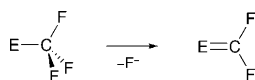


Trapping a Difluorocarbene–Platinum Fragment by Base Coordination**

Sonia Martínez-Salvador, Babil Menjón, Juan Forniés,* Antonio Martín, and Isabel Usón

Dedicated to Prof. Dr. H. W. Roesky on the occasion of his 75th birthday

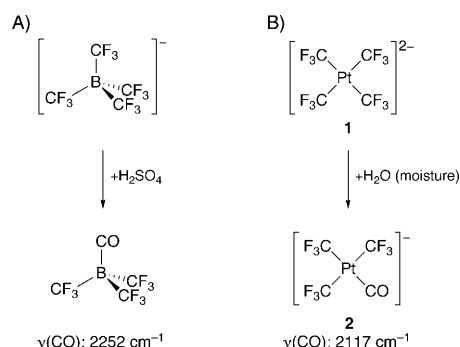
The trifluoromethyl group (CF₃) when bound to an element E of medium to high electronegativity behaves as a monovalent substituent with a high thermal stability and a marked chemical inertness. This low-reactivity profile together with its unique combination of electronic and steric properties have definitely encouraged the increasing use of CF₃ as a robust terminal group in modern organic chemistry.^[1] When bound to an electropositive atom, however, CF₃ becomes more reactive: α -fluoride elimination and the formation of a difluorocarbene unit (Scheme 1) is a general reaction path-



Scheme 1. α -Fluoride elimination process operating in trifluoromethyl derivatives of electropositive elements E.

way for such [E]–CF₃ species. This kind of reaction may occur spontaneously or require the action of an acid. The failure of preparations of LiCF₃ ($\chi_{\text{Li}} = 0.97$)^[2] has been attributed to the ready decomposition into LiF and :CF₂ even at very low temperatures.^[3] At the other extreme is the case of the highly stable tetrahedral anion [B(CF₃)₄][–], which required treatment with concentrated H₂SO₄ (Scheme 2A)^[4] to be brought into reaction ($\chi_{\text{B}} = 2.01$).^[2] The process presumably goes through the unstable difluorocarbene intermediate B(CF₃)₃(CF₂), which undergoes subsequent hydrolysis to give eventually the unusual carbonyl derivative B(CF₃)₃(CO).

Transition metals (TMs) belong to the class of moderately electropositive elements ($\chi_{\text{TM}} = 1.22$ – 1.75)^[2] and are therefore intermediate cases. This feature, together with the richness in



Scheme 2. Hydrolytic processes undergone by homoleptic tetrakis(trifluoromethyl) derivatives of A) main-group element boron (with K⁺ as counterion) or B) transition-metal element platinum (with [NBu₄]⁺ as counterion).

reactivity made possible by the availability of d orbitals, makes them attractive as potential agents leading to C–F bond activation,^[5] which is the reason why the chemistry of trifluoromethyl–transition-metal derivatives is receiving much current attention.^[6,7]

We have now observed that [NBu₄]₂[Pt(CF₃)₄] (**1**)^[8] undergoes a hydrolytic process to give the monocarbonyl derivative [NBu₄][Pt(CF₃)₃(CO)] (**2**) in high yield (Scheme 2B; for experimental details, see the Supporting Information). The reaction takes place under mild conditions and is effected simply by moisture. The ease with which one of the Pt-bound CF₃ groups in **1** is transformed into CO contrasts with other known precedents that require treatment of the appropriate trifluoromethylplatinum complex with acids as strong as HBF₄/Et₂O or HClO₄/H₂O.^[9] In this context, it is also interesting to note that, although a number of compounds containing the [TM]–CF₂ unit are known for Group 8 and 9 metals,^[10] none have been isolated for Pt, probably because of the high electrophilic character of the [Pt]–CF₂ moiety. The transformation of one of the anionic CF₃ groups within the square-planar (SP-4), homoleptic unit [Pt(CF₃)₄]^{2–} into the neutral, poorly σ -donating CO ligand deactivates the resulting [Pt(CF₃)₃(CO)][–] ion towards further hydrolysis. Compound **2** is, in fact, a fairly stable white solid, which can be handled in the air without alteration.

The structure of the (SP-4)-[Pt(CF₃)₃(CO)][–] ion (Figure 1) was established by X-ray diffraction methods^[11] on single crystals of the salt [PPh₄][Pt(CF₃)₃(CO)] (**2'**), which was obtained by following a simple metathetical process. The Pt–C(CF₃) bond lengths in **2'** are insensitive to the *trans*-standing ligand (CO vs. CF₃)^[12] and do not appreciably differ

