# Activation of C−F and C−H Bonds by Platinum in Trifluorinated [C,N,N′] Ligands. Crystal Structures of $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)(2,4\text{-}C_6H_2F_2)\}]$ and $[PtMe\{Me_2NCH_2CH_2N{=}CH(2,3,4\text{-}C_6HF_3)\}]$

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Trifluorinated ligands $Me_2NCH_2CH_2N{=}CHR$ (R = 2,4,6-$C_6H_2F_3$ (**2a**), 2,3,6-$C_6H_2F_3$ (**2b**)) react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) to yield the [C,N,N′] saturated cyclometalated platinum(IV) compounds $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)(C_6H_2F_2)\}]$ (**4**) arising from C−F bond activation followed by acetone addition on the iminic bond of the coordinated ligand. The reactions of the platinum substrate with trifluorinated ligands $Me_2NCH_2CH_2N{=}CHR$ (R = 2,3,4-$C_6H_2F_3$ (**2c**), 2,4,5-$C_6H_2F_3$ (**2d**), 3,4,5-$C_6H_2F_3$ (**2e**)) containing only one or no fluorine atom in the *ortho* positions yield the [C,N,N′] cyclometalated platinum(II) compounds $[PtMe(Me_2NCH_2CH_2N{=}CHC_6HF_3)]$ (**5**) by *ortho* metalation with loss of methane. Compounds **5** react with methyl iodide to yield the [C,N,N′] unsaturated cyclometalated platinum(IV) compounds $[PtIMe_2(Me_2NCH_2CH_2N{=}CHC_6HF_3)]$ (**6**) and with triphenylphosphine to produce the displacement of the $NMe_2$ moiety and the formation of [C,N] cyclometalated compounds $[PtMe(PPh_3)(Me_2NCH_2CH_2N{=}CHC_6HF_3)]$ (**7c**). When there is a fluorine atom adjacent to platinum ($F^5$), the displacement of both nitrogen donor atoms takes place upon reaction with $PPh_3$ to yield the compounds $[PtMe(PPh_3)_2(Me_2NCH_2CH_2N{=}CHC_6HF_3)]$ (**7d**,**e**). All compounds were characterized by elemental analyses and NMR spectroscopy, and $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)(2,4\text{-}C_6H_2F_2)\}]$ (**4a**) and $[PtMe\{Me_2NCH_2CH_2N{=}CH(2,3,4\text{-}C_6HF_3)\}]$ (**5c**) were characterized crystallographically.

## Introduction

In spite of the fact that aryl C−F bonds are among the strongest known, a number of systems capable of activating these bonds have been reported and the subject has recently been reviewed.[1] Interest in this field arises from the fact that carbon−fluorine bond activation is a fundamental step in the development of metal-based catalysts for the functionalization of organofluorine compounds.[2] Moreover, the resulting fluoride complexes might function as metal-based receptors for organic molecules, since it has been shown that tungsten-bound fluoride shows a propensity to engage in hydrogen bonding.[3]

The ability to produce chelated-assisted aryl C−F oxidative-addition processes has been attributed to the basicity, chelating nature, and restricted conformation of the ligand, as well as to the perfluorination of the aryl ring. For instance, successful intramolecular C−F bond activation has been reported for the ligand $Me_2NCH_2CH_2N{=}CHC_6F_5$ at electron-rich metal centers, such as W(0)[4] and Pt(II).[5] While intramolecular activation of C−F bonds at W(0) can be extended to substrates containing only difluoro- or monofluoro-substituted aromatic rings,[6] such processes fail at Pt(II). In the latter case, either no reaction occurs, as for the ligand $Me_2NCH_2CH_2N{=}CH(2,6\text{-}C_6H_3F_2)$, or C−H bond activation takes place, as for the ligand $Me_2NCH_2CH_2N{=}CH(2\text{-}C_6H_4F)$.[5] On the other hand, attempts to achieve intramolecular activation of aryl C−X or aryl C−H bonds in related saturated ligands $Me_2NCH_2CH_2N(Me)CH_2R$ have been unsuccessful both at platinum(II)[7] and at tungsten(0).[8] The greater tendency to form unsaturated metallacycles containing the C=N group (*endo*-cycles) than saturated metallacycles has been attributed to restricted rotation about the C=N bond and to conjugation of the C=N bond with the aryl ring.[9]

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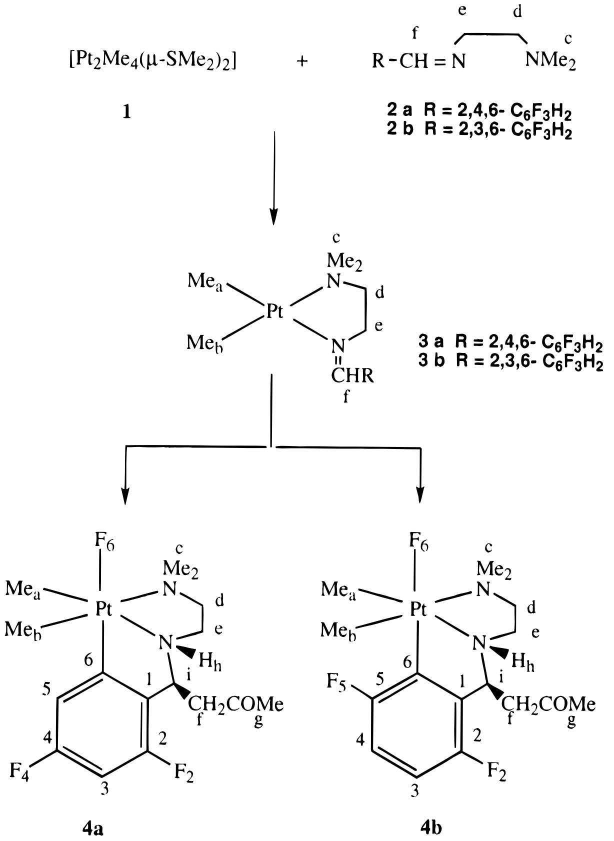
**Scheme 1**



In order to gain further insights into the scope and limitations of the chelate-assisted oxidative addition of C−F bonds and into the competitive C−H bond activation, we decided to extend our studies to several trifluoro derivatives $Me_2NCH_2CH_2N{=}CH(C_6H_2F_3)$. Trifluoroaryl groups containing two, one, or no fluorine atom in the *ortho* positions were selected for this study. Results for related ligands with a single nitrogen donor, $RCH{=}NCH_2Ph$, have been reported elsewhere,[10] and hence a comparison between bidentate [C,N] and terdentate [C,N,N′] systems could be established.

## Results and Discussion

The ligands $Me_2NCH_2CH_2N{=}CHR$ were prepared from reaction of the corresponding aldehyde and dimethylethylenediamine in toluene and were characterized by $^1H$ and $^{19}F$ NMR spectra and MS/CI.

**Reactions of the Ligands $Me_2NCH_2CH_2N{=}CHR$ (R = 2,4,6-$C_6H_2F_3$, 2,3,6-$C_6H_2F_3$).** The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with ligands $Me_2NCH_2CH_2N{=}CHR$ (R = 2,4,6-$C_6H_2F_3$ (**2a**), 2,3,6-$C_6H_2F_3$ (**2b**)) were carried out in acetone solution at room temperature, and the results are summarized in Scheme 1. Compounds $[PtMe_2(Me_2NCH_2CH_2N{=}CHR)]$ (**3**) could be detected in acetone-$d_6$ solution when the reactions were monitored by $^1H$ NMR. As reported for analogous compounds,[5] two methylplatinum resonances were observed with $^2J(PtH)$ values of 84 and 92 Hz. The imine proton also couples with $^{195}Pt$. Resonances for $CH_2$ and aromatic protons are overlapped with those of the unreacted ligand. The reaction proceeds in acetone solution to yield the compounds $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)(2,4\text{-}C_6H_2F_2)\}]$ (**4a**) and $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)(2,5\text{-}C_6H_2F_2)\}]$ (**4b**), respectively, as insoluble white compounds which were characterized by elemental analysis, IR, and FAB-MS and an X-ray determination for **4a**. Compounds **4** were sufficiently soluble in $CDCl_3$ solution so as to be characterized by $^1H$ and $^{19}F$ (**4b**) NMR spectroscopy. The presence of ketone and NH groups is confirmed by IR spectroscopy. Two methyl resonances were observed with $^2J(PtH)$ values in the range 63−70 Hz. These resonances appear as singlets for **4a**, but for **4b**, the axial methyl resonance appears as a doublet and the equatorial methyl resonance appears as a doublet of doublets due to couplings with one ($F^6$) or with two ($F^6$ and $F^5$) fluorine atoms. All protons in both $NMe_2$ and $CH_2CH_2$ groups are diastereotopic, and all resonances could be assigned by $^1H{-}^1H$ COSY experiments. For **4b**, the presence of a Pt−F bond was further proved by the observation of a resonance in the $^{19}F$ NMR spectrum at −235 ppm. Although **4a** was not soluble enough to run a $^{19}F$ NMR spectrum and no couplings with fluorine were observed in the $^1H$ NMR spectrum, the presence of a Pt−F bond was confirmed in the solid state by the crystal structure determination. The lack of hydrogen−fluorine couplings may suggest that the fluorine dissociates from the platinum atom center in solution. In the FAB mass spectra of compounds **4**, the molecular peak was not observed but fragments corresponding to loss of a fluorine atom were present in both cases.

