# Synthesis and molecular structures of platinum(II) and platinum(IV) diimine complexes possessing fluoroalkyl ligands<sup>1</sup>

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**Abstract:** A range of Pt-diimine complexes possessing fluoroalkyl and hydrofluoroalkyl ligands were synthesized from the readily prepared [Pt(diimine)Me<sub>2</sub>] complexes and the appropriate iodofluoroalkane. For complexes with diimine ligands containing substituents in the 2,6-positions of the aryl group, Pt(II) complexes were obtained due to in situ reductive elimination of MeI, while for complexes with diimine ligands of smaller steric demands (possessing substituents in the 3,5-positions or the 4-position), Pt(IV) complexes were obtained. Attempts to convert the Pt(IV) complexes to the desired Pt(II) species via reductive elimination of MeI, methane, or ethane resulted in either no reaction or degradation of the starting complex. Fluoroalkyl(methyl)platinum(II) complexes were then converted to the fluoroalkyliodoplatinum(II) complexes via addition of I<sub>2</sub> or by reaction with aq HI. Several complexes have been characterized crystallographically.

Key words: fluoroalkyl, organometallic synthesis, structure, platinum.

**Résumé :** Utilisant comme produit de départ des iodofluoroalcanes appropriés et des complexes [Pt(diimine)Me<sub>2</sub>] qui peuvent facilement être préparés, on a préparé un éventail de complexes Pt-diimine portant des ligands fluoroalkyles et hydrofluoroalkyles. Pour les complexes avec des ligands diimines portant des substituants dans les positions 2,6 du groupe aryle, on a obtenu des complexes de Pt(II) en raison d'une élimination réductrice in situ de MeI alors qu'on a obtenu des complexes de Pt(IV) avec pour les complexes avec des ligands diimines dont les demandes stériques sont plus faibles (qui portent des substituants dans les positions 4 ou 3,5). Des essais en vue de transformer les complexes de Pt(IV) en espèces Pt(II) désirées par le biais d'une élimination réductrice de MeI, de méthane ou d'éthane n'ont pas donné de réaction ou une dégradation du complexe de départ. Les complexes fluoroalkyl(méthyl)platine(II) ont ensuite été transformés en complexes fluoroalkyliodoplatine(II) par le biais d'une addition de I<sub>2</sub> ou par une réaction avec du HI aqueux. Plusieurs complexes ont été cristallisés par diffraction des rayons X.

Mots clés : fluoroalkyle, organométallique, synthèse, structure, platine.

[Traduit par la Rédaction]

## Introduction

Much recent work within our research group has focussed upon the synthesis of late transition metal-fluoroalkyl complexes, particularly those of metals from groups 9 (1–9) and 10 (10–12), utilizing oxidative addition of iodoperfluoroalkanes (11). While many such complexes have been synthesized previously using oxidative addition reactions (13–18), we have shown that such a route can often lead to fluoro-

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alkylation at ligand sites rather than at the metal center in both early and late transition metals (19–22).

There have been many studies of oxidative addition of alkyl halides to square-planar Pt(II) precursors (23–27). In the majority of cases, the reaction of bromo- and iodoalkanes with dimethylplatinum(II) complexes occurs via a polar  $S_N 2$  mechanism to give a Pt(IV) complex with kinetically controlled trans stereochemistry (23), although subsequent isomerization has been shown in some cases to afford the cis product (28). On occasion, cationic five-coordinate intermediates have been detected spectroscopically (29). These five-coordinate species in the oxidative addition reaction have also been shown to serve as key intermediates for reductive elimination of methyl iodide or ethane from Pt(IV) (30–32).

The oxidative addition reactions of iodofluoroalkanes to transition metals is unlikely to proceed via polar  $S_N^2$  attack by the metal at carbon due to the unfavourable polarity of the C<sup> $\delta$ </sup>----I<sup> $\delta$ +</sup> bond (33, 34). In previous systems involving reactions of primary iodoperfluoroalkanes, we have postulated that the reactions proceeded via electron transfer to the iodofluoroalkane, followed by rapid loss of iodide from the

resultant radical anion, and very fast trapping of the fluoroalkyl radical at the metal (21, 22).

While most studies of oxidative addition - reductive elimination to Pt(II) centers have involved complexes bearing monodentate or bidentate phosphorus ligands, complexes with chelating nitrogen ligands have also been examined (23). cis-Dialkyl- and -diarylplatinum(II) complexes with nitrogen donor ligands usually react with alkyl halides to afford the trans oxidative addition product (35-38). The corresponding cis-isomer can be formed either by a competitive cis oxidative addition pathway, or by trans oxidative addition with subsequent isomerization of the platinum(IV) product to a thermodynamically more stable cis-isomer (23). Dimethylplatinum(II) complexes possessing pyridine (35), 2,2'-bipyridine (39), 1,10-phenanthroline (39, 40), bis(ptolylimino)acenaphthene (41), bis(phenylimino)camphane (41), various diimine ligands (42, 43), and tetramethylethylenediamine (tmeda) (44, 45) have been studied.

We have previously reported on the reactions of  $[Pt(tmeda)Me_2]$  with fluoroalkyl iodides to give Pt(IV) and Pt(II) fluoroalkyl complexes (11). Here we report on the corresponding reactions of dimethylplatinum(II) complexes bearing diimine ligands.

# **Results and discussion**

#### Synthesis

In contrast to the very facile oxidative addition reactions of [Pt(tmeda)Me<sub>2</sub>] with fluoroalkyl iodides (11), the corresponding reactions of the [Pt(diimine)Me<sub>2</sub>] complexes 1 and 2 required heating at reflux in ethyl acetate to afford the fluoroalkyl Pt(IV)-diimine complexes 3-6 (Scheme 1). To reduce the possibility of light-induced radical chemistry of the fluoroalkyl iodides, the reactions were performed in the dark, although no attempts were made to evaluate whether light actually does cause problems in these cases. When [Pt(diimine)Me<sub>2</sub>] complexes 7 and 8 were used, which possess a diimine ligand containing a 2,6-dimethylaryl fragment, the products formed were always the Pt(II) complexes 9–12 (Scheme 2). This can be ascribed to steric congestion around the Pt(IV) centre (initially formed by oxidative addition of the  $R_f I$  to the [Pt(diimine)Me<sub>2</sub>] complex), resulting in in situ reductive elimination of MeI to form the square planar Pt(II) complex.