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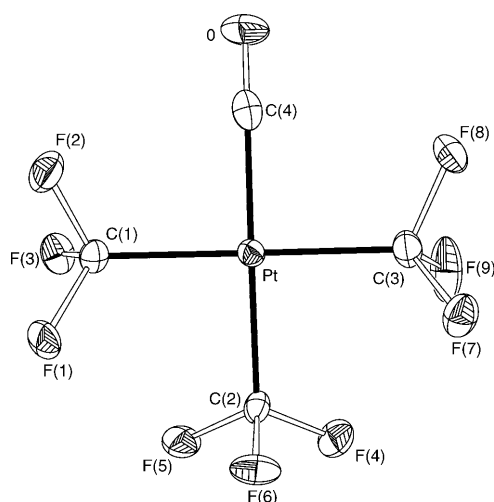
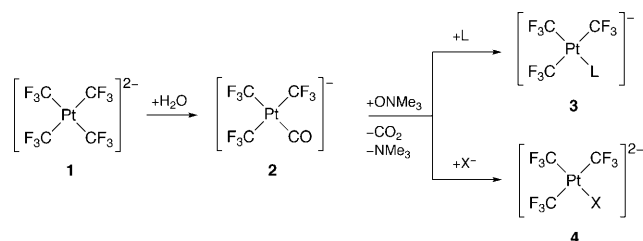


Figure 1. Thermal ellipsoid diagram (50% probability) of the $[\text{Pt}(\text{CF}_3)_3(\text{CO})]^-$ ion in **2'**. Selected bond lengths [pm] and angles $^\circ$ with estimated standard deviations: Pt–C(1) 207.5(4), Pt–C(2) 206.3(3), Pt–C(3) 206.5(3), Pt–C(4) 191.3(4), C(4)–O 113.4(4), average C–F 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).

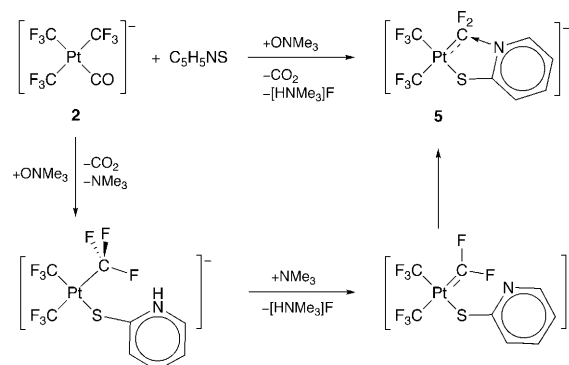
from those observed in the precursor species **1** (average Pt–C(CF_3) bond length 205.0(4) pm).^[8] The $\nu(\text{CO})$ frequency in **2'** is the highest within the $[\text{PtR}_3(\text{CO})]^-$ series: 2117 ($\text{R} = \text{CF}_3$) > 2084 ($\text{R} = \text{C}_6\text{F}_5$) > 2073 cm^{-1} ($\text{R} = \text{C}_6\text{Cl}_5$),^[13] thus denoting the lower electron density on the metal center where $\text{R} = \text{CF}_3$. This lack of electron density on the metal appears to be the main reason for the enhanced stability against hydrolysis of **2** (or **2'**) with respect to its parent species **1**.

Compound **2** reacts with a number of neutral (L) or anionic (X^-) ligands in the presence of trimethylamine *N*-oxide (ONMe_3), undergoing efficient replacement of CO by the incoming ligand L or X^- (Scheme 3). Following this procedure, a series of mono- or dianionic complexes of formula $[\text{NBu}_4][\text{Pt}(\text{CF}_3)_3(\text{L})]$ ($\text{L} = \text{CNCMe}_3$ (**3a**), PPh_3 (**3b**),^[14] $\text{P}(\text{2-MeC}_6\text{H}_4)_3$ (**3c**) and $[\text{NBu}_4]_2[\text{Pt}(\text{CF}_3)_3\text{X}]$ ($\text{X} = \text{Cl}$ (**4a**), Br (**4b**), I (**4c**)) can be easily obtained. Treatment of **2** with pyridin-2-thiol ($\text{C}_5\text{H}_5\text{NS}$) in the presence of ONMe_3 unexpectedly gave the *gem*-difluorinated metallacyclic com-



Scheme 3. Synthesis of the mono- or dianionic tris(trifluoromethyl)platinate(II) derivatives: $[\text{NBu}_4][\text{Pt}(\text{CF}_3)_3(\text{L})]$ ($\text{L} = \text{CNCMe}_3$ (**3a**), PPh_3 (**3b**), $\text{P}(\text{2-MeC}_6\text{H}_4)_3$ (**3c**) and $[\text{NBu}_4]_2[\text{Pt}(\text{CF}_3)_3\text{X}]$ ($\text{X} = \text{Cl}$ (**4a**), Br (**4b**), I (**4c**)). See the Supporting Information for experimental details.

pound $[\text{NBu}_4][\text{Pt}(\text{CF}_3)_2(\text{CF}_2\text{NC}_5\text{H}_4\text{S}-\kappa\text{C},\kappa\text{S})]$ (**5**) in good yield (Scheme 4; upper path). The reaction involves not only replacement of the CO ligand at **2** as observed in the



Scheme 4. Experimentally observed (upper path) formation of compound **5** (see the Supporting Information for details) together with the suggested reaction mechanism (lower path).

preceding cases, but also entails C–F bond activation and C–N coupling. This complex reaction can be rationalized by means of the following simple steps (Scheme 4; lower path): 1) ONMe_3 -assisted replacement of the CO ligand at **2** by the thione tautomer of $\text{C}_5\text{H}_5\text{NS}$; 2) α -fluoride elimination in one of the CF_3 groups *cis* to the S-donor atom promoted by the neighboring and moderately acidic pyridinium moiety,^[15,16] and 3) attack at the highly electrophilic C atom of the resulting difluorocarbene fragment by the *N*-donor atom of the anchored pyridine ligand.

