Effect of Fluorine Substituents in Intramolecular Activation of C—F and C—H Bonds by Platinum(II)

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The bifunctional iminic ligands $C_6F_5CH{=}NCH_2(2\text{-}C_6H_4X)$ (X = H, Cl, Br) and $ArCH{=}NCH_2\text{-}C_6H_5$ (Ar = 2,3,6-$C_6H_2F_3$, 2,4,6-$C_6H_2F_3$) react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give, *via* oxidative addition of the C–F bonds, platinum(IV) products in which the fluorine ligand and the aryl carbon are mutually *cis*. Further reaction of these compounds with PPh_3 takes place to give a displacement reaction of SMe_2 for PPh_3 which is shown from NMR data to occur with isomerization, resulting in a *trans* arrangement of the fluorine ligand and the aryl carbon. No reaction is observed when the ligand $2,6\text{-}C_6H_3F_2CH{=}NCH_2C_6H_5$ is treated with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, indicating the importance of the increase of fluorination in the ring for C–F bond activation. Ligands $ArCH{=}NCH_2(2\text{-}C_6H_4Cl)$ (Ar = 2-C_6H_4F, 3-C_6H_4F, 4-C_6H_4F, 3,5-$C_6H_3F_2$) also react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give platinum(II) complexes by ortho metalation with loss of methane. Again, the presence of fluorine substituents in the ligands is shown to increase, mainly *via* inductive effects, the reactivity of C–H bonds. The kinetics of formation of both types of compounds has been studied, and a trend in the activation enthalpy values that parallels the electron-withdrawing effects in the iminic ring is obtained.

Introduction

There is an increasing interest in C—F bond activation, but due to their high dissociation energy, carbon—fluorine bonds were considered for many years one of the least reactive of the various chemical bonds capable of undergoing oxidative addition to metal centers. Nevertheless, several examples of activation of C—F have been reported for d- and f-block metals.[1-11] The cleavage of C—F bonds by nucleophiles has also been described in fluoroarenes.[12] The first well-defined systems demonstrating oxidative addition of C—F bonds to tungsten(0)[1] and platinum(II)[2] metal centers occurred in an intramolecular way and involved perfluorinated aromatic rings. Chelate-assisted C—F bond activation in less fluorinated tungsten(0) systems was later reported.[3] On the other hand, hexafluorobenzene reacts with rhodium(I) compounds[4] in a photochemical process to yield a π-C_6F_6 coordination compound followed by a C—F insertion product and with $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ to produce intermolecular C—F and intramolecular C—H activation reactions.[5] The reaction of hexafluorobenzene with a highly reactive platinum(0) fragment has also been reported[6] and yields exclusively the C—F insertion product.

It seems that perfluorination enhances the reactivity of the C—F bond for both inter- and intramolecular systems. This fact is very remarkable, since the reported C—F bond dissociation energy is higher for C_6F_5 (154 kcal/mol) than for C_6H_4F (133 kcal/mol),[1b] and for this reason it is interesting to report any new results in this field. In this paper we deal with intramolecular oxidative addition of C—F bonds to platinum(II) both in C_6F_5 and in the less fluorinated imine ligands $ArCH{=}NCH_2Ar'$. We have already reported for related ligands that the imine functionality appears to be quite important in directing the regiochemistry of C—X bond activation. In this work we study the effect of fluorine substituents in both C—F and C—H bond activation in order to establish the importance of electronic effects, mainly inductive, in the selectivity of the process. A preliminary account of part of this work has already been published.[13]

Results and Discussion

Activation of C–F Bonds. The reactions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1) with imines $C_6F_5CH{=}NCH_2(2\text{-}C_6H_4X)$ (2) (see Chart I) were carried out in acetone solution at room temperature, and the results are summarized in Scheme I. Although platinum(II) compounds arising from coordination of the ligands have been reported for analogous

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(1) (a) Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091. (b) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221. (c) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1988.

(2) (a) Anderson, C. M.; Puddephatt, R. J.; Ferguson, G.; Lough, A. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1297. (b) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 1177.

(3) Lucht, B. L.; Poss, M. J.; King, M. A.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1991**, 400.

(4) (a) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928. (b) Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 264. (c) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429.

(5) Klahn, A. H.; Moore, M. H.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1992**, 1699.

(6) Hofman, P.; Unfried, G. *Chem. Ber.* **1992**, *125*, 659.

(7) (a) Park, S.; Roundhill, D. M. *Inorg. Chem.* **1989**, *28*, 2905. (b) Park, S.; Pontier-Johnson, M.; Roundhill, D. M. *Inorg. Chem.* **1990**, *29*, 2689.

(8) Watson, P. L.; Tulip, Y. H.; Williams, I. *Organometallics* **1990**, *9*, 1999.

(9) Burk, M. J.; Staley, D. L.; Tumas, W. *J. Chem. Soc., Chem. Commun.* **1990**, 809.

(10) Blum, O.; Frolow, F.; Milstein, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 258.

(11) Burns, C. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1989**, 136.

(12) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J.; Fernández-Baeza, A.; Jones, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 794 and references therein.

(13) Crespo, M.; Martinez, M.; Sales, J. *J. Chem. Soc., Chem. Commun.* **1992**, 822.

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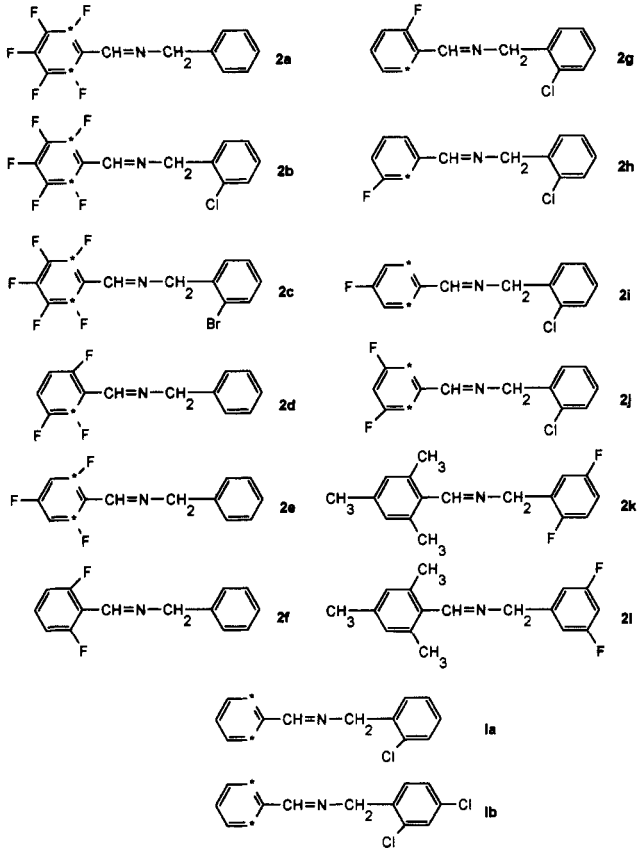
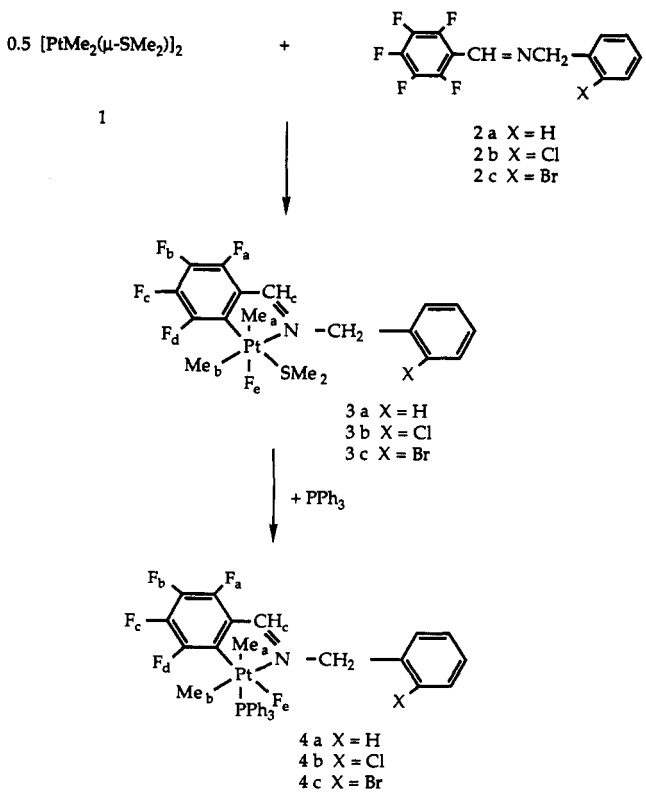
Chart I[a]



[a] The asterisk indicates the activated position.