Owing to the solubility of **7** in hexane, the desired perfluoroalkyl complexes could also be obtained by heating at reflux in hexane for 8 h. The use of hexane, however, only resulted in better yields when the perfluoroalkyl group was  $C_3F_7$ . Hexane also afforded straightforward isolation of the Pt(II) complexes, which are insoluble in hexane. Unfortunately, the lack of hexane solubility for dimethyl complexes possessing other diimine ligands (**1**, **2**, and **8**) precluded its use as a general solvent for the synthesis of these complexes.

Before ethyl acetate was found to facilitate these oxidative addition reactions of [Pt(diimine)Me<sub>2</sub>] complexes with iodofluoroalkanes, attempts were made to use benzene as a solvent. However, when benzene was used, the reaction was incomplete after heating at reflux for 24 h, and there was formation of elemental Pt. NMR of the crude reaction mixtures showed approximately 30%–40% conversion to the desired products after 24 h. However, isolation of the oxidative addition products proved unsuccessful due to the very similar solubilities exhibited by the starting materials, free diimine ligand, and the oxidative addition products. The subsequent choice of ethyl acetate was based solely upon its slightly lower boiling point as compared to benzene, as previous experience within our research group has shown that certain oxidative addition reactions can be very temperature dependent (46). It may also have proven to be a fortuitous choice for a reaction that may proceed via a fluoroalkyl radical, since electrostatic repulsion of the oxygen atoms of the ethyl acetate has been shown to significantly inhibit hydrogen atom abstraction by fluoroalkyl radicals when compared with rates of abstraction from alkanes (47), thereby perhaps increasing the yield of organometallic product.

The Pt(IV) species obtained were invariably those in which the perfluoroalkyl moiety was mutually trans to the iodo ligand, giving rise to complexes with  $C_s$  symmetry, as shown for complexes 3, 4, and 6. The <sup>19</sup>F NMR spectrum of 3 reveals two resonances for the m-CF<sub>3</sub> groups of the diimine ligand indicating that there is no free rotation about the N-aryl bonds on the NMR timescale. However, the <sup>19</sup>F NMR spectrum of **4** reveals only one resonance for the m-CF<sub>3</sub> groups of the diimine ligand indicating apparently free rotation of the aryl moiety, or an accidental equivalence of  $CF_3$  resonances. In the case of 5, the presence of a stereocenter at the  $\alpha$ -C of the fluoroalkyl group results in a complex with  $C_1$  symmetry. This is highlighted clearly in the <sup>1</sup>H NMR spectrum of this complex in which the Pt-bound methyl groups, the CH<sub>3</sub> groups of the diimine backbone, and the m-CF<sub>3</sub> substituents of the aryl rings display nonequivalence (two of which are coincident), indicating that rotation of the aryl rings is slow on the NMR timescale.

Attempts to convert the Pt(IV) complexes to Pt(II) species with procedures that we have used successfully for such reductions in cases when the ligands involved are tmeda, 1,2bis(diphenylphosphino)ethane, or 1,2-bis(dimethylphosphino)ethane proved unsuccessful. The methods attempted to achieve this reduction included: (i) removal of iodide using AgBF<sub>4</sub> and heating at reflux in acetone to eliminate ethane, followed by addition of NaI to form the iodoplatinum(II) complex (32); (ii) heating a solution of the complex in the presence of NEt<sub>3</sub>, to form the insoluble [Et<sub>3</sub>NMe]I complex upon thermal elimination of MeI (11); and (iii) reaction of the complex with NaBH<sub>4</sub> (to convert the iodo ligand to a hydride) and then stirring at room temperature to allow the complex to thermally eliminate methane. In the first case, the starting complexes were obtained without any observable isomerization, while degradation of the Pt(IV) complex to elemental platinum occurred in the last two methods.

As discussed above, the only instances in which Pt(II) complexes were obtained were from reactions in which the diimine ligand possessed the 2,6-dimethylaryl substituent. The NMR spectra of these complexes are very diagnostic as the backbone protons (or methyl groups) of the diimine ligand are inequivalent due to the  $C_s$  symmetry of the square-planar complexes. In the <sup>1</sup>H NMR spectrum, the diimine backbone protons of complexes 9 and 10 exhibit Pt satellites: in the case of 9, these <sup>3</sup> $J_{PtH}$  coupling constants were 36 Hz ( $\delta$  9.01 ppm) and 84 Hz ( $\delta$  8.93 ppm), while for 10 the coupling constants were 37 Hz ( $\delta$  9.20 ppm) and 42 Hz ( $\delta$  9.06 ppm), respectively. A similar coupling was

Scheme 1.

Scheme 2.



previously seen in numerous unsymmetrical platinum diimine complexes (42, 48–54). Tilset (49) assigned the protons on the diimine backbone using a variety of NMR techniques, with the smaller coupling being ascribed to those protons transoid to the methyl ligand. Thus, some indication as to the relative trans-influence of the two different fluoroalkyl ligands in these complexes can be obtained: the partially fluorinated ligand (CFHCF<sub>3</sub>) exerts a stronger trans influence than the perfluorinated ligand ( $C_3F_7$ ). The complexes possessing methyl substitution of the diimine backbone (complexes **11** and **12**) do not exhibit any coupling to Pt.

The [Pt(diimine)( $R_f$ )Me] complexes **9–12** are readily converted to the iodo complexes **13–16** via two methods, each of which results in selective cleavage of the Pt—CH<sub>3</sub> bond rather than the Pt—fluoroalkyl bond. The first involves the reaction of the complex with I<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, possibly resulting in the formation of a transient diiodo–Pt(IV) complex, which undergoes thermal reductive elimination of MeI. The second pathway involves reaction of the methyl complex with 1 equiv. of aq HI in toluene (Scheme 2), resulting in the gen-

eration of methane followed by trapping of the resulting cationic Pt(II) fragment with iodide. Both methods afford the iodo complexes in 70%–80% yield after recrystallization from dichloromethane–hexane.

