

How to cite: *Angew. Chem. Int. Ed.* **2024**, e202403108
 doi.org/10.1002/anie.202403108

Mechanistic Investigations

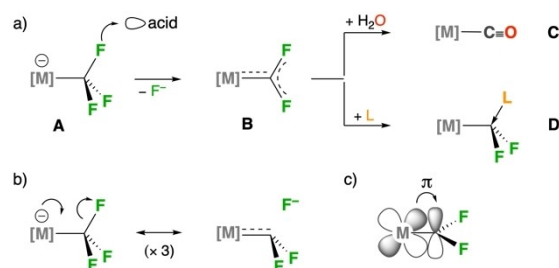
 The CF₃ Group as a Synthon of the CF⁺ Unit in Palladium Chemistry

Daniel Joven-Sancho, Miguel Baya, Antonio Martín, Jesús Orduna, and Babil Menjón*

Dedicated to Prof. Dr. Dieter Naumann

Abstract: The homoleptic trifluoromethyl-palladium(II) complex [Pd(CF₃)₄]²⁻ (**1**) is shown to be highly active towards amines. Thus, when treated with primary amines RNH₂, it readily undergoes aminolysis of one of the CF₃ ligands affording the isocyanide complexes [(CF₃)₃Pd(CNR)]⁻ (R = aryl). In this process the original CF₃ group undergoes total defluorination. Interestingly, the reaction of **1** with secondary amines R₂NH proceeds with loss of just two F-substituents, whereby the Fischer-type fluoroaminocarbene complexes [(CF₃)₃Pd-(CFNR₂)]⁻ are formed (R = Et, Ph). The reaction of **1** with diamines affords different [(CF₃)₃Pd(NHC)]⁻ complexes containing sterically non-demanding NHC ligands. Representative examples of various topologies are reported based on the common imidazolidin-2-ylidene or benzimidazolin-2-ylidene rings as well as the expanded-ring perimidin-2-ylidene. This metal-tailored synthetic route, where a CF₃ group acts as a pre-carbenic unit, is unprecedented in the vast NHC-chemistry. It takes place under very mild conditions and is envisaged to be extensible to other non-isolable NHC ligands. The key difluorocarbene intermediate [(CF₃)₃Pd(CF₂)]⁻ is experimentally detected.

The trifluoromethyl group is a common source of difluorocarbene in transition-metal (TM) chemistry.^[1] Defluorination of the former usually requires the action of a Brønsted or Lewis acid of varied strength^[2] (Scheme 1a) depending of the extent of the negative hyperconjugation operating in the [M⁺]CF₃ unit (Scheme 1b).^[3] In fact, the [M⁺]CF₃ and [M]CF₂ entities can be considered as conjugate species in the fluoride exchange process: **A** ⇌ **B** + F⁻. The stability of



Scheme 1. Acid-promoted fluoride abstraction from a CF₃ group affording a difluorocarbene unit and ensuing typical reactivity (a), together with the negative hyperconjugation underlying the intimate relationship between the [M⁺]CF₃ and [M]CF₂ units (b) and the possible π bonding interaction in the latter (c).

the difluorocarbene moiety thus formed, [M]CF₂, greatly varies with the metal, its oxidation state and the ancillary ligands in the complex. The underlying reason for this variation is the extent of π -back donation from occupied M(d) orbitals to the C(p) orbital perpendicular to the CF₂ plane (Scheme 1c). The steady stabilization of the d orbitals on moving rightwards in the TM series results in less efficient π -back donation in late-TMs. The corresponding M–CF₂ bond length becomes longer and the mentioned C(p) orbital becomes less populated thus rendering the carbene C atom more electrophilic. For this reason the [M]CF₂ unit becomes less stable and more reactive, which explains the scarcity of terminal [M]CF₂ units in very late-TMs.^[4] In fact, very few terminal difluorocarbene complexes of low-valent Ni(0), Pd(0), Cu(I) and Au(I) (all of them d¹⁰ ions) have been detected or isolated thus far.^[5] The low stability and high reactivity of the [M]CF₂ unit is even more pronounced as the metal oxidation states increases. In fact, the only precedents for late-TMs in a higher oxidation state are the d⁸ complexes [M(PCP)(CF₂)]⁺ (M = Ni, Pd)^[6] and [trans-PtH(CF₂)(PPh₃)₂]⁺.^[7] In a number of instances, the electrophilic [M]CF₂ unit can be stabilized by coordination of a donor, [M]CF₂·L (**D**).^[8]