Scheme I



reactions,[2,14,15] they were not detected for these systems when the reaction was monitored by ^{1}H NMR. In all cases, a single compound was formed, ruling out the activation of the other C—X bond present in the ligand. For these systems, C—F bonds are selectively activated even in the presence of weaker C—H, C—Cl, or C—Br bonds. The resulting compounds **3** are not amenable to recrystallization due to their low stability, and thus, satisfactory analysis could not be obtained. However, they were properly characterized by ^{1}H and ^{19}F NMR spectra; their triphenylphosphine derivatives **4** were fully characterized (see below). Two methyl resonances coupled with ^{195}Pt appear in the ^{1}H NMR spectra, and the coupling constant values are typical for platinum(IV) complexes with a *fac*-PtC_3 stereochemistry. The resonance assigned to the axial methyl group appears as a doublet due to coupling with the fluorine atom F_e, and the downfield methyl resonance shows a pattern consisting of a doublet of doublets due to coupling to the nonequivalent fluorine atoms F_d and F_e. The presence of a Pt—F bond was proved by the observation of a resonance in the ^{19}F NMR spectra at $\delta(^{19}F)$ *ca.* −259 ppm (J(PtF) = 133–151 Hz). The other four fluorine resonances appear in the aromatic region, and their assignment was confirmed by a spectral simulation of these resonances for compound **3b** (see Figure 1) using the parameters listed in the Experimental Section.

These results can be related to the fact that activation of the C—F bond leads to an unsaturated metallacycle containing the C=N group (*endo*-cycle), while activation of the C—X bond would lead to a saturated metallacycle (*exo*-cycle). It has already been reported that the imine functionality is quite important in directing the regiochemistry of C—X bonds; for instance, activation of a C—H bond to give an *endo*-cycle takes place in preference to activation of a weaker C—Cl bond.[15] However, activation of a C—Br bond takes place for the C_6H_5-CH=NCH_2(2-C_6H_4Br) ligand, while for **2c** exclusive activation of the C—F bond occurs. It is clear that the higher reactivity of C—F bonds for the latter ligand may be attributed, at least in part, to the electron-withdrawing effect of the fluorine atoms in the perfluorinated group.

In order to investigate this fact, less fluorinated ligands were tested. For both trifluorinated ligands **2d** and **2e**, activation of C—F bonds was achieved. However, no reaction was observed when difluorinated ligand **2f** was treated with **1** under the same conditions, and unreacted imine together with metallic platinum and SMe_2 were recovered from the reaction mixture. It has been suggested for platinum[6] and ytterbium[11] systems that the C—F bond activation for C_6F_6 can be related in thermodynamic terms to the strength of the M—F and M—C_6F_5 bonds formed. Taking into account that the strength of the Pt—C bond increases with the increasing electronegativity of the aryl group, the different reactivity of **2f** when compared to **2d** and **2e** could be related to the stronger Pt—C bond arising from the last two species. Furthermore, the expected strength of the Pt—F bond in this system is not very large, as attempts to prepare the Pt—F compound *via* halide exchange, as reported for tungsten systems,[1b] have been unsuccessful. For instance, [$PtMe_2Cl(C_6H_3ClCH$=$NCH_2C_6H_5)(SMe_2)$] fails to react with KF under the conditions reported for the tungsten system. For ligand **2f**, the low stability expected for the corresponding compound **3** would also prevent its detection.

^{1}H and ^{19}F NMR point to the formation of compounds

(14) Anderson, C. M.; Crespo, M.; Jennings, M. C.; Lough, A. J.; Ferguson, G.; Puddephatt, R. J. *Organometallics* **1991**, *10*, 2672.

(15) Crespo, M.; Martinez, M.; Sales, J.; Solans, X.; Font-Bardía, M. *Organometallics* **1992**, *11*, 1288.

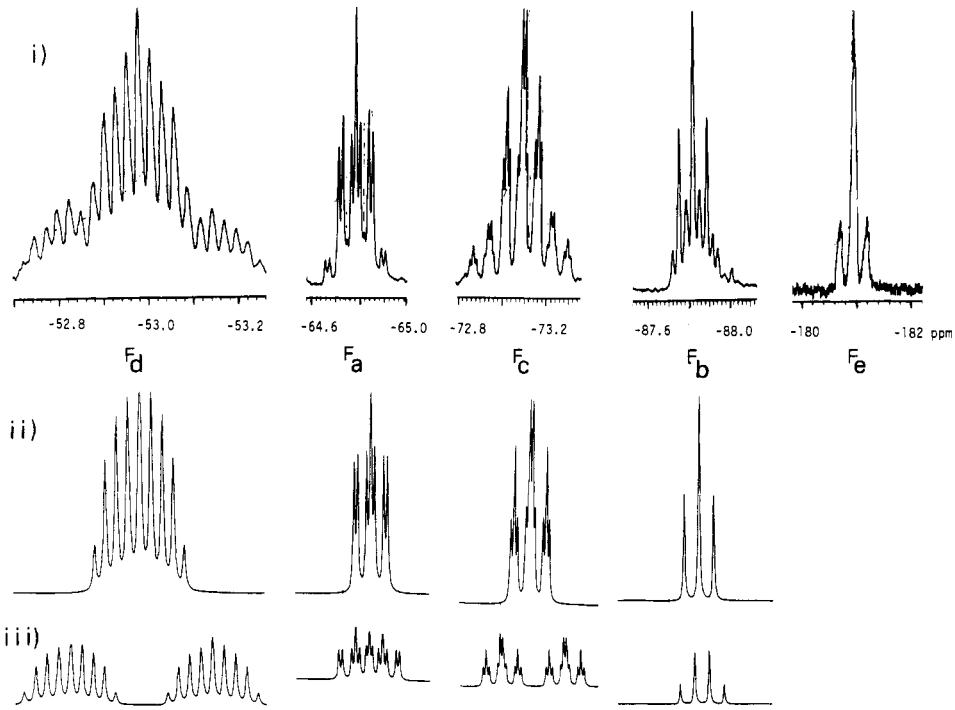
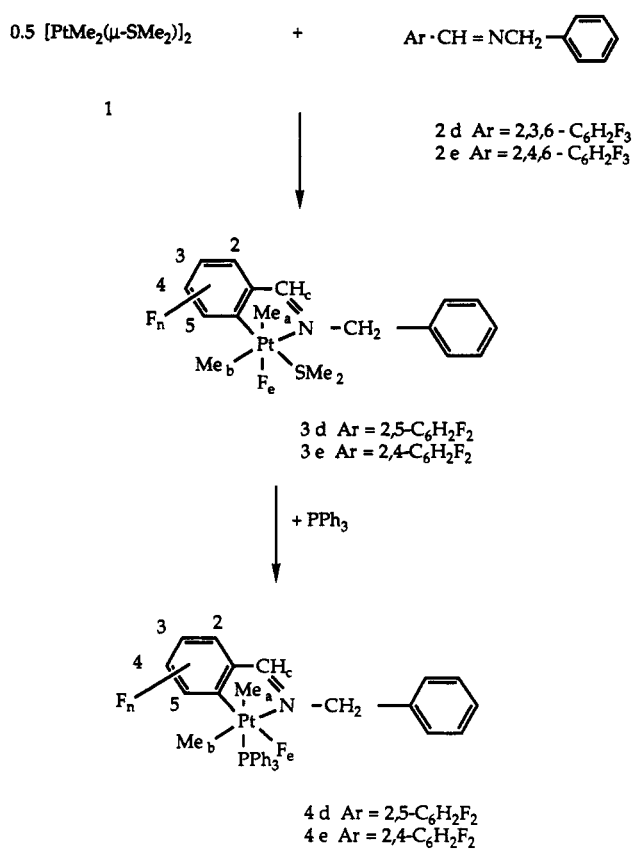


Figure 1. (i) ^{19}F NMR spectrum of compound **3b**. (ii) PANIC simulation of the nonactive Pt isotopomer. (iii) PANIC simulation of the ^{195}Pt isotopomer.

