Stepwise Degradation of Trifluoromethyl Platinum(II) Compounds

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Dedicated to Professor Pascual Román on the occasion of his 65th birthday

Abstract: The action of moisture on the homoleptic organoplatinum(II) compound $[NBu_4]_2[Pt(CF_3)_4]$ (1) gives rise to the carbonyl derivative [NBu₄]- $[Pt(CF_3)_3(CO)]$ (2), which is itself moisture stable. However, treatment of compound 2 with HCl(aq) results in the formation of [NBu₄][cis-Pt- $(CF_3)_2Cl(CO)$] (3), which undergoes degradation of an additional CF₃ group by further treatment with HCl(aq) in large excess, affording [NBu4][cis-Pt- $(CF_3)Cl_2(CO)$] (4). The carbonyl derivatives 2-4 are fairly stable species, in which the CO ligand, however, can be readily extruded by reaction with trimethylamine N-oxide (ONMe₃). Thus, compound 2 reacts with $ONMe_3$ in the presence of a number of neutral or

Introduction

 σ -Organotransition-metal compounds, [M]–R, typically react with Brønsted acids, HA, by undergoing M–C σ-bond cleavage.^[1] As a result, RH is released and a vacant site at the metal coordination environment is created, which, in the absence of any better ligand, can be occupied by the anion A⁻ (if this is electrophilic enough) or the solvent. This procedure has been extensively used in transition-metal chemistry to create vacant coordination sites at the metal center. The organyl groups R include the simplest alkyl group, methyl (CH₃), that releases methane upon protonation (Scheme 1).^[2-4] Sharply different behavior is observed, however, for the perfluorinated homologue, that is, trifluoro-

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anionic ligands affording a series of
singly or doubly charged derivatives
with the general formulae [NBu₄][Pt-
(CF₃)₃(L)] [L=CNtBu (**5**), PPh₃ (**6**), P-
(*o*-tolyl)₃ (**7**), tht (**8**; tht=tetrahydro-
thiophene)] and [NBu₄]₂[Pt(CF₃)₃X]
[X=Cl (**9**), Br (**10**), I (**11**)], respective-
ly. Compound **2** also reacts with
ONMe₃ and pyridin-2-thiol (C₅H₅NS)
giving rise to the five-membered
metallacyclic derivative [NBu₄][Pt-
(CF₃)₂(CF₂NC₅H₄S-
$$\kappa$$
C, κ S)] (**12**), which
can be viewed as a difluorocarbene
species stabilized by intramolecular

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treatment of compound 3 with ONMe₃ in the presence of C5H5NS yields the four-membered metallacyclic compound $[NBu_4][Pt(CF_3)_2(NC_5H_4S \kappa N, \kappa S$] (13). The geometries of the metallacycles in compounds 12 and 13 are compared. In the absence of any additional ligand, compound 3 undergoes dimerization producing the dinuclear species $[NBu_4]_2[{Pt(CF_3)_2}_2(\mu Cl_{2}$ (14). Halide abstraction in the latter compound with AgClO₄ in THF yields the solvento compound cis-[Pt- $(CF_3)_2(thf)_2$] (15). The highly labile character of the THF ligands in compound 15 makes this species a convenient synthon of the "cis-Pt(CF₃)₂" unit.

base coordination. On the other hand,

methyl (CF₃). In this case, acidic treatment promotes C–F bond activation resulting in fluoride release and formation of a difluorocarbene–metal unit (Scheme 1).^[5] The involvement of the [M]=CF₂ unit has been established in several instances by spectroscopic detection, isolation, and even structural determination of the corresponding species. Most usually, however, the [M]=CF₂ unit is too unstable to be isolated or even detected and reacts readily with nucleophiles, such as OH_2 , evolving further into more stable species such as [M]–CO (hydrolysis).

Lewis acids as, for instance, SbF_5 and even unsaturated centers near the CF_3 group are also able to bring about the same reactivity pattern. Thus, compound $[Ru]-CF_3$, where $[Ru]=RuH(PtBu_2Me)_2(CO)$, has been found to be in rapid



Scheme 1. Reactions usually found in methyl- or trifluoromethyl derivatives of transition metals (M) upon treatment with Brønsted acids.

equilibrium with $F-[Ru]=CF_2$ by spin saturation transfer techniques (¹⁹F NMR spectroscopy), whereby the unsaturated Ru center acts as an intramolecular Lewis acidic center.^[6]

The stability of trifluoromethyl derivatives of main-

group elements other than carbon, [E]-CF₃, may also be diminished by the action of Brønsted or Lewis acids. Thus, although CF₃O⁻ salts of fairly large cations are reasonably stable,^[7] the corresponding protonated species CF₃OH decomposes at -20 °C into F₂CO and HF.^[8] Moreover, the instability of the homoleptic species B(CF₃)₃ has been attributed to the presence of a vacant p orbital on the boron atom that would enable a fluorine 1,2-shift from the carbon atom to the Lewis-acidic boron center.^[9] In keeping with this suggestion is the enhanced stability of the saturated, four-substituted (tetrahedral) species $[B(CF_3)_4]^-$, in which all valence orbitals are involved in chemical bonding. This homoleptic species complying with the octet rule requires treatment with concentrated H₂SO₄ to promote degradation of just one CF₃ group, thereby giving rise to the unusual carbonyl derivative (CF₃)₃B(CO).^[10]

Further to a previous communication,^[11] here we report on the stepwise degradation of trifluoromethyl groups in the homoleptic organoplatinum(II) derivative $[NBu_4]_2[Pt(CF_3)_4]$ (1) promoted by Brønsted acids, H₂O or HCl(aq), affording complete series of mononuclear [NBu₄][Ptthe $(CF_3)_{3-x}Cl_x(CO)$] compounds (x=0-2). Indirect evidence for the intermediacy of highly electrophilic $[Pt]=CF_2$ species has been attained through the isolation and structural characterization of a donor-stabilized species of the type [Pt]= CF_2 ·L (see compound 12). The synthesis of the solvento derivative cis-[Pt(CF₃)₂(thf)₂] is also reported. Due to the high lability of the THF ligand, the latter compound can be considered as a convenient synthon of the "cis-Pt(CF₃)₂" unit.

Results and Discussion

Stepwise degradation of CF₃ groups: The square-planar, homoleptic trifluoromethyl platinum(II) derivative [NBu₄]₂[Pt- $(CF_3)_4$ (1) is a well-behaved species with a fairly high thermal stability: in the solid state, it decomposes at about 255°C (thermogravimetrical analysis). This compound is known to readily undergo oxidative addition of halogens (Cl₂, Br₂, or I₂)^[12] as well as CF₃I.^[13] These reactions take place quantitatively (¹⁹F NMR spectroscopy) and in a stereoselective way, giving rise to the corresponding octahedral organoplatinum(IV) derivatives [NBu₄]₂[trans-Pt(CF₃)₄RX] $(R/X = Cl/Cl, Br/Br, I/I, CF_3/I)$. Compound 1, however, has been found to be water sensitive in solution, as it readily suffers hydrolysis by the simple action of moisture. Thus, compound 1 in moist Me₂CO is quantitatively transformed $(^{19}\text{F NMR spectroscopy})$ into $[\text{NBu}_4][\text{Pt}(\text{CF}_3)_3(\text{CO})]$ (2) in 72 h at room temperature (Scheme 2). From the reaction



Scheme 2. Stepwise degradation of the CF_3 groups in trifluoromethyl platinum(II) compounds starting from the homoleptic derivative 1 ([NBu₄]⁺ is the counterion in all cases).

medium, compound **2** can be isolated as a white, air-stable solid in 82 % yield.

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Compounds **1** and **2** provide a nice example evidencing that transformation of an anionic CF_3 ligand into a neutral CO ligand involves a decrease in the electron charge on the metal center and hence a deactivation of the resulting complex species towards subsequent hydrolytic processes, as it had already been noted by Appleton et al.^[14]

We were not able to obtain single crystals of compound 2 that were suitable for X-ray diffraction purposes. Nevertheless, the structure of the $[Pt(CF_3)_3(CO)]^-$ anion was established by X-ray diffraction methods on single crystals of $[PPh_4][Pt(CF_3)_3(CO)]$ (2'). This salt was readily obtained by following a simple metathetical process (see the Experimental Section). The Pt^{II} center is in a square-planar (SP-4) environment as expected for a four-coordinate d⁸ species (Figure 1). The two mutually trans-standing CF₃ groups are virtually in line with the central atom, C(1)-Pt-C(3): 175.9(1)°, whereas the other two ligands deviate slightly from linearity: C(2)-Pt-C(4): 171.9(1)°. This notwithstanding, the sum of all angles between adjacent ligands amounts to 360.6°. All three Pt-CF₃ bond lengths are indistinguishable within the experimental error (206.8(4) pm average)value) regardless of the different nature of the ligands in the trans position (CF₃ vs. CO). These distances do not significantly depart from those observed in the homoleptic derivative 1 (205.0(5) pm average value).^[12] The Pt-CO bond distance, 191.3(4) pm, is the longest observed for any Q-



Figure 1. Displacement-ellipsoid diagram (50% probability) of [Pt-(CF₃)₃(CO)]⁻ as found in single crystals of compound **2'**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pt-C(1) 207.5(4), Pt-C(2) 206.3(3), Pt-C(3) 206.5(3), Pt-C(4) 191.3(4), C(4)-O 113.4(4), average C-F 136.8(4); C(1)-Pt-C(2) 91.1(1), C(1)-Pt-C(3) 175.9(1), C(1)-Pt-C(4) 89.7(1), C(2)-Pt-C(3) 89.5(1), C(2)-Pt-C(4) 171.9(1), C(3)-Pt-C(4) 90.3(1), Pt-C(4)-O 172.3(3), average Pt-C-F 115.1(2), average F-C-F' 103.3(3).

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[PtX₃(CO)] species (Q⁺ being a cation) for which the molecular structure is known (Table 1).^[15–19] It is still significantly shorter than that found in the octahedral (*OC*-6) Pt^{IV} car-

Table 1. Spectroscopic (IR) and structural data of the monocarbonyl platinum(II) compounds $Q[PtX_3(CO)]$.