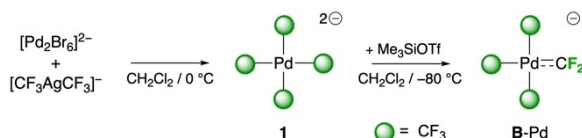
Based on our own experience with the homoleptic platinum(II) complex [Pt(CF₃)₄]²⁻,^[9] we turned to study the reactivity of the lighter homologous palladium(II) complex [Pd(CF₃)₄]²⁻ originally prepared by Naumann.^[10] Enhanced C–F activity has been found and exploited in various amination processes enabling facile access to fluoroaminocarbene and NHC units (Fischer and Wanzlick carbenes, respectively). The key difluorocarbene intermediate [(CF₃)₃Pd(CF₂)]⁻ (**B**-Pd) is also detected.

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Inspired by Pérez-Temprano's work^[11] we have succeeded to prepare the homoleptic compound $[\text{PPh}_4][\text{Pd}(\text{CF}_3)_4]$ (**1**) by reacting $[\text{NBu}_4][\text{Pd}_2\text{Br}_6]$ with $[\text{PPh}_4][\text{CF}_3\text{AgCF}_3]$ (Scheme 2). After the appropriate workup, compound **1** was isolated as a white solid in 66 % yield and was characterized by analytical and spectroscopic methods. The structure of the $[\text{Pd}(\text{CF}_3)_4]^{2-}$ anion has been first determined by single-crystal X-ray diffraction (sc-XRD) analysis.^[12] It has an almost perfect square-planar (*SP*-4) geometry (Figure 1a, Table 1) with the interatomic Pd–C distance (206.5(2) pm av.) being comparable to the Pt–C distance (205.0(4) pm, av.) found in the heavier homologous complex.^[13] The corresponding Ni–C distance in $[\text{PPh}_4][\text{Ni}(\text{CF}_3)_4]$ is, in turn, substantially shorter: 193.0(4) pm, av.^[14] It is worth noting that the Ni complex shows an apparent D_{2d} distortion (*trans* C–Ni–C 167.3(2)° av.), whereas the anion of **1** is strictly planar (*trans* C–Pd–C 180°), as imposed by symmetry (Table 1). In fact, the palladium complex has the



Scheme 2. Synthesis of **1** and its transformation into $[(\text{CF}_3)_3\text{Pd}(\text{CF}_2)]^-$ (B-Pd).

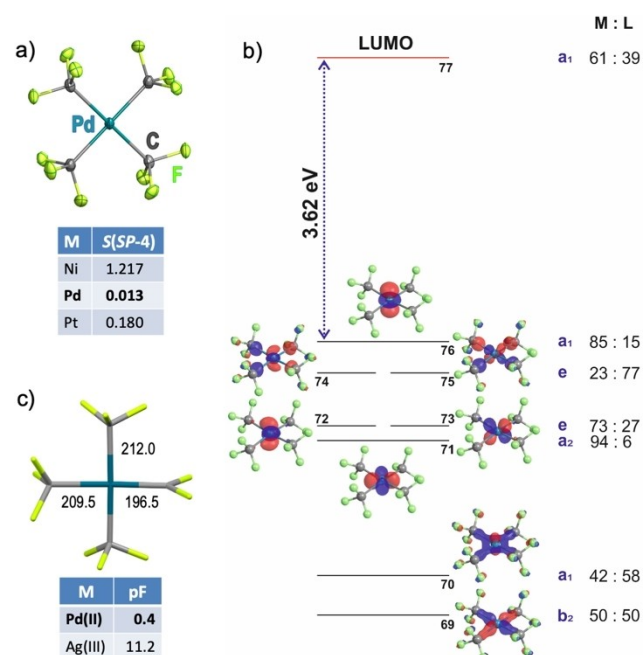


Figure 1. (a) Displacement-ellipsoid diagram (50% probability) of the $[\text{Pd}(\text{CF}_3)_4]^{2-}$ anion as found in single crystals of **1** (relevant geometric parameters given in Table 1) and $S(\text{SP-4})$ values^[15] for all three Group 10 $[\text{M}(\text{CF}_3)_4]^{2-}$ anions. (b) Calculated electronic structure of the $[\text{Pd}(\text{CF}_3)_4]^{2-}$ anion with indication of the percental M:L contribution to each level. (c) Optimized structure of $[(\text{CF}_3)_3\text{Pd}(\text{CF}_2)]^-$ (B-Pd) with indication of the calculated M–C bond lengths [pm] and the pF value^[18] compared to that corresponding to the Ag(III) homologous complex. (See Supporting Information for details)

