Carbenes

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Trapping a Difluorocarbene–Platinum Fragment by Base Coordination**

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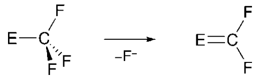
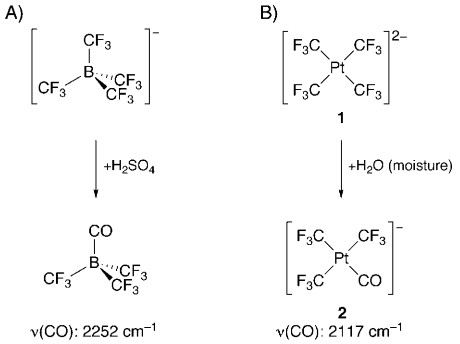
Dedicated to Prof. Dr. H. W. Roesky on the occasion of his 75th birthday

The trifluoromethyl group (CF_3) 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 CF_3 as a robust terminal group in modern organic chemistry.[1] When bound to an electropositive atom, however, CF_3 becomes more reactive: α-fluoride elimination and the formation of a difluorocarbene unit (Scheme 1) is a general reaction pathway for such [E]−CF_3 species. This kind of reaction may occur spontaneously or require the action of an acid. The failure of preparations of $LiCF_3$ ($\chi_{Li} = 0.97$)[2] has been attributed to the ready decomposition into LiF and :CF_2 even at very low temperatures.[3] At the other extreme is the case of the highly stable tetrahedral anion $[B(CF_3)_4]^-$, which required treatment with concentrated H_2SO_4 (Scheme 2 A)[4] to be brought into reaction ($\chi_B = 2.01$).[2] The process presumably goes through the unstable difluorocarbene intermediate $B(CF_3)_3(CF_2)$, which undergoes subsequent hydrolysis to give eventually the unusual carbonyl derivative $B(CF_3)_3(CO)$.



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

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



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 $[NBu_4]^+$ as counterion).

We have now observed that $[NBu_4]_2[Pt(CF_3)_4]$ (**1**)[8] undergoes a hydrolytic process to give the monocarbonyl derivative $[NBu_4][Pt(CF_3)_3(CO)]$ (**2**) in high yield (Scheme 2 B; 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 CF_3 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 HBF_4/Et_2O or $HClO_4/H_2O$.[9] In this context, it is also interesting to note that, although a number of compounds containing the [TM]=CF_2 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]=CF_2 moiety. The transformation of one of the anionic CF_3 groups within the square-planar (*SP*-4), homoleptic unit $[Pt(CF_3)_4]^{2-}$ into the neutral, poorly σ-donating CO ligand deactivates the resulting $[Pt(CF_3)_3(CO)]^-$ 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)-$[Pt(CF_3)_3(CO)]^-$ ion (Figure 1) was established by X-ray diffraction methods[11] on single crystals of the salt $[PPh_4][Pt(CF_3)_3(CO)]$ (**2′**), which was obtained by following a simple metathetical process. The Pt−C(CF_3) bond lengths in **2′** are insensitive to the *trans*-standing ligand (CO vs. CF_3)[12] and do not appreciably differ

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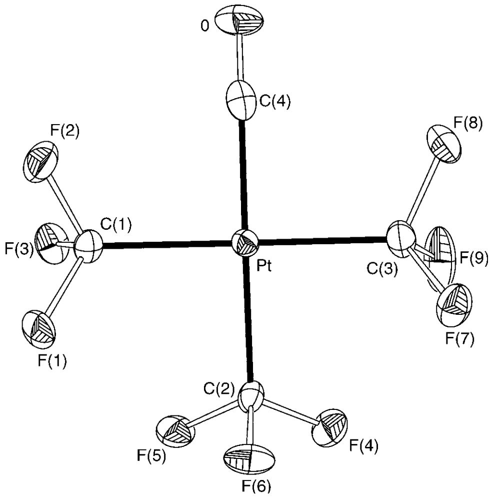
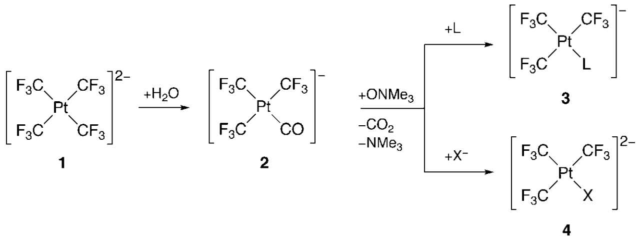


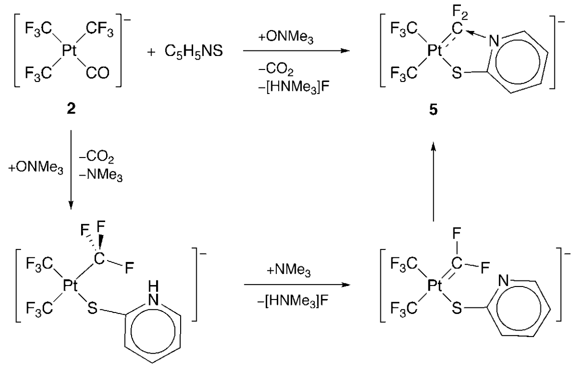
Figure 1. Thermal ellipsoid diagram (50 % probability) of the $[Pt(CF_3)_3(CO)]^-$ ion in **2'**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pt–C(1) 207.5(4), Pt–C(2) 206.3(3), Pt–C(3) 206.5(3), Pt–C(4) 191.3(4), C(4)–O 113.4(4), average C–F 136.8(4), C(1)-Pt-C(2) 91.1(1), 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).