	$ ilde{ u}(\mathrm{CO})^{[\mathrm{a}]}$ $[\mathrm{cm}^{-1}]$	Pt-C(CO) [pm]	C–O [pm]	Pt-C-O [°]
$[PPh_4][Pt(CF_3)_3(CO)]$ (2')	2117	191.3(4)	113.4(4)	172.3(3)
$[NBu_4][Pt(C_6F_5)_3(CO)]$	2084 ^[b]	-	-	-
$[NBu_4][Pt(C_6Cl_5)_3(CO)]$	2073 ^[b]	-	_	-
[NBu ₄][PtCl ₃ (CO)]	2098 ^[c]	$182(1)^{[d]}$	$112(2)^{[d]}$	$178(2)^{[d]}$
[NBu ₄][PtBr ₃ (CO)]	2089 ^[c]	$186(1)^{[e]}$	$111(1)^{[e]}$	177(2) ^[e]
$[N(PPh_3)_2][PtI_3(CO)]$	2075 ^[f]	182.2(8) ^[f]	113.5(7) ^[f]	178.6(6) ^[f]

[a] In CH₂Cl₂. [b] Reference [15]. [c] Reference [16]. [d] Reference [17].
 [e] Reference [18]. [f] Reference [19].

bonyl derivative $[PPh_4][Pt(CF_3)_5(CO)]$ (Pt^w-CO: 203.0(3) pm)^[13] in contrast with the expected variation with the oxidation state of the metal. Aside from this remarkable difference, the structural parameters associated with the *trans* CF₃-Pt-CO unit within the (*SP*-4)-[Pt(CF₃)₃(CO)]⁻ and the (*OC*-6)-[Pt(CF₃)₅(CO)]⁻ anions are surprisingly similar.

The ¹⁹F NMR spectrum of compound **2** in CD₂Cl₂ (Figure 2) consists of a quartet at $\delta = -22.1$ ppm and a septet at $\delta = -31.9$ ppm in 2:1 integrated ratio straightforwardly assignable to each kind of chemically inequivalent CF₃ groups mutually coupled with ⁴*J*(¹⁹F,¹⁹F)=3.9 Hz. Both signals are flanked by ¹⁹⁵Pt satellites. The rather different ²*J*(¹⁹⁵Pt,¹⁹F) values observed (518 vs. 769 Hz) evidence the higher *trans* influence of the CF₃ group compared with that of the CO ligand. This difference is not reflected, however, in the structural parameters (see above).

The IR spectrum of compound **2** (or **2'**) in CH₂Cl₂ shows a sharp signal at $\tilde{v} = 2117 \text{ cm}^{-1}$ assignable to the v(CO) mode. This is the highest \tilde{v} (CO) value observed for any known carbonyl derivative with [PtX₃(CO)]⁻ stoichiometry



Figure 2. Room-temperature ${}^{19}\text{F}$ NMR spectrum of compound **2** in CD₂Cl₂ with spectral parameters indicated. Both signals belong to the same spin system, as they are mutually coupled with ${}^{4}\textit{I}({}^{19}\text{F},{}^{19}\text{F})\!=\!3.9$ Hz.

(Table 1), thus denoting the least electron density on the metal center in the case where $R = CF_3$. This fact is in keeping with the high electronegativity assigned to the CF_3 group ($\chi = 3.49$), which is even higher than that of Cl ($\chi = 3.16$).^[20] The CF₃ group also gives rise to the highest $\tilde{\nu}(CO)$ values within both the $[Pt^{\nu}X_5(CO)]^-$ and the [AuX(CO)] monocarbonyl series ($X = CF_3$, Cl, Br).^[13,21] All these observations are incompatible with the recently suggested idea that the CF₃ group should be an even better donor group than a methyl group.^[22]

Compound 2 in Me₂CO reacts at 0°C with an excess of concentrated HCl(aq) giving rise to [NBu4][cis-Pt- $(CF_3)_2Cl(CO)$] (3, Scheme 2) in a stereoselective way (¹⁹F NMR spectroscopy). The reaction probably proceeds by degradation of an additional CF₃ group and formation of the intermediate species cis-[Pt(CF₃)₂(CO)₂] that would be unstable in the presence of Cl⁻ and would eventually afford compound 3. From the reaction medium, compound 3 can be isolated as a white solid in 74% yield. It must be noted that neutralization of the excess acid is required before attempting to concentrate the initial solution, otherwise, the product obtained is contaminated with significant amounts of [NBu₄][cis-Pt(CF₃)Cl₂(CO)] (4). The latter compound can be obtained in pure form and in good yield (67%) by prolonged treatment of compound 2 with a large excess of concentrated HCl(aq) at room temperature (Scheme 2). Compound 4 had been previously obtained in 23% yield by reaction of $[Pt(CF_3)_2(nbd)]$ (nbd=norbornadiene) with $[NBu_4]Cl$ in an attempt to prepare $[NBu_4]_2[{Pt(CF_3)_2}_2(\mu-$ Cl)₂] (14, see below) that resulted in undesired hydrolysis of one of the CF₃ groups.^[14] Compound **4** is remarkably inert towards acidic attack as noted earlier.^[14]

The stereochemistry of compound **3** can be readily established by spectroscopic methods. The ¹⁹F NMR spectrum of compound **3** in CD₂Cl₂ (Figure 3) shows two equally intense



Figure 3. Room-temperature ^{19}F NMR spectrum of compound **3** in CD₂Cl₂ with spectral parameters indicated. Both signals belong to the same spin system, as they are mutually coupled with $^{4}J(^{19}F,^{19}F)=4.3$ Hz. The signal marked with an asterisk corresponds to a small amount of compound **4** present in the sample.

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signals ($\delta = -16.5, -34.9$ ppm) that belong to the same spin system as they are mutually coupled with a common ⁴J- $({}^{19}F, {}^{19}F) = 4.3$ Hz. These signals correspond to the two chemically inequivalent CF₃ groups in a *cis* arrangement. They are flanked by ¹⁹⁵Pt satellites with ${}^{2}J({}^{195}Pt, {}^{19}F)$ values of 833 and 722 Hz, respectively. By analogy with the spectroscopic properties of compound 2 we assign the lower-frequency signal to the CF₃ group trans to the CO ligand. It is interesting to note that the $\tilde{v}(CO)$ value in the IR spectrum of compound **3** in CH₂Cl₂ ($\tilde{\nu} = 2119 \text{ cm}^{-1}$) is not significantly different than that observed for compound 2 ($\tilde{\nu} = 2117 \text{ cm}^{-1}$). Thus, replacement of a CF₃ group by a Cl ligand in a *cis* position has a little effect on the Pt-CO unit. On the other hand, the $\tilde{\nu}(CO)$ value of compound 4 in CH₂Cl₂ shows a distinct drop. The observed value ($\tilde{\nu} = 2100 \text{ cm}^{-1}$) is close to reported for the chloro-carbonyl that derivative $[PtCl_3(CO)]^-$ under the same conditions $(\tilde{\nu}=2098 \text{ cm}^{-1})^{[16]}$ and hence points to the CO ligand being located trans to Cl in agreement with the cis geometry previously assigned to compound 4.^[14]

CO replacement reactions: Given the ease with which compound **2** is obtained as well as its reasonable stability, we decided to further examine its chemical behavior. Compound **2** was found to react with trimethylamine N-oxide, ONMe₃, in the presence of a number of neutral or anionic ligands (Scheme 3) affording a series of singly or doubly charged



Scheme 3. Synthesis of the mono- or di-anionic tris(trifluoromethyl)platinate(II) derivatives **5–11** by replacement of the CO ligand in compound **2** ($[NBu_4]^*$ is the counterion in all cases).

derivatives with the general formulae $[NBu_4][Pt(CF_3)_3(L)]$ [L=CN*t*Bu (5), PPh₃ (6), P(*o*-tolyl)₃ (7), tht (8, tht=tetrahydrothiophene)] and $[NBu_4]_2[Pt(CF_3)_3X]$ [X=Cl (9), Br (10), I (11)], respectively. All these compounds have been isolated in reasonable yields and have been characterized by analytical and spectroscopic methods.

The ¹⁹F NMR spectra of all those compounds but **7** show a similar pattern to that observed for the parent species **2** (Figure 2) consisting of a quartet and a septet with a 2:1 integrated ratio. The specific spectral parameters for each compound are given where appropriate in the Experimental Section. The halo-compounds **9–11** provide a homogeneous series that is particularly suited for the purposes of comparison. The signals corresponding to the mutually *trans*-standing CF₃ groups are observed to appear at higher frequencies

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with decreasing electronegativity of the halogen (Figure 4). This effect was also observed within the related $[NBu_4]_2[Pt^{IV}-(CF_3)_5X]$ series^[13] where it was rationalized suggesting that



Figure 4. ¹⁹F NMR chemical shifts observed in the doubly charged species (*SP*-4)-[Pt(CF₃)₃X]²⁻ (X = Cl, Br, I) with long bars representing the positions of mutually *trans*-standing CF₃ groups. The corresponding ²*J*(¹⁹⁵Pt,¹⁹F) values [Hz] are given in parentheses.

increased electron density on the metal in the order Cl < Br < I would favor the overlap between filled F(p) and M(d) orbitals and hence the downfield shift of the resonance as the result of paramagnetic screening.^[23] However, the signals corresponding to the CF₃ group *trans* to X show the opposite trend (Figure 4). The result is that the separation between the signals corresponding to the chemically inequivalent CF₃ groups, $\Delta \delta$, decreases with the decreasing electronegativity of X. Both signals become almost coincident and even reverse their positions with the heaviest halogen atom X=I. The ²J(¹⁹⁵Pt,¹⁹F) values associated with the septet signals (\approx 940 Hz) are substantially larger than those associated with the quartet ones (\approx 520 Hz). This fact is assignable to the much higher *trans* influence of the CF₃ group in comparison with the halo ligands.^[24]

The ¹⁹F NMR spectra of the singly charged [NBu₄][Pt- $(CF_3)_3(L)$] compounds (5-8) show less-defined trends, as expected from the diversity of the donor atoms as well as from the different π -donor/-acceptor abilities of each kind of ligand. Thus, in compound 8 containing the σ - and π -donor ligand THT, the quartet appears more shielded than the septet, the latter signal showing a substantially larger $^{2}J(^{195}\text{Pt},^{19}\text{F})$ value (868 Hz) than the former one (490 Hz). In compound 5, which contains the σ -donor and π -acceptor ligand CNtBu, the signals appear in reverse order, that is, the septet being more shielded than the quartet as in compound 2 (L=CO). The ${}^{2}J({}^{195}\text{Pt},{}^{19}\text{F})$ value associated with the septet is 725 Hz, whereas that associated with the quartet is 529 Hz. The ¹⁹F and ³¹P NMR spectra of compound **6** in solution are in keeping with those previously observed for the tetramethylammonium salt [NMe₄][Pt(CF₃)₃(PPh₃)].^[25] The ¹⁹F NMR spectrum of compound 7 shows three equally intense signals, denoting that all three CF₃ groups are chemically inequivalent. This would suggest that rotation of the otolyl groups about the P-C bonds is restricted. In order to verify the diastereotopic character of the two mutually trans-standing CF_3 groups in compound 7, we sought to gain more detailed structural information on this chemical species.