The crystal and molecular structures of **5** have been established by single-crystal X-ray diffraction methods.^[11] The Pt center is in an approximate $SP-4$ environment (Figure 2) formed by two terminal CF_3 groups and the S- and C-donor atoms of the metallacycle. The Pt–C(CF_3) bond lengths are

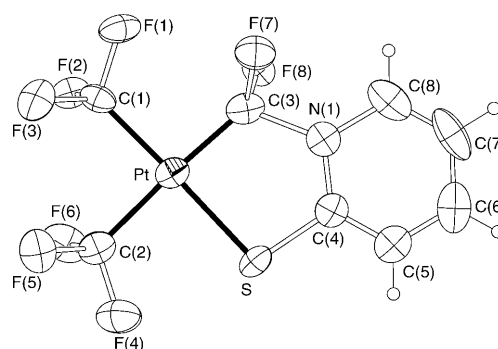
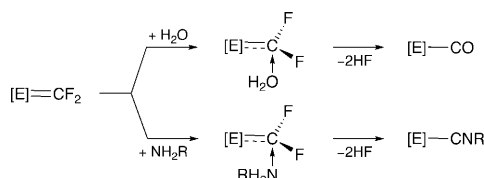


Figure 2. Thermal ellipsoid diagram (50% probability) of one of the two disordered $[\text{Pt}(\text{CF}_3)_2(\text{CF}_2\text{NC}_5\text{H}_4\text{S}-\kappa\text{C},\kappa\text{S})]^-$ ions in **5**. Selected bond lengths [pm] and angles $^\circ$ with estimated standard deviations: Pt–C(1) 200.1(9), 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).

virtually identical and slightly shorter than those found in the related species **1** and **2'**. The 5-membered metallacycle has a bite angle that is large enough not to induce heavy angular distortions in the overall *SP*-4 geometry around the Pt atom. The Pt–S bond length [231.0(5) pm] is typical of a terminal thiolatoplatinum(II) complex (ca. 232 pm).^[17] At first sight, this metallacycle could appear as a Pt derivative of a fluorinated *N*-ylide ligand. However, a closer look reveals geometric parameters associated with the CF₂ unit that are inconsistent with this bonding scheme. Thus, the N–C(CF₂) bond [160(3) pm] is much longer than that previously observed for an N(sp²)–C(CF₂) single bond (ca. 145 pm).^[18] The Pt–C(3)–F(7) and Pt–C(3)–F(8) bond angles are approximately 120° and significantly wider than the Pt–C–F angles associated with a terminal CF₃ group (ca. 115°). Moreover, the Pt–C(CF₂) bond length [185(2) pm] is much shorter than the usual Pt–C(CF₃) bonds (ca. 205 pm) and is comparable to the Pt–C(CO) bond length found in **2'** [191.3(4) pm]. In fact, the Pt–C(CF₂) bond length is quite similar to the Ir–C(CF₂) ones found in structurally characterized difluorocarbene–iridium compounds, such as [Ir(CF₃)(=CF₂)(CO)(PPh₃)₂] [187.4(7) pm],^[19] [Ir(η⁵-C₅Me₅)(=CF₂)(CO)] [185.5(13) pm],^[20] and [Ir(η⁵-C₅Me₅)(=CF₂)(PMe₃)] [185.4(11) pm].^[16] All these structural features suggest that compound **5** can be more appropriately described as a pyridine-stabilized difluorocarbene–platinum derivative. Related structural patterns had been observed in pyridine-stabilized silylene–metal derivatives^[21] in which the longer Si–N bond (ca. 195 pm vs. 170–176 pm for a normal Si–N single bond) was taken as evidence of a dative bond.^[22,23] In view of its structural properties, compound **5** can be considered a valid model for the initial step operating in the solvolysis (including hydrolysis) of difluorocarbene–element derivatives (Scheme 5).^[24] Of particular relevance to the present case is



Scheme 5. Suggested reaction path for solvolytic processes undergone by difluorocarbene element species.

the transformation of the [E]=CF₂ unit into a coordinated isocyanide ([E]–CNR), which is effected by reaction with a primary amine (NH₂R; Scheme 5).^[19] The reasonable stability of **5** can be attributed to the lack of H atoms bound to the N-donor atom as well as to the chelate effect.

In short, the homoleptic compound [NBu₄]₂[Pt(CF₃)₄] (**1**) was found to undergo stepwise CF₃ degradation under mild conditions. Evidence for the intermediacy of highly reactive [Pt]=CF₂ species was attained by the isolation of the ligand-stabilized adduct **5**, in which the CF₂ unit still preserves much of its original carbene nature.

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