Scheme II



3 as depicted in Scheme II. However, complexes **3d** and **3e** could not be isolated in a pure form from the reaction mixture due to their low stability. As for previously reported ligands, only a single compound is formed in each case. For both platinum(IV) compounds, the axial methyl resonance appears as a doublet due to the coupling with the fluorine bound to platinum, F_e; however, the other methyl resonance appears as a doublet for **3e** and as a doublet of doublets for **3d**. This result shows that, in **3d**, the equatorial methyl group is coupled to F_e and F_5. Thus, of the two nonequivalent C—F bonds in **2d**, only 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, thus explaining the high reactivity of the perfluorinated group.

As shown in Schemes I and II, the reaction of compounds **3** with triphenylphosphine gave compounds **4**. These have been characterized by elemental analysis and ^1H, ^{31}P, and ^{19}F NMR spectra. For compounds **4a–c**, two methylplatinum resonances appear at δ 0.77–0.90 ppm (J(HPt) = 54–56 Hz) and δ 1.70–1.72 ppm (J(HPt) = 63–65 Hz). Both signals are coupled with the phosphorus atom and with F_e, and the signal for the equatorial methyl is also coupled with F_d. The ^{19}F NMR spectra shows five distinct resonances; one of them appears as a doublet at δ ca. −280 ppm (J(FPt) = 226–254 Hz, J(FP) = 28 Hz), confirming the presence of a Pt—F bond. The coupling constant J(FP) was further confirmed by ^{31}P NMR. The increase in the coupling of F_e with platinum and the decrease in the coupling of the axial methyl with platinum, compared with the values for compounds **3**, suggests the stereochemistry shown in Scheme I, that is, structure **4** having the methyl group *trans* to PPh_3 and the F_e *trans* to the electron-withdrawing group, C_6F_4. Assuming that the stereochemistry of compounds **3** is as shown in Scheme I, the substitution reaction of SMe_2 for PPh_3 occurs with isomerization, as previously reported for analogous compounds.[15]

Similar results were obtained for compounds **4d** and **4e**, although for the latter the coupling of the equatorial methyl with F_5 is missing due to the absence of a fluorine substituent in an *ortho* position (see Figure 2). The presence of a Pt—F bond is confirmed by a resonance at high field in the ^{19}F NMR; the smaller values obtained for J(FPt), when compared with those for the pentafluo-

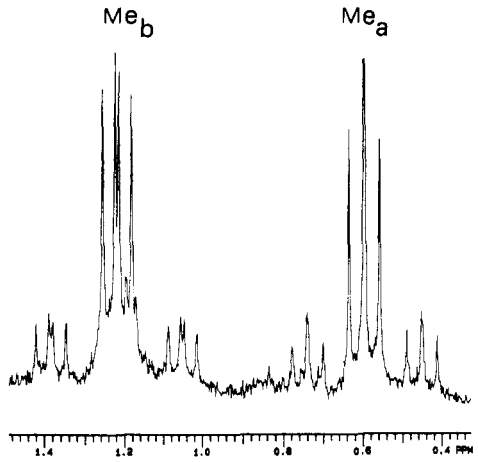
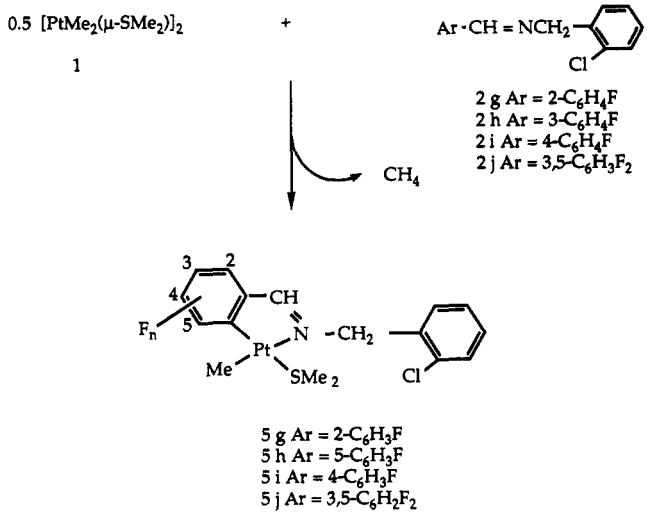


Figure 2. ^{1}H NMR spectrum in the methyl region for compound **4e**.

Scheme III



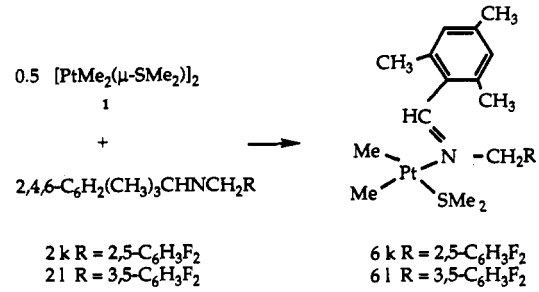
rophenyl derivatives, are consistent with the larger *trans* influence of the less fluorinated groups.

Activation of C–H Bonds in Fluorinated Ligands. The reactions of **1** with **2g–j** (see Chart I) were carried out at room temperature in acetone solution, and the results are shown in Scheme III. In all cases, platinum(II) compounds are formed due to C—H bond activation followed by methane elimination, as already described for analogous systems.[14,15] Compounds **5** were characterized by elemental analyses and ^{1}H and ^{19}F NMR spectra. The single platinum—methyl resonance, coupled with ^{195}Pt, appears in the ^{1}H NMR as a singlet for **5g** and **5i** but as a doublet (due to coupling with one fluorine atom) for **5h** and **5j**. The ^{19}F NMR spectra consist of a single resonance coupled with ^{195}Pt for **5g–i** and of two distinct resonances for **5j**, one of them coupled with ^{195}Pt.

Ligand **2g** could react in several ways, both producing a C—F or C—H bond activation to give *endo*-metallacycles and, less likely, giving a C—Cl or C—H bond activation to produce *exo*-metallacycles. The exclusive formation of the platinum(II) compound **5g** indicates that C—H bond activation to give an *endo*-cycle is the most favored of these four processes. For ligands **2h–j** without a fluorine atom in an *ortho* position the *endo* C—H bond activation occurs as expected.[15]

For ligands **2i** and **2j** the aryl group is symmetric and both *ortho* hydrogen atoms are equivalent, while for **2h** they are nonequivalent. The observation that for **5h** the methyl–platinum resonance is coupled with one fluorine atom (J(HF) = 5.5 Hz), and the fluorine atom is coupled with platinum (J(FPt) = 108 Hz), indicates that only the C—H bond having a fluorine atom in an *ortho* position is exclusively activated in **2h**. As already pointed out for ligand **2d**, the presence of the fluorine substituents can be decisive in the selectivity of these processes.

Scheme IV



In order to extend the study of the effect of electron-withdrawing groups, we have tested the reaction of **1** with fluorinated ligands that could activate the formation of an *exo*-cycle *via* a C—H bond activation. The ligand 2,4,6-$C_6H_2(CH_3)_3CH{=}NCH_2(2\text{-}C_6H_4Cl)$ is known to react with **1** to produce a C—Cl bond activation, the mesityl group in this system effectively preventing the formation of *endo*-cycles, while C—H bond activation was not observed for the 2,4,6-$C_6H_2(CH_3)_3CH{=}NCH_2C_6H_5$ ligand.[15] Ligands **2k** and **2l** (see Chart I), having activating fluorine substituents, could, in principle, yield five-membered metallacycles if C—H bond activation took place in the benzylic ring to produce an *exo*-cycle. The results of these reactions are summarized in Scheme IV.