The crystal and molecular structures of $[NBu_4][Pt-(CF_3)_3[P(o-tolyl)_3]]$ (7) have been determined by single-crystal X-ray methods. The local coordination environment of the Pt atom in the $(SP-4)-[Pt(CF_3)_3[P(o-tolyl)_3]]^-$ species (Figure 5) is comparable to that observed for compound 2'



Figure 5. Displacement-ellipsoid diagram (50% probability) of $[Pt-(CF_3)_3[P(o-tolyl)_3]]^-$ as found in single crystals of compound **7**. Selected bond lengths [pm] and angles [^o] with estimated standard deviations: Pt-C(1) 207.4(2), Pt-C(2) 207.7(2), Pt-C(3) 207.3(2), Pt-P 233.80(6), average P-C 183.2(2), average C-F 137.3(3); C(1)-Pt-C(2) 87.11(9), C(1)-Pt-C(3) 171.36(9), C(1)-Pt-P 91.14(6), C(2)-Pt-C(3) 86.78(9), C(2)-Pt-P 176.55(6), C(3)-Pt-P 95.27(6), average C-P-C' 104.1(1), average Pt-P-C 114.48(7), average Pt-C-F 115.48(15), average F-C-F' 102.8(2).

(Figure 1). Replacement of CO in compound 2' by a phosphine ligand has no significant effect on the Pt-CF₃ distances. In fact, the three Pt-CF₃ distances in compound 7 (207.5(2) pm average value) are not only indistinguishable one from another, but also quite similar to those observed in compound 2' (see above). The much higher steric demand of the P(o-tolyl)₃ ligand with respect to CO might be responsible for the more pronounced bending apart of the mutually trans-standing CF₃ groups in the corresponding [Pt- $(CF_3)_3(L)$ ⁻ with L=CO or P(o-tolyl)₃. Thus, the C(1)-Pt-C(3) angle in 7 (171.36(9)°) clearly departs from linearity. The Pt-P distance, 233.80(6) pm, is comparable to that observed in [NMe₄][Pt(CF₃)₃(PPh₃)] (235.3(5) pm).^[25] The helical arrangement of the aryl rings in the phosphine ligand with approximate local C_3 symmetry does not match the binary local symmetry around the Pt atom and results in the absence of any symmetry element within the $[Pt(CF_3)_3]P(o$ tolyl)₃]⁻ species. This makes the two mutually *trans*-standing CF₃ groups diastereotopic as, in fact, observed in the ¹⁹F NMR spectrum of compound **7** in CD₂Cl₂. Free rotation of the o-tolyl groups about the P-C bonds at a sufficiently high rate (in the NMR time scale) would introduce an apparent symmetry element and would render both mutually trans-standing CF₃ groups chemically and magnetically equivalent. This point, however, could not be verified because decomposition of the sample occurred before even approaching the expected coalescence.

The dianionic species **9–11** are moisture sensitive and need to be stored under anhydrous conditions in order to prevent decomposition. Any of the ligands used other than CO seems to increase the electron density on the metal center, thereby enhancing the reactivity of the CF_3 groups. Thus, the action of moisture on compound **9**, for instance, resulted in hydrolytic degradation of one of the mutually *trans*-standing CF_3 groups affording compound **3** (Scheme 4).



Scheme 4. Hydrolytic process undergone by the dianionic tris(trifluoromethyl)platinate(II) derivative 9 caused by the action of moisture ($[NBu_4]^+$ is the counterion).

Stabilization of a difluorocarbene unit by base coordination: From the results presented in the previous section it becomes clear that: 1) the CO molecule in compound **2** can be replaced (Scheme 3) by a wide range of ligands, and 2) that the resulting compounds are more prone to suffer CF₃ degradation than the parent species (see, e.g., Scheme 4). Taking these two experimental features into account, we carried out the reaction of compound **2** with pyridine-2-thiol, C_5H_5NS , in the presence of ONMe₃ aiming to prepare a mononuclear^[26] or possibly a dinuclear^[27] trifluoromethyl platinum(II) compound containing the deprotonated pyridin-2-thiolato, $C_5H_4NS^-$, ligand. Instead, a compound with the formula [NBu₄][Pt(CF₃)₂(CF₂NC₅H₄S)] (**12**) was obtained (Scheme 5, upper path), which can be isolated as a



Scheme 5. Experimentally observed (upper path) formation of the fivemembered heterometallacyclic compound **12** together with the suggested reaction mechanism (lower path) ($[NBu_4]^+$ is the counterion in all cases).

yellowish solid in 77% yield. The reaction outcome, although unexpected, still follows the premises stated above. The compound originally aimed for in this reaction was obtained by a different procedure (see below).

The precise nature of compound **12** was established by single-crystal X-ray diffraction methods. The anion [Pt-

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 $(CF_3)_2(CF_2NC_5H_4S-\kappa C,\kappa S)]^-$ turned out to contain a *gem*-difluorinated five-membered metallacycle (Figure 6). In the crystal, although the cation is perfectly ordered, the complex



Figure 6. Displacement-ellipsoid diagram (50% probability) of [Pt- $(CF_3)_2(CF_2NC_5H_4S-\kappa C,\kappa S)$]⁻ as found in single crystals of compound **12**. The second component of the disorder is omitted for clarity. Selected bond lengths [pm] and angles [^o] with estimated standard deviations: Pt-C(1) 200.1(9), Pt-C(2) 202.9(9), Pt-C(3) 185(2), Pt-S 231.0(5), average C-F(CF_3) 137.8(14), C(3)-N(1) 160(3), C(3)-F(7) 142.2(15), C(3)-F(8) 141.3(16), S-C(4) 174(4); C(1)-Pt-C(2) 89.7(3), C(1)-Pt-C(3) 93.5(7), C(1)-Pt-S 178.2(3), C(2)-Pt-C(3) 176.1(6), C(2)-Pt-S 88.6(3), C(3)-Pt-S 88.2(6), Pt-C(3)-F(7) 122.5(12), Pt-C(3)-F(8) 122.9(12), F(7)-C(3)-F(8) 98.0(13). Standard deviations are thought to be underestimated on account of the disorder.

anion is disordered over two discrete sites. The disorder consists of a 180° rotation around the axis bisecting the $Pt(CF_3)_2$ unit and thus leading to two alternative locations of the ligand forming the metallacycle. The C and S donor atoms of the heterocyclic ligand together with the terminal CF₃ groups form a slightly distorted SP-4 environment for the Pt^{II} center, yet all the donor atoms and the Pt center are in the same plane. The most salient feature of compound 12 is the nature of the metallacycle: although, in principle, it could be considered to be a Pt derivative of a fluorinated Nylide ligand,^[28] the structural data would suggest that it could be described as a Pt-difluorocarbene unit stabilized by base coordination. To begin with, the Pt-CF₂ distance, 185 pm, is shorter than the terminal Pt-CF₃ single bonds within the same molecule (201 pm in average), being closer to the Pt-CO bond length found in the monocarbonyl derivative 2', that is, 191.3(4) pm. The $Pt-CF_2$ distance in compound 12 is in the range of the Ir-CF₂ distances found in structurally characterized difluorocarbeneiridium compounds such as $[Ir(CF_3)(=CF_2)(CO)(PPh_3)_2]$ $(187.4(7) \text{ pm})^{[29]}$ [(η^{5} -C₅Me₅)Ir(=CF₂)(CO)] (185.5(13) pm)^[30] or $[(\eta^5-C_5Me_5)Ir(=CF_2)(PMe_3)]$ (185.4(11) pm).^[31] Finally, the N(1)-C(3) bond length, 160 pm, appears longer than that typically found for a $N-C(sp^3)$ single bond in N-alkyl pyridinium compounds, that is, 148.5(9) pm average.^[32] The latter value is not significantly altered on fluorination of the N-alkyl group. Thus, a N–C(sp³) bond length of 146(1) pm has been observed in the solid-state structure of 1-(4-dimethylaminopyridinium)-1,1,2,2-tetrafluoroethane bromide.^[33] The long N-C bond found in compound 12 can be considered as evidence for some dative bond character.^[34] Similar structural features were found, for instance, in the pyridine

(py)-stabilized silylene-metal compound $cis-[(\eta^5-C_5Me_5)W(CO)_2H(=SiPh_2\cdot py)]$,^[35–38] which exhibits a short W–Si distance and a long Si–N bond length. It is interesting to note that the fluorinated metallacyclic organonickel(II) compound I depicted in Scheme 6 was best described "as a



Scheme 6. Cationic five-membered metallacyclic compounds of Group 10 metals ($[PF_6]^-$ is the counterion in both cases).

phosphine-stabilized carbenium complex rather than a phosphonium ylide complex".^[39] On the other hand, the non-fluorinated metallacyclic organoplatinum(II) compound **II** (Scheme 6) has been described recently to arise by intermolecular C–N coupling between the carbene carbon-donor atom of the corresponding alkylidene precursor species and the heterocyclic nitrogen-donor atom of free 4-dimethylaminopyridine (py*). The resulting C–N distance, 151.2(3) pm, compares well with that found in *N*-alkyl pyridinium compounds (see above) and thus points to a pyridinium ylide structure in this case.^[40] Both compounds **I** and **II**, as well as compound **12**, seem to benefit from the stabilizing chelate effect.

The ¹⁹F NMR spectrum of compound **12** in CD₂Cl₂ shows three signals in a 3:3:2 integrated ratio (Figure 7) and is in keeping with the solid-state structure. The equally intense signals are assignable to the terminal CF₃ groups, whereas the complex multiplet appearing at $\delta = -55.85$ ppm is assigned to the CF₂ unit. We attribute the signal appearing at $\delta = -22.5$ ppm with ²J(¹⁹⁵Pt,¹⁹F)=525 Hz to the CF₃ group *trans* to a carbon atom due to its higher multiplicity. The signal appearing at $\delta = -23.6$ ppm with ²J(¹⁹⁵Pt,¹⁹F)=788 Hz



Figure 7. Room-temperature ${}^{19}\text{F}\,\text{NMR}$ spectrum of compound 12 in CD_2Cl_2 with spectral parameters indicated.

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shows lower multiplicity and can thus be assigned to the CF_3 group *trans* to the S atom.

The reaction of compound **3** with pyridin-2-thiol in the presence of ONMe₃ afforded $[NBu_4][Pt(CF_3)_2(NC_5H_4S)]$ (**13**), which was isolated as a yellow solid in reasonable yield (Scheme 7). This compound is instrumental in order to establish useful spectroscopic and structural comparisons with the related metallacyclic derivative **12**.



Scheme 7. Synthesis of the four-membered heterometallacyclic compound 13 ([NBu₄]⁺ is the counterion).