The formation of compounds **4** involves C−F bond activation and subsequent *cis* addition of a C−H bond of acetone across the C=N bond of the coordinated ligand. It has been suggested that for the analogous pentafluorophenyl derivative the latter process is induced by coordination to platinum(IV) and by the strongly electronegative pentafluorophenyl group. Our present result shows that this unusual addition of a C−H bond of acetone to an imine group takes place also for less fluorinated terdentate [C,N,N′] systems. It is worth noting that this process does not take place for the compound $[PtFMe_2(PhCH_2N{=}CHC_6F_4)(SMe_2)]$ containing a bidentate [C,N] metallacycle. The strain of the rigid [C,N,N′] imine ligand coordinated in a *meridional* fashion induces the addition of acetone to the imine so that the more flexible resulting saturated ligand may adopt a *facial* coordination. Both *facial* and *meridional* coordination have been reported for related [C,N,N′] saturated ligands.[11]

In spite of the fact that C−F activation in saturated ligands has been reported to be unsuccessful, the stable saturated cyclometalated compounds **4a** and **4b** can be obtained via formation of an *endo*-cycle followed by addition of acetone. This result indirectly proves that C−F activation reactions are governed by kinetic rather than thermodynamic factors. Mechanistic studies for related systems have recorded greater negative activation entropy values for the formation of saturated metallacycles than for that of unsaturated cycles.[12] Since **4b** consists of a single isomer and the equatorial methyl is coupled to $F^6$ and $F^5$, it may be assumed that of the two non-equivalent *ortho* C-F bonds in **2b**, only

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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 4a**

| | | | |
|---|---|---|---|
| Pt−C(1) | 1.973(3) | N(1)−C(8) | 1.495(5) |
| Pt−C(15) | 2.031(5) | N(2)−C(9) | 1.509(5) |
| Pt−C(16) | 2.046(4) | C(6)−C(7) | 1.519(4) |
| Pt−F(3) | 2.079(2) | C(7)−C(12) | 1.538(4) |
| Pt−N(1) | 2.160(3) | C(8)−C(9) | 1.501(5) |
| Pt−N(2) | 2.256(3) | C(12)−C(13) | 1.484(5) |
| O−C(13) | 1.205(5) | C(13)−C(14) | 1.478(6) |
| F(1)−C(3) | 1.378(4) | N(1)−H(1) | 0.99(4) |
| F(2)−C(5) | 1.342(5) | N(1)−F(3*) | 2.74(5) |
| N(1)−C(7) | 1.475(4) | H(1)−F(3*) | 1.76(4) |
| C(1)−Pt−C(15) | 89.0(2) | C(9)−N(2)−Pt | 103.8(2) |
| C(1)−Pt−C(16) | 97.0(2) | C(6)−C(1)−Pt | 114.1(2) |
| C(15)−Pt−C(16) | 87.4(2) | C(3)−C(2)−C(1) | 120.6(4) |
| C(1)−Pt−F(3) | 174.31(10) | C(4)−C(3)−C(2) | 123.3(4) |
| C(15)−Pt−F(3) | 89.9(2) | C(1)−C(6)−C(7) | 119.9(3) |
| C(16)−Pt−F(3) | 88.6(2) | N(1)−C(7)−C(6) | 110.2(3) |
| C(1)−Pt−N(1) | 83.18(13) | N(1)−C(7)−C(12) | 110.1(3) |
| C(15)−Pt−N(1) | 95.2(2) | C(6)−C(7)−C(12) | 112.7(3) |
| C(16)−Pt−N(1) | 177.5(2) | N(1)−C(8)−C(9) | 110.3(3) |
| F(3)−Pt−N(1) | 91.36(11) | C(8)−C(9)−N(2) | 110.9(3) |
| C(1)−Pt−N(2) | 92.64(14) | C(13)−C(12)−C(7) | 114.2(3) |
| C(15)−Pt−N(2) | 176.78(14) | O−C(13)−C(14) | 121.5(4) |
| C(16)−Pt−N(2) | 95.1(2) | O−C(13)−C(12) | 121.9(3) |
| F(3)−Pt−N(2) | 88.20(11) | C(14)−C(13)−C(12) | 116.6(4) |
| N(1)−Pt−N(2) | 82.31(13) | Pt−N(1)−H(1) | 105.0(2) |
| C(7)−N(1)−Pt | 110.1(2) | N(1)−H(1)−F(3*) | 174(2) |
| C(8)−N(1)−Pt | 107.1(2) | | |

that having a fluorine atom in the adjacent position is selectively activated. This fact shows that the electron-withdrawing effect of the adjacent fluorine atom, inductive in nature, is decisive in enhancing the reactivity of C-F bonds. Moreover, the fluorine atom at position 5, may be crucial in preventing the solvolysis of the Pt-F bond observed for **4a**.

**Crystal Structure of 4a.** Suitable crystals of **4a** were grown in acetone solution. The crystal structure is composed of pairs of molecules forming centrosymmetric dimers. H(1) was located from a difference synthesis and refined isotropically. The value of the angle N(1)−H(1)−F(3*) is 174(2)°, and the short H(1)···F(3*) distance between pairs of molecules (1.76(4) Å) is indicative of intermolecular hydrogen bonding. The basicity of the fluoride in analogous tungsten systems has been attributed to the inability of the 18-electron metal center to accept $\pi$-donation from the fluoride, and thus it is expected to increase if fluorination of the aryl ring decreases.[13] Although the difference is not significant, a shorter N(1)···F(3*) distance between pairs of molecules (2.74(5) Å) is obtained for **4a** as compared to $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4\}]$ [2.805(10) Å].[5] The molecular structure is shown in Figure 1 and confirms the geometry predicted from spectroscopic and analytical data. The platinum atoms are octahedrally coordinated by three carbon atoms in a facial arrangement, two nitrogen atoms, and a fluoride ligand. The saturated tridentate [C,N,N′] ligand adopts a facial coordination.

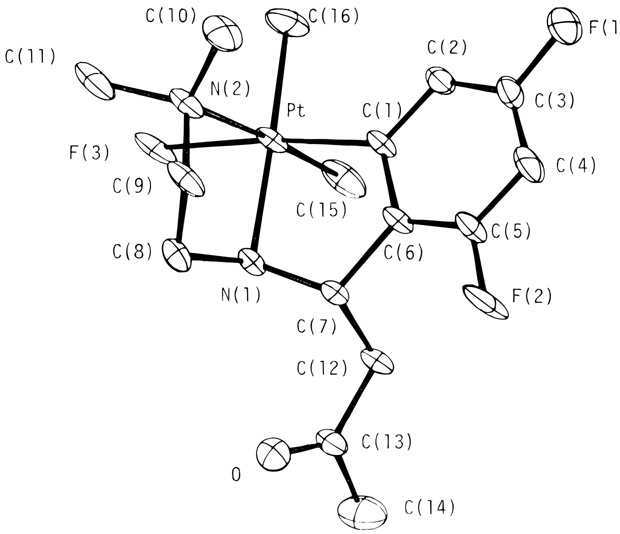


**Figure 1.** View of the molecular structure of compound **4a**.

Molecular dimensions are given in Table 1. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 82.31(13)−97.0(2)°; the smallest angles correspond to the terdentate ligand. The metallacycle has an envelope structure, and displacements from the least-squares plane are as follows: Pt, −0.034; N(1), 0.025; C(1), 0.052; C(6), −0.043; C(7), −0.227 Å. A comparison of structural features for **4a** and related saturated or unsaturated platinum(IV) metallacycles is presented in Table 2. All bond distances and angles in the coordination sphere of platinum are in the expected range for this type of compound. Although differences are not significant, the Pt−F bond distance is slightly longer (2.079(2) Å) than in $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COMe)C_6F_4\}]$ (2.070(5) Å),[5] in agreement with the greater *trans* influence of a less fluorinated group (see Table 2).

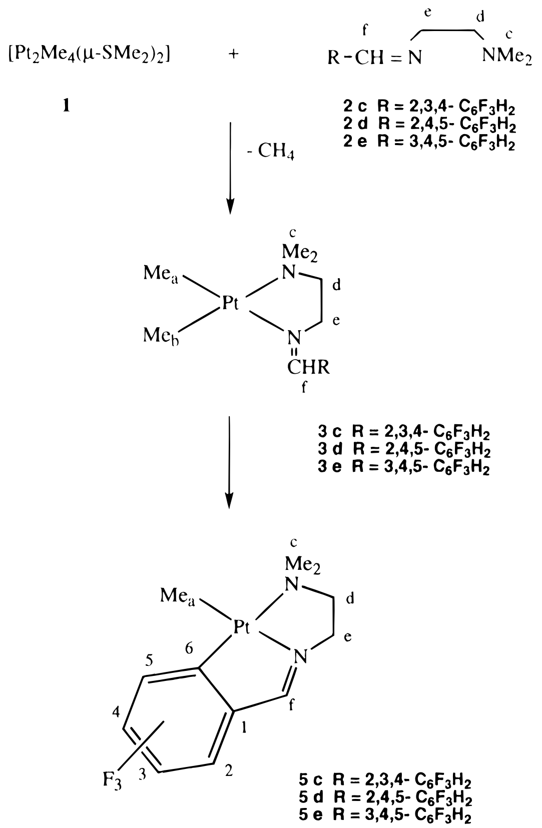
**Reactions of the Ligands $Me_2NCH_2CH_2N{=}CHR$ (R = 2,3,4-$C_6H_2F_3$, 2,4,5-$C_6H_2F_3$, 3,4,5-$C_6H_2F_3$).** The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) with ligands $Me_2NCH_2CH_2N{=}CHR$ (R = 2,3,4-$C_6H_2F_3$ (**2c**), 2,4,5-$C_6H_2F_3$ (**2d**), 3,4,5-$C_6H_2F_3$ (**2e**)) were carried out in acetone or toluene solution at room temperature, and the results are summarized in Scheme 2. In this case, as described for ligands **2a** and **2b**, the compounds $[PtMe_2(Me_2NCH_2CH_2N{=}CHR)]$ (**3**) could also be detected. In all cases, platinum(II) compounds $[PtMe(Me_2NCH_2CH_2N{=}CHR)]$ (**5**) were formed due to C−H bond activation followed