The NMR spectra of the iodo complexes are very similar to those of the methyl analogues. As was the case for the methyl complexes, the backbone protons of the diimine ligand in complexes **13** and **14** display platinum coupling: for **13**,  ${}^{3}J_{\text{PtH}} = 102 \text{ Hz}$  ( $\delta$  9.00 ppm) and 40 Hz ( $\delta$  8.62 ppm), while for **14**,  ${}^{3}J_{\text{PtH}} = 100 \text{ Hz}$  ( $\delta$  9.16 ppm) and 38 Hz ( $\delta$  8.68 ppm). Presumably, the large difference in the coupling constants for both complexes may be explained by the large cis-effect exerted by the iodo ligand. As was the case in the methyl complexes, no platinum satellites were observed for those complexes possessing methyl substitution on the backbone of the diimine ligand.

#### **Crystal structures**

X-ray diffraction quality crystals were obtained for several of the Pt(IV) complexes by slow recrystallization from  $CH_2Cl_2$ -hexane. Crystal structures were obtained for com-



Fig. 1. ORTEP diagram of the non-hydrogen atoms of 3, showing the atom labelling scheme. Thermal ellipsoids are shown at 30% probability.

Fig. 2. ORTEP diagram of the non-hydrogen atoms of 4, showing the atom labelling scheme. Thermal ellipsoids are shown at 30% probability.



plexes 3 (Fig. 1), 4 (Fig. 2), and 5 (Fig. 3). Details of the crystal data and structure determinations of all complexes are presented in Table 1. Selected bond lengths and angles for the coordination sphere of Pt are given in Table 2. For easy comparison, a common numbering scheme has been adopted: in the Pt(IV) complexes, the equatorial plane corresponds to the plane of N(1) and N(2) of the diimine ligand

and C(1) and C(2) of the two methyl groups, while C(3) (the  $\alpha$ -carbon of the perfluoroalkyl moiety) is always trans to I.

The structures obtained for complexes 3 and 4 display disorder in the CF<sub>3</sub> groups of the diimine ligand, and, in the case of the structures for 4 and 5, a small amount of disorder is also observed in the perfluoroalkyl moiety.

The crystal structures of complexes 3, 4, and 5 show the



Fig. 3. ORTEP diagram of the non-hydrogen atoms of 5, showing the atom labelling scheme. Thermal ellipsoids are shown at 30% probability.

Table 1. Summary of X-ray crystallographic data collection, solution, and refinement parameters for complexes 3, 4, 5, and 11.

Complex	3	4	5	11
Formula	$C_{25}H_{18}F_{19}IN_2Pt$	$C_{24}H_{19}F_{16}IN_2Pt$	$C_{24}H_{19}F_{16}IN_2Pt$	$C_{24}H_{27}F_7N_2Pt$
Space group	$P2_1/n$	$P2_1/n$	<i>P</i> -1	$P2_1/n$
a (Å)	14.0822(6)	14.5331(1)	8.3105(5)	8.3273(5)
<i>b</i> (Å)	9.2888(4)	9.3944(7)	11.8465(8)	13.0769(7)
<i>c</i> (Å)	24.2972(1)	23.4593(17)	31.026(2)	23.0810(13)
α (°)	90.00	90.00	95.757(1)	90.00
β (°)	101.885(1)	101.229(1)	92.018(1)	90.109(1)
γ (°)	90.00	90.00	108.0410(10)	90.00
V (Å <sup>3</sup> )	3110.1(2)	3141.6(4)	2882.6(3)	2513.4(2)
Ζ	4	4	4	4
Crystal colour, habit	Yellow, block	Amber, block	Yellow, block	Red, block
$D(\text{calcd.}) (\text{g/cm}^3)$	2.198	2.033	2.215	1.775
$\mu (mm^{-1})$	5.639	5.562	6.061	5.649
Т (К)	100(2)	295(2)	100(2)	173(2)
Total data	7346	6160	18 522	15 786
Unique data $(R_{int})$	6757(0.0232)	4764(0.0262)	12 959(0.0207)	5856(0.0280)
R1, wR2 $(I > 2\sigma(I))$	0.0406, 0.0994	0.0513, 0.1496	0.0405, 0.0948	0.0778, 0.2135
All data	0.0441, 0.1015	0.0679, 0.1612	0.0530, 0.1002	0.0979, 0.2551

Pt(IV) center to have approximate octahedral geometry. There is only a subtle deviation from the ideal angle of  $180^{\circ}$  for C(3)-Pt-I(1), with **5** showing the largest discrepancy with an angle of  $175.8(3)^{\circ}$ . The deviation is also observed for the C(3)-Pt-N(1) angle in **5**, which exhibits a value of  $96.7(3)^{\circ}$ , while complexes **3**, and **4** have angles close to  $90^{\circ}$ . In all structures, there is deviation from the expected angles in the plane of the Pt atom: the C(1)-Pt-C(2) angles are reduced substantially (especially in the case of **4** and **5**), presumably due to the bulk of the aryl groups on the diimine ligand. As a consequence, the C(1)-Pt-N(2) and the C(2)-Pt-N(1) bond angles are all in the region of  $100^{\circ}$ . The Pt—C(1) and Pt—

C(2) bond lengths for **3** and **5** are similar in all cases and are identical for each complex, except for complex **4**, in which there is a significant variation between the two bond lengths (2.072(11) Å and 2.031(12) Å, respectively). The source of this bond length variation is not clear. The Pt—C(3) bond lengths for **3** (2.129(8) Å) and **5** (2.076(8) Å) are significantly different, with an unexpectedly shorter bond to the partially hydrogenated  $\alpha$ -CFH group. However, the Pt—I bond lengths for **3** (2.6769(4) Å) and **5** (2.7447(5) Å) do display the expected trend for the trans-influence of the alkyl group, with a greater degree of fluorination affording a weaker trans-influence (10, 55). Because the Pt—N(1) and



Fig. 4. ORTEP diagram of the non-hydrogen atoms of 11, showing the atom labelling scheme. Thermal ellipsoids are shown at 30% probability.

Table 2. Selected bond lengths (Å) and angles (°) for the coordination sphere of platinum in complexes 3, 4, 5, and 11.