Table 1: Relevant structural parameters of the mononuclear complexes $[\text{PPh}_4]_n[(\text{CF}_3)_3\text{Pd}(\text{L})]$, as established by sc-XRD methods.^[a]

L	Pd–L [pm]	LPd–CF ₃ [pm] ^[b]	av. Pd–C ₂ [pm] ^[d]	CF ₃ –Pd–L [°] ^[c]
CF ₃ (1)	–	–	206.5(2)	180 ^[e]
PhNC (2)	198.9(2)	205.2(2)	206.4(2)	176.90(6)
<i>o</i> -FC ₆ H ₄ NC (3)	198.4(3)	203.7(3)	206.7(4)	173.6(1)
<i>o</i> -(NH ₂)C ₆ H ₄ NC (4)	198.7(2)	204.8(2)	206.1(3)	178.3(1)
Ph ₂ NC(F) (6)	199.5(2)	204.4(2)	205.7(2)	176.19(7)
PhNHC ₂ H ₄ NPhCF (7)	201.3(2)	204.7(2)	206.0(2)	178.03(7)
SiMe (9)	203.2(3)	205.0(3)	205.2(3)	176.6(1)
BnIme ₂ (10) ^[f]	203.5(1)	206.1(2)	206.6(2)	175.34(6)
BnIHMe (11) ^[g]	203.2(2)	205.3(2)	205.2(2)	175.9(7)
PPh ₃ ^[h]	238.2(4)	205(2)	208.6(10)	177.9(6)

[a] Full details given in the Supporting Information. [b] The Pd–CF₃ distance *trans* to the neutral ligand L is here indicated. [c] Average of the independent Pd–CF₃ bond lengths in *trans* arrangement. [d] *trans*-standing C–Pd–L unit. [e] Imposed by symmetry: the Pd atom lays at an inversion center. [f] BnIme₂ = *N,N'*-dimethylbenzimidazolin-2-ylidene. [g] BnIHMe = *N*,*m*-methylbenzimidazolin-2-ylidene. [h] Ref. [10]

most regular geometry of all three $[\text{M}(\text{CF}_3)_4]^{2-}$ anions in the Group 10 metals, as clearly indicated by the corresponding values of continuous shape measure (Figure 1) for square-planar geometry, $S(\text{SP-4}) = 1.217$ (Ni), 0.013 (Pd), 0.18 (Pt).^[15]

The electronic structure of the $[\text{Pd}(\text{CF}_3)_4]^{2-}$ anion has been studied by computational methods at the DFT/M06 level (Figure 1b). We find that the frontier MOs are mainly contributed by the metal: the HOMO has 85 % Pd d_{z^2} character and the LUMO has 61 % Pd participation. The MOs with major contribution of the d_{xy} and the degenerate (d_{xz} , d_{yz}) metal AOs (levels 71–73) are quite close to the HOMO (level 76). The bonding MO with $d_{x^2-y^2}$ metal character (level 69) has equal contribution from the ligand system (50:50), which we take as clear evidence for covalency in the Pd–C bond. The electronic structure is therefore in agreement with the ligand-field model and in line with that previously calculated for the heavier Pt(II)^[13] and the lighter Ni(II)^[14] homologues. It is, however, in contrast to that of the silver(III) complex $[\text{Ag}(\text{CF}_3)_4]^-$, which was identified as a clear case of ligand-field inversion.^[16] The contrasting electronic structure of these isoelectronic and isostructural species of the neighbour elements Pd and Ag is particularly relevant and denotes a sharp break between Groups 10 and 11.^[17] A structural comparison of this homologous couple reveals that the M–C bond length is elongated on going from Pd (206.5(2) pm av.) to Ag (209.8(2) pm av.),^[16] whereas the opposite applies to the corresponding C–F bond: 138.5(2) (Pd) vs. 134.4(3) (Ag) pm av. A shorter M–C bond and a longer C–F one can be taken as evidence of increased negative hyperconjugation operating in the CF₃ group of the Pd(II) complex (Scheme 1b). Accordingly, the energy required to release a single F[−] anion from complex **1** is fairly low as estimated by calculation: 4.3 kcalmol^{−1}. The conjugate difluorocarbene complex $[(\text{CF}_3)_3\text{Pd}(\text{CF}_2)]^-$ (Figure 1c) shows, in turn, a remarkably low fluoride-ion affinity (FIA) with an equally low pF value (0.4) in the Christie's quantitative scale for