Reaction of **1** with **2k** and **2l** was followed by ^{1}H NMR and produces a mixture of starting materials and the coordination compounds **6** that arise from the coordination of the imine to the platinum(II) through the nitrogen. The coordination of the imine is proved by the observation of platinum satellites for the iminic proton resonance (δ 9.3 ppm; J(HPt) = 50 Hz) and the presence of two nonequivalent methyl–platinum resonances, both coupled with platinum (see Experimental Section). After 24 h, the reacting mixture remains practically unchanged and thereafter a slow decomposition yields uncoordinated iminic ligand, SMe_2, and metallic platinum. Even when a large excess of the imine is used, no cyclometalated platinum(II) compounds were observed. A similar result was obtained when activating substituents such as Cl and CF_3 were present in the benzylic ring.[15] The effect of electron-withdrawing substituents does not seem important enough as to overcome the unfavorable formation of an *exo*-metallacycle through C—H bond activation.

Mechanistic Studies. The reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with several imine ligands was studied kinetically in acetone solution by means of UV–visible spectroscopy. The *in situ* monitoring of these processes *via* ^{1}H NMR and UV–visible spectroscopy proved that the reactions followed were the C—X bond activations observed in the preparative work. Only Pt(II) cyclometalated complexes (**5g–j**) show definite absorption maxima in acetone solution (λ 390 nm (1800–1900 M^{-1} cm^{-1}) and λ 368 nm (2100–2300 M^{-1} cm^{-1})), the rest of the compounds showing only increasing absorbance from 370 to 330 nm, whereafter the acetone background cannot be subtracted. At the working wavelength an increase of the extinction coefficient from

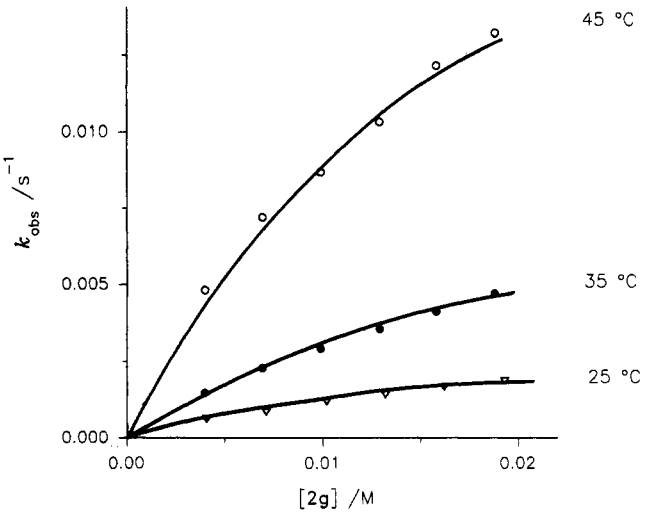


Figure 3. Typical k_{obs} *versus* [imine] plots for the reaction of **1** with imine **2g** at different temperatures.

ca. 50 to *ca.* 2000 M^{-1} cm^{-1} occurs. The observed rate constants were [imine]-dependent, and when pseudo-first-order conditions were used ([imine] ≫ 20[Pt_2]), well-behaved first-order absorbance *versus* time traces were obtained. No dependence on platinum complex concentration was observed in the range of concentrations used ((5–10) × 10^{-4} M). Table i (supplementary material) collects all k_{obs} values obtained as a function of imine concentration and temperature for each ligand used. Figure 3 shows a typical k_{obs} *versus* [imine] plot from which a rate law such as $k_{obs} = k[\text{imine}]/(K + [\text{imine}])$ can be determined.[16]

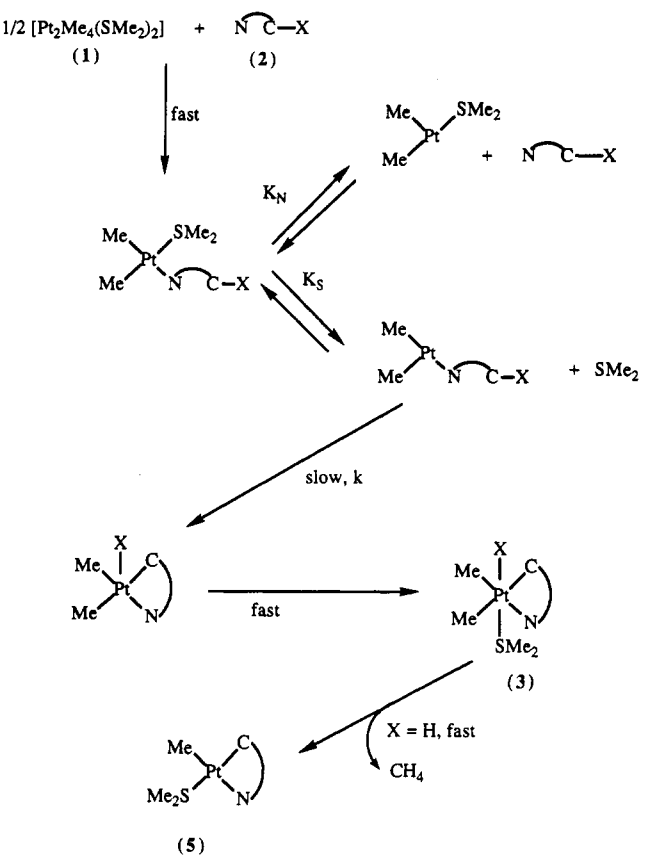
The reaction mechanism shown in Scheme V, proposed for the overall process, is in agreement with the experimental data obtained. Coordination of the iminic nitrogen to platinum in compound **1** to yield a monomeric species is fast;[17] such compounds have been detected by ^{1}H NMR for some of the previously studied reactions.[15] In order to explain the data obtained, this monomeric tetracoordinate complex must be in equilibrium with two tricoordinate species. In one the imine ligand has been lost, and in the other the SMe_2 stabilizing ligand has dissociated. Such equilibria to form [$PtMe_2(SMe_2)$] and [$PtMe_2$(imine)] account for both the [imine] dependence and the previously observed [SMe_2]-retardation effect, respectively.[15] On the other hand, these monomeric tricoordinate species have already been postulated in some reaction mechanisms of the Pt(II) dimer **1**,[18a] as well as in substitution reactions on Pt(II) monomers.[18b,c]

According to the reaction mechanism shown in Scheme V, rate law 1 can be obtained

$$k_{obs} = \frac{\dfrac{kK_s}{K_s + [SMe_2]}[\text{imine}]}{\dfrac{K_N[SMe_2]}{K_s + [SMe_2]} + [\text{imine}]} \qquad (1)$$

where

Scheme V



$$K_s = [[PtMe_2(\text{imine})]][SMe_2]/[[PtMe_2SMe_2(\text{imine})]]$$

$$K_N = [[PtMe_2SMe_2]][\text{imine}]/[[PtMe_2SMe_2(\text{imine})]]$$

In the absence of added SMe_2 the [SMe_2] term becomes negligible when compared with K_s and expression 1 becomes $k_{obs} = k[\text{imine}]/((K_N[SMe_2]/K_s) + [\text{imine}])$, where $K_N[SMe_2]/K_s = [[PtMe_2SMe_2]][\text{imine}]/[[PtMe_2(\text{imine})]]$ now represents the relative amount of tricoordinate [$PtMe_2SMe_2$] with respect to [$PtMe_2$(imine)] under the conditions of our study. As already observed,[15] the relative ratio from equilibria N and S favors the dissociation of the imine *versus* that of the SMe_2 for all complexes to the same extent, within the experimental error involved in kinetically determined equilibrium ratios ($K_N[SMe_2]/K_s$ = 0.003–0.03 M), as would be expected from the stronger soft–soft bond of the latter.