Complex	3	4	5	11
Bond angles (	(Å)			
Pt-C(1)	2.065(6)	2.072(11)	2.053(7)	2.047(9)
Pt—C(2)	2.066(5)	2.031(12)	2.055(7)	2.032(9)
Pt—C(3)	2.129(8)	2.228(9)	2.076(9)	_
Pt—N(1)	2.175(4)	2.178(6)	2.187(5)	2.133(7)
Pt—N(2)	2.170(5)	2.183(7)	2.178(5)	2.077(8)
Pt—X	2.6769(4)	2.6963(8)	2.7447(5)	
Bond angles (	(°)			
C(1)-Pt- $C(2)$	88.2(2)	85.4(5)	85.1(3)	87.2(6)
C(1)-Pt-C(3)	94.3(2)	92.0(4)	88.1(4)	_
C(1)-Pt-N(1)	172.5(2)	173.3(4)	174.5(3)	171.0(6)
C(1)-Pt-N(2)	98.8(2)	99.4(4)	100.2(2)	93.9(6)
C(1)-Pt-X	87.53(18)	89.5(3)	91.0(2)	_
C(2)-Pt-C(3)	91.1(2)	91.1(4)	88.1(4)	_
C(2)-Pt-N(1)	98.7(2)	100.7(4)	100.2(2)	101.8(4)
C(2)-Pt-N(2)	172.3(2)	174.4(4)	174.7(2)	176.1(5)
C(2)-Pt-X	88.81(16)	88.0(3)	91.3(2)	_
C(3)-Pt-N(1)	88.43(19)	90.7(3)	96.7(3)	_
C(3)-Pt-N(2)	91.4(2)	91.5(3)	92.4(3)	_
C(3)-Pt-X	178.12(16)	178.2(2)	175.8(3)	_
N(1)-Pt-N(2)	74.08(17)	74.4(3)	74.48(18	77.1(4)
N(1)-Pt-X	89.72(11)	87.91(17)	87.57(13	_
N(2)-Pt-X	88.46(12)	89.13(16)	88.49(13	_

Pt—N(2) bond lengths for **3**, **4**, and **5** are similar in all cases and show no significant variation within each complex, there is clearly no cis-effect in the differently fluorinated alkyl groups.

No meaningful comparisons between the Pt(IV)-diimine complexes and the analogous Pt(IV)-tmeda complexes can be made, as the tmeda complexes isomerize from the initial trans-product to form the thermodynamically favored cisproduct.<sup>3</sup>

Crystallization of **11** from  $CH_2Cl_2$ -hexane afforded red plates that were suitable for X-ray diffraction studies. The ORTEP diagram for complex **11** is shown in Fig. 4. Selected bond lengths and angles for the coordination sphere of Pt are given in Table 2. The numbering scheme adopted for complex **11** has N(1) trans to C(1) (the methyl group), while N(2) is trans to C(2) (the  $\alpha$ -carbon of the perfluoroalkyl moiety).

The structure shows the complex is square planar, with no significant deviations of the ligands from the plane, but with significant bond angle deviations due to the steric bulk of the perfluoroalkyl ligand. The C(2)-Pt-N(2) bond angle of 176.1(5)° is close to the ideal angle, however, there is significant deviation observed for the C(1)-Pt-N(1) which has a bond angle of  $171.0(6)^\circ$ . Similarly, the C(2)-Pt-N(1) bond angle ( $101.8(6)^\circ$ ) shows a large distortion that is attributable to the steric requirements of the perfluoroalkyl moiety. Variations in the bond lengths to the Pt atom are also observed which is a consequence of the relative magnitude of the trans-influence for methyl and perfluoroalkyl ligands: the

<sup>3</sup>Our initial observations on this reaction were that the cis-product was formed. More careful studies have shown that the trans-isomer is the kinetic product. R.P. Hughes, M.A. Meyer, A.J. Ward, A. Williamson. Unpublished results.

Pt—C(1) bond length is 2.047(9) Å, while the Pt—C(2) bond length is slightly shorter at 2.032(9) Å. However, it is in the Pt—N bond lengths that the trans-effect is most clearly manifested: the Pt—N(1) bond length (trans to methyl) is 2.133(7) Å, while the Pt—N(2) bond length (trans to  $C_3F_7$ ) is 2.077(8) Å.

Comparison of the structure obtained for 11 and that obtained previously for  $[Pt(tmeda)(C_3F_7)Me]$  (11) reveals that the presence of the diimine ligand results in significant steric crowding around the Pt center, and thus, there is some variation in bond lengths and bond angles between the two complexes. For example, the Pt-C(1) and Pt-C(2) bond lengths for the tmeda complex are 2.148(18) Å and 2.01(2)Å, respectively, compared to 2.047(9) Å and 2.032(9) Å for the same bonds in complex 11. The Pt-N(1) and Pt-N(2)are 2.14(2) Å and 2.172(19) Å, respectively, for the tmeda complex, while they are 2.133(7) Å and 2.077(8) Å for 11. Significant variation in bond angles is observed between the two complexes: C(1)-Pt-C(2) for **11** is 87.2(6)° and for the tmeda complex is  $88.3(9)^{\circ}$ ; C(1)-Pt-N(2) for **11** is  $93.9(6)^{\circ}$ and for the tmeda complex is 92.3(8)°; C(2)-Pt-N(2) for 11 is  $101.8(6)^{\circ}$  and for the tmeda complex is  $97.7(9)^{\circ}$ . While these large variations are probably attributable solely to the large steric bulk of the diimine aryl groups, the data for the tmeda complex are of poor quality and preclude any more meaningful comparisons.

## **Experimental section**

#### **General considerations**

Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen (which had been deoxy-genated over BASF catalyst), and dried using Aquasorb<sup>®</sup>. Solvents were deoxygenated and dried over activated alumina using an apparatus modified from that described in the literature (56). <sup>1</sup>H (300 MHz), <sup>19</sup>F (282 MHz), and <sup>31</sup>P (121.4 MHz) NMR spectra were recorded on a Varian Unity-300 spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of TMS (<sup>1</sup>H, referenced to solvent) or internal CFCl<sub>3</sub> (<sup>19</sup>F). Coupling constants are reported in Hertz (Hz). Microanalyses were performed by Schwartzkopf Microanalytical Laboratory (Woodside, N.Y.).