Lewis acidity (Table S22).^[18] This picture suggesting enhanced reactivity of the CF₃ group in complex **1** finds experimental support, as we will show next. The homologous silver(III) difluorocarbene complex (CF₃)₃Ag(CF₂) should be, in turn, strongly fluorophilic according to its high pF value (11.2).^[19]

The first experimental evidence of high C–F activity in **1** is the detection in its MS of a distinct peak corresponding to the conjugate difluorocarbene complex **B**-Pd with the characteristic isotopic pattern and the correct exact mass

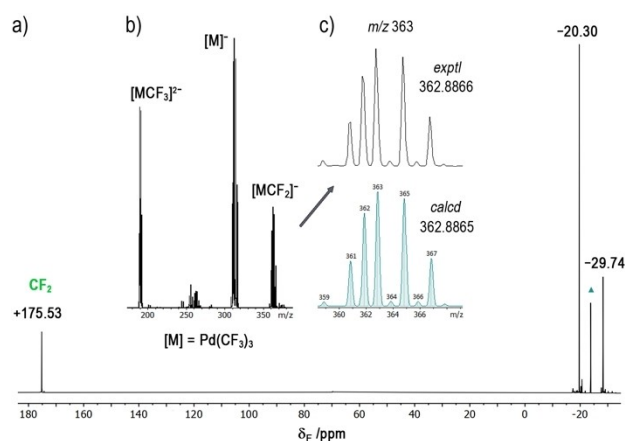
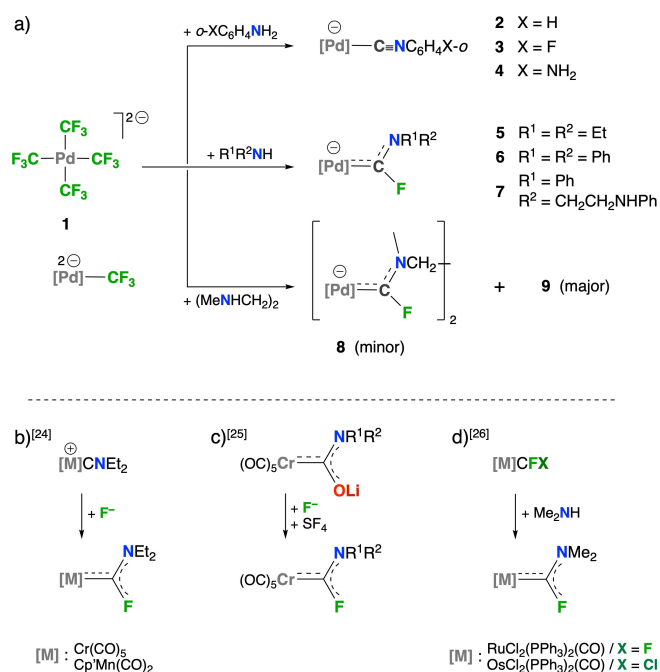


Figure 2. Spectroscopic detection of the difluorocarbene complex [(CF₃)₃Pd(CF₂)][−] (**B**-Pd): ¹⁹F NMR at −60 °C (a) and ESI-MS (b). The pattern of the characteristic MS peak as well as the exact mass (c) are fully satisfactory (Table S1). In the ¹⁹F NMR spectrum, unreacted **1** (▲, < 10%) is still observed.



