)$ was also formed, along with small amounts of another, unidentified, complex.

$Pt(–CF_2CH_3)I(NBD)$ (**16**) was unstable at ambient temperature in acetone solution, decomposing within 24 h. Attempts to obtain **16** as a pure solid were unsuccessful. In the expectation that the bis(diphenylphosphino)ethane (dppe) derivative, $Pt(–CF_2CH_3)I(dppe)$ (**19**) would possess enhanced stability, dppe was added to the reaction mixture. A sample of $Pt(CF_3)I(dppe)$ (**17**) was prepared separately, to allow peaks from **17** to be assigned, and NMR data had been reported previously for $Pt(CH_3)I(dppe)$ (**18**) [12]. $Pt(–CF_2CH_3)I(dppe)$ (**19**) gave characteristic ^{31}P and ^{195}Pt spectra. In the ^{31}P spectrum, each signal appeared as a 1:2:1 triplet, from coupling with the two ^{19}F nuclei, with satellites from coupling with ^{195}Pt. The smaller Pt–P coupling constant (1472 Hz) was assigned to the phosphorus atom *trans* to $–CF_2CH_3$, and the larger to the phosphorus atom *trans* to iodide. The ^{195}Pt NMR spectrum in CD_2Cl_2 showed a doublet of doublets of triplets, from coupling to two non-equivalent ^{31}P nuclei, and two equivalent ^{19}F nuclei. The ^{195}Pt shift, −4833 ppm, was comparable to those of other complexes PtRI(dppe) (Table 2). The ^{19}F NMR spectrum showed a doublet of doublets of quartets (from coupling with two non-equivalent ^{31}P nuclei and three ^1H nuclei) with satellites from coupling to ^{195}Pt. In the ^1H NMR spectrum, the methyl group of **19** showed a doublet of triplets (coupling to two ^{19}F nuclei, and coupling resolved to only one ^{31}P nucleus) with satellites.

It was possible to isolate small quantities of pure **19** from the reaction mixture, as described in the Experimental section.

Other complexes *cis*-$Pt(CH_3)(CF_3)L_2$ did not react with iodide. For example, $Pt(CH_3)(CF_3)(bipy)$ (**10**) remained unchanged when treated in acetone with one mole equivalent of sodium iodide for ten days.

4. Discussion

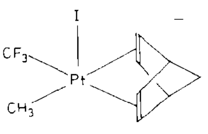
4.1. The reactions of $Pt(CH_3)(CF_3)(NBD)$ (1) with neutral ligands

The ligand displacement reactions described above show that **1** is intermediate between $Pt(CH_3)_2(NBD)$ (**2**) and $Pt(CF_3)_2(NBD)$ (**3**) in its reactivity toward displacement of NBD by other neutral ligands, L. Thus, **1** reacts readily with CH_3CN, which also readily displaces NBD from **3** [6] but does not react with **2** [5]. On the other hand, **1** does not react with DMF, which easily displaces NBD from **3** to give *cis*-$Pt(CF_3)_2(DMF$-$O)_2$ [6].

The only isomer of *cis*-$Pt(CH_3)(CF_3)(DMSO)_2$ which could be detected was that in which both of the DMSO ligands are coordinated through sulfur, **12**. In this respect, the behaviour is similar to that of *cis*-$Pt(CH_3)_2(DMSO$-$S)_2$ [5,22,23] and *cis*-$Pt(C_6H_5)_2(DMSO$-$S)_2$ [23,24], but contrasts with that of *cis*-$Pt(CF_3)_2(DMSO)_2$, for which small amounts of *cis*-$Pt(CF_3)_2(DMSO$-$S)_2$ exist in equilibrium with a much larger proportion of *cis*-$Pt(CF_3)_2(DMSO$-$S)(DMSO$-$O)$ [6]. The presence of two relatively bulky trifluoromethyl groups in this complex probably causes one of the DMSO ligands to adopt the sterically less demanding coordination through oxygen. In **12**, the electronically-preferred configuration with both DMSO ligands S-bound is stable.

4.2. Reaction of $Pt(CH_3)(CF_3)(NBD)$ (1) with iodide

The products from reaction of **1** with iodide were quite unexpected. *Cis*-$Pt(CH_3)_2(NBD)$ (**2**) underwent only a slow decomposition reaction when iodide was added [5]. With *cis*-$Pt(CF_3)_2(NBD)$, the initial reaction was displacement of NBD to give $[\{Pt(CF_3)_2(\mu\text{-}I)\}_2]^{2-}$ (**4**) (Scheme 1) [6]. With more iodide, *cis*-$Pt(CF_3)(CO)I_2^-$, **7**, was formed, presumably *via* reaction of a highly reactive difluorocarbene intermediate, **6**, with traces of moisture. The trifluoromethyl group in the intermediate complex *cis*-$Pt(CF_3)_2I_2^{2-}$, which was not observed, must be highly activated toward loss of F^-. This is probably associated with the high negative charge on this complex. In the reaction of **1** with iodide, all of the products detected still contained coordinated norbornadiene. The first stage in the reaction of **1** with iodide is probably the formation of a five-coordinate complex **20**. The negative charge on this species may activate the trifluoromethyl group toward loss of F^- (possibly assisted by traces of H^+) to give a difluorocarbene intermediate, **21**. Insertion of the difluorocarbene moiety into the Pt–CH_3 bond (or, perhaps more correctly, migration of the methyl carbon to the difluorocarbene group) would then give the product **16**.