Iodoperfluoroalkanes were purchased from PCR, (except for CF<sub>3</sub>CFHI, which was purchased from ABCR) treated with  $Na_2S_2O_3$  to remove residual  $I_2$ , and vacuum distilled before use. The complexes [Pt(3,5-(CF<sub>3</sub>)<sub>2</sub>ArN=C(Me)C(Me)=N-3,5-(CF<sub>3</sub>)<sub>2</sub>Ar)Me<sub>2</sub>] (1) (57), [Pt(4-MeArN=CHCH=N-4-MeAr)Me<sub>2</sub>] (2) (58), [Pt(2,6-Me\_2ArN=CHCH=N-2,6-Me\_2Ar)Me\_2] (7) (59), and [Pt(2,6-Me\_2ArN=C(Me)C(Me)=N-2,6-Me\_2Ar)Me\_2] (8) (59) were prepared as reported previously.

## trans-[1,2-Bis(3,5-bis(trifluoromethylphenylimino)-1,2dimethylethane]dimethyl(heptafluoropropyl)iodoplatinum(IV) (3)

To a solution of 1 (100 mg, 0.14 mmol) in degassed ethyl acetate (10 mL) was added heptafluoropropyl iodide (30 mL, 0.20 mmol) and the reaction mixture was heated at reflux for 2 h in the absence of light. The solvent was removed in vacuo. The residue was recrystallized from

CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford the product as an orange powder (86 mg, 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 8.44 (s, 2H, Ar*H*), 7.96 (s, 2H, Ar*H*), 7.37 (s, 2H, Ar*H*), 2.49 (s, 6H,  ${}^{4}J_{PtH} = 5$  Hz, N=C(C*H*<sub>3</sub>)), 1.37 (s, 6H,  ${}^{2}J_{PtH} = 73$  Hz, PtC*H*<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>) δ (ppm): -63.34 (s, 6F, *m*-ArC*F*<sub>3</sub>), -63.47 (s, 6F, *m*-ArC*F*<sub>3</sub>), -80.07 (t, 3F,  ${}^{4}J_{FF} = 13$  Hz,  ${}^{4}J_{PtF} = 9$  Hz, CF<sub>2</sub>C*F*<sub>3</sub>), -90.08 (m, 2F,  ${}^{2}J_{PtF} = 298$  Hz, PtC*F*<sub>2</sub>), -122.03 (m, 2F, C*F*<sub>2</sub>C*F*<sub>3</sub>). Anal. calcd. for C<sub>25</sub>H<sub>18</sub>F<sub>19</sub>IN<sub>2</sub>Pt (%): C 29.17, H 1.77; found (%): C 29.37, H 1.65.

#### trans-[1,2-Bis(3,5-bis(trifluoromethylphenylimino)-1,2dimethylethane]iododimethyl-(2H-tetrafluoroethyl)platinum(IV) (4)

To a solution of **1** (100 mg, 0.14 mmol) in degassed ethyl acetate (10 mL) was added iodo-2*H*-tetrafluoroethane (23  $\mu$ L, 0.20 mmol) and the reaction mixture was heated at reflux in the absence of light for 2 h. The solution was cooled and the solvent removed in vacuo. The residue was extracted with hot hexanes until no colour persisted in the washings. The volume of the combined extracts was reduced in vacuo to 5 mL and cooled to -30 °C. The product was obtained by filtration as a yellow powder (86 mg, 66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 8.42 (s, 2H, ArH), 7.94 (s, 2H, ArH), 7.45 (s, 2H, ArH), 5.45 (tt, <sup>2</sup>J<sub>FH</sub> = 55 Hz, <sup>3</sup>J<sub>FF</sub> = 6 Hz, <sup>2</sup>J<sub>PtH</sub> = 11 Hz CF<sub>2</sub>H), 2.47 (s, 6H, <sup>4</sup>J<sub>PtH</sub> = 5 Hz, N=C(CH<sub>3</sub>)), 1.26 (s, 6H, <sup>2</sup>J<sub>PtH</sub> = 72 Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -63.30 (s, 12F, *m*-ArCF<sub>3</sub>), -90.98 (dt, 2F, <sup>3</sup>J<sub>FF</sub> = 3 Hz, <sup>3</sup>J<sub>FF</sub> = 6 Hz, <sup>2</sup>J<sub>PtH</sub> = 55 Hz, <sup>2</sup>J<sub>PtH</sub> = 27 Hz, CF<sub>2</sub>CF<sub>2</sub>H). Anal. calcd. for C<sub>24</sub>H<sub>19</sub>F<sub>16</sub>IN<sub>2</sub>Pt (%): C 29.98, H 2.00; found (%): C 30.21, H 1.87.

## trans-[1,2-Bis(3,5-bis(trifluoromethylphenylimino)-1,2dimethylethane]dimethyliodo(1H-tetrafluoroethyl)platinum(IV) (5)

To a solution of 1 (100 mg, 0.14 mmol) in degassed ethyl acetate (10 mL) was added iodo-1H-tetrafluoroethane (23 µL, 0.20 mmol) and the reaction mixture was heated at reflux in the absence of light for 2 h. The solution was cooled and the solvent removed in vacuo. The residue was extracted with hot hexanes until no colour persisted in the washings. The volume of the combined extracts was reduced in vacuo to 5 mL and cooled to -30 °C. The product was obtained by filtration as a yellow powder (85 mg, 65%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 8.73 (bs, 1H, ArH), 8.39 (s, 1H, ArH), 7.94 (s, 2H, ArH), 7.41 (bs, 2H, ArH), 6.5) (s, 1II,  $^{2}J_{FH} = 47$  Hz,  $^{3}J_{FF} = 10$  Hz,  $^{2}J_{PtH} = 410$  Hz, CFH), 2.48 (s, 3H,  $^{4}J_{PtH} = 5$  Hz, N=C(CH<sub>3</sub>)), 2.45 (s, 3H,  $^{4}J_{PtH} = 5$  Hz, N=C(CH<sub>3</sub>)), 1.27 (d, 3H,  $^{4}J_{FH} = 1$  Hz,  $^{2}J_{PtH} = 70$  Hz, PtCH<sub>3</sub>), 1.12 (s, 3H,  $^{2}J_{PtH} = 71$  Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCL)  $\delta$  (npm): 63 18 (s, 3E m ArCE) 63 27 (s, 2E m  $(CDCl_3) \delta$  (ppm): -63.18 (s, 3F, m-ArCF<sub>3</sub>), -63.27 (s, 3F, m-ArCF<sub>3</sub>), -63.32 (s, 6F, *m*-ArCF<sub>3</sub>), -72.95 (dd, 3F,  ${}^{3}J_{\text{FF}}$  = 11 Hz,  ${}^{3}J_{FH} = 11$  Hz,  ${}^{3}J_{PtF} = 61$  Hz, CFHCF<sub>3</sub>), -191.43 (dq, 1F,  ${}^{3}J_{FF} = 11$  Hz,  ${}^{3}J_{FH} = 47$  Hz,  ${}^{2}J_{PtF} = 135$  Hz, CFHCF<sub>3</sub>). Anal. calcd. for C<sub>24</sub>H<sub>19</sub>F<sub>16</sub>IN<sub>2</sub>Pt (%): C 29.98, H 2.00; found (%): C 29.87, H 1.99. X-ray diffraction quality crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>-hexane.