from those observed in the precursor species **1** (average Pt–$C(CF_3)$ bond length 205.0(4) pm).[8] The ν(CO) frequency in **2'** is the highest within the $[PtR_3(CO)]^-$ series: 2117 ($R = CF_3$) > 2084 ($R = C_6F_5$) > 2073 cm^{-1} ($R = C_6Cl_5$),[13] thus denoting the lower electron density on the metal center where $R = CF_3$. 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 $[NBu_4][Pt(CF_3)_3(L)]$ ($L = CNCMe_3$ (**3a**), PPh_3 (**3b**),[14] $P(2\text{-}MeC_6H_4)_3$ (**3c**)) and $[NBu_4]_2[Pt(CF_3)_3X]$ (X = Cl (**4a**), Br (**4b**), I (**4c**)) can be easily obtained. Treatment of **2** with pyridin-2-thiol (C_5H_5NS) in the presence of $ONMe_3$ unexpectedly gave the *gem*-difluorinated metallacyclic compound $[NBu_4][Pt(CF_3)_2(CF_2NC_5H_4S\text{-}\kappa C,\kappa S)]$ (**5**) in good yield (Scheme 4; upper path). The reaction involves not only replacement of the CO ligand at **2** as observed in the 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 C_5H_5NS; 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.



Scheme 3. Synthesis of the mono- or dianionic tris(trifluoromethyl)platinate(II) derivatives: $[NBu_4][Pt(CF_3)_3(L)]$ ($L = CNCMe_3$ (**3a**), PPh_3 (**3b**), $P(C_6H_4Me\text{-}2)_3$ (**3c**)) and $[NBu_4]_2[Pt(CF_3)_3X]$ (X = Cl (**4a**), Br (**4b**), I (**4c**)). See the Supporting Information for experimental details.



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

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

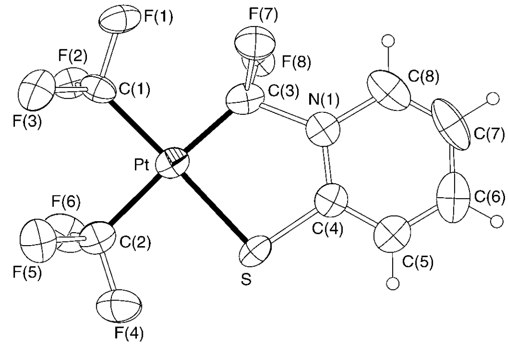
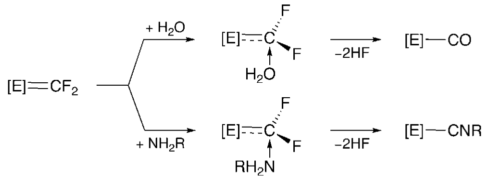


Figure 2. Thermal ellipsoid diagram (50 % probability) of one of the two disordered $[Pt(CF_3)_2(CF_2NC_5H_4S\text{-}\kappa C,\kappa S)]^-$ ions in **5**. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Pt–C(1) 200.1(9), Pt–C(2) 202.9(9), Pt–C(3) 185(2), Pt–S 231.0(5), average 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 CF$_2$ unit that are inconsistent with this bonding scheme. Thus, the N–C(CF$_2$) bond [160(3) pm] is much longer than that previously observed for an N(sp^2)–C(CF$_2$) 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 CF$_3$ group (ca. 115°). Moreover, the Pt–C(CF$_2$) bond length [185(2) pm] is much shorter than the usual Pt–C(CF$_3$) 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(CF$_2$) bond length is quite similar to the Ir–C(CF$_2$) ones found in structurally characterized difluorocarbene–iridium compounds, such as [Ir(CF$_3$)(=CF$_2$)(CO)(PPh$_3$)$_2$] [187.4(7) pm],[19] [Ir(η^5-C$_5$Me$_5$)(=CF$_2$)(CO)] [185.5(13) pm],[20] and [Ir(η^5-C$_5$Me$_5$)(=CF$_2$)(PMe$_3$)] [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 the transformation of the [E]=CF$_2$ unit into a coordinated isocyanide ([E]–CNR), which is effected by reaction with a primary amine (NH$_2$R; 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.



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

In short, the homoleptic compound [NBu$_4$]$_2$[Pt(CF$_3$)$_4$] (**1**) was found to undergo stepwise CF$_3$ degradation under mild conditions. Evidence for the intermediacy of highly reactive [Pt]=CF$_2$ species was attained by the isolation of the ligand-stabilized adduct **5**, in which the CF$_2$ unit still preserves much of its original carbene nature.

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