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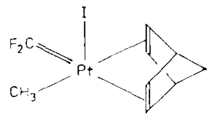

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Apart from the example shown in Scheme 1, many reports have previously appeared of difluorocarbene complexes formed from trifluoromethyl precursors [25–31], or of products formed by reaction of a difluorocarbene intermediate with other reagents [30,32]. Burrell *et al.* [33] described the reaction of *trans*-$Rh(CF_3)(CO)(PPh_3)_2$ with dry HCl gas to produce $Rh(CHF_2)Cl_2(PPh_3)_2$, which may be considered as arising from hydride migration to difluorocarbene in an intermediate Rh(III)–CF_2 complex. Difluoromethyl complexes of ruthenium(II) [26] and iridium(III) [31] also probably arise from analogous reactions.

The details of reactions which would lead to PtRI(NBD) (R = CH_3 (**15**), CF_3 (**14**)) are not obvious. Perhaps a complex sequence of redox reactions is involved.

4.3. NMR spectra

The complex $Pt(CH_3)(CF_3)$(dppe) (**8**) provides an additional compound in the extensive series Pt $(CH_3)X$(dppe) for which ^{31}P NMR data are available [12]. The Pt–P coupling constants provide a direct confirmation that the NMR trans influence of trifluoromethyl is slightly less than that of methyl, as previously proposed [7,12,13]. NMR data are now also available for a number of complexes Pt(R)I(dppe). From the value of ^1J(Pt–P) *trans* to $-CF_2CH_3$ in **19** (1472 Hz) compared with that *trans* to methyl in **18** (1726 Hz [11]) and *trans* to trifluoromethyl in **17** (1784 Hz), the NMR *trans* influence of the difluoroethyl group is significantly greater than that of the other alkyl groups.

Table 4 shows some comparative data for coupling constants between ^{195}Pt and nuclei in methyl and trifluoromethyl groups. It is evident that $^2J(Pt–CH_3)$ values differ only slightly (< 3 Hz) between *cis*-$Pt(CH_3)_2L_2$ and *cis*-$Pt(CH_3)(CF_3)L_2$. Differences between ^1J(Pt–C) (methyl) values tend to be larger. The greater susceptibility of ^1J(Pt–C) (methyl) to cis influences compared with $^2J(Pt–CH_3)$ has been previously noted [34–36]. The Pt–CF_3 coupling constants in complexes *cis*-$Pt(CF_3)_2L_2$ are consistently smaller in magnitude than for corresponding complexes in the series *cis*-$Pt(CH_3)(CF_3)L_2$. We have previously noted [8] that $^2J(Pt–CF_3)$ in trifluoromethylplatinum(IV) complexes is much more sensitive to the influence of *cis*-ligands than $^2J(Pt–CH_3)$ in corresponding methyl complexes.

From the limited ^{195}Pt chemical shift data available, it appears that replacing a methyl group in a platinum(II) complex by a trifluoromethyl group usually causes a shift to higher field. For example, δ_{Pt} for $Pt(CH_3)_2$(dppe) is −4685 [37] and for $Pt(CH_3)(CF_3)$(dppe) (**8**) −4819; for $Pt(CH_3)_2$(NBD) (**2**) δ_{Pt} is −3618, for $Pt(CH_3)(CF_3)$(NBD) (**1**) − 3869, and for $Pt(CF_3)_2$(NBD) (**3**) −3971 [6]; for *cis*-$Pt(CH_3)(CF_3)py_2$ (**10**), −3711 and for *cis*-$Pt(CF_3)_2py_2$ −3827 [6]. This trend contrasts with that observed for platinum(IV) complexes, for which replacement of a methyl group by a trifluoromethyl group causes a shift to lower field [8]. An exception to this general trend for platinum(II) complexes is the pair of compounds PtRI(dppe), with R = CH_3 (δ_{Pt} −4967) and R = CF_3 (δ_{Pt} −4950).

TABLE 4. Comparative coupling constant data [a]

L_2	*Cis*-$Pt(CH_3)_2L_2$		*Cis*-$Pt(CH_3)(CF_3)L_2$			*Cis*-$Pt(CF_3)_2L_2$
	$^2J(Pt–CH_3)$	$^1J(Pt–CH_3)$	$^2J(Pt–CH_3)$	$^1J(Pt–CH_3)$	$^2J(Pt–CF_3)$	$^2J(Pt–CF_3)$
dppe	71.4 [12]	610 [37]	68.1	573	685	627 [b] [2]
(DMSO-*S*)$_2$	78 [23]		79.4		807	711 [6]
bipy	85.0 [38]		86.8		809	741 [2]
(py)$_2$	86.1 [5]	689 [5]	87.6	798	861	794 [6]
tmen	86.0 [2]	826 [5]	88.2	841	841	752 [2]
NBD	89.8 [5]	815 [5]	89.1	788	894	811 [6]
$(CH_3CN)_2$					906	864 [6]

[a] Coupling constants in Hz. Where values are not from this work, references are given in parentheses. [b] Value for *cis*-$Pt(CF_3)_2(PMe_2Ph)_2$.

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