Table I collects all k values obtained for the systems studied at different temperatures, as well as the thermal activation parameters derived from Eyring plots. The activation enthalpy and entropy values are in the same range for all the systems studied, indicating a common mechanism for all reactions.[19] All the activation entropy values are clearly negative, in agreement with a concerted mechanism with a highly ordered transition state allowing a tricentered C—Pt—X interaction.[20] An isokinetic plot of the activation parameters obtained, for both these systems and systems studied previously,[15] gives a very

(16) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1961.
(17) Rashidi, M.; Fakhroeian, Z.; Puddephatt, R. J. *J. Organomet. Chem.* **1991**, *406*, 261.
(18) (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (b) Frey, U.; Helm, L.; Merbach, A. E.; Romeo, R. *J. Am. Chem. Soc.* **1989**, *111*, 8161. (c) Romeo, R.; Grassi, A.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4383.
(19) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; VCH: Weinheim, Germany, 1991.
(20) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

Table I. First-Order Rate Constants and Thermal Activation Parameters for the Bond-Activation Reactions Studied in Acetone Solution at Various Temperatures

ligand (act. bond)	T/°C	10^3k/s^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
2a[a] (C—F)	25	3.38 ± 0.43	30 ● 4	−198 ± 15
	35	4.70 ± 0.70		
	45	7.81 ± 0.47		
2b[a] (C—F)	25	1.41 ± 0.22	36 ± 1	−186 ± 3
	35	2.42 ± 0.26		
	45	3.88 ± 0.62		
2c[a] (C—F)	25	1.32 ± 0.11	35 ± 8	−189 ± 25
	35	2.59 ± 0.26		
	45	3.57 ± 0.72		
2d (C—F)	15	0.71 ± 0.08	63 ± 4	−90 ± 11
	25	1.73 ± 0.05		
	35	3.67 ± 0.09		
	45	9.42 ± 0.85		
2e[a] (C—F)	15	0.54 ± 0.09	54 ± 1	−129 ± 4
	25	1.09 ± 0.14		
	35	2.24 ± 0.29		
	45	4.96 ± 0.23		
2g (C—H)	25	4.97 ± 0.57	61 ± 3	−85 ± 9
	35	12.4 ± 1.1		
	45	26.5 ± 2.5		
2h (C—H)	25	2.81 ± 0.11	53 ± 1	−114 ± 3
	35	6.04 ± 0.40		
	45	12.5 ± 0.4		
2i[a] (C—H)	25	3.32 ± 0.10	62 ± 3	−92 ± 9
	35	7.20 ± 0.21		
	45	18.2 ± 1.8		
2j[a] (C—H)	25	3.43 ± 0.32	43 ± 1	−154 ± 3
	35	6.41 ± 0.54		
	45	11.5 ± 2.8		
Ia[a]	15	0.81 ± 0.11	68 ± 5	−75 ± 18
	25	1.6 ± 0.1		
	35	5.4 ± 0.2		
	45	12 ± 2		
Ib[a]	25	2.5 ± 0.3	75 ± 1	−48 ± 16
	35	5.5 ± 0.8		
	45	17 ± 3		

[a] A statistical factor of $^1/_2$ applies to the first-order rate constants, accounting for the two positions available for the reaction on the ligand.

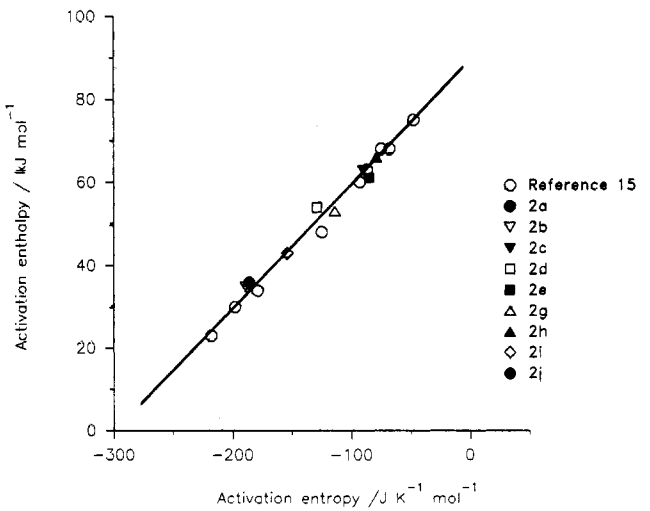


Figure 4. Isokinetic plot for the 1 + imine systems studied (isokinetic temperature 23 °C).

good straight line, as shown in Figure 4. This indicates that, even with so many different iminic ligands and activated bonds, the reactions probably take place *via* a common mechanism involving a tricentered transition state. Consequently, a limiting S_N2 mechanism, or even an electron-transfer process from the metal center to the fluorinated ring, as suggested for an Ir system,[10] seems unlikely for the fluorinated **2a–e** iminic ligands.

From the activation parameters shown in Table I, it is clear that fluorine substituents in positions *ortho* to the activated bond, in ligands **2h** and **2j**, promote a facile enthalpic process for the activation of the C—H bonds when compared with the simpler **Ia** and **Ib** ligands previously studied.[15] Furthermore, this effect seems to be somehow cumulative, as shown by the difference in $\Delta H^{\ddagger}$ values for the **2h** and **2j** C—H activation processes. In this respect, it is important to note that the presence of fluorine substituents in other positions of the iminic ring does not have such a dramatic effect on the activation parameters. The thermal activation parameters obtained for the C—H bond activation process for imines **2g** and **2i** are only slightly different from those of the unsubstituted **Ia** imine ligand. An inductive effect occurring from the adjacent *ortho* fluorine substituent has to be mainly responsible for the differences in the decrease of the enthalpy of activation. As for mesomeric effects, the fluorine substituents in positions *ortho* with respect to the C—H activated bond (imines **2h** and **2j**) would disfavor this bond activation.[21] The large decrease in activation enthalpy as one goes from **Ia** to **2h** and **2j** suggests that the effect due to resonance is negligible in these cases.

Preliminary experiments done with an imine similar to **2j**, but substituted by chlorine, show that even for this sterically hindered system, although an activation enthalpy slightly less favorable is found, activation of the C—H bond takes place. The fine tuning between steric and electronic factors that seems to operate for the bond activation processes in these systems is currently being studied further.

As for the C—F bond activation, the thermal activation parameters obtained indicate that ligands with perfluorinated iminic rings such as **2a–c** show a surprisingly low activation enthalpy; for these systems a value of *ca.* 35 kJ/mol is obtained. Comparison of this value with that obtained for the C—H bond activation in ligands **Ia** and **Ib** indicates that the ease of bond activation does not parallel the difference in strength between C—F and C—H bonds. This fact is not in accordance with the previously found trend in $\Delta H^{\ddagger}$ values for *endo* C—X bond activation reactions, which was parallel to the C—X bond strength. In this respect, for ligands **2d** and **2e** the activation enthalpy obtained is somehow larger than that for the perfluorinated ring. If only inductive effects, similar to those observed for the C—H bond activation for ligands **2g–j**, are responsible for this effect, there should be a clear difference in the activation parameters for ligands **2d** and **2e**. The values obtained for the activation enthalpies for these ligands are very similar; furthermore, if differences are significant, the value obtained for **2d** is even larger, indicating that the inductive effects are not solely responsible for the C—F activation in these systems. Activation of the C—F bonds in ligand **2f** does not take place under the same conditions, although at 15 °C the reaction seems to take place; after less than 1 half-life the absorbance *versus* time traces start showing signs of decomposition, as already observed in the preparative work, thus preventing any evaluation of the thermal activation parameters.