## trans-[1,2-Bis(4-methylphenylimino)ethane]dimethyl(heptafluoropropyl)iodoplatinum(IV) (6)

To a suspension of 2 (100 mg, 0.22 mmol) in hexane

(10 mL) was added C<sub>3</sub>F<sub>7</sub>I (47 µL, 0.33 mmol) and the reaction mixture was refluxed for 8 h. The solution was cooled and the solvent removed in vacuo. Recrystallization from hot hexane afforded the product as an orange microcrystalline solid (104 mg, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 8.67 (t, 2H, <sup>3</sup>J<sub>PtH</sub> = 26 Hz, N=CH), 7.45 (m, 4H, ArH), 7.31 (m, 4H, ArH), 2.44 (s, 6H, ArCH<sub>3</sub>), 1.77 (t, 6H, <sup>2</sup>J<sub>PtH</sub> = 74 Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -80.01 (t, 3F, <sup>4</sup>J<sub>FF</sub> = 12 Hz, <sup>4</sup>J<sub>PtF</sub> = 18 Hz, CF<sub>3</sub>), -91.93 (qt, 2F, <sup>2</sup>J<sub>PtF</sub> = 362 Hz, <sup>4</sup>J<sub>FF</sub> = 12 Hz, <sup>3</sup>J<sub>FF</sub> = 3 Hz, PtCF<sub>2</sub>), -121.79 (m, 2F, CF<sub>2</sub>CF<sub>3</sub>). Anal. calcd. for C<sub>21</sub>H<sub>22</sub>F<sub>7</sub>IN<sub>2</sub>Pt (%): C 33.29, H 2.93; found (%): C 33.83, H 3.12.

#### [1,2-Bis(2,6-dimethylphenylimino)ethane](heptafluoropropyl)methylplatinum(II) (9)

To a solution of **7** (100 mg, 0.20 mmol) in hexane (10 mL) was added  $C_3F_7I$  (44 µL, 0.31 mmol) and the reaction mixture was heated at reflux for 18 h. The solution was cooled. Filtration and washing with hexane afforded the product as a maroon microcrystalline solid (146 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 9.01 (t, 1H, <sup>3</sup>J<sub>Pt-H</sub> = 36 Hz, N=CH), 8.93 (t, 1H, <sup>3</sup>J<sub>PtH</sub> = 84 Hz, N=CH), 7.21 (s, 4H, *m*-ArH), 7.14 (m, 2H, *p*-ArH), 2.28 (s, 12H, CH<sub>3</sub>), 1.21 (t, 3H, <sup>2</sup>J<sub>PtH</sub> = 88 Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -79.98 (t, 3F, <sup>4</sup>J<sub>PtF</sub> = 36 Hz, <sup>4</sup>J<sub>FF</sub> = 10 Hz, CF<sub>3</sub>), -94.74 (q, 2F, <sup>2</sup>J<sub>PtF</sub> = 420 Hz, <sup>4</sup>J<sub>FF</sub> = 10 Hz, PtCF<sub>2</sub>), -120.33 (s, 2F, <sup>3</sup>J<sub>PtF</sub> = 116 Hz, CF<sub>2</sub>CF<sub>3</sub>). Anal. calcd. for C<sub>22</sub>H<sub>23</sub>F<sub>7</sub>N<sub>2</sub>Pt (%): C 41.06, H 3.61; found (%): C 41.04, H 3.69.

## [1,2-Bis(2,6-dimethylphenylimino)ethane](1H-tetrafluoroethyl)methylplatinum(II) (10)

To a solution of **7** (100 mg, 0.20 mmol) in ethyl acetate (10 mL) was added iodo-1*H*-tetrafluoroethane (70 mg, 0.31 mmol) and the reaction mixture was heated at reflux for 12 h in the absence of light. The solvent was removed in vacuo and the residue was washed with hexane until no colour persisted in the washings. The product was obtained as purple needles after recrystallization from chloroform–hexane (50 mg, 45%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 9.20 (s, 1H, <sup>3</sup>J<sub>PtH</sub> = 37 Hz, N=CH), 9.06 (s, 1H, <sup>3</sup>J<sub>PtH</sub> = 42 Hz, N=CH), 7.24–7.15 (m, 6H, ArH), 6.03 (dq, 1H, <sup>2</sup>J<sub>FH</sub> = 50 Hz, <sup>3</sup>J<sub>FH</sub> = 11 Hz, <sup>2</sup>J<sub>PtF</sub> = 61 Hz, CFH), 2.36 (s, 3H, ArCH<sub>3</sub>), 2.29 (s, 3H, ArCH<sub>3</sub>), 2.27 (s, 3H, ArCH<sub>3</sub>), 2.20 (s, 3H, ArCH<sub>3</sub>), 1.36 (s, 3H, <sup>2</sup>J<sub>PtH</sub> = 86 Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): –70.69 (dd, 3F, <sup>3</sup>J<sub>FH</sub> = 14 Hz, <sup>3</sup>J<sub>FF</sub> = 14 Hz, <sup>3</sup>J<sub>PtF</sub> = 14 Hz, CF<sub>3</sub>), –212.28 (dq, 1F, <sup>2</sup>J<sub>FH</sub> = 50 Hz, <sup>3</sup>J<sub>FF</sub> = 14 Hz, <sup>2</sup>J<sub>PtF</sub> = 327 Hz, CFH). Anal. calcd. for C<sub>21</sub>H<sub>24</sub>F<sub>4</sub>N<sub>2</sub>Pt•0.5CHCl<sub>3</sub> (%): C 40.65, H 3.90; found (%): C 41.37, H 3.74.