**Table 2. Bond Lengths (Å) and Bond Angles (deg) for Cyclometalated Platinum(IV) and Platinum(II) Compounds**

| | Pt−X | Pt−N | Pt−C(Ar) | Pt−Me | N(1)−Pt−C(Ar) | N(1)−Pt−N(2) |
|---|---|---|---|---|---|---|
| $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COCH_3)R\}]$ (**4a**; R = 2,4-$C_6H_2F_2$) | 2.079(2) | 2.160(3)[a]<br>2.256(3)[c] | 1.973(3) | 2.046(4)[b]<br>2.031(5)[d] | 83.18(13) | 82.31(13) |
| $[PtFMe_2\{Me_2NCH_2CH_2NHCH(CH_2COCH_3)R\}]$[e] (R = $C_6F_4$) | 2.070(5) | 2.173(9)[a]<br>2.242(10)[c] | 1.978(9) | 2.060(14)[b]<br>2.038(14)[d] | 82.7(4) | 81.5(4) |
| $[PtClMe_2\{Me_2NCH_2CH_2N{=}CHR\}]$[f] (R = 2-$C_6H_3Cl$) | 2.456(3) | 2.045(13)[a]<br>2.254(11)[c] | 1.999(12) | 2.068(15)[b]<br>2.036(13)[d] | 81.7(5) | 81.2(4) |
| $[PtMe(Me_2NCH_2CH_2N{=}CHR]$ (**5c**; R = 2,3,4-$C_6HF_3$) | | 2.009(6)[a]<br>2.160(7)[c] | 1.996(8) | 2.040(8)[b] | 80.9(3) | 82.1(3) |
| $[PtMe(PPh_3)(RCH{=}NCH_2Ph)]$[g] (R = 2,3,4-$C_6HF_3$) | | 2.156(8)[a] | 2.026(8) | 2.118(9)[b] | 78.4(4) | |

[a] N(1), NH, or imine. [b] Me *trans* to N(1). [c] N(2), $NMe_2$. [d] Me *trans* to N(2). [e] Reference 5. [f] Reference 14. [g] Reference 10b.

**Scheme 2**



by methane elimination, as already reported for analogous systems.[10,14] Compounds **5** were characterized by elemental analysis, FAB-MS, and $^1$H and $^{19}$F NMR and UV−visible spectra. Compound **5c** was also characterized crystallographically. The single platinum−methyl resonance, coupled with $^{195}$Pt, appears in the $^1$H NMR as a singlet for **5c** and as a doublet (due to coupling with one fluorine atom) for **5d** and **5e**. Three distinct fluorine signals appear in the aromatic region in the $^{19}$F NMR spectra.

Ligands **2c** and **2d** could lead either to C−F or to C−H bond activation. The exclusive formation of the platinum(II) compounds indicate that C−H bond activation is most favored, even when an electron-withdrawing fluorine substituent is present in a position adjacent to the C−F bond (**2c**). These results together with those previously obtained for fluorinated ligands $Me_2NCH_2CH_2N{=}CHR$ ($R = C_6F_5$, 2,6-$C_6H_3F_2$)[5] indicate that C−F bond activation is produced only if the aryl ring contains at least three fluorine atoms, two of them in *ortho* positions. Analogous results have been obtained for related ligands with the single nitrogen donor $RCH{=}NCH_2Ph$.[10]

**Crystal Structure of 5c.** Suitable crystals of **5c** were grown in toluene solution. The crystal structure is composed of discrete molecules separated by van der Waals distances. The structure is shown in Figure 2, and molecular dimensions are listed in Table 3. The coordination sphere of platinum is square-planar. The metallacycle is approximately planar; the largest deviation from the mean plane determined by the five atoms is −0.0095 Å for N(1). The metallacycle is nearly coplanar with the coordination plane, the dihedral angle being 0.28°. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 80.9(3)−98.8(4)°, the smallest angles corresponding to the terdentate ligand. Bond lengths and angles are well within the range of values obtained for analogous cyclometalated platinum(II) compounds.[10b,15] A comparative study of structural features for **5c** and [PtMe(PPh$_3$)(2,3,4-$C_6HF_3CH{=}NCH_2Ph$)] is presented in Table 2. An analysis of these values reveals that Pt−N and Pt−C bond lengths are shorter for the terdentate [C,N,N′] than for the bidentate [C,N] system, and in the former the metallacycle is smaller (perimeter 8.177 Å *versus* 8.305 Å). This fact, as well as the greater distortion of the coordination sphere of the platinum in the PPh$_3$ derivative, is consistent with the steric requirements of the bulky phosphine. On the other hand, differences in the Pt−N and Pt−C bond lengths between related platinum(II) and platinum(IV) compounds are not significant.

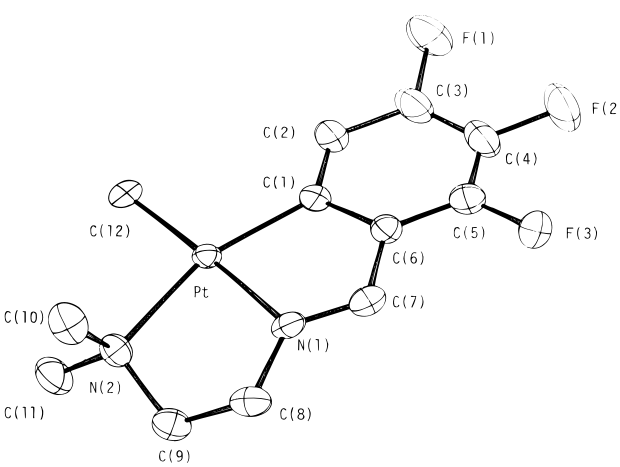


**Figure 2.** View of the molecular structure of compound **5c**.

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 5c**

| | | | |
|---|---|---|---|
| Pt−C(1) | 1.996(8) | F(3)−C(5) | 1.355(10) |
| Pt−N(1) | 2.009(6) | N(2)−C(9) | 1.460(13) |
| Pt−C(12) | 2.040(8) | N(1)−C(7) | 1.285(11) |
| Pt−N(2) | 2.160(7) | N(1)−C(8) | 1.459(11) |
| F(1)−C(3) | 1.357(12) | C(6)−C(7) | 1.471(12) |
| F(2)−C(4) | 1.350(11) | C(8)−C(9) | 1.532(13) |

| | | | |
|---|---|---|---|
| C(1)−Pt−N(1) | 80.9(3) | C(7)−N(1)−Pt | 117.8(6) |
| C(1)−Pt−C(12) | 98.8(4) | C(8)−N(1)−Pt | 115.7(5) |
| N(1)−Pt−C(12) | 178.5(3) | C(6)−C(1)−Pt | 112.0(6) |
| C(1)−Pt−N(2) | 163.0(3) | C(1)−C(6)−C(7) | 115.4(7) |
| N(1)−Pt−N(2) | 82.1(3) | N(1)−C(7)−C(6) | 113.8(7) |
| C(12)−Pt−N(2) | 98.1(3) | N(1)−C(8)−C(9) | 106.6(6) |
| C(9)−N(2)−Pt | 103.1(5) | N(2)−C(9)−C(8) | 112.3(7) |
| C(7)−N(1)−C(8) | 126.5(7) | | |

**Reactivity of the Cyclometalated Compounds 5.** It has been shown that potentially terdentate chelating ligands [N,C,N′][16] and [C,N,N′][17] may adopt different bonding modes and hapticities, which is relevant in

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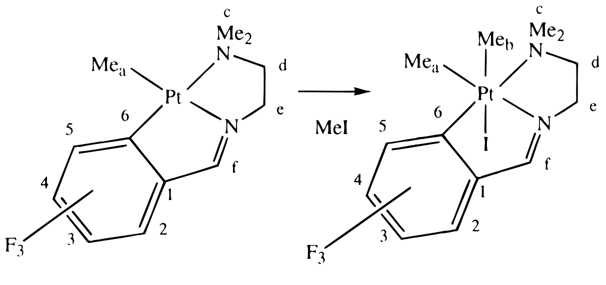
**Scheme 3**



5 c R = 2,3,4- $C_6F_3H_2$
5 d R = 2,4,5- $C_6F_3H_2$
5 e R = 3,4,5- $C_6F_3H_2$

6 c R = 2,3,4- $C_6F_3H_2$
6 d R = 2,4,5- $C_6F_3H_2$
6 e R = 3,4,5- $C_6F_3H_2$

relation to catalytic processes. In order to explore the bonding abilities of the terdentate $Me_2NCH_2CH_2N{=}CHR$ in these systems, we studied the reactivity of the cyclometalated compounds **5**.