Scheme 3. a) Reactivity of **1** with primary and secondary amines. b–d) Procedures leading to the known fluoroaminocarbene metal pre-cursors, all of them involving mid-TMs (Cp' = η⁵-C₅H₄Me).^[24–26]

(Figure 2; Table S1). Moreover, we also succeeded to detect complex **B**-Pd in solution by treating **1** with Me₃SiOTf in CH₂Cl₂ at −80 °C (Scheme 2): The low-temperature ¹⁹F NMR spectrum (Figure 2a) shows a downfield signal at δ_F = +175.53 ppm characteristic of a [M]CF₂ unit.^[5–7]

Compound **1** readily reacts with aniline under very mild conditions (Scheme 3a) to afford the isocyanide complex [PPh₄][(CF₃)₃Pd(CNPh)] (**2**), which can be isolated in 75 % yield. In the process, small amounts of the hydrolysis product [(CF₃)₃Pd(CO)][−] (**C**-Pd) are always formed, but are cleanly eliminated with the appropriate workup. The introduction of an electron-withdrawing (F) or electron-donor (NH₂) substituent in *ortho* position of the aniline phenyl ring has no significant effect in the reaction outcome with the corresponding complexes **3** and **4** being isolated in ca. 70 % yield (Scheme 3a). This one-step operational transformation is unprecedented and reveals an unusual activity of the CF₃ group. Amination of transient or isolated difluorocarbene metal complexes to afford the corresponding isocyanides was already known.^[21] In our system, however, the high activity of the CF₃ group makes a separate activation step unnecessary. The reagent-compatibility issue is particularly critical in the case of amines, as they would be neutralized by any acid (Brønsted or Lewis) used to promote the initial defluorination step, as generally required (Scheme 1a). The reaction is also highly selective, whereby a single CF₃ group is transformed. The high selectivity relies on the deactivation suffered by the complex upon replacement of a charged CF₃ group by a neutral one (RNC). This deactivation had already been noted^[20] and will equally operate in all subsequent reactions.

The ¹⁹F NMR spectra of compounds **2–4** show a common pattern consisting of a quartet (mutually *trans* CF₃ groups: CF₃—Pd—CF₃) and a septet (CF₃ group *trans* to the heteroligand: CF₃—Pd—L) in 2:1 integrated ratio (Figures S2–S4).^[22] The crystal and molecular structures of compounds **2–4** have been established by sc-XRD methods.^[12] The structure of the anion of **2** is shown in Figure 3a. The observed Pd—CNR bond lengths in all these *SP*-4 complexes are in the narrow range between 198.4(2) and 198.9(2) pm (Table 1), in good agreement with the standard value in four-coordinate isocyanide complexes of palladium: 197.8 pm.^[23a] In the crystal of **4**, both H atoms of the pendant amino function build a network of intra- and intermolecular H-bonding interactions with neighboring F atoms (Figure S14). The tautomerization of **4** will be commented below.

The unusually high activity of complex **1** towards anilines can be extended to secondary amines. Thus, compound **1** readily reacts with the equimolar amount of R₂NH (Scheme 3a) affording the Fischer-type carbene complexes [PPh₄]-[(CF₃)₃Pd(CFNR₂)] [R = Et (**5**), Ph (**6**)], which are isolated as analytically pure solids. It is worth noting that one of the C–F bonds in the original CF₃ group is preserved in the final product. The remaining F atom in the carbene ligand shows characteristic signals at δ_F +29.79 (**5**) and +49.75 (**6**) ppm in the corresponding ¹⁹F NMR spectra (Figures S5 and S6). This distinct nucleus is thus strongly deshielded with respect to the accompanying CF₃ groups, which show the typical pattern of the (CF₃)₃ML unit (see above) in the usual range

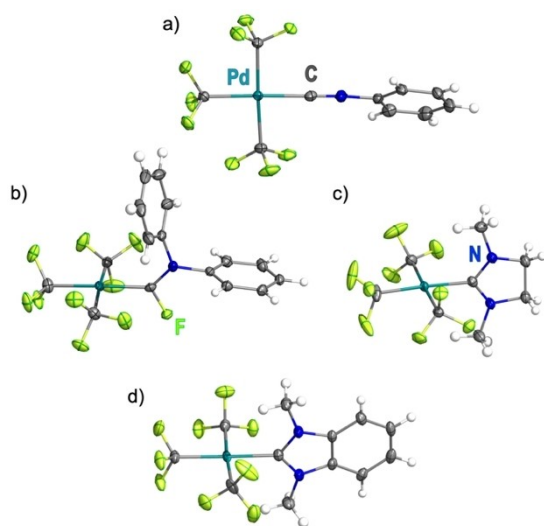


Figure 3. Displacement-ellipsoid diagram (50% probability) of the $[(\text{CF}_3)_3\text{Pd}(\text{CNPh})]^-$ (a), $[(\text{CF}_3)_3\text{Pd}(\text{CFNPh}_2)]^-$ (b), $[(\text{CF}_3)_3\text{Pd}(\text{SiMe})]^-$ (c), and $[(\text{CF}_3)_3\text{Pd}(\text{BnIme}_2)]^-$ (d) anions as found in single crystals of **2**, **6**, **9** and **10**, respectively (relevant geometric parameters given in Table 1).