# [1,2-Bis(2,6-dimethylphenylimino)-1,2-dimethylethane](heptafluoropropyl)methylplatinum(II) (11)

To a solution of **8** (100 mg, 0.19 mmol) in ethyl acetate (10 mL) was added  $C_3F_7I$  (42 µL, 0.29 mmol) and the reaction mixture was heated under reflux in the absence of light for 2 h. The solution was cooled and the solvent removed in vacuo. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–hexane. Filtration afforded the complex as a purple powder (66 mg, 51%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.19 (m, 4H, *p*-ArH), 7.12 (s, 2H, *p*-ArH), 2.21 (s, 12H, *o*-ArCH<sub>3</sub>), 1.73 (s, 3H, N=C(CH<sub>3</sub>)), 1.63 ((s, 3H, N=C(CH<sub>3</sub>)), 0.70 (t, 3H, <sup>2</sup>J<sub>PtH</sub> = 86 Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -80.01 (tt, 3F,

 ${}^{4}J_{\text{FF}} = 10 \text{ Hz}, {}^{4}J_{\text{PtF}} = 19 \text{ Hz}, \text{ C}F_3$ , -93.51 (tq, 2F,  ${}^{4}J_{\text{FF}} = 10 \text{ Hz}, {}^{2}J_{\text{PtF}} = 410 \text{ Hz}, \text{ PtC}F_2$ ), -119.74 (t, 2F,  ${}^{3}J_{\text{PtF}} = 119 \text{ Hz}, \text{ C}F_2\text{C}F_3$ ). Anal. calcd. for  $\text{C}_{24}\text{H}_{27}\text{F}_7\text{N}_2\text{Pt}$  (%): C 42.92, H 4.06; found (%): C 43.1, H 4.12.

## [1,2-Bis(2,6-dimethylphenylimino)-1,2-dimethylethane]methyl(1H-tetrafluoroethyl)platinum(II) (12)

To a solution of **8** (100 mg, 0.19 mmol) in ethyl acetate (10 mL) was added  $C_3F_7I$  (42 µL, 0.29 mmol) and the reaction mixture was heated under reflux in the absence of light for 24 h. The solution was cooled and the solvent reduced to 5 mL in vacuo. Hexane was added. Filtration afforded the product as a purple microcrystalline powder (100 mg, 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.30–7.17 (m, 6H, Ar*H*), 5.63 (dq, 1H, <sup>2</sup>J<sub>FH</sub> = 49 Hz, <sup>3</sup>J<sub>FH</sub> = 13 Hz, <sup>2</sup>J<sub>PtH</sub> = 52 Hz, CF*H*), 2.28 (s, ArCH<sub>3</sub>), 1.66 (s, 3H, N=C(CH<sub>3</sub>)), 1.35 (s, 3H, N=C(CH<sub>3</sub>)), 1.10 (s, 3H, <sup>2</sup>J<sub>PtH</sub> = 86 Hz, PtCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -70.73 (dd, 3F, <sup>3</sup>J<sub>FH</sub> = 13 Hz, <sup>3</sup>J<sub>FF</sub> = 14 Hz, CF<sub>3</sub>), -211.64 (dq, 1F, <sup>2</sup>J<sub>FH</sub> = 49 Hz, <sup>3</sup>J<sub>FF</sub> = 14 Hz, CFH). Anal. calcd. for C<sub>23</sub>H<sub>28</sub>F<sub>4</sub>N<sub>2</sub>Pt (%): C 45.76, H 4.69; found (%): C 45.77, H 4.53.

#### [1,2-Bis(2,6-dimethylphenylimino)ethane](heptafluoropropyl)iodoplatinum(II) (13)

#### Method 1:

To a solution of **9** (100 mg, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added iodine (39 mg, 0.16 mmol) and the reaction mixture was stirred in the dark for 12 h. The solvent was reduced in volume to approximately 5 mL in vacuo. Hexane was added to precipitate the product as a brown powder. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane at –30 °C afforded the product as an umber microcrystalline solid (94 mg, 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 9.00 (t, 1H, <sup>3</sup>J<sub>PtH</sub> = 102 Hz, N=CH), 8.62 (t, 1H, <sup>3</sup>J<sub>PtH</sub> = 40 Hz, N=CH), 7.23–7.15 (m, 6H, ArH), 2.33 (s, 6H, CH<sub>3</sub>), 2.30 (s, 6H, CH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -80.08 (t, 3F, <sup>4</sup>J<sub>FF</sub> = 11 Hz, CF<sub>3</sub>), -80.83 (tqd, 2F, <sup>2</sup>J<sub>PtF</sub> = 288 Hz, <sup>4</sup>J<sub>FF</sub> = 11 Hz, <sup>5</sup>J<sub>FH</sub> = 4 Hz, PtCF<sub>2</sub>), -114.69 (t, 2F, <sup>5</sup>J<sub>PtF</sub> = 72 Hz, CF<sub>2</sub>CF<sub>3</sub>). Anal. calcd. for C<sub>21</sub>H<sub>20</sub>F<sub>7</sub>IN<sub>2</sub>Pt (%): C 33.39, H 2.67; found (%): C 32.65, H 2.57.

#### Method 2:

To a solution of **9** (100 mg, 0.16 mmol) in toluene (10 mL) was added hydriodic acid (57% w/w, 20  $\mu$ L, 0.16 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo and the residue recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford the product as an umber microcrystalline powder (83 mg, 78%).