The crystal and molecular structures of compound **13** were established by single-crystal X-ray diffraction methods. A drawing of the mononuclear complex anion [Pt- $(CF_3)_2(NC_5H_4S-\kappa N,\kappa S)$]⁻ is given in Figure 8. The small bite



Figure 8. Displacement-ellipsoid diagram (50% probability) of [Pt- $(CF_3)_2(NC_5H_4S-\kappa N,\kappa S)$]⁻ as found in single crystals of compound **13**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pt-C(1) 197.4(4), Pt-C(2) 199.1(4), Pt-N(1) 209.2(3), Pt-S 239.5(1), S-C(3) 174.2(4), N(1)-C(3) 136.9(4), average C-F 137.3(4); C(1)-Pt-C(2) 91.55(16), C(1)-Pt-N(1) 168.52(14), C(1)-Pt-S 100.00(12), C(2)-Pt-N(1) 99.84(13), C(2)-Pt-S 168.12(11), N(1)-Pt-S 68.70(8), Pt-S-C(3) 80.58(12), Pt-N(1)-C(3) 101.6(2), Pt-N(1)-C(7) 138.6(3), N(1)-C(3)-S 109.1(3), average Pt-C-F 115.9(3), average F-C-F' 102.3(3).

angle of the chelating pyridin-2-thiolato ligand results in an acute N-Pt-S angle, $68.70(8)^\circ$, and consequently in heavy angular distortions around the Pt center from an ideal *SP*-4 geometry. The metal coordination environment, although far from square, is indeed planar, because the sum of the angles between donor atoms in adjacent positions amounts to $360.1(1)^\circ$. The CF₃ coordination sites are negligibly affected by the aforementioned angular distortions, as these ligands form almost a right angle: C(1)-Pt-C(2): 91.55(16)°. The Pt-C bond distances, Pt-C(1): 197.4(4) and Pt-C(2): 199.1(4) pm, are indistinguishable within the experimental

error in spite of the different nature of the donor atoms in *trans* positions: a hard and neutral nitrogen atom versus a soft and anionic sulphur atom. These Pt–C bond lengths (198.2(4) pm average value) are comparable to those observed in compound **12** (201.5 pm average value). The fourmembered metallacycle in compound **13** is obviously more strained than the five-membered one in compound **12**. The slightly elongated Pt–S distance found in compound **13** (239.5(1) pm) compared to that observed in compound **12** (231.0 pm), can be assigned to the unfavorable ring strain in the former case. The overall geometry of the Pt(NC₅H₄S- $\kappa N,\kappa S$) unit in compound **13** is similar to those observed in the related [Pt(NC₅H₄S- $\kappa N,\kappa S$)(PR₃)₂]⁺ salts (PR₃=PPh₃,^[41] $\frac{1}{2}$ 1,1'-bis(diphenylphosphino)ferrocene.^[42]

The ¹⁹F NMR spectrum of compound **13** in [D₆]acetone (Figure 9) shows two quartet signals at $\delta = -19.8$ and -22.0 ppm, which we respectively assign to the CF₃ groups



Figure 9. Room-temperature ${}^{19}\text{F}$ NMR spectrum of compound **13** in [D₆]acetone with spectral parameters indicated. Both signals belong to the same spin system, as they are mutually coupled with ${}^4J({}^{19}\text{F},{}^{19}\text{F})=2.5$ Hz.

trans to the sulphur atom and to the nitrogen atom based on the higher value of ${}^{2}J({}^{195}\text{Pt},{}^{19}\text{F})$ associated with the former signal (830 vs. 754 Hz). Both signals show a common coupling constant of ${}^{4}J({}^{19}\text{F},{}^{19}\text{F})=2.5$ Hz.

The synthetic procedures leading to compounds **12** (Scheme 5) and **13** (Scheme 7) can be considered to involve similar chemical processes. In a first step, the CO ligand in both precursor species **2** and **3** would be replaced by the thione tautomer of the C_3H_5NS ligand (e.g., lower path in Scheme 5). This is a reasonable assumption, because monodentate κS coordination is the most widespread for the C_5H_5S molecule throughout the periodic table.^[43] The resulting pyridinium species would undergo deprotonation with abstraction of a neighboring halide and formation of the corresponding [NHMe₃]X salt (X=F, Cl). Abstraction of an α -fluorine atom in the former case^[44] would render a highly electrophilic difluorocarbene unit that would readily react with the pyridine nucleophile resulting in an intramolecular C–N coupling and the eventual formation of the five-mem-

bered metallacycle found in compound **12** (lower path in Scheme 5). On the other hand, abstraction of the Pt-bound Cl ligand in the latter case would result in the four-membered metallacycle found in compound **13**, where the deprotonated $C_5H_4NS^-$ ligand is acting as a bifunctional ligand through both its soft and hard donor atoms.

Nucleophilic substitutions at the Fischer transition-metal carbene compounds are important chemical processes usually assumed to proceed through a four-substituted intermediate.^[45] Compound **12** provides a structural model for an early stage in the referred process, namely that in which the nucleophile approaches the reactive $C(sp^2)$ center (**A** in Scheme 8a). This may be extended to other chemical pro-



Scheme 8. Suggested reaction paths for nucleophilic attack at metalbounded carbene carbon atoms resulting in a) nucleophilic substitution (generic process) and b) hydrolysis of a difluorocarbene unit.

cesses involving nucleophilic attack at a metal-bounded carbene carbon atom.^[46] In the particular case in which the carbene unit is $:CF_2$ and the nucleophile is $:OH_2$, we get a plausible mechanism for the hydrolytic processes undergone by the trifluoromethyl derivatives 1-3 presented above (Scheme 2). All these processes can be rationalized with a common overall reaction path entailing the following steps (Scheme 8b): 1) acid-promoted activation of an α -fluorine atom resulting in F⁻ loss and formation of a highly electrophilic difluorocarbene-metal unit; 2) nucleophilic attack at the carbon atom by the OH_2 molecule giving rise first to a donor-acceptor adduct A and then to a tetrahedral ylid species B-sometimes termed alternatively as onium or zwitterionic; 3) the latter unstable species would further evolve under formal loss of HF and formation of the metalcoordinated carbonyl unit. Only the carbonyl derivative, 2, resulting from the first degradation process in compound 1 seems to be sufficiently stable to be isolated. The dicarbonyl species presumably resulting from the degradation of any additional CF3 group would be unstable under the reaction conditions and would undergo spontaneous replacement of CO by Cl⁻. As indicated above, the Pt-bound CO ligand can in fact be replaced by a number of better ligands including Cl⁻ (Scheme 3). Thus, the whole series of chlorocarbonyl platinum(II) derivatives 2-4 can be understood as the result of repeated and alternating CF_3 degradation and CO substitution processes.

Synthesis of a "Pt(CF₃)₂" synthon: When compound 3 is reacted with ONMe₃ in the absence of any added ligand, the dinuclear species $[NBu_4]_2[{Pt(CF_3)_2}_2(\mu-Cl)_2]$ (14) is formed (Scheme 9). In the absence of any better ligand, the residual



Scheme 9. Dimerization undergone by compound 3 under CO extrusion in the absence of any better ligand ($[NBu_4]^+$ is the counterion) together with the synthesis of the neutral solvent derivative **15**.

nucleophilicity of the terminal Cl ligand is able to promote dimerization of $[Pt(CF_3)_2Cl]^-$ units giving rise to the doublebridging system in 14. Compound 14 had purportedly been detected in solution, but had not been isolated due to its readiness to suffer hydrolysis.^[14] We succeeded in isolating compound 14 as a white, moisture-sensitive solid in approximately 60% yield. The ¹⁹F NMR spectrum of compound **14** shows a singlet at $\delta = -22.9$ ppm flanked by ¹⁹⁵Pt satellites with ${}^{2}J({}^{195}\text{Pt},{}^{19}\text{F}) = 907$ Hz. This coupling constant has a similar value to that found for the CF3 group trans to Cl in compound 5 (922 Hz). However, the spectroscopic parameters observed for compound 14 significantly depart from those previously reported^[14] and thus, the latter most probably correspond to a different chemical species. At this point, it is interesting to note that compound 14 regenerates the parent species 3 (¹⁹F NMR and IR spectroscopy) upon treatment with CO at room temperature and under normal pressure (Scheme 9). This fact strongly supports the formulation of compound 14 as a dinuclear compound with a doublebridging system that is reversibly formed and broken by CO loss or uptake.

Compound **14** reacts with the stoichiometrically required amount of AgClO₄ in THF (Scheme 9) affording *cis*-[Pt-(CF₃)₂(thf)₂] (**15**). After the appropriate work up, this solvento derivative can be isolated as a yellowish solid in 60 % yield. The ¹⁹F NMR spectrum in CD₂Cl₂ shows a singlet at $\delta = -26.6$ ppm flanked by ¹⁹⁵Pt satellites with ²J(¹⁹⁵Pt,¹⁹F) = 929 Hz. This coupling constant is slightly larger than that found in the dinuclear precursor species **14**. The large ²J(¹⁹⁵Pt,¹⁹F) value suggests that the CF₃ group is *trans* to a ligand with moderate *trans* influence, thus indicating that compound **15** adopts a global *cis* geometry in solution. The solid-state stereochemistry of cis-[Pt(CF₃)₂(thf)₂] (15) has been unambiguously established by single-crystal X-ray diffraction methods (Figure 10). The sum of the angles be-



Figure 10. Displacement-ellipsoid diagram (50% probability) of *cis*-[Pt-(CF₃)₂(thf)₂] as found in single crystals of compound **15**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pt-C(1) 196(1), Pt-C(2) 194(1), Pt-O(1) 211.4(7), Pt-O(2) 211.6(7); C(1)-Pt-C(2) 90.7(4), C(1)-Pt-O(1) 92.0(4), C(1)-Pt-O(2) 175.4(4), C(2)-Pt-O(1) 177.3(4), C(2)-Pt-O(2) 93.9(4), O(1)-Pt-O(2) 83.4(3).

tween adjacent ligands amounts exactly to 360°. The Pt-C distances are indistinguishable within the experimental error (195(1) pm average value) and considerably shorter than those found in the anionic derivatives 2' and 7 presented above (≈ 207 pm). The crystal and molecular structure of the neutral species $[Pt(CF_3)_2(nbd)]$ has been previously reported,^[47] but the large standard deviation estimated for the corresponding Pt–CF₃ bond lengths (202(4) and 207(4) pm) precludes detailed comparison with the current results. The Pt-O distance (211.5(7) pm average value) is significantly shorter than that found in the neutral zwitterionic species $[{Ph_2B(CH_2PPh_2)_2 - \kappa^2 P}]PtMe(thf)] \cdot 2THF: 217.0(4) pm.^{[48]} It$ is, in turn, comparable to the Pd-O distance in the related solvento compound *cis*-[Pd(C₆F₅)₂(thf)₂]: 212.1(3) pm.^[49] This resemblance is in keeping with the similar covalent radii assigned to Pd and Pt atoms when involved in single bonds: $r_1(Pd) = 120 \text{ pm}$ versus $r_1(Pt) = 123 \text{ pm}$.^[50] The Pt- CF_3 distance in compound 15 is also similar to the Pd-C₆F₅ distance in cis-[Pd(C₆F₅)₂(thf)₂] (196.4(4) pm average value), regardless of the presumably different hybridization of the carbon donor atom in each case.