The reactions of compounds **5** with methyl iodide were carried out in acetone solution and are summarized in Scheme 3. Oxidative addition of alkyl halides to platinum(II) substrates is well-documented; in particular, studies concerning compounds $[PtMe_2(NN)]$ (where NN is a bidentate nitrogen donor) have been reported, and experimental evidence points to *trans* stereochemistry in the resulting platinum compounds.[7,18] This process is inhibited by steric hindrance or by the presence of highly electron-withdrawing groups, as in $[Pt(4\text{-}CF_3\text{-}C_6H_4)_2(NN)]$.[19] Studies of cyclometalated platinum(II) compounds have also been reported to yield platinum(IV) compounds[20] or, more unexpectedly, either an arenonium platinum(II) compound or zwitterionic dinuclear platinum complexes arising from dissociation of the amine arm of the ligand.[21]

Upon addition of methyl iodide to a solution of compounds **5** in acetone, the color of the solution rapidly changed from red to yellow, and platinum(IV) compounds $[PtIMe_2(Me_2NCH_2CH_2N{=}CHC_6HF_3)]$ (**6**) were isolated. Thus, in these systems, the electron-withdrawing fluorine substituents do not prevent the oxidative addition. Compounds **6** were characterized by elemental analysis and NMR spectroscopy. The methyl−platinum resonances show couplings with ${}^{195}$Pt, and ${}^{2}J$(H−Pt) values are consistent with the oxidation state of platinum. In addition, for **6d** and **6e**, the equatorial methyl is coupled with one fluorine atom ($F^5$). As reported for analogous compounds, the methyl *trans* to iodide appears at higher fields as compared to the methyl groups *trans* to nitrogen atoms. Dissociation and methylation of the amine arm of the terdentate ligand may be disregarded, since diastereotopic methyl groups of the $NMe_2$ unit are coupled with platinum. The resonance due to the imine proton appears at $\delta$ *ca.* 9 ppm with platinum satellites (${}^{3}J$(H−Pt) = *ca.* 50 Hz) and indicates that the addition of acetone to the C=N bond of the ligand, as observed in compounds **4**, does not take place in this system. In the ${}^{19}$F NMR, three distinct resonances appear in the aromatic region, and *J*(F−Pt) values are smaller than for the corresponding platinum(II) compounds.

The reactions of compounds **5** with triphenylphosphine are summarized in Scheme 4. Compound **5c** reacted with $PPh_3$ in a 1:1 molar ratio in acetone solution to yield compound **7c**, which results from a displacement reaction of the $NMe_2$ moiety for $PPh_3$. The lability of the Pt−$NMe_2$ bond has previously been proved for platinum(IV) compounds containing a *meridional* [C,N,N′] tridentate ligand.[14] Compound **7c** is a yellow solid that was characterized by elemental analysis and ${}^{1}$H, ${}^{19}$F, and ${}^{31}$P NMR. Both the methyl and the imine groups are coupled with ${}^{195}$Pt, and the methyl group appears as a doublet due to coupling with the phosphorus atom. No platinum satellites are observed for the dimethylamino group, thus ruling out the possibility of pentacoordination of the platinum. The presence of $PPh_3$ coordinated to platinum is further confirmed by ${}^{31}$P NMR.

Compounds **5d** and **5e**, however, under the same reaction conditions gave compounds **7d** and **7e**, in which both nitrogen atoms were displaced by 2 equiv of $PPh_3$, along with platinum(0) and free ligand. Attempts to obtain compounds containing 1 equiv of $PPh_3$ were unsuccessful. Compounds **7d** and **7e**, best obtained from reaction of the corresponding compound **5** with 2 equiv of $PPh_3$, are white solids which were characterized by elemental analysis and ${}^{1}$H, ${}^{19}$F, and ${}^{31}$P NMR. The methyl group is coupled with two nonequivalent phosphorus atoms and is also coupled with ${}^{195}$Pt. Both dimethylamino and imine groups lack platinum satellites. The ${}^{31}$P NMR spectra show two sets of resonances due to the nonequivalent phosphorus atoms, both coupled with platinum. Spectral evidence points to the fact that the imine is acting as a monodentate ligand through the aryl carbon and the planar coordination of the platinum(II) is completed with one methyl group and two nonequivalent phosphorus atoms. Large *J*($F^5$−Pt) values for compounds **7d** and **7e**, in comparison to the values for cyclometalated compounds **5d** and **5e**, arise from a perpendicular orientation of the aryl group to the coordination plane.

Attempts to obtain an analogous compound for ligand **2c** were unsuccessful, since the reaction of **5c** with an excess of $PPh_3$ yielded **7c**, which does not react further with the phosphine. Thus, for compound **5c**, the metallacycle is not cleaved upon reaction with $PPh_3$. The differences in reactivity toward $PPh_3$ can be attributed to the presence of a fluorine atom in the position adjacent to the Pt−C(aryl) bond ($F^5$). An analogous result has been obtained for the ligands $RCH{=}NCH_2Ph$ and has been explained by the unfavorable steric repulsion between the methyl group and $F^5$ in chelated [C,N] compounds. The cleavage of the metallacycle would relieve the steric crowding in the coordination sphere of platinum.

## Conclusions

Although most examples of C(aryl)−F bond activation have been reported for systems which meet the condi-

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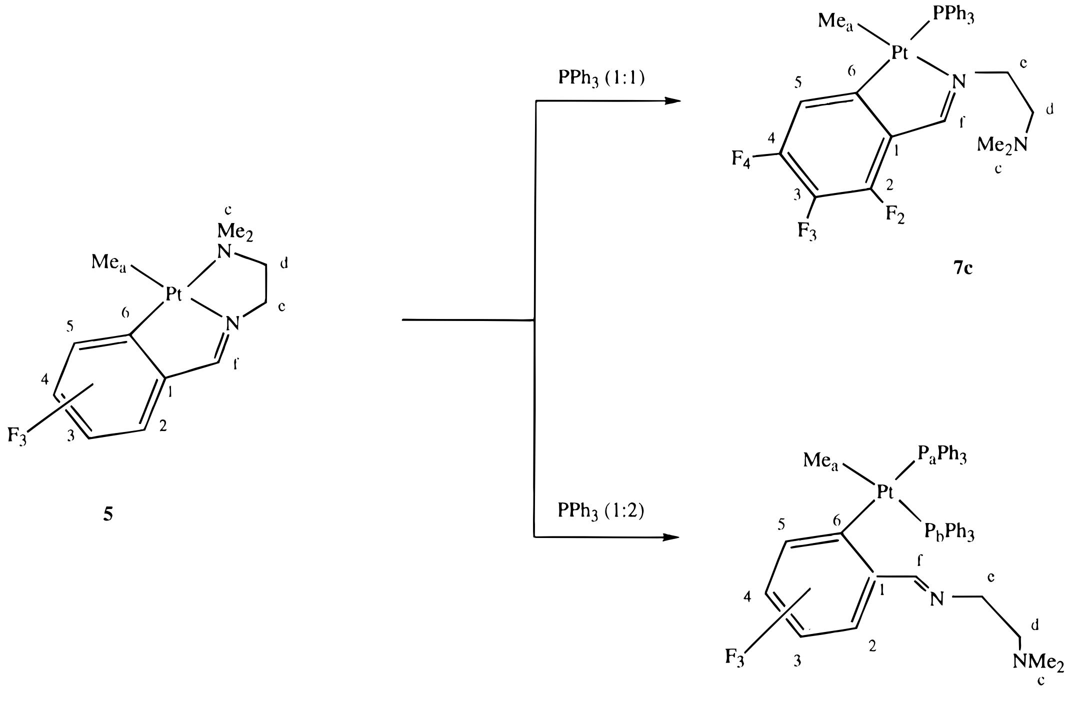
**Scheme 4**



7 d R = 2,4,5- $C_6F_3H_2$
7 e R = 3,4,5- $C_6F_3H_2$

tions of perfluorination of the aryl ring and unsaturation of the formed metallacycle, our results prove that C—F bond activation can be extended to trifluorinated systems such as ligands **2a** and **2b**, leading to the stable saturated platinum(IV) metallacycles **4a** and **4b**. The overall process takes place via C—F bond activation, followed by addition of acetone to the imine bond. On the other hand, trifluorinated ligands **2c**—**e**—containing one or no fluorine atoms in the *ortho* positions—produce exclusively C—H bond activation which, followed by methane elimination, leads to platinum(II) metallacycles **5**. For these compounds, dissociation of the dimethylamino group from platinum takes place readily upon reaction with triphenylphosphine. However, the stronger bond of the iminic nitrogen to platinum is cleaved only if there is a fluorine atom ($F^5$) adjacent to the Pt—C(aryl) bond in a process similar to that reported for analogous bidentate [C,N] systems. These results show that potentially terdentate ligands **2** may adopt either anionic terdentate [C,N,N′], bidentate [C,N], or monodentate [C] coordination modes, in addition to neutral bidentate [N,N′] observed in compounds **3**.