#### [1,2-Bis(2,6-dimethylphenylimino)ethane](1H-tetrafluoroethyl)iodoplatinum(II) (14)

To a solution of **10** (100 mg, 0.19 mmol) in toluene (10 mL) was added HI (57% w/w, 33 µL, 0.29 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo and the residue recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford the product as a black powder (86 mg, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 9.16 (s, 1H, <sup>3</sup>J<sub>PtH</sub> = 100 Hz, N=CH), 8.68 (s, 1H, <sup>3</sup>J<sub>PtH</sub> = 38 Hz, N=CH), 7.25-7.15 (m, 6H, ArH), 6.09 (dq, 1H, <sup>2</sup>J<sub>FH</sub> = 50 Hz, <sup>3</sup>J<sub>FH</sub> = 11 Hz, <sup>2</sup>J<sub>PtH</sub> = 61 Hz, Hz, CFH), 2.39 (s, 3H, ArCH<sub>3</sub>), 2.26 (s, 3H, ArCH<sub>3</sub>), 2.29 (s, 3H, ArCH<sub>3</sub>), 2.25 (s,

3H, ArCH<sub>3</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -68.61 (dd, 3F, <sup>3</sup>J<sub>FH</sub> = 15 Hz, <sup>3</sup>J<sub>FF</sub> = 11 Hz, <sup>2</sup>J<sub>PtF</sub> = 91 Hz, *CF*<sub>3</sub>), -211.67 (dq, 1F, <sup>2</sup>J<sub>FH</sub> = 50 Hz, <sup>3</sup>J<sub>FF</sub> = 11 Hz, <sup>2</sup>J<sub>PtF</sub> = 359 Hz, *CF*H). Anal. calcd. for C<sub>20</sub>H<sub>21</sub>F<sub>4</sub>IN<sub>2</sub>Pt (%): C 34.94, H 3.09; found (%): C 35.32, H 3.36.

#### [1,2-Bis(2,6-dimethylphenylimino)-1,2-dimethylethane](heptafluoropropyl)iodoplatinum(II) (15)

To a solution of **11** (100 mg, 0.15 mmol) in toluene (5 mL) was added HI (57% w/w, 100 µL, excess) and the reaction mixture was stirred at room temperature for 8 h. The solvent was removed in vacuo. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the supernatant solution filtered. The solvent was reduced in vacuo to 5 mL and hexane was added. Filtration afforded the product as a brick-red powder (82 mg, 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.23–7.13 (m, 6H, Ar*H*), 2.26 (s, 6H, ArC*H*<sub>3</sub>), 2.23 (s, 6H, ArC*H*<sub>3</sub>), 2.22 (s, 3H, N=C(C*H*<sub>3</sub>)), 1.84 (s, 3H, N=C(C*H*<sub>3</sub>)). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -79.65 (qt, 3F, <sup>4</sup>J<sub>FF</sub> = 11 Hz, <sup>3</sup>J<sub>FF</sub> = 4 Hz, <sup>2</sup>J<sub>PtF</sub> = 290 Hz, C*F*<sub>3</sub>), -93.46 (t, 2F, <sup>4</sup>J<sub>FF</sub> = 11 Hz, <sup>4</sup>J<sub>PtF</sub> = 38 Hz, PtC*F*<sub>2</sub>), -114.06 (t, 2F, <sup>3</sup>J<sub>FF</sub> = 4 Hz, <sup>3</sup>J<sub>PtF</sub> = 68 Hz, C*F*<sub>2</sub>C*F*<sub>3</sub>). Anal. calcd. for C<sub>23</sub>H<sub>24</sub>F<sub>7</sub>IN<sub>2</sub>Pt (%): C 35.26, H 3.09; found (%): C 35.15, H 3.32.

# [1,2-Bis(2,6-dimethylphenylimino)-1,2-dimethylethane](1H-tetrafluoroethyl)iodoplatinum(II) 16

To a solution of **12** (100 mg, 0.17 mmol) in CHCl<sub>3</sub> (10 mL) was added HI (21  $\mu$ L, 0.17 mmol) and the reaction mixture was stirred at room temperature overnight. The solvent was removed in vacuo. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to afford the product as a deep orange powder (88 mg, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.23–7.08 (m, 6H, Ar*H*), 5.60 (dq, <sup>2</sup>J<sub>FH</sub> = 50 Hz, <sup>3</sup>J<sub>FH</sub> = 11 Hz, <sup>2</sup>J<sub>PtH</sub> = 51 Hz, CF*H*), 2.20 (s, 9H, 3 × *ArCH*<sub>3</sub>), 1.56 (s, 3H, Ar*CH*<sub>3</sub>), 1.26 (s, 3H, C(C*H*<sub>3</sub>)), 1.02 (s, 3H, <sup>4</sup>J<sub>PtH</sub> = 86 Hz, *C*(CH<sub>3</sub>)). <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): -70.74 (dd, 3F, <sup>3</sup>J<sub>FF</sub> = 11 Hz, <sup>3</sup>J<sub>FH</sub> = 11 Hz, <sup>3</sup>J<sub>PtF</sub> = 136 Hz, *CF*<sub>3</sub>), -211.69 (dq, 1F, <sup>2</sup>J<sub>PH</sub> = 50 Hz, <sup>3</sup>J<sub>FF</sub> = 15 Hz, <sup>2</sup>J<sub>PtF</sub> = 388 Hz, *CF*H). Anal. calcd. for C<sub>22</sub>H<sub>25</sub>F<sub>4</sub>IN<sub>2</sub>Pt (%): C 36.93, H 3.53; found (%): C 36.71, H 3.40.

# Crystallographic structural determinations

Diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer. Crystal data collection and refinement parameters are provided in Table 1.<sup>4</sup> The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures on reflection intensities ( $F^2$ ). SADABS absorption corrections were applied to all structures (60). All non-hydrogen atoms were refined with anisotropic displacement coefficients except the C and F atoms of disordered groups. The F atoms of CF<sub>3</sub> groups in **3**, **4**, and **5** and -CF<sub>2</sub>-CHF<sub>2</sub>, -CHF-CF<sub>3</sub> ligands in **4** and **5** are disordered. Hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (5.10) program libraries (61).

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<sup>&</sup>lt;sup>4</sup> Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A OS2, Canada. For information on obtaining material electronically go to http://www.ncc.ca/cisti/irm/unpub\_e.shtml. CCDC 204287 (3), 204288 (4), 204289 (5), and 204290 (11) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1233 336033; or deposit@ccdc.cam.ac.uk).

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