By using the Ahrland–Chatt–Davies classification,^[51] Ptⁿ is considered as a *class b* acidic center, whereas THF belongs to the *class a* ligands. This means that the Ptⁿ–OC₄H₈ bond should not be particularly strong.^[52] Furthermore, the THF ligand would be expected to be highly labile as it has been found, for instance, in the related perhalophenyl derivatives *cis*-[Pt(C₆X₅)₂(thf)₂] (X=F, Cl).^[53] The lability of the THF ligands in compound **15** has been confirmed by reac-

tion with norbornadiene at room temperature (Scheme 9), whereby THF is cleanly replaced by the diene molecule, giving rise to $[Pt(CF_3)_2(nbd)]^{[14,54]}$ in quantitative yield (¹⁹F NMR spectroscopy). This reaction builds a link with previously established results and qualifies compound **15** as a convenient synthon of the "Pt(CF₃)₂" moiety—being even more efficient than the previously used $[Pt(CF_3)_2(nbd)]$ compound.^[14,54]

Conclusion

Increasingly harsher conditions are required (Scheme 2) to achieve the stepwise degradation of CF₃ groups in the homoleptic trifluoromethyl platinum(II) derivative [NBu₄]₂[Pt- $(CF_3)_4$ (1). Thus, the action of moisture at room temperature is enough to transform compound 1 into the monocarbonyl derivative $[NBu_4][Pt(CF_3)_3(CO)]$ (2). Treatment of the latter compound with an excess of concentrated HCl(aq) at 0°C produces degradation of a second CF₃ group affording the chloro-carbonyl derivative $[NBu_4][cis-Pt(CF_3)_2Cl(CO)]$ (3). An additional CF_3 group can be degraded by the action of an excess of concentrated HCl(aq) on compound 2 at room temperature, resulting in the stereospecific formation of [NBu₄][cis-Pt(CF₃)Cl₂(CO)] (4), which stands further acidic attack. This provides a complete and, as far as we know, unprecedented series of trifluoromethyl-metal compounds obtained as the result of acid-promoted α -fluorine abstraction processes immediately followed by hydrolysis of the ensuing difluorocarbene-platinum(II) unit (Scheme 8b).

Indirect evidence of the involvement of the $[Pt]=CF_2$ unit in these degradative processes has been gained through investigation of the reaction of compound **2** with pydirin-2thiol, C₃H₅NS, whereby $[NBu_4][Pt(CF_3)_2(CF_2NC_5H_4S <math>\kappa C,\kappa S)]$ (**12**) was formed (Scheme 5). This *gem*-difluorinated five-membered metallacyclic compound can, in fact, be considered as a difluorocarbene–metal derivative stabilized by intramolecular base coordination in view of its molecular structure (Figure 6). Moreover, compound **12** is a valid model for the initial step operating in the many processes involving nucleophilic attack at an electrophilic carbon atom (Scheme 8a)—in particular in the hydrolysis of $[M]=CF_2$ to give [M]–CO (Scheme 8b).

The stability of the unusual species 12 may be mainly due to the absence of substituents at the pyridine nitrogen atom that might act as suitable leaving groups. The chelating effect of the bidentate ligand will probably add to the global stabilization of the metallacyclic compound. The synthesis of compound $[NBu_4][Pt(CF_3)_2(NC_5H_4S-\kappa N,\kappa S)]$ (13) containing a more strained four-membered metallacycle is also reported. The structural features of compounds 12 (Figure 6) and 13 (Figure 8), which differ only in terms of the presence or absence of a difluorocarbene CF_2 unit inserted in the Pt– N bond, are suitably compared.

The CO ligand in the carbonyl derivative **2** can be replaced, in the presence of $ONMe_3$, by a number of neutral (L) or anionic (X⁻) ligands giving rise to a variety of mono-

nuclear trifluoromethyl platinum(II) derivatives with the general formulae [NBu₄][Pt(CF₃)₃(L)] (**5–8**) and [NBu₄]₂[Pt-(CF₃)₃X] (**9–11**), respectively (Scheme 2). Additionally, the ONMe₃-assisted extrusion of the CO ligand in the carbonyl derivative **3** gives rise, in the absence of any added ligand, to the dinuclear species [NBu₄]₂[Pt(CF₃)₂(µ-Cl)₂] (**14**), which is itself a suitable precursor of the solvento derivative *cis*-[Pt(CF₃)₂(thf)₂] (**15**). The THF ligands in the latter compound are more labile than the diene ligands in the well-known species [Pt(CF₃)₂(cod)]^[55] (cod=1,5-cyclooctadiene) and [Pt(CF₃)₂(nbd)].^[14,47] Compound **15** can thus be considered as a more convenient synthon of the "*cis*-Pt(CF₃)₂" unit.

Experimental Section

General procedures and materials: Unless otherwise stated, the reactions and manipulations were carried out under purified argon by using Schlenk techniques. Solvents were dried by using an MBraun SPS-800 System. Compound [NBu₄]₂[Pt(CF₃)₄] (1) was obtained as described elsewhere.^[12] Elemental analyses were carried out by using a Perkin-Elmer 2400 CHNS/O Series II microanalyzer. IR spectra of KBr discs were recorded on the following Perkin-Elmer spectrophotometers: 883 (4000-200 cm⁻¹) or Spectrum One (4000-350 cm⁻¹); an ATR device was used to register the IR spectrum of compound 15 in order to avoid substitution of the highly labile THF ligand. NMR spectra were recorded on any of the following spectrometers: Varian Gemini-300, Bruker ARX 300, or Bruker ARX 400. Unless otherwise stated, the spectroscopic measurements were carried out at room temperature. Chemical shifts of the measured nuclei (δ in [ppm]) are given with respect to the standard references in use: SiMe₄ (¹H and ¹³C), CFCl₃ (¹⁹F), and 85% aqueous H₃PO₄ (³¹P). NMR parameters associated with the cations are unexceptional and are therefore omitted.

Synthesis of [NBu₄][Pt(CF₃)₃(CO)] (2): Compound 1 (1.50 g, 1.57 mmol) was dissolved in wet Me₂CO (25 cm³) and after four days at room temperature under air, the solvent was evaporated to dryness. Treatment of the resulting residue with iPrOH (5 cm³) gave rise to a white solid, which was filtered, washed with n-hexane, and vacuum dried to give compound **2** (0.86 g, 1.28 mmol, 82 %). ${}^{13}C{}^{19}F{}$ NMR (100.577 MHz, CD₂Cl₂): $\delta =$ 174.21 (s, ${}^{1}J({}^{195}\text{Pt}, {}^{13}\text{C}) = 1103 \text{ Hz}$, CO), 138.19 (s, ${}^{1}J({}^{195}\text{Pt}, {}^{13}\text{C}) = 1144 \text{ Hz}$, mutually trans-standing CF₃), 133.71 ppm (s, ${}^{1}J({}^{195}Pt, {}^{13}C) = 1777 \text{ Hz}, \text{ CF}_{3}$ *trans* to CO); ¹⁹F NMR (376.308 MHz, CD₂Cl₂): $\delta = -22.10$ (q, ${}^{2}J({}^{195}\text{Pt},{}^{19}\text{F}) = 518$, ${}^{4}J({}^{19}\text{F},{}^{19}\text{F}) = 3.9 \text{ Hz}$, 6F; mutually *trans*-standing CF₃), -31.90 ppm (septet, ${}^{2}J({}^{195}\text{Pt}, {}^{19}\text{F}) = 769 \text{ Hz}$, 3F; CF₃ trans to CO); IR (KBr): $\tilde{\nu} = 2968$ (s), 2879 (m), 2121 (s, C=O), 1475 (s), 1381 (w), 1255 (m), 1158 (s), 1135 (m), 1096 (vs), 1081 (s), 1014 (vs), 977 (s), 895 (w), 880 (w, $[NBu_4]^+$), 801 (w), 738 (w, $[NBu_4]^+$), 547 cm⁻¹ (w); IR (CH₂Cl₂): $\tilde{\nu} = 2117 \text{ cm}^{-1}$ (s, C=O); elemental analysis calcd (%) for C₂₀H₃₆F₉NOPt: C 35.7, H 5.4, N 2.1; found: C 35.9, H 5.45, N 2.1.

Synthesis of [PPh₄][Pt(CF₃)₃(CO)] (2'): Compound 2' was obtained in 92% yield by metathesis of compound 2 with [PPh₄]Br in Me₂CO/*i*PrOH at room temperature. ¹⁹F NMR data in CD₂Cl₂ are coincident with those of compound 2; IR (KBr): $\tilde{\nu}$ =2106 (vs, C≡O), 1587 (w), 1485 (m), 1438 (s), 1340 (w), 1316 (w), 1189 (w), 1149 (vs), 1110 (vs), 1094 (vs), 1033 (s), 1019 (vs), 1008 (vs), 995 (s), 975 (s), 848 (w), 754 (m), 751 (m), 724 (s), 689 (s), 527 (vs), 444 (w), 294 cm⁻¹ (w); IR (CH₂Cl₂): $\tilde{\nu}$ =2117 cm⁻¹ (s, CO); elemental analysis calcd (%) for C₂₈H₂₀F₉OPPt: C 43.7, H 2.6; found: C 43.55, H 2.5.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *i*PrOH (15 cm³) into a solution of 15 mg of compound **2'** in Me₂CO (15 cm³) at 4 °C.