From a qualitative point of view, it is clear that at least three fluorine substituents have to be present in the ring in order to activate a C—F bond. If the possible mesomeric

(21) Sykes, P. *A Guidebook to Mechanisms in Organic Chemistry*; Longman: London, 1981.

effects of the fluorine substituents are looked into, imine **2d** has an *ortho* nucleophilic substitition-deactivating fluorine while ligand **2e** has none. Nevertheless, as already shown for the C—H activation processes, the inductive nucleophilic substitution-activating effect of the *ortho* fluorine in imine **2d** should completely counterbalance this effect.[21] Simple inductive and mesomeric effects do not seem to apply to these C—F bond iminic systems. The overall differences in the symmetry of the iminic ring could be responsible for the differences in reactivity of the **2d–f** iminic ligands. Again, as already pointed out,[1b] the electrophilicity of the carbon in the activated position of the ring is of vital importance in promoting the C—F bond activation; consequently, an increase in the fluorination character of the ring seems to play a major or very important role in this bond activation.

Conclusions. Intramolecular activation of C—F bonds has been achieved at platinum(II) not only for C_6F_5 but also for trifluorinated ligands containing two fluorine substituents in *ortho* positions. The reaction is favored for the more fluorinated systems, and the difluorinated ligand **2f** fails to react. The presence of a fluorine substituent in the position *ortho* to the C—F bond to be activated is decisive in the selectivity of the process, as also observed in C—H bond activation of the **2h** ligand. These effects, though, are not entirely similar for C—H and C—F bond activation. While for C—H bond activation the thermal activation parameters indicate that the inductive effects of neighboring C—F bonds are decisive, for C—F bond activation several effects have to be considered, the electrophilicity of the carbon atom attached to the Pt(IV) center playing a very important role in the oxidative-addition reaction.

As a result of the combined effect of the presence of the imine functionality and fluorine substituents, C—F bonds are activated even in the presence of weaker C—X bonds (X = H, Cl, Br). However, in spite of the increase in reactivity and selectivity for the fluorinated systems the unfavorable formation of an *exo*-metallacycle has not been achieved for these ligands.

Experimental Section

^1H, $^{31}P\{^1H\}$, and ^{19}F NMR spectra were recorded by using Varian Gemini 200 (200 MHz), Bruker WP 80 SY (32.4 MHz), and Varian XL 300 FT (282.2 MHz) spectrometers, respectively, and referenced to $SiMe_4$, H_3PO_4, and CCl_3F, respectively. δ values are given in ppm and J values in Hz. The simulation of the ^{19}F NMR spectrum of **3b** was carried out using the program PANIC provided by Bruker.[22] Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (CSIC).

Kinetics. All spectra were recorded on an HP 8452A instrument equipped with a multicell holder thermostated (±0.2 °C) by an external circulator. All kinetic runs were followed at 340 nm in acetone solutions, where the differences in absorbance between the initial and final species were large enough and, importantly, where there was no interference from the solvent. Pseudo-first-order conditions were used for all runs, and absorbance *versus* time traces were fitted to exponential form by the Marquardt algorithm. All the k_{obs} errors were in the range of 3–5% of the actual value obtained, indicating a very good fit up to 4–5 half-lives. The platinum concentration was within the $(5–10) \times 10^{-4}$ M range and was achieved by the addition of small quantities (0.1–0.2 cm^3) of a concentrated stock solution (kept at −10 °C) to a previously thermostated solution of the ligand.

The k_{obs} *versus* [imine] plots were fitted by unweighted least squares by the standard kinetic software of an HP 8452A instrument. Thermal activation parameters were derived from standard Eyring plots by the same method.

Compounds. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1) was prepared by the literature method.[18a]

Compounds **2** were prepared by reaction of 5 mmol of the corresponding aldehyde with an equimolar amount of the benzylamine in ethanol. The mixture was refluxed for 2 h, and the solvent was removed under vacuum to yield either white solids (**2a–c**, **2g–l**) or yellow oils (**2d–f**) (see Chart I).[23] Table ii (supplementary material) collects spectroscopic data for these compounds.

Compounds **3a–c** (see Scheme I) were prepared by the following procedure: 100.0 mg (0.17 mmol) of **1** and 0.35 mmol of the corresponding imine were dissolved in acetone. The mixture was stirred for 24 h, and the solvent was removed under vacuum. The residue was washed with hexane, and white compounds were obtained.

$[PtMe_2F(SMe_2)(C_6F_4CH{=}NCH_2C_6H_5)]$ (3a). Yield: 129 mg (65%). Mp: 85 °C dec. ^1H NMR (acetone-d_6): δ 0.89 [d, J(PtH) = 67, $J(F_eH)$ = 7.2, Me_a], 1.54 [dd, J(PtH) = 64, $J(F_eH)$ = 9.3, $J(F_dH)$ = 7.2, Me_b], 5.17 [m, CH_2], 9.18 [d, J(PtH) = 47, CHN], 2.02 [s, SMe_2]. ^{19}F NMR (acetone-d_6): δ −258.2 [s, J(PtF) = 151, F_e], −165.5 [m, J(PtF) = 18, $J(F_bF_a)$ = 19, $J(F_bF_c)$ = 19, F_b], −152.0 [m, J(PtF) = 80, $J(F_cF_d)$ = 22, $J(F_cF_b)$ = 19, $J(F_aF_c)$ = 4, $J(F_cH_c)$ = 4, F_c], −143.2 [m, J(PtF) = 29, $J(F_aF_b)$ = 19, $J(F_aF_d)$ = 14, $J(F_aF_c)$ = 4, F_a], −131.5 [m, J(PtF) = 104, $J(F_dF_c)$ = 22, $J(F_dF_a)$ = 14, $J(F_dMe_b)$ = 7, F_d].

$[PtMe_2F(SMe_2)(C_6F_4CH{=}NCH_2C_6H_4Cl)]$ (3b). Yield: 147 mg (70%). Mp: 87 °C dec. ^1H NMR (acetone-d_6): δ 0.95 [d, J(PtH) = 67, $J(F_eH)$ = 7.2, Me_a], 1.56 [dd, J(PtH) = 64, $J(F_eH)$ = 9.6, $J(F_dH)$ = 7.2, Me_b], 5.30 [m, CH_2], 8.95 [s, J(PtH) = 48, CHN], 2.07 [s, SMe_2]. ^{19}F NMR (acetone-d_6): δ −259.4 [s, J(PtF) = 143, F_e], −166.3 [m, J(PtF) = 18, $J(F_bF_a)$ = 19, $J(F_bF_c)$ = 19, F_b], −151.6 [m, J(PtF) = 81, $J(F_cF_d)$ = 22, $J(F_cF_b)$ = 19, $J(F_aF_c)$ = 4, $J(F_cH_c)$ = 4, F_c], −143.3 [m, J(PtF) = 30, $J(F_aF_b)$ = 19, $J(F_aF_d)$ = 14, $J(F_aF_c)$ = 4, F_a], −131.5 [m, J(PtF) = 90, $J(F_dF_c)$ = 22, $J(F_dF_a)$ = 14, $J(F_dMe_b)$ = 7, F_d].

$[PtMe_2F(SMe_2)(C_6F_4CH{=}NCH_2C_6H_4Br)]$ (3c). Yield: 163 mg (72%). Mp: 95 °C dec. ^1H NMR (acetone-d_6): δ 0.98 [d, J(PtH) = 67, $J(F_eH)$ = 7.5, Me_a], 1.58 [dd, J(PtH) = 64, $J(F_eH)$ = 9.6, $J(F_dH)$ = 7.5, Me_b], 5.29 [m, CH_2], 8.87 [s, J(PtH) = 47, CHN], 2.12 [s, J(PtH) = 13, SMe_2]. ^{19}F NMR (acetone-d_6): δ −259.6 [s, J(PtF) = 133, F_e], −166.2 [m, J(PtF) = 18, $J(F_bF_a)$ = 19, $J(F_bF_c)$ = 19, F_b], −151.4 [m, J(PtF) = 81, $J(F_cF_d)$ = 22, $J(F_cF_b)$ = 19, $J(F_aF_c)$ = 4, $J(F_cH_c)$ = 4, F_c], −143.2 [m, J(PtF) = 30, $J(F_aF_b)$ = 19, $J(F_aF_d)$ = 15, $J(F_aF_c)$ = 4, F_a], −131.4 [m, J(PtF) = 90, $J(F_dF_c)$ = 22, $J(F_dF_a)$ = 15, $J(F_dMe_b)$ = 7, F_d].