Formation of cyclometalated platinum(IV) compounds **6** by oxidative addition of methyl iodide to compounds **5** in acetone is not followed by addition of acetone to the C=N bond, as observed in compounds **4**. Thus, for this process to take place the presence of both a terdentate [C,N,N′] and a fluorine ligand coordinated to platinum(IV) are required, regardless of the fluorination of the aryl ring. The strain of the rigid [C,N,N′] imine ligand facilitates this process as well as the easy cleavage of the Pt—$NMe_2$ bond in compounds **5**.

## Experimental Details

$^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded by using Varian Gemini 200 ($^1H$, 200 MHz), Varian 500 ($^1H-^1H$ COSY, 500 MHz), Bruker 250 ($^{31}P$, 101.25 MHz), and Varian Unity-300 ($^{19}F$, 282.22 MHz) spectrometers and referenced to $SiMe_4$ ($^1H$), $CFCl_3$ ($^{19}F$), and $H_3PO_4$ ($^{31}P$). $\delta$ values are given in ppm and *J* values in Hz. UV—visible spectra were recorded in a Shimadzu UV-160 A spectrophotometer. IR spectra were recorded as KBr disks on a Nicolet 520 FT-IR spectrometer. Microanalyses and mass spectra (CI and FAB) were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona.

**Preparation of the Compounds.** The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) was prepared by the method reported in the literature.[22]

Compounds **2** were prepared by the reaction of 5 mmol of the corresponding aldehyde with an equimolecular amount of dimethylethylenediamine in toluene. After it was stirred for 30 min, the reaction mixtures were dried over anhydrous $Na_2SO_4$, and the solvent was removed in a rotary evaporator to yield yellow oils (yield 80—85%).

**2,4,6-$C_6H_2F_3CH{=}NCH_2CH_2NMe_2$ (2a).** $^1H$ NMR ($CDCl_3$): $\delta$ 2.31 [s, 6H, Me]; 2.67 [t, 2H, $^3J(H^d-H^e) = 7$, $H^d$]; 3.78 [t, 2H, $^3J(H^d-H^e) = 7$, $H^e$]; 6.70 [t, 2H, $^3J(H-F) = 6$, aromatics]; 8.43 [s, 1H, $H^f$]. $^{19}F$ NMR ($CDCl_3$): $\delta$ −110.68 [dd, 2F, $^3J(F-H) = 6$, $^4J(F-F) = 6$, $F^{2,6}$]; −104.84 [tt, 1F, $^4J(F-F) = 6$, $^3J(F-H) = 6$, $F^4$]. MS/CI-$NH_3$ (*m*/*z*): 231 ($[M + H]^+$).

**2,3,6-$C_6H_2F_3CH{=}NCH_2CH_2NMe_2$ (2b).** $^1H$ NMR ($CDCl_3$): $\delta$ 2.31 [s, 6H, Me]; 2.68 [t, 2H, $^3J(H^d-H^e) = 7$, $H^d$]; 3.81 [t, 2H, $^3J(H^d-H^e) = 7$, $H^e$]; {6.87 [m, 1H, $J(H-F) = 9$, $J(H-F) = 4$, $J(H-H) = 2$], 7.17 [m, 1H, H], aromatics}; 8.49 [s, 1H, $H^f$]. $^{19}F$ NMR ($CDCl_3$): $\delta$ −142.73 [m, 1F, $^3J(F^2-F^3) = 19$, $^5J(F^6-F^3) = 15$, $^3J(H^4-F^3) = 10$, $^4J(H^5-F^3) = 4$, $F^3$]; −137.96 [dd, 1F, $^3J(F^3-F^2) = 19$, $^4J(F^2-F^6) = 9$, $F^2$]; −119.91 [m, 1F, $^5J(F^6-F^3) = 15$, $^4J(F^6-F^2) = 10$, $^3J(F^6-H^5) = 5$, $F^6$]. MS/CI-$NH_3$ (*m*/*z*): 231 ($[M + H]^+$).

**2,3,4-$C_6H_2F_3CH{=}NCH_2CH_2NMe_2$ (2c).** $^1H$ NMR ($CDCl_3$): $\delta$ 2.31 [s, 6H, Me]; 2.65 [t, 2H, $^3J(H^d-H^e) = 7$, $H^d$]; 3.77 [t, 2H, $^3J(H^d-H^e) = 7$, $H^e$]; {7.01 [m, 1H]; 7.74 [m, 1H], aromatics}; 8.51 [s, 1H, $H^f$]. $^{19}F$ NMR ($CDCl_3$): $\delta$ −167.60 [td, 1F, $^3J(F^4-F^3) = {}^3J(F^2-F^3) = 18$, $^4J(F^3-H^5) = 6$, $F^3$]; −149.67 [m, 1F,

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(22) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

$^3J$(F$^3$−F$^4$) = 18, $^4J$(F$^2$−F$^4$) = $^3J$(F$^4$−H$^5$) = 9, F$^4$]; −137.54 [dd, 1F, $^3J$(F$^2$−F$^3$) = 18, $^4J$(F$^2$−F$^4$) = 9, F$^2$]. MS/CI-NH$_3$ (*m*/*z*): 231 ([M + H]$^+$).

**2,4,5-C$_6$H$_2$F$_3$CH=NCH$_2$CH$_2$NMe$_2$ (2d).** $^1$H NMR (CDCl$_3$): *δ* 2.31 [s, 6H, Me]; 2.64 [t, 2H, $^3J$(H$^d$−H$^e$) = 7, H$^d$]; 3.75 [td, 2H, $^3J$(H$^d$−H$^e$) = 7, $^4J$(H$^e$−H$^f$) = 1, H$^e$]; {6.93 [td, 1H, $^3J$(H−F) = 10, $^4J$(H−F) = 4]; 7.81 [m, 1H, $^3J$(H−F) = 10], aromatics}; 8.49 [t, 1H, $^4J$(H$^e$−H$^f$) = 1, H$^f$]. $^{19}$F NMR (CDCl$_3$): *δ* −142.62 [m, 1F, F$^5$]; −130.10 [m, 1F, $^3J$(F$^4$−F$^5$) = 21, $^4J$(F$^2$−F$^4$) = $^3J$(F$^4$−H$^3$) = 10, $^4J$(F$^4$−H$^6$) = 4, F$^4$]; −124.45 [m, 1F, F$^2$]. MS/CI-NH$_3$ (*m*/*z*): 231 ([M + H]$^+$).

**3,4,5-C$_6$H$_2$F$_3$CH=NCH$_2$CH$_2$NMe$_2$ (2e).** $^1$H NMR (CDCl$_3$): *δ* 2.31 [s, 6H, Me]; 2.64 [t, 2H, $^3J$(H$^d$−H$^e$) = 7, H$^d$]; 3.71 [t, 2H, $^3J$(H$^d$−H$^e$) = 7, H$^e$]; 7.38 [dd, 2H, $^3J$(H−F) = 8, $^4J$(H−F) = 6, aromatics]; 8.18 [s, 1H, H$^f$]. $^{19}$F NMR (CDCl$_3$): *δ* −157.62 [tt, 1F, $^3J$(F$^3$−F$^4$) = $^3J$(F$^5$−F$^4$) = 20, $^4J$(F$^4$−H$^2$) = $^4J$(F$^4$−H$^6$) = 6, F$^4$]; −134.41 [dd, 2F, $^3J$(F−F) = 20, $^3J$(F−H) = 8, F$^3$, F$^5$]. MS/CI-NH$_3$ (*m*/*z*): 231 ([M + H]$^+$).

Compounds **3** were characterized by the following procedure: a 20.0 mg (0.035 mmol) amount of complex **1** and 0.07 mmol of the corresponding imine were dissolved in 0.6 mL of acetone-*d*$_6$, and the $^1$H NMR spectrum was recorded.

**[PtMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,4,6-C$_6$H$_2$F$_3$)}] (3a).** $^1$H NMR (acetone-*d*$_6$): *δ* −0.21 [s, 3H, $^2J$(H−Pt) = 92, Me$^b$]; 0.35 [s, 3H, $^2J$(H−Pt) = 85, Me$^a$]; 9.17 [s, 1H, $^3J$(H−Pt) = 52, H$^f$].

**[PtMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,3,6-C$_6$H$_2$F$_3$)}] (3b).** $^1$H NMR (acetone-*d*$_6$): *δ* −0.22 [s, 3H, $^2J$(H−Pt) = 92, Me$^b$]; 0.36 [s, 3H, $^2J$(H−Pt) = 85, Me$^a$]; 9.27 [s, 1H, $^3J$(H−Pt) = 53, H$^f$].

**[PtMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,3,4-C$_6$H$_2$F$_3$)}] (3c).** $^1$H NMR (acetone-*d*$_6$): *δ* −0.04 [s, 3H, $^2J$(H−Pt) = 92, Me$^b$]; 0.43 [s, 3H, $^2J$(H−Pt) = 85, Me$^a$]; 9.34 [s, 1H, $^3J$(H−Pt) = 44, H$^f$].

**[PtMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,4,5-C$_6$H$_2$F$_3$)}] (3d).** $^1$H NMR (acetone-*d*$_6$): *δ* −0.12 [s, 3H, $^2J$(H−Pt) = 92, Me$^b$]; 0.32 [s, 3H, $^2J$(H−Pt) = 85, Me$^a$]; 9.25 [s, 1H, $^3J$(H−Pt) = 42, H$^f$].