Synthesis of $[NBu_4][cis-Pt(CF_3)_2Cl(CO)]$ (3): An excess of concentrated HCl(aq) (1.38 cm³, 16.72 mmol) was added to a solution of compound 2

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(0.75 g, 1.11 mmol) in Me₂CO (25 cm³) at 0 °C (ice bath). After four days of stirring at that temperature, the reaction medium was neutralized with an aqueous solution of K2CO3 and the white precipitate formed was filtered off. The filtrate was concentrated to dryness and the resultant residue was washed with H_2O (3×5 cm³), vacuum dried, and re-dissolved in CH₂Cl₂ (10 cm³). The solution was dried with anhydrous MgSO₄, which was subsequently filtered off. The filtrate was concentrated to dryness and by treating the resultant residue with Et₂O (5 cm³) a white solid formed, which was filtered, washed with *n*-hexane $(2 \times 3 \text{ cm}^3)$ and vacuum dried to give compound 3 (0.53 g, 0.83 mmol, 74%). ¹⁹F NMR (282.231 MHz, CD₂Cl₂): $\delta = -16.5$ (q, ${}^{4}J({}^{19}F, {}^{19}F) = 4.3$, ${}^{2}J({}^{195}Pt, {}^{19}F) =$ 833 Hz, 3F; CF₃ trans to Cl), -34.9 ppm (q, ${}^{2}J({}^{195}\text{Pt}, {}^{19}\text{F}) = 722 \text{ Hz}, 3\text{ F};$ CF₃ trans to CO); IR (KBr): $\tilde{\nu}$ =2967 (s), 2878 (m), 2117 (s, C=O), 1486 (s), 1467 (m), 1383 (m), 1261 (w), 1141 (vs), 1092 (vs), 1029 (vs), 1007 (vs), 997 (vs), 880 (m, [NBu₄]⁺), 800 (m), 741 (m, [NBu₄]⁺), 712 (w), 543 (w), 493 (w), 319 cm⁻¹ (w, Pt–Cl); IR (CH₂Cl₂): $\tilde{\nu} = 2119$ cm⁻¹ (s, CO); elemental analysis calcd (%) for C₁₉H₃₆ClF₆NOPt: C 35.7, H 5.7, N 2.2; found: C 35.6, H 5.5, N 2.3.

Synthesis of [NBu₄][*cis*-Pt(CF₃)Cl₂(CO)] (4): An excess of concentrated HCl(aq) (0.46 cm³, 5.57 mmol) was added to a solution of compound **2** (0.25 g, 0.37 mmol) in Me₂CO (10 cm³) at room temperature and the mixture was stirred for 12 h at room temperature. The reaction medium was concentrated to dryness. By treating the resulting residue with *i*PrOH (5 cm³) a white solid formed, which was filtered, washed with *n*-hexane (2×3 cm³), and vacuum dried to yield compound **4** (0.15 g, 0.25 mmol, 67%). Multinuclear NMR spectroscopic properties in solution are in keeping with literature values;^[14] IR (KBr): $\tilde{\nu}$ =2967 (s), 2874 (w), 2096 (vs, C=O), 1485 (m), 1465 (w), 1383 (w), 1142 (m), 1108 (vs), 1030 (vs), 881 (m, [NBu₄]⁺), 800 (w), 741 (m, [NBu₄]⁺), 553 (w), 504 (w), 492 (w), 344 (w, Pt-Cl), 304 cm⁻¹ (w, Pt-Cl); IR (CH₂Cl₂): $\tilde{\nu}$ =2100 cm⁻¹ (s, C=O); elemental analysis calcd (%) for C₁₈H₃₆Cl₂F₃NOPt: C 35.7, H 6.0, N 2.3; found: C 35.8, H 5.8, N 2.3.

Synthesis of [NBu₄][Pt(CF₃)₃(CN*t***Bu)] (5): ONMe₃ (28 mg, 0.37 mmol) was added to a solution of compound 2** (0.25 g, 0.37 mmol) and CN*t*Bu (0.21 cm³, 1.86 mmol) in CH₂Cl₂ (15 cm³) at room temperature. After 2 h of stirring, the solution was concentrated to dryness. By treating the resulting residue with *i*PrOH (2 cm³) at 0°C, a white solid formed, which was filtered, washed with cold *i*PrOH (2 cm³) and *n*-hexane (3 cm³), and vacuum dried to give compound **5** (0.19 g, 0.26 mmol, 70%). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = -1.51$ ppm (CMe₃); ¹⁹F NMR (282.231 MHz, CD₂Cl₂): $\delta = -22.22$ (q, ²*l*(¹⁹⁵Pt, ¹⁹F) = 529, ⁴*l*(¹⁹F)¹⁹F) = 3.4 Hz, 6 F; mutual ly *trans*-standing CF₃), -27.28 ppm (septet, ²*l*(¹⁹⁵Pt, ¹⁹F) = 725 Hz, 3 F; CF₃ *trans* to CN*t*Bu); IR (KBr): $\tilde{\nu} = 2970$ (m), 2880 (w), 2218 (s, C=N), 1481 (m), 1461 (w), 1376 (w), 1146 (vs), 1084 (vs), 1024 (m), 993 (vs), 959 (m), 883 (w, [NBu₄]⁺), 799 (w), 739 cm⁻¹ (w, [NBu₄]⁺); elemental analysis calcd (%) for C₂₄H₄₅F₉N₂Pt: C 39.6, H 6.2, N 3.85; found: C 39.4, H 6.0, N 3.8.

Synthesis of [NBu₄][Pt(CF₃)₃(PPh₃)] (6): ONMe₃ (28 mg, 0.37 mmol) was added to a solution of compound **2** (0.25 g, 0.37 mmol) and PPh₃ (0.29 g, 1.11 mmol) in CH₂Cl₂ (15 cm³) at room temperature. After 2 h of stirring, the solution was concentrated to dryness. By treating the resulting residue with Et₂O (3×5 cm³), a white solid formed, which was filtered and vacuum dried to give compound **6** (0.26 g, 0.29 mmol, 77%). The NMR spectroscopic properties associated with the anion [Pt(CF₃)₃(PPh₃)]⁻ in solution are in keeping with those reported for the [NMe₄] + salt;^[25] IR (KBr): $\tilde{\nu}$ = 2965 (m), 2935 (w), 2876 (m), 1482 (m), 1458 (sh), 1438 (m), 1382 (w), 1315 (w), 1139 (s), 1099 (m), 1073 (vs), 988 (vs), 938 (w), 893 (w), 881 (w, [NBu₄]⁺), 803 (w), 744 (m), 698 (m), 532 (m), 511 (w), 498 (w), 375 (w), 363 cm⁻¹ (w); elemental analysis calcd (%) for C₃₇H₅₁F₉NPPt: C 49.0, H 5.7, N 1.5; found: C 48.9, H 5.6, N 1.6.

Synthesis of [NBu₄][Pt(CF₃)₃[P(C₆H₄Me-2)₃] (7): Compound 7 was prepared from compound 2 (0.25 g, 0.37 mmol), P(C₆H₄Me-2)₃ (0.34 g, 1.11 mmol), and ONMe₃ (28 mg, 0.37 mmol) by using a similar procedure to that just described for the synthesis of compound 6. Complex 7 was obtained as a white solid (0.24 g, 0.25 mmol, 68%). ¹H NMR (400 MHz, CD₂Cl₂): δ =7-9 (overlapping m, 12H; aromatic), 1.84 (brs, 3H; CH₃), 1.42 ppm (brs, 6H; CH₃); ¹⁹F NMR (376.308 MHz, CD₂Cl₂): δ =-21.47 (brd, ²*J*(¹⁹⁵Pt,¹⁹F)=467 Hz, 3F; one of the mutually *trans*-standing CF₃),

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 $\begin{array}{l} -23.62 \ (br d, \ ^2J(^{195}Pt,^{19}F)=468 \ Hz, \ 3F; \ one \ of \ the \ mutually \ trans-standing \ CF_3), \ -24.54 \ ppm \ (d, \ ^3J(^{31}P,^{19}F)=56, \ ^2J(^{195}Pt,^{19}F)=728 \ Hz, \ 3F; \ CF_3 \ trans \ to \ P); \ ^{31}P\{^1H\} \ NMR \ (161.923 \ MHz, \ CD_2Cl_2): \ \delta=20.47 \ ppm \ (q \ of \ not \ well-resolved \ septets, \ ^{3}J(^{19}F,^{31}P)=56 \ (trans), \ ^{3}J(^{19}F,^{31}P) \ \approx 7 \ (cis), \ ^{1}J(^{195}Pt,^{31}P)=2169 \ Hz); \ IR \ (KBr): \ \tilde{\nu}=2964 \ (m), \ 2935 \ (sh), \ 2877 \ (m), \ 1592 \ (w), \ 1566 \ (w), \ 1473 \ (m), \ 1469 \ (m), \ 1382 \ (m), \ 1279 \ (w), \ 1204 \ (w), \ 1136 \ (s), \ 1074 \ (vs), \ 1018 \ (m), \ 994 \ (vs), \ 883 \ (w, \ [NBu_4]^+), \ 803 \ (w), \ 757 \ (m), \ 722 \ (w), \ 562 \ (w), \ 539 \ (w), \ 517 \ (w), \ 481 \ (m), \ 466 \ cm^{-1} \ (sh); \ elemental \ analysis \ calcd \ (\%) \ for \ C_{40}H_{57}F_9NPPt: \ C \ 50.6, \ H \ 6.05, \ N \ 1.5; \ found: \ C \ 49.8, \ H \ 6.5, \ N \ 1.1. \end{array}$

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (10 cm^3) into a solution of compound **7** (15 mg) in CH₂Cl₂ (5 cm^3) at 4 °C.

Synthesis of [NBu₄][Pt(CF₃)₃(tht)] (8): Compound **8** was prepared from compound **2** (0.25 g, 0.37 mmol), THT (0.16 cm³, 1.86 mmol), and ONMe₃ (28 mg, 0.37 mmol) by using a similar procedure to that just described for the synthesis of compound **5**. Complex **8** was obtained as a white solid (0.20 g, 0.27 mmol, 73%). Elemental analysis calcd (%) for C₂₃H₄₄F₉NPtS: C 37.7, H 6.05, N 1.9, S 4.4; found: C 37.4, H 5.9, N 2.0, S 4.3. IR (KBr): $\bar{\nu}$ =2966 (m), 2878 (w), 1525 (w), 1474 (w), 1383 (w), 1257 (w), 1146 (s), 1082 (vs), 1051 (w), 1021 (sh), 995 (s), 883 (w, [NBu₄]⁺), 805 (w), 739 (w, [NBu₄]⁺), 504 cm⁻¹ (w); ¹H NMR (400 MHz, CD₂Cl₂): δ =3.08 (m, ³*J*(¹⁹⁵Pt,¹H)=25 Hz, 4H; α-CH₂), 1.90 ppm (m, 4H; β-CH₂); ¹⁹F NMR (376.308 MHz, CD₂Cl₂): δ =-22.0 (septet, ⁴*J*(¹⁹F,¹⁹F)=3.8, ²*J*(¹⁹⁵Pt,¹⁹F)=868 Hz, 3F; CF₃ trans to THT), -24.1 ppm (q, ²*J*(¹⁹⁵Pt,¹⁹F)=490 Hz, 6F; mutually trans-standing CF₃).