Compounds **3d** and **3e** (see Scheme II) were characterized in acetone-d_6 solution but could not be isolated in a pure form.

$[PtMe_2F(SMe_2)(2,5\text{-}C_6H_2F_2CH{=}NCH_2C_6H_5)]$ (3d). ^1H NMR (acetone-d_6): δ 0.89 [d, J(PtH) = 67, $J(F_eH)$ = 7.3, Me_a], 1.53 [dd, J(PtH) = 64, $J(F_eH)$ = 9.2, $J(F_5H)$ = 7.2, Me_b], 5.2 [m, CH_2], 9.12 [s, J(PtH) = 47, CHN], 2.34 [s, J(PtH) = 24, SMe_2]. ^{19}F NMR (acetone-d_6): δ −255.4 [s, br, J(PtF) = 90, F_e], −141.1 [m, J(PtF) = 26, F_2], −122.98 (m, F_5).

$[PtMe_2F(SMe_2)(2,4\text{-}C_6H_2F_2CH{=}NCH_2C_6H_5)]$ (3e). ^1H NMR (acetone-d_6): δ 0.79 [d, J(PtH) = 66, $J(F_eH)$ = 7.4, Me_a], 1.16 [d, J(PtH) = 65, $J(F_eH)$ = 7.4, Me_b], 5.2 (m, CH_2), 9.0 [s, J(PtH) = 49, CHN], 2.33 [s, J(PtH) = 25, SMe_2].

Compounds **4a–c** (see Scheme I) were prepared by the following procedure: 50 mg of the corresponding complex **3** was dissolved in acetone, and the equimolar amount of triphenylphosphine was added. The solution was stirred for 48 h, and the solvent was removed under vacuum. The residue was washed with hexane and diethyl ether and recrystallized from acetone–hexane.

$[PtMe_2F(PPh_3)(C_6F_4CH{=}NCH_2C_6H_5)]$ (4a). Yield: 47 mg (70%). Mp: 137 °C dec. Anal. Calcd for $C_{34}H_{29}F_5NPPt$: C,

(22) *PANIC, Parameter Adjustment in NMR by Iteration Calculation*; Bruker Analytische Messtechnik GMBH: Karlsruhe, Germany, 1985.

(23) Bigelow, L. A.; Eatough, H. In *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1944; Vol. 1.

52.85; H, 3.78; N, 1.81. Found: C, 52.46; H, 3.74; N, 1.68. ^{1}H NMR (acetone-d_6): δ 0.77 [t, J(PtH) = 55, $J(F_eH)$ = 7.5, J(PH) = 7.5, Me_a], 1.70 [q, J(PtH) = 63, $J(F_eH)$ = 7.5, $J(F_dH)$ = 7.5, J(PH) = 7.5, Me_b] {4.40 (d), 5.0 (d), J(HH) = 14, CH_2, AB pattern}, 8.70 [s, J(PtH) = 50, CHN]. ^{19}F NMR (acetone-d_6): δ −278.5 [d, J(PtF) = 226, J(PF) = 28, F_e], −167.9 [m, J(PtF) = 18, $J(F_bF_a)$ = 20, $J(F_bF_c)$ = 19, F_b], −152.1 [m, J(PtF) = 77, $J(F_cF_d)$ = 22, $J(F_cF_b)$ = 19, $J(F_aF_c)$ = 4, $J(F_cH_c)$ = 4, F_c], −143.7 [m, J(PtF) = 30, $J(F_aF_b)$ = 20, $J(F_aF_d)$ = 14, $J(F_aF_c)$ = 4, F_a], −129.4 [m, J(PtF) = 79, $J(F_dF_c)$ = 22, $J(F_dF_a)$ = 14, $J(F_dMe_b)$ = 7, F_d]. ^{31}P NMR (acetone): δ −2.64 [d, J(PtP) = 993, J(FP) = 30].

[PtMe$_2$F(PPh$_3$)(C$_6$F$_4$CH=NCH$_2$C$_6$H$_4$Cl)] (4b). Yield: 50 mg (75%). Mp: 145 °C dec. Anal. Calcd for $C_{34}H_{28}ClF_5NPPt$: C, 50.59; H, 3.50; N, 1.73. Found: C, 50.79; H, 3.60; N, 1.59. ^{1}H NMR (acetone-d_6): δ 0.87 [t, J(PtH) = 54, $J(F_eH)$ = 7.5, J(PH) = 7.5, Me_a], 1.72 [q, J(PtH) = 65, $J(F_eH)$ = 7.5, $J(F_dH)$ = 7.5, J(PH) = 7.5, Me_b] {4.70 (d), 5.15 (d), J(HH) = 16, CH_2, AB pattern}, 8.40 [s, J(PtH) = 50, CHN]. ^{19}F NMR (acetone-d_6): δ −280.5 [d, J(PtF) = 254, J(PF) = 28, F_e], −257.3 [m, J(PtF) = 18, $J(F_bF_a)$ = 19, $J(F_bF_c)$ = 19, F_b], −151.8 [m, J(PtF) = 79, $J(F_cF_d)$ = 22, $J(F_cF_b)$ = 19, $J(F_aF_c)$ = 4, $J(F_cH_c)$ = 4, F_c], −143.9 [m, J(PtF) = 30, $J(F_aF_b)$ = 19, $J(F_aF_d)$ = 14, $J(F_aF_c)$ = 4, F_a], −129.4 [m, J(PtF) = 79, $J(F_dF_d)$ = 22, $J(F_dF_a)$ = 14, $J(F_dMe_b)$ = 7, F_d]. ^{31}P NMR (acetone): δ −2.24 [d, J(PtP) = 992, J(FP) = 30].

[PtMe$_2$F(PPh$_3$)(C$_6$F$_4$CH=NCH$_2$C$_6$H$_4$Br)] (4c). Yield: 50 mg (76%). Mp: 153 °C dec. Anal. Calcd for $C_{34}H_{28}BrF_5NPPt$: C, 47.95; H, 3.31; N, 1.65. Found: C, 48.10; H, 3.25; N, 1.43. ^{1}H NMR (acetone-d_6): δ 0.90 [t, J(PtH) = 56, $J(F_eH)$ = 7.5, J(PH) = 7.5, Me_a], 1.72 [q, J(PtH) = 64, $J(F_eH)$ = 7.5, $J(F_dH)$ = 7.5, J(PH) = 7.5, Me_b] {4.70 (d), 5.15 (d), J(HH) = 17, CH_2, AB pattern}, 8.40 [s, J(PtH) = 50, CHN]. ^{19}F NMR (acetone-d_6): δ −280.6 [d, J(PtF) = 254, J(PF) = 28, F_e], −167.9 [m, J(PtF) = 18, $J(F_bF_a)$ = 19, $J(F_bF_c)$ = 19, F_b], −151.7 [m, J(PtF) = 80, $J(F_cF_d)$ = 22, $J(F_cF_b)$ = 19, $J(F_aF_c)$ = 4, $J(F_cH_c)$ = 4, F_c], −144.0 [m, J(PtF) = 30, $J(F_aF_b)$ = 19, $J(F_aF_d)$ = 15, $J(F_aF_c)$ = 4, F_a], −129.4 [m, J(PtF) = 79, $J(F_dF_c)$ = 22, $J(F_dF_a)$ = 15, $J(F_dMe_b)$ = 7, F_d]. ^{31}P NMR (acetone): δ −2.44 [d, J(PtP) = 979, J(FP) = 30].

Compounds **4d** and **4e** (see Scheme II) were prepared by adding the equimolar amount of triphenylphosphine to the reaction mixture obtained from 40 mg (70 mmol) of complex **1** and 32 mg (130 mmol) of the corresponding imines **2d** and **2e**. The mixture was stirred for 24 h, a small amount of [PtMe$_2$(PPh$_3$)$_2$] was filtered off, the solvent was removed in vacuo, and the residue was washed with hexane and ether.