**[PtMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(3,4,5-C$_6$H$_2$F$_3$)}] (3e).** $^1$H NMR (acetone-*d*$_6$): *δ* 0.01 [s, 3H, $^2J$(H−Pt) = 92, Me$^b$]; 0.04 [s, 3H, $^2J$(H−Pt) = 85, Me$^a$]; 2.72 [s, 6H, $^3J$(H−Pt) = 22, Me$^c$]; 3.67 [t, 2H, $^3J$(H$^d$−H$^e$) = 6, H$^d$]; 4.06 [t, 2H, $^3J$(H$^d$−H$^e$) = 6, H$^e$]; {7.54 [dd, 1H, $^3J$(H−F) = 7, $^4J$(H−F) = 7]; 8.48 [dd, 1H, $^3J$(H−F) = 9, $^4J$(H−F) = 7], aromatics}; 9.16 [s, 1H, $^3J$(H−Pt) = 44, H$^f$].

Compounds **4** were obtained by adding a solution of 3.4 × 10$^{-4}$ mol of the corresponding imine in acetone (10 mL) to a solution of 100 mg (1.7 × 10$^{-4}$ mol) of compound **1** in acetone. The mixture was stirred for 16 h, and the resulting white crystals were filtered and dried under vacuum.

**[PtFMe$_2${Me$_2$NCH$_2$CH$_2$NHCH(CH$_2$COMe)(2,4-C$_6$H$_2$F$_2$)}] (4a).** Yield: 150 mg (84%). Anal. Calcd for C$_{16}$H$_{25}$F$_3$N$_2$OPt. C, 37.43; H, 4.91; N, 5.45. Found: C, 37.12; H, 4.94; N, 5.26. FAB(+) (NBA, *m*/*z*): 479 ([M − CH$_3$ − F]$^+$). IR: *ν*(N−H) 3086 cm$^{-1}$, *ν*(C=O) 1725 cm$^{-1}$. $^1$H NMR (CDCl$_3$): *δ* 1.03 [s, 3H, $^2J$(H−Pt) = 67, Me$^b$]; 1.05 [s, 3H, $^2J$(H−Pt) = 66, Me$^a$]; {2.13 [s, 3H, $^3J$(H−Pt) = 17]; 2.21 [s, 3H], Me$^c$}; {2.44 [td, 1H, $^2J$(H−H) = 12, $^3J$(H−H) = 2]; 2.49 [td, 1H, $^2J$(H−H) = 12, $^3J$(H−H) = 2], 3.26 [m, 1H]; 3.62 [m, 1H], H$^d$, H$^e$}; 2.55 [d, 3H, *J*(H−H) = 2, Me$^g$]; {2.89 [dd, 1H, $^2J$(H−H) = 19, $^3J$(H−H) = 2]; 2.97 [dd, 1H, $^2J$(H−H) = 19, $^3J$(H−H) = 10], H$^f$}; 4.51 [d, 1H, $^3J$(H−H) = 10, H$^i$]; 5.0 [br, 1H, H$^h$]; {6.47 [ddd, 1H, *J*(H−F) = 11, *J*(H−F) = 9, *J*(H−H) = 2]; 6.66 [dd, 1H, *J*(H−Pt) = 57, *J*(H−F) = 9], aromatics}.

**[PtFMe$_2${Me$_2$NCH$_2$CH$_2$NHCH(CH$_2$COMe)(2,5-C$_6$H$_2$F$_2$)}] (4b).** Yield 140mg (78%). Anal. Calcd for C$_{16}$H$_{25}$F$_3$N$_2$OPt: C, 37.43; H, 4.91; N, 5.45. Found: C, 37.09; H, 5.00; N, 5.31. FAB(+) (NBA, *m*/*z*): 442 ([M − CH$_3$ − CH$_2$COCH$_3$]$^+$), 464 ([M − 2CH$_3$ − F]$^+$), 479 ([M − CH$_3$ − F]$^+$), 483 ([M − 2CH$_3$]$^+$), 494 ([M − F]$^+$). IR: *ν*(N−H) = 3080 cm$^{-1}$, *ν*(C=O) = 1725 cm$^{-1}$. $^1$H NMR (CDCl$_3$): *δ* 1.12 [d, 3H, $^2J$(H−Pt) = 70, *J*(H−F) = 8, Me$^b$]; 1.42 [dd, 3H, $^2J$(H−Pt) = 63, *J*(H−F) = 9, *J*(H−F) = 8, Me$^a$]; {2.22 [s, 3H, $^3J$(H−Pt) = 18]; 2.25 [s, 3H], Me$^c$}; {2.44 [m, 2H]; 3.22 [dd, 1H, $^2J$(H−H) = 13, $^3J$(H−H) = 2]; 3.59 [m, 1H], H$^d$, H$^e$}; 2.54 [d, 3H, *J*(H−H) = 2, Me$^g$]; {2.89 [dd, 1H, $^2J$(H−H) = 19, $^3J$(H−H) = 1]; 3.08 [dd, 1H, $^2J$(H−H) = 19, $^3J$(H−H) = 11], H$^f$}; 4.62 [d, 1H, $^3J$(H−H) = 11, H$^i$]; 5.27 [br, 1H, H$^h$]; {6.57 [m, 1H]; 6.63 [m, 1H], aromatics}. $^{19}$F NMR (CDCl$_3$): *δ* −105.72 [t, 1F, *J* = 8, F$^2$], −122.44 [m, 1F, F$^5$], −235.40 [s, 1F, F$^6$].

Compounds **5** were obtained by adding a solution of 3.4 × 10$^{-4}$ mol of the corresponding imine in acetone (10 mL) to a solution of 100 mg (1.7 × 10$^{-4}$ mol) of compound **1** in acetone. The mixture was stirred for 16 h, and the solvent was removed under vacuum. The residue was washed with hexane to yield red solids, which were filtered, washed with hexane, and dried under vacuum.

**[PtMe{Me$_2$NCH$_2$CH$_2$N=CH(2,3,4-C$_6$HF$_3$)}] (5c).** Yield: 130 mg (85%). Anal. Calcd for C$_{12}$H$_{15}$F$_3$N$_2$Pt: C, 32.81; H, 3.44; N, 6.38. Found: C, 32.12; H, 3.40; N, 6.11. FAB(+) (NBA, *m*/*z*): 423 ([M − CH$_3$]$^+$), 439 ([M]$^+$), 578 ([M − CH$_3$ +NBA$^+$]). UV−vis (acetone): *λ* 415 nm (*ϵ* = 1169 M$^{-1}$ cm$^{-1}$), *λ* 335 nm (*ϵ* = 1693 M$^{-1}$ cm$^{-1}$). $^1$H NMR (acetone-*d*$_6$): *δ* 0.76 [s, 3H, $^2J$(H−Pt) = 79, Me$^a$]; 2.76 [s, 6H, $^3J$(H−Pt) = 23, Me$^c$]; 3.21 [t, 2H, $^3J$(H−Pt) = 15, $^3J$(H$^d$−H$^e$) = 6, H$^d$]; 4.20 [t, 2H, $^3J$(H−H) = 6, H$^e$]; 6.95 [m, 1H, $^3J$(H$^5$−F$^4$) = 11, $^4J$(H$^5$−F$^3$) = 7, $^5J$(H$^5$−F$^2$) = 2, aromatic]; 8.98 [s, 1H, $^3J$(H−Pt) = 62, H$^f$]. $^{19}$F NMR (acetone-*d*$_6$): *δ* −169.81 [td, 1F, $^3J$(F$^3$−F$^4$) = $^3J$(F$^3$−F$^2$) = 20, $^4J$(F$^3$−H$^5$) = 7, F$^3$]; −135.69 [m, 1F, $^4J$(F−Pt) = 76, $^3J$(F$^2$−F$^3$) = 20, $^4J$(F$^2$−F$^4$) = 6, F$^2$]; −128.58 [m, 1F, $^4J$(F−Pt) = 80, $^3J$(F$^4$−F$^3$) = 20, $^3J$(F$^4$−H$^5$) = 11, $^4J$(F$^2$−F$^4$) = 6, F$^4$].

**[PtMe{Me$_2$NCH$_2$CH$_2$N=CH(2,4,5-C$_6$HF$_3$)}] (5d).** Yield 120 mg (78%). Anal. Calcd for C$_{12}$H$_{15}$F$_3$N$_2$Pt: C, 32.81; H, 3.44; N, 6.38. Found: C, 33.24; H, 3.44; N, 6.32. FAB(+) (NBA, *m*/*z*): 420 ([M − F]$^+$), 423 ([M − CH$_3$]$^+$), 439 ([M]$^+$). UV−vis (acetone): *λ* 409 nm (*ϵ* = 2822 M$^{-1}$ cm$^{-1}$), *λ* 335 nm (*ϵ* = 3055 M$^{-1}$ cm$^{-1}$). $^1$H NMR (acetone-*d*$_6$): *δ* 1.07 [d, 3H, $^2J$(H−Pt) = 77, *J*(H−F) = 4, Me$^a$]; 2.78 [s, 6H, $^3J$(H−Pt) = 25, Me$^c$]; 3.24 [t, 2H, $^3J$(H−Pt) = 15, $^3J$(H−H) = 6, H$^d$]; 4.14 [t, 2H, $^3J$(H−H) = 6, H$^e$]; 6.62 [m, 1H, aromatic]; 9.06 [s, 1H, $^3J$(H−Pt) = 62, H$^f$]. $^{19}$F NMR (acetone-*d*$_6$): *δ* −132.3 [td, 1F, $^3J$(F−Pt) = 195, $^3J$(F$^4$−F$^5$) = $^5J$(F$^5$−F$^2$) = 20, $^4J$(F$^5$−H$^3$) = 6, F$^5$]; −130.8 [dt, 1F, $^4J$(F−Pt) = 122, $^3J$(F$^4$−F$^5$) = 20, $^3J$(F$^4$−H$^3$) = $^4J$(F$^4$−F$^2$) = 6, F$^4$]; −120.95 [m, 1F, $^4J$(F−Pt) = 55, F$^2$].