Synthesis of [NBu₄]₂[Pt(CF₃)₃Cl] (9): ONMe₃ (28 mg, 0.37 mmol) was added to a solution of compound **2** (0.25 g, 0.37 mmol) and [NBu₄]Cl (0.52 g, 1.86 mmol) in CH₂Cl₂ (15 cm³) at room temperature. After 2 h of stirring, the solution was concentrated to dryness. By treating the resulting residue with *i*PrOH (3 cm³) at 0 °C, a white solid formed, which was filtered, washed with cold *i*PrOH (2×2 cm³) and *n*-hexane (3 cm³) and vacuum dried to give compound **9** (0.24 g, 0.26 mmol, 70 %). ¹⁹F NMR (282.231 MHz, CD₂Cl₂): $\delta = -16.49$ (septet, ⁴*J*(¹⁹F,¹⁹F) = 3.8, ²*J*(¹⁹⁵Pt,¹⁹F) = 922 Hz, 3F; CF₃ *trans* to Cl), -24.72 pm (q, ²*J*(¹⁹⁵Pt,¹⁹F) = 517 Hz, 6F; mutually *trans*-standing CF₃); IR (KBr): $\tilde{\nu} = 2964$ (vs), 2876 (s), 1482 (vs), 1419 (w), 1383 (m), 1349 (w), 1169 (w), 1139 (s), 1071 (vs), 1063 (vs), 1006 (s), 985 (vs), 957 (vs), 907 (m), 892 (m), 877 (m, [NBu₄]⁺), 797 (w), 748 (m, [NBu₄]⁺), 327 (m, Pt–Cl), 314 cm⁻¹ (w); elemental analysis calcd (%) for C₃₅H₇₂ClF₉N₂Pt: C 45.6, H 7.9, N 3.0; found: C 45.6, H 8.0, N 3.0.

Synthesis of [NBu₄]₂[Pt(CF₃)₃Br] (10): Compound **10** was prepared from compound **2** (0.25 g, 0.37 mmol), [NBu₄]Br (0.60 g, 1.86 mmol), and ONMe₃ (28 mg, 0.37 mmol) by using a similar procedure to that just described for the synthesis of compound **9**. Complex **10** was obtained as a white solid (0.27 g, 0.28 mmol, 75%). ¹⁹F NMR (282.231 MHz, CD₂Cl₂): $\delta = -18.31$ (septet, ⁴*J*(¹⁹F,¹⁹F)=4.1, ²*J*(¹⁹⁵Pt,¹⁹F)=947 Hz, 3F; CF₃ *trans* to Br), -23.86 ppm (q, ²*J*(¹⁹⁵Pt,¹⁹F)=519 Hz, 6F; mutually *trans*-standing CF₃); IR (KBr): $\bar{\nu}$ =2962 (vs), 2875 (s), 1482 (vs), 1420 (w), 1382 (m), 1348 (w), 1166 (w), 1137 (s), 1071 (vs), 1060 (vs), 1010 (s), 985 (vs), 960 (vs), 906 (m), 886 (m), 877 (m, [NBu₄]⁺), 802 (w), 786 (w), 740 cm⁻¹ (m, [NBu₄]⁺); elemental analysis calcd (%) for C₃₅H₇₂BrF₉N₂Pt: C 43.5, H 7.5, N 2.9; found: C 43.6, H 7.85, N 2.8.

Synthesis of [NBu₄]₂[Pt(CF₃)₃I] (11): Compound **11** was prepared from compound **2** (0.25 g, 0.37 mmol), [NBu₄]I (0.69 g, 1.86 mmol), and ONMe₃ (28 mg, 0.37 mmol) by using a similar procedure to that just described for the synthesis of compound **9**. Complex **11** was obtained as a white solid (0.31 g, 0.31 mmol, 82 %). ¹⁹F NMR (282.231 MHz, CD₂Cl₂): $\delta = -19.48$ (central signal heavily overlapped with the other one, ²*J*(¹⁹⁵Pt,¹⁹F)=520 Hz, 6F; mutually *trans*-standing CF₃), -19.53 ppm (central signal heavily overlapped with the other one, ²*J*(¹⁹⁵Pt,¹⁹F)=947 Hz, 3F; CF₃ *trans* to 1); IR (KBr): $\tilde{\nu} = 2959$ (vs), 2874 (s), 1481 (s), 1420 (w), 1382 (m), 1348 (w), 1166 (w), 1134 (s), 1109 (m), 1069 (vs), 1012 (s), 983 (vs), 969 (vs), 897 (m), 893 (m), 880 (m, [NBu₄]⁺), 798 (w), 738 (m, [NBu₄]⁺), 506 cm⁻¹ (w); elemental analysis calcd (%) for C₃₅H₇₂F₉IN₂Pt: C 41.5, H 7.2, N 2.8; found: C 41.5, H 7.5, N 3.0.

Synthesis of $[NBu_4][Pt(CF_3)_2(CF_2NC_5H_4S-\kappa C_5\kappa S)]$ (12): ONMe₃ (28 mg, 0.37 mmol) was added to a solution of compound 2 (0.25 g, 0.37 mmol)

and C₅H₅NS (45 mg, 0.41 mmol) in CH₂Cl₂ (15 cm³) at room temperature. After 3 h of stirring, the solution was concentrated to dryness. By treating the resulting residue with iPrOH (3 cm³) at 0°C, a yellowish solid formed, which was filtered, washed with cold *i*PrOH $(2 \times 2 \text{ cm}^3)$ and *n*hexane (3 cm^3) , and vacuum dried to yield compound 12 (0.21 g, 0.28 mmol, 77 %). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 8.11$ (ddd, ³J- $(H^5, H^6) = 6.8, {}^4J(H^4, H^6) = 1.5, {}^5J(H^3, H^6) = 0.75 \text{ Hz}, 1 \text{ H}; H^6), 7.52 \text{ (ddd, } {}^3J\text{-}$ $(H^3, H^4) = 8.4, {}^{3}J(H^4, H^5) = 6.8 \text{ Hz}, 1 \text{ H}; H^4), 7.44 (ddd, {}^{4}J(H^3, H^5) = 1.4 \text{ Hz}, 1 \text{ H}; H^3), 6.89 \text{ ppm} (ddd, 1 \text{ H}; H^5); {}^{13}C{}^{19}\text{F} \text{ NMR} (100.577 \text{ MHz}, 100.577 \text{ MHz})$ [D₆]acetone): $\delta = 174.07$ (CS), 145.69 (s, ${}^{1}J({}^{195}\text{Pt}, {}^{13}\text{C}) = 1067$ Hz; CF₂), 140.42 (d, ${}^{1}J({}^{1}H,{}^{13}C) = 167 \text{ Hz}$; C⁴H), 140.24 (s, ${}^{1}J({}^{195}\text{Pt},{}^{13}C) = 1287 \text{ Hz}$; CF₃ trans to CF₂), 137.03 (d, ${}^{1}J({}^{1}H,{}^{13}C) = 187$ Hz; C⁶H), 131.31 (s, ${}^{1}J({}^{195}\text{Pt},{}^{13}\text{C}) = 1918 \text{ Hz}; \text{ CF}_{3} \text{ trans to S}, 128.75 \text{ (d, } {}^{1}J({}^{1}\text{H},{}^{13}\text{C}) = 173 \text{ Hz};$ ¹⁹F NMR 116.33 ppm (d, ${}^{1}J({}^{1}H,{}^{13}C) = 167$ Hz; C⁵H); $C^{3}H$), (282.231 MHz, CD₂Cl₂): $\delta = -22.5$ (br, ${}^{2}J({}^{195}Pt, {}^{19}F) = 525$ Hz, 3F; CF₃ *trans* to C), -23.6 br, ${}^{2}J({}^{195}\text{Pt}, {}^{19}\text{F}) = 788$ Hz, 3 F; CF₃ *trans* to S), -55.85 ppm (br, ${}^{2}J({}^{195}\text{Pt}, {}^{19}\text{F}) = 392 \text{ Hz}, 2\text{ F}; \text{ CF}_{2}$); IR (KBr): $\tilde{\nu} = 2965$ (s), 2877 (m), 1618 (s), 1546 (s), 1480 (s), 1463 (s), 1419 (s), 1380 (w), 1270 (m), 1262 (m), 1180 (w), 1130 (vs), 1107 (m), 1073 (vs), 1051 (s), 1014 (vs), 985 (vs), 959 (vs), 881 (w; [NBu₄]⁺), 841 (m), 801 (w), 776 (m), 749 (w), 738 (w, $[NBu_4]^+$), 666 (w), 597 (w), 493 (w), 478 (w), 372 cm⁻¹ (w); elemental analysis calcd (%) for $C_{24}H_{40}F_8N_2PtS\colon C$ 39.2, H 5.5, N 3.8, S 4.4; found: C 40.15, H 5.7, N 4.0, S 5.0.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (15 cm^3) into a solution of compound **12** (15 mg) in CH₂Cl₂ (5 cm^3) at 4 °C.