[PtMe$_2$F(PPh$_3$)(2,5-C$_6$H$_2$F$_2$CH=NCH$_2$C$_6$H$_5$)] (4d). Yield: 50 mg (52%). Mp: 118 °C dec. Anal. Calcd for $C_{34}H_{31}F_3NPPt$: C, 55.43; H, 4.24; N, 1.90. Found: C, 55.23; H, 4.18; N, 1.70. ^{1}H NMR (acetone-d_6): δ 0.72 [t, J(PtH) = 58, $J(F_eH)$ = 7.5, J(PH) = 7.5, Me_a], 1.65 [dt, J(PtH) = 64, $J(F_5H)$ = 8.6, $J(F_eH)$ = 6.6, J(PH) = 8.6, Me_b] {4.10 (d), 4.80 (d), J(HH) = 15, CH_2, AB pattern}, 8.60 [s, J(PtH) = 50, CHN]. ^{19}F NMR (acetone-d_6): δ −274.2 [d, J(PtF) = 181, J(PF) = 33, F_e], −107.7 [m, J(FH) = 10, platinum satellites as shoulders], −123.8 [m, J(PtF) = 49]. ^{31}P NMR (acetone): δ −2.14 [d, J(PtP) = 970, J(FP) = 30].

[PtMe$_2$F(PPh$_3$)(2,4-C$_6$H$_2$F$_2$CH=NCH$_2$C$_6$H$_5$)] (4e). Yield: 60 mg (63%). Mp: 143 °C dec. Anal. Calcd for $C_{34}H_{31}F_3NPPt$: C, 55.43; H, 4.24; N, 1.90. Found: C, 55.29; H, 4.32; N, 1.87. ^{1}H NMR (acetone-d_6): δ 0.59 [t, J(PtH) = 58, $J(F_eH)$ = 7.6, J(PH) = 7.6, Me_a], 1.21 [dd, J(PtH) = 66, $J(F_eH)$ = 6.4, J(PH) = 8.2, Me_b] {4.40 (d), 5.00 (d), J(HH) = 15, CH_2, AB pattern}, 8.45 [s, J(PtH) = 49, CHN]. ^{19}F NMR (acetone-d_6): δ −286.3 [d, J(PtF) = 148, J(PF) = 30, F_e], −115.0 [t, J(PtF) = 46, $J(F_2H_3)$ = 9, $J(F_2F_4)$ = 9, F_2], −105.4 [m, J(PtF) = 61, $J(F_4H_3)$ = 9, $J(F_4H_5)$ = 9, $J(F_4F_2)$ = 9, $J(F_4H_c)$ = 3, F_4]. ^{31}P NMR (acetone): δ −1.98 [d, J(PtP) = 966, J(FP) = 31].

Compounds **5** (see Scheme III) were prepared by the following procedure: 100 mg (0.17 mmol) of complex **1** and 0.35 mmol of the corresponding imine were dissolved in acetone. The mixture was stirred for 24 h, and the solvent was removed under vacuum. The residue was washed with hexane, and orange-yellow compounds were obtained and recrystallized from acetone–hexane.

[PtMe(SMe$_2$)(2-C$_6$H$_3$FCH=NCH$_2$C$_6$H$_4$Cl)] (5g). Yield: 130 mg (72%). Mp: 132 °C dec. Anal. Calcd for $C_{17}H_{19}ClFNSPt$: C, 39.35; H, 3.69; N, 2.70. Found: C, 39.28; H, 3.67; N, 2.63. ^{1}H NMR (acetone-d_6): δ 0.95 [s, J(PtH) = 83, Me], 5.32 [s, J(PtH) = 14, CH_2], 9.14 [s, J(PtH) = 55, CHN], 2.05 [s, J(HPt) = 28, SMe_2]. ^{19}F NMR (acetone-d_6): δ −119.6 [dd, J(PtF) = 60, J(HF) = 11, 6].

[PtMe(SMe$_2$)(5-C$_6$H$_3$FCH=NCH$_2$C$_6$H$_4$Cl)] (5h). Yield: 128 mg (71%). Mp: 134 °C dec. Anal. Calcd for $C_{17}H_{19}ClFNSPt$: C, 39.35; H, 3.69; N, 2.70. Found: C, 39.09; H, 3.59; N, 2.62. ^{1}H NMR (acetone-d_6): δ 1.23 [d, J(PtH) = 81, J(HF) = 5.5, Me], 5.23 [s, J(PtH) = 15, CH_2], 9.00 [s, J(PtH) = 53, CHN], 2.03 [s, J(HPt) = 31, SMe_2]. ^{19}F NMR (acetone-d_6): δ −98.2 [m, J(PtF) = 108].

[PtMe(SMe$_2$)(4-C$_6$H$_3$FCH=NCH$_2$C$_6$H$_4$Cl)] (5i). Yield: 152 mg (84%). Mp: 115 °C dec. Anal. Calcd for $C_{17}H_{19}ClFNSPt$: C, 39.35; H, 3.69; N, 2.70. Found: C, 39.10; H, 3.70; N, 2.53. ^{1}H NMR (acetone-d_6): δ 0.88 [s, J(PtH) = 82, Me], 5.23 [s, J(PtH) = 13, CH_2], 8.85 [s, J(PtH) = 58, CHN], 2.05 [s, J(HPt) = 24, SMe_2]. ^{19}F NMR (acetone-d_6): δ −115.1 [m, J(PtF) = 75, J(HF) = 10, 9, 6].

[PtMe(SMe$_2$)(3,5-C$_6$H$_2$F$_2$CH=NCH$_2$C$_6$H$_4$Cl)] (5j). Yield: 159 mg (85%). Mp: 136 °C dec. Anal. Calcd for $C_{17}H_{18}ClF_2NSPt$: C, 38.03; H, 3.38; N, 2.61. Found: C, 37.60; H, 3.39; N, 2.47. ^{1}H NMR (acetone-d_6): δ 1.21 [d, J(PtH) = 81, $J(F_5H)$ = 5.5, Me], 5.25 [s, J(PtH) = 12, CH_2], 9.03 [s, J(PtH) = 53, CHN], 2.03 [s, J(HPt) = 32, SMe_2]. ^{19}F NMR (acetone-d_6): δ −94.8 [m, J(PtF) = 105, F_5], −122.3 [m, J(FF) = 9.6, J(HF) = 7.9, F_3].

Compounds **6** (see Scheme IV) were detected by ^{1}H NMR upon dissolution of 20 mg of compound **1** and the equimolar amount of **2k** or **2l** in acetone-d_6.

[PtMe$_2$(SMe$_2$){2,4,6-C$_6$H$_2$(CH$_3$)$_3$CH=NCH$_2$(2,5-C$_6$H$_3$F$_2$)}] (6k). ^{1}H NMR (acetone-d_6): δ 0.11 [s, J(PtH) = 87, Me], 0.43 [s, J(PtH) = 87, Me], 2.20 [s, CH_3, 3H], 2.24 [s, CH_3, 6H], 1.45 [s, J(PtH) = 28, SMe_2], 5.2 [s, J(PtH) = 22, CH_2], 9.35 [s, J(PtH) = 50, CHN].

[PtMe$_2$(SMe$_2$){2,4,6-C$_6$H$_2$(CH$_3$)$_3$CH=NCH$_2$(3,5-C$_6$H$_3$F$_2$)}] (6l). ^{1}H NMR (acetone-d_6): δ 0.14 [s, J(PtH) = 85, Me], 0.41 [s, J(PtH) = 85, Me], 2.14 [s, CH_3, 3H], 2.22 [s, CH_3, 6H], 1.48 [s, J(PtH) = 31, SMe_2], 5.1 [s, J(PtH) = 23, CH_2], 9.30 [s, J(PtH) = 51, CHN].

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Supplementary Material Available: Tables of observed rate constants for all the reactions studied and of spectroscopic data for ligands **2** (5 pages). Ordering information is given on any current masthead page.

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