**[PtMe{Me$_2$NCH$_2$CH$_2$N=CH(3,4,5-C$_6$HF$_3$)}] (5e).** Yield: 130 mg (85%). Anal. Calcd for C$_{12}$H$_{15}$F$_3$N$_2$Pt: C, 32.81; H, 3.44; N, 6.38. Found: C, 33.24; H, 3.44; N, 6.32. FAB(+) (NBA, *m*/*z*): 420 ([M − F]$^+$), 423 ([M − CH$_3$]$^+$), 439 ([M]$^+$), 578 ([M − CH$_3$ + NBA$^+$]). UV−vis (acetone): *λ* 410 nm (*ϵ* = 1893 M$^{-1}$ cm$^{-1}$), *λ* 334 nm (*ϵ* = 2184 M$^{-1}$ cm$^{-1}$). $^1$H NMR (acetone-*d*$_6$): *δ* 1.04 [d, 3H, $^2J$(H−Pt) = 77, *J*(H−F) = 4, Me$^a$]; 2.75 [s, 6H, $^3J$(H−Pt) = 25, Me$^c$]; 3.20 [t, 2H, $^3J$(H−H) = 6, H$^d$]; 4.11 [t, 2H, $^3J$(H−H) = 6, H$^e$]; 7.2 [m, 1H, aromatic]; 8.87 [s, 1H, $^3J$(H−Pt) = 61, H$^f$]. $^{19}$F NMR (acetone-*d*$_6$): *δ* −155.0 [m, 1F, $^4J$(F−Pt) = 100, $^3J$(F$^5$−F$^4$) = 24, $^3J$(F$^3$−F$^4$) = 18, $^4J$(F$^4$−H$^2$) = 7, F$^4$]; −143.7 [m, 1F, $^3J$(F$^3$−F$^4$) = 18, $^3J$(F$^3$−H$^2$) = 10, $^4J$(F$^3$−F$^5$) = 4, F$^3$]; −118.5 [d, 1F, $^3J$(F−Pt) = 198, $^3J$(F$^5$−F$^4$) = 24, F$^5$].

Compounds **6** were prepared by adding an excess of methyl iodide (0.1 mL) to a solution of 30 mg (0.068 mmol) of the corresponding compound **5** in acetone. The mixtures were stirred for 15 min, and the solvent was removed under vacuum to yield light yellow solids.

**[PtIMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,3,4-C$_6$HF$_3$)}] (6c).** Yield: 30 mg (76%). Anal. Calcd for C$_{13}$H$_{18}$F$_3$IN$_2$Pt: C, 26.86; H, 3.12; N, 4.82. Found: C, 27.23; H, 3.23; N, 4.80. $^1$H NMR (acetone-*d*$_6$): *δ* 0.80 [s, 3H, $^2J$(H−Pt) = 71, Me$^b$]; 1.13 [s, 3H, $^2J$(H−Pt) = 64, Me$^a$]; {2.68 [s, 3H, $^3J$(H−Pt) = 18], 3.20 [s, 3H, $^3J$(H−Pt) = 13] Me$^c$}; {4.18 [m], 4.30 [m] H$^d$, H$^e$}; 6.84 [m, 1H, H$^5$]; 8.96 [s, 1H, $^3J$(H−Pt) = 50, H$^f$]. $^{19}$F NMR (acetone-*d*$_6$): *δ* −166.49 [td, 1F, $^5J$(F−Pt) = 12, $^3J$(F$^2$−F$^3$) = $^3J$(F$^4$−F$^3$) = 19, $^4J$(F$^3$−H$^5$) = 8, F$^3$]; −133.03 [dd, 1F, $^4J$(F−Pt) = 42, $^3J$(F$^2$−F$^3$) = 19, $^4J$(F$^2$−F$^4$) = 8, F$^2$]; −125.06 [dt, 1F, $^4J$(F−Pt) = 47, $^3J$(F$^4$−F$^3$) = 19, $^3J$(F$^2$−F$^4$) = $^4J$(F$^4$−H$^5$) = 8, F$^4$].

**[PtIMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,4,5-C$_6$HF$_3$)}] (6d).** Yield: 25 mg (63%). Anal. Calcd for C$_{13}$H$_{18}$F$_3$IN$_2$Pt: C, 26.86; H, 3.12; N, 4.82. Found: C, 27.21; H, 3.19; N, 4.84. $^1$H NMR (acetone-$d_6$): $\delta$ 0.90 [s, 3H, $^{2}J$(H−Pt) = 71, Me$^{b}$]; 1.51 [d, 3H, $^{2}J$(H−Pt) = 63, $J$(H−F) = 5, Me$^{a}$]; {2.67 [s, 3H, $^{3}J$(H−Pt) = 20], 3.18 [s, 3H, $^{3}J$(H−Pt) = 15] Me$^{c}$}: {3.3 [m, 1H], 4.2 [m, 1H], 4.28 [m, 2H], H$^{d}$, H$^{e}$}; 6.89 [m, 1H, H$^{3}$]; 9.03 [d, 1H, $^{3}J$(H−Pt) = 47, $J$(H−H) = 1, H$^{f}$]. $^{19}$F NMR (acetone-$d_6$): $\delta$ −129.14 [m, 1F, $^{5}J$(F−Pt) = 84, $^{3}J$(F$^{5}$−F$^{4}$) = 23, $^{5}J$(F$^{2}$−F$^{5}$) = 17, $^{4}J$(F$^{5}$−H$^{3}$) = 5, F$^{5}$]; −122.09 [m, 1F, $^{4}J$(F−Pt) = 73, $^{3}J$(F$^{5}$−F$^{4}$) = 23, $^{4}J$(F$^{2}$−F$^{4}$) = 11, $^{3}J$(F$^{3}$−H$^{3}$) = 5, F$^{4}$]; −112.86 [m, 1F, $^{4}J$(F−Pt) = 32, $^{5}J$(F$^{2}$−F$^{5}$) = 17, $^{4}J$(F$^{2}$−F$^{4}$) = 10, $^{3}J$(F$^{2}$−H$^{3}$) = 5, F$^{2}$].

**[PtIMe$_2${Me$_2$NCH$_2$CH$_2$N=CH(3,4,5-C$_6$HF$_3$)}] (6e).** Yield: 25 mg (63%). Anal. Calcd for $C_{13}H_{18}F_3IN_2Pt$: C, 26.86; H, 3.12; N, 4.82. Found: C, 27.20; H, 3.25; N, 4.92. $^{1}$H NMR (acetone-$d_6$): $\delta$ 0.89 [s, 3H, $^{2}J$(H−Pt) = 70, Me$^{b}$]; 1.49 [d, 3H, $^{2}J$(H−Pt) = 63, $J$(H−F) = 5, Me$^{a}$]; {2.66 [s, 3H, $^{3}J$(H−Pt) = 19], 3.17 [s, 3H, $^{3}J$(H−Pt) = 15] Me$^{c}$}; {3.2 [m, 1H], 4.2 [m, 1H], 4.27 [m, 2H], H$^{d}$, H$^{e}$}; 7.47 [m, 1H, $^{3}J$(F$^{3}$−H$^{2}$) = 10, $^{4}J$(F$^{4}$−H$^{2}$) = 7, H$^{2}$]; 8.86 [d, 1H, $^{3}J$(H−Pt) = 51, $J$(H−H) = 1, H$^{f}$]. $^{19}$F NMR (acetone-$d_6$): $\delta$ −151.51 [m, 1F, $^{5}J$(F−Pt) = 57, $^{3}J$(F$^{5}$−F$^{4}$) = 23, $^{3}J$(F$^{4}$−F$^{3}$) = 19, $^{4}J$(F$^{4}$−H) = 7, F$^{4}$]; −140.42 [m, 1F, $^{3}J$(F$^{3}$−F$^{4}$) = 19, $^{3}J$(F$^{3}$−H$^{2}$) = 10, $^{4}J$(F$^{3}$−F$^{5}$) = 5, F$^{3}$]; −121.25 [m, 1F, $^{4}J$(F−Pt) = 84, $^{3}J$(F$^{4}$−F$^{5}$) = 22, $^{4}J$(F$^{3}$−F$^{5}$) = $^{5}J$(H$^{2}$−F$^{5}$) = 5, $^{5}J$(F$^{5}$−H$^{f}$) = 1, F$^{5}$].

Compounds **7** were obtained by adding 1 equiv (**7c**) or 2 equiv (**7d**, **7e**) of PPh$_3$ to a solution of 50 mg (0.114 mol) of the corresponding compound **5** in acetone. The mixture was stirred for 30 min, and the solvent was removed under vacuum. The residue was washed with hexane to yield orange (**7c**) or white (**7d**, **7e**) solids, which were filtered, washed with hexane, and dried under vacuum.