Synthesis of [NBu₄][Pt(CF₃)₂(NC₅H₄S-κN,κS)] (13): Compound 13 was prepared from compound 3 (0.25 g, 0.39 mmol), pyridin-2-thiol (48 mg, 0.43 mmol), and ONMe₃ (30 mg, 0.39 mmol) by using a similar procedure to that just described for the synthesis of compound 5. Upon mixing the reagents, a slight precipitate formed (probably [NHMe₃]Cl), which was filtered off before proceeding farther. Complex 13 was obtained as a yellow solid (0.15 g, 0.22 mmol, 56 %). ¹H NMR (400 MHz, [D₆]acetone): $\delta = 7.91 \text{ (ddd, } {}^{3}J(\mathrm{H}^{5},\mathrm{H}^{6}) = 5.3, {}^{4}J(\mathrm{H}^{4},\mathrm{H}^{6}) = 1.7, {}^{3}J({}^{195}\mathrm{Pt},{}^{1}\mathrm{H}) = 31 \mathrm{Hz}, 1 \mathrm{H};$ H⁶), 7.26 (ddd, ${}^{3}J(H^{3},H^{4}) = 8.2$, ${}^{3}J(H^{4},H^{5}) = 6$ Hz, 1H; H⁴), 6.68 (ddd, ${}^{4}J$ - $(H^{3}, H^{5}) \approx 0.8 \text{ Hz}, 1 \text{ H}; H^{5}), 6.49 \text{ ppm} (ddd, 1 \text{ H}; H^{3}); {}^{13}\text{C}{}^{19}\text{F} \text{ NMR}$ (100.577 MHz, [D₆]acetone): $\delta = 182.03$ (CS), 145.46 (d, ${}^{1}J({}^{1}H, {}^{13}C) =$ 177 Hz, C⁴H), 136.24 (d, ${}^{1}J({}^{1}H,{}^{13}C) = 162$ Hz; C⁶H), 127.45 (d, ${}^{1}J$ - $({}^{1}H, {}^{13}C) = 174 \text{ Hz}; C^{3}H), 124 \text{ (s, } {}^{1}J({}^{195}\text{Pt}, {}^{13}C) = 1921 \text{ Hz}; CF_{3} \text{ trans to S}),$ 116.07 (d, ${}^{1}J({}^{1}H, {}^{13}C) = 168 \text{ Hz}; C^{5}H), 114.95 \text{ ppm}$ (s, ${}^{1}J({}^{195}\text{Pt}, {}^{13}C) =$ 1923 Hz; CF₃ trans to N); ¹⁹F NMR (376.308 MHz, [D₆]acetone): $\delta =$ -19.8 (q, ${}^{4}J({}^{19}F,{}^{19}F) = 2.5$, ${}^{2}J({}^{195}Pt,{}^{19}F) = 830$ Hz; CF₃ trans to S), $-22.02 \text{ ppm} (q, {}^{2}J({}^{195}\text{Pt}, {}^{19}\text{F}) = 754 \text{ Hz}; \text{ CF}_{3} \text{ trans to N}); \text{ IR (KBr): } \tilde{\nu} = 2962$ (s), 2877 (s), 1613 (w), 1582 (vs), 1552 (w), 1483 (s), 1459 (m), 1445 (m), 1427 (s), 1381 (m), 1275 (w), 1243 (w), 1128 (vs), 1100 (m), 1070 (vs), 1041 (m), 1017 (vs), 982 (vs), 957 (sh), 882 (m; [NBu₄]⁺), 801 (w), 761 (s), 739 (w, [NBu₄]⁺), 729 (m), 652 (w), 494 (w), 462 (w), 420 cm⁻¹ (w); elemental analysis calcd (%) for $C_{23}H_{40}F_6N_2PtS$: C 40.3, H 5.9, N 4.1, S 4.7; found: C 40.1, H 5.7, N 4.4, S 4.7.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (15 cm^3) into a solution of compound **13** (15 mg) in CH₂Cl₂ (5 cm^3) at 4 °C.

Synthesis of [NBu₄]₂[Pt(CF₃)₂]₂(**μ**-**Cl**)₂] (14): Compound 14 was prepared from compound 3 (0.50 g, 0.78 mmol) and ONMe₃ (60 mg, 0.78 mmol) by using a similar procedure to that just described for the synthesis of compound 5. Complex 14 was obtained as a white solid (0.28 g, 0.23 mmol, 58 %).¹⁹F NMR (282.231 MHz, CD₂Cl₂): $\delta = -22.89$ ppm (s, ²*J*(¹⁹⁵Pt,¹⁹F)=907 Hz); IR (KBr): $\tilde{\nu}$ =2966 (m), 2877 (w), 1470 (s), 1383 (w), 1261 (w), 1127 (vs), 1096 (m), 1069 (vs), 1046 (vs), 987 (vs), 926 (w), 878 (m, [NBu₄]⁺), 801 (w), 739 (s), 711 (w), 482 (w), 328 (m, Pt-Cl), 310 cm⁻¹ (m); elemental analysis calcd (%) for C₁₈H₃₆ClF₆NPt: C 35.4, H 5.9, N 2.3; found: C 35.1, H 6.05, N 2.2.

Synthesis of *cis*-[**Pt(CF₃)₂(thf)₂]** (15): AgClO₄ (85 mg, 0.41 mmol) was added to a solution of compound 14 (0.25 g, 0.20 mmol) in THF (20 cm³) at 0 °C under light exclusion and the mixture was stirred at the same temperature for 1 h. The resulting suspension was evaporated to dryness, the residue was extracted with Et_2O (30 cm³), and the insoluble components (AgCl and [NBu₄]ClO₄) were filtered off. The filtrate was evaporated to

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Table 2. Crystal data and structure refinement for compounds 2', 7, 12, 13, and 15.

	2'	7	12	13	15
formula	C ₂₈ H ₂₀ F ₉ OPPt	C40H57F9NPPt	$C_{24}H_{40}F_8N_2PtS$	$C_{23}H_{40}F_6N_2PtS$	$C_{10}H_{16}F_6O_2Pt$
M _r	769.50	948.93	735.73	685.72	477.32
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$Pca2_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	C2/c
a [pm]	2494.52(4)	1006.43(1)	1140.7(7)	924.89(1)	1912.99(6)
b [pm]	709.00(2)	2547.30(2)	1643.9(10)	1739.14(3)	919.96(3)
<i>c</i> [pm]	1484.80(3)	1554.01(1)	1472.7(10)	1670.28(3)	1531.49(5)
β [°]	90	97.605(1)	92.553(11)	91.052(2)	92.752(3)
$V [nm^3]$	2.62604(10)	3.94894(6)	2.759(3)	2.68621(7)	2.69212(15)
Z	4	4	4	4	8
$\rho_{\rm calcd} [\rm g cm^{-3}]$	1.946	1.596	1.771	1.696	2.355
$\mu [{\rm mm}^{-1}]$	5.490	3.666	5.232	5.356	10.489
F(000)	1480	1912	1456	1360	1784
2θ range [°]	7.6-57.9	7.6-50.2	3.7-50.0	7.7–53.2	7.8-50.2
reflns collected	15965	37360	14271	17509	8778
unique reflns	5103	7001	4865	5603	2391
R(int)	0.0204	0.0210	0.0753	0.0370	0.0585
transmission max/min	0.8526/0.3294	0.3149/0.4609	0.8180/0.4527	0.8143/0.2232	0.3022/0.1088
data/restraints/parameters	5103/1/361	7001/0/469	4865/553/408	5603/0/298	2391/242/238
final R indices $[I > 2\sigma(I)]^{[a]}$	$R_1 = 0.0172$	$R_1 = 0.0168$	$R_1 = 0.0502$	$R_1 = 0.0263$	$R_1 = 0.0357$
	$wR_2 = 0.0373$	$wR_2 = 0.0425$	$wR_2 = 0.1007$	$wR_2 = 0.0632$	$wR_2 = 0.0883$
R indices (all data)	$R_1 = 0.0223$	$R_1 = 0.0190$	$R_1 = 0.0865$	$R_1 = 0.0338$	$R_1 = 0.0454$
	$wR_2 = 0.0379$	$wR_2 = 0.0433$	$wR_2 = 0.1119$	$wR_2 = 0.0672$	$wR_2 = 0.0916$
$\operatorname{GOF}^{[b]}$ on F^2	1.016	1.065	1.028	1.046	1.016
absolute structure parameter	0.011(5)	-	_	-	-

[a] $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0$; $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$; $w = [\sigma^2(F_0^2) + (g_1P)^2 + g_2P]^{-1}$; $P = (1/3)[\max\{F_0^2, 0\} + 2F_c^2]$. [b] Goodness-of-fit = $[\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$; $w = [\sigma^2(F_0^2) + (g_1P)^2 + g_2P]^{-1}$; $P = (1/3)[\max\{F_0^2, 0\} + 2F_c^2]$. [b] Goodness-of-fit = $[\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$; $N = [\sigma^2(F_0^2) + (g_1P)^2 + g_2P]^{-1}$; $P = (1/3)[\max\{F_0^2, 0\} + 2F_c^2]$. [b] Goodness-of-fit = $[\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$; $P = (1/3)[\max\{F_0^2, 0\} + 2F_c^2]$. [b] Goodness-of-fit = $[\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$; $P = (1/3)[\max\{F_0^2, 0\} + 2F_c^2]$.

approximately 5 cm³ and *n*-hexane (30–40 cm³) was added. By allowing the mixture to stand at -35 °C for over one day, a yellow solid was obtained, which was filtered and vacuum dried to give compound **15** (0.12 g, 0.25 mmol, 61 %). ¹H NMR (300 MHz, CD₂Cl₂): δ = 4.02 (m, 4 H; α -CH₂), 1.97 ppm (m, 4H; β -CH₂); ¹⁹F NMR (282.231 MHz, CD₂Cl₂): δ = -26.6 ppm (s, ²*J*(¹⁹⁵Pt, ¹⁹F) = 929 Hz); IR (ATR): $\tilde{\nu}$ = 2971 (w), 2905 (w), 1484 (w), 1473 (w), 1461 (w), 1367 (w), 1349 (w), 1248 (w), 1142 (s), 1111 (m), 1078 (s), 1047 (s), 999 (sh), 978 (vs), 917 (m), 866 (s, THF: C-O-C), ^[56] 826 (m), 716 (w), 689 (w), 542 (w), 532 cm⁻¹ (w); elemental analysis calcd (%) for C₁₀H₁₆F₆O₂Pt: C 25.2, H 3.4; found: C 25.35, H 3.23.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane (15 cm³) into a solution of compound **15** (15 mg) in CH₂Cl₂ (5 cm³) at -35 °C.

X-ray structure determinations: Crystal data and other details of the structure analyses are presented in Table 2. Suitable crystals for X-ray diffraction studies, obtained as indicated in the corresponding experimental entry, were mounted at the end of quartz fibers. The radiation used in all cases was graphite monochromated Mo_{Ka} (λ = 71.073 pm). X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected for absorption by using the CrysAlis RED program.^[57]

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 with SHELXL-97.^[58] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the CH_3 atoms). In the structure of compound **12**, the electrondensity map clearly showed that the anion was disordered by a twofold rotation over two sets of positions, apparent at the sites of the atoms of the $CF_2NC_5H_4S$ ligand as the disorder leads the CF_3 groups to practically coincide with their counterparts. The geometry of the $CF_2NC_5H_4S$ ligand as well as the atomic displacement parameters were tightly restrained to be equal in both sites. A common occupation parameter was refined for all the atoms making up one site and the final values adopted were 0.56/ 0.44. It has to be considered that correlation among alternative atoms occupying close sites is bound to induce some distortion in the geometry determined, yet the connectivity and bond length range are clearly established. One of the CF₃ groups was disordered adopting two different rotational positions around the Pt–C bond, as has frequently been encountered. The occupation for the alternative sites was refined while restraining the atomic displacement parameters to be similar. In the structure of compound **15**, both the α -CH₂ units of the THF ligands and the F atoms were disordered over two sets of positions. Weak restraints were used in the geometry and thermal parameters of these disordered atoms. Fullmatrix least-squares refinement of these models against F^2 converged to final residual indices given in Table 2.

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CCDC-749438 (2'), 893040 (7), 749437 (12), 893038 (13), and 893039 (15) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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