**[PtMe(PPh$_3$){Me$_2$NCH$_2$CH$_2$N=CH(2,3,4-C$_6$HF$_3$)}] (7c).** Yield: 65 mg (81%). Anal. Calcd for $C_{30}H_{30}F_3N_2PPt$: C, 51.35; H, 4.31; N, 3.99. Found: C, 50.68; H, 4.54; N, 3.63. $^{1}$H NMR (acetone-$d_6$): $\delta$ 0.61 [d, 3H, $^{2}J$(H−Pt) = 81, $^{3}J$(H−P) = 7, Me$^{a}$]; 1.79 [t, 2H, $^{3}J$(H−H) = 6, H$^{d}$]; 1.92 [s, 6H, Me$^{c}$], 3.22 [t, 2H, $^{3}J$(H−H) = 6, H$^{e}$]; 7.30−7.73 [16H, aromatic]; 8.89 [s, 1H, $^{3}J$(H−Pt) = 59, H$^{f}$]. $^{19}$F NMR (acetone-$d_6$): $\delta$ −170.96 [td, 1F, $^{3}J$(F$^{3}$−F$^{2}$) = $^{3}J$(F$^{3}$−F$^{4}$) = 18, $^{4}J$(F$^{3}$−H$^{5}$) = 5, F$^{3}$]; −140.05 [m, 1F, $^{4}J$(F−Pt) = 44, $^{3}J$(F$^{2}$−F$^{3}$) = 18, F$^{2}$]; −132.32 [dd, 1F, $^{4}J$(F−Pt) = 53, $^{3}J$(F$^{4}$−F$^{3}$) = 18, $^{3}J$(F$^{4}$−H$^{5}$) = 10, F$^{4}$]. $^{31}$P NMR (acetone-$d_6$): $\delta$ 30.87 [s, $J$(P−Pt) = 2385].

**[PtMe(PPh$_3$)$_2${Me$_2$NCH$_2$CH$_2$N=CH(2,4,5-C$_6$HF$_3$)}] (7d).** Yield: 80 mg (73%). Anal. Calcd for $C_{48}H_{45}F_3N_2P_2Pt$: C, 59.81; H, 4.70; N, 2.91. Found: C, 59.32; H, 4.70; N, 2.87. $^{1}$H NMR (acetone-$d_6$): $\delta$ 0.19 [dd, 3H, $^{2}J$(H−Pt) = 65, $^{3}J$(H−P$^{b}$) = 8, $^{3}J$(H−P$^{a}$) = 6, Me$^{a}$]; 2.26 [s, 6H, Me$^{c}$]; 2.54 [t, 2H, $^{3}J$(H−H) = 7, H$^{e}$]; 3.83 [t, 2H, $^{3}J$(H−H) = 7, H$^{d}$]; 6.3 [m, H$^{3}$]; 7.00−7.55 [m, 30H, aromatic]; 8.89 [d, 1H, $J$(H−F) = 1, H$^{f}$]. $^{19}$F NMR (acetone-$d_6$): $\delta$ −135.88 [m, 1F, $^{4}J$(F−Pt) = 108, $^{3}J$(F$^{5}$−F$^{4}$) = 33, $^{4}J$(F$^{4}$−F$^{2}$) = $^{3}J$(F$^{4}$−H$^{3}$) = 10, $^{4}J$(F$^{4}$−P$^{a}$) = 4, F$^{4}$]; −120.32 [m, 1F, F$^{2}$]; −117.81 [m, 1F, $^{3}J$(F−Pt) = 470, $^{3}J$(F$^{5}$−F$^{4}$) = 33, $^{5}J$(F$^{5}$−F$^{2}$) = $^{4}J$(F$^{5}$−P$^{a}$) = 15, $^{4}J$(F$^{5}$−H$^{3}$) = 6, F$^{5}$]. $^{31}$P NMR (acetone-$d_6$): $\delta$ 25.49 [d, $^{2}J$(P−P) = 15, $J$(P−Pt) = 1989, P$^{b}$]; 25.83 [m, $J$(Pt−Pt) = 2382, P$^{a}$].

**[PtMe(PPh$_3$)$_2${Me$_2$NCH$_2$CH$_2$N=CH(3,4,5-C$_6$HF$_3$)}] (7e).** Yield: 85 mg (77%). Anal. Calcd for $C_{48}H_{45}F_3N_2P_2Pt$: C, 59.81; H, 4.70; N, 2.91. Found: C, 58.93; H, 4.69; N, 2.84. $^{1}$H NMR (acetone-$d_6$): $\delta$ 0.20 [dd, 3H, $^{2}J$(H−Pt) = 65, $^{3}J$(H−P$^{b}$) = 8, $^{3}J$(H−P$^{a}$) = 7, Me$^{a}$]; 2.18 [s, 6H, Me$^{c}$]; 2.42 [m, 2H, H$^{e}$]; 3.68 [m, 2H, H$^{d}$]; 7.05−7.43 [m, 31H, aromatic]; 9.20 [d, 1H, $J$(H−H) = 3, H$^{f}$]. $^{19}$F NMR (acetone-$d_6$): $\delta$ −163.05 [m, 1F, $^{4}J$(F−Pt) = 88, $^{3}J$(F$^{5}$−F$^{4}$) = 30, $^{3}J$(F$^{3}$−F$^{4}$) = 19, $^{4}J$(F$^{4}$−H$^{2}$) = 7, F$^{4}$]; −147.05 [m, 1F, F$^{3}$]; −112.40 [m, 1F, $^{3}J$(F−Pt) = 415, $^{3}J$(F$^{5}$−F$^{4}$) = 30, $^{4}J$(F$^{5}$−P$^{a}$) = 15, $^{4}J$(F$^{5}$−F$^{3}$) = 4, F$^{5}$]. $^{31}$P NMR (acetone-$d_6$): $\delta$ 25.42 [d, $^{2}J$(P−P) = 15, $J$(P−Pt) = 1907, P$^{b}$]; 26.00 [m, $J$(P−Pt) = 2300, P$^{a}$].

**Table 4. Crystallographic Data and Details of the Refinements for Compounds 4a and 5c**

| formula | **4a** | **5c** |
|---|---|---|
| formula | $C_{16}H_{25}F_3N_2OPt$ | $C_{12}H_{15}F_3N_2Pt$ |
| fw | 513.47 | 439.35 |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/a$ |
| $a$, Å | 8.068(3) | 8.127(4) |
| $b$, Å | 10.2740(8) | 16.4270(12) |
| $c$, Å | 12.0189(12) | 10.2377(9) |
| α, deg | 114.170(8) | 90 |
| $\beta$, deg | 104.22(2) | 101.12 |
| $\gamma$, deg | 90.893(13) | 90 |
| $V$, Å$^3$ | 873.4(3) | 1341.1(7) |
| $D_c$, g cm$^{-3}$ | 1.952 | 2.175 |
| $Z$ | 2 | 4 |
| $F$(000) | 496 | 824 |
| cryst size, mm$^3$ | 0.1 × 0.1 × 0.1 | 0.1 × 0.1 × 0.2 |
| $\lambda$(Mo Kα), Å | 0.710 69 | 0.710 69 |
| $T$, K | 293(2) | 293(2) |
| no. of rflns collected | 5074 | 4202 |
| $R$ | 0.032 | 0.047 |
| $R_w(F^2)$ | 0.0742 | 0.1132 |
| no. of refined params | 217 | 174 |
| max shift/esd | 0.49 | 0.00 |
| max and min diff peaks, e Å$^{-3}$ | +0.984 and −0.935 | +0.631 and −0.612 |

**X-ray Structure Analysis. Data Collection.** Prismatic crystals were selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections (12° < $\theta$ < 21°) and refined by least-squares methods. Intensities were collected with graphite-monochromated Mo Kα radiation, using the $\omega/2\theta$ scan technique. For **4a**, 5074 reflections were measured in the range 1.93° < $\theta$ < 29.96°; 4562 were assumed as observed, applying the condition $I > 2\sigma(I)$. For **5c**, 4202 reflections were measured in the range 2.03° < $\theta$ < 29.97°; 3905 were nonequivalent by symmetry, and 2935 were assumed as observed, applying the condition $I > 2\sigma(I)$. Absorption correction was made from $\psi$ scans;[23] maximum and minimum transmission factors were 0.894 and 0.475 for **4a** and 0.763 and 0.421 for **5c**. Further details are given in Table 4.

**Structure Solution and Refinement.** The structures were solved by Patterson Syntheses, using the SHELXS computer program,[24] and refined by the full-matrix least-squares method, with the SHELX93 computer program.[25] The function minimized as $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1245P)^2]^{-1}$ for **4a**, $w = [\sigma^2(I) + (0.0859P)^2 + 0.8780P]^{-1}$ for **5c**, and $P = (|F_o|^2 + 2|F_c|^2)/3$. $f$, $f'$, and $f''$ were taken from ref 26. For **4a**, 1 hydrogen atom (H(1)) was located from a difference synthesis and refined isotropically and 24 hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. For **5c**, six hydrogen atoms were located from a difference synthesis and nine hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final $R$ factors, the number of refined parameters, and the maximum and minimum peaks in the final difference synthesis are given in Table 4.

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**Supporting Information Available:** Tables giving all bond lengths and angles, refined and calculated atomic coordinates, and anisotropic thermal parameters for **4a** and **5c** (13 pages). Ordering information is given on any current masthead page.

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