(−20 to −40 ppm). In the ^{13}C NMR spectra, the carbene-C signal was located at δ_{C} 224.7 (**5**) and 232.2 (**6**) ppm. The connection of the distinct F nucleus with the carbene-C atom was confirmed by heterocorrelation NMR experiments. The presence of the fluoroaminocarbene ligand in complex **6** was confirmed by sc-XRD methods (Figure 3b).^[12] The C–F bond length in the carbene moiety (134.55(18) pm) perfectly matches that tabulated for a $\text{C}(\text{sp}^2)\text{--F}$ bond (134.0(13) pm),^[23b] which indicates little π delocalization of the F(p) electron density onto the carbene C atom. On the other hand, the C–N bond (130.3(2) pm) is comparable to the $\text{C}=\text{N}^{(+)}$ double bond in furoxan (131.6 (9) pm), where the N atom also bears a formal positive charge (furoxan = 1,2 λ^5 ,5-oxadiazol-2-one).^[23b] This shortening suggests significant π -donation from the amine NR_2 group, which results in a $\text{C}=\text{N}$ double bond, in keeping with the planarity of the N atom: $\Sigma(\text{C}=\text{N}=\text{C}')=360.0(1)^\circ$. The structure of the $[(\text{CF}_3)_3\text{Pd}(\text{CFNPh}_2)]^-$ anion was also optimized in the gas phase and found to be in good agreement with that experimentally found in the crystal (Figure S17b). The double-bond character of the $\text{FC}=\text{NR}_2$ unit is further confirmed by the chemical inequivalence of the R substituents in the ^1H and ^{13}C NMR spectra of compounds **5** and **6**. It also explains the formation of two isomers of **7** (Scheme 3a) in the reaction of **1** with a secondary amine bearing different substituents, $\text{R}^1\text{R}^2\text{NH}$, as commented in detail in the Supporting Information.

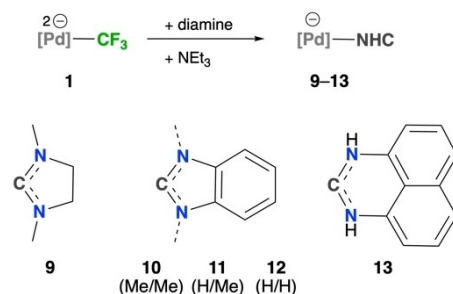
Fluoroaminocarbene ligands are extremely rare and limited to mid-TMs. It was Fischer who prepared the earliest precedents by fluoride addition to electrophilic carbynes $[\text{M}]\equiv\text{CNEt}_2$ of Cr and Mn (Scheme 3b).^[24] The remaining precedents were prepared starting from a preformed metal-carbene moiety of either Group 6 (Scheme 3c)^[25] or Group 8 metals (Scheme 3d).^[26] In our system, direct transformation of the CF_3 group into a CFNR_2 unit takes place straightfor-

wardly under very mild conditions. The one-pot process certainly involves the difluorocarbene $[(\text{CF}_3)_3\text{Pd}(\text{CF}_2)]^-$ (**B-Pd**) intermediate, but there is no need to prepare it in a separate step because of the high activity of the C–F unit in the starting material **1**.

The reaction of **1** with the 1,2-diamine $\text{MeNHCH}_2\text{CH}_2\text{NHMe}$ (dmeda) in the presence of NEt_3 afforded the NHC-complex $[(\text{CF}_3)_3\text{Pd}(\text{SiMe})]^-$ (**9**) as the major product (Scheme 3a). The formation of the dinuclear complex **8** as a minor product^[12] suggests the intermediacy of a mononuclear fluoroaminocarbene complex similar to **7**, which undergoes subsequent ring closure. The overall process involves full defluorination of a single CF_3 group and cyclisation. The generality of our simple, one-pot procedure was demonstrated by using a set of carefully selected diamines, which furnish representative examples of NHC ligands with various ring topologies (Scheme 4). In this way, complexes **9–13** were actually obtained and spectroscopically characterized. Two roughly related precedents of our methodology require prior synthesis of the highly active dichlorocarbene complexes $[\text{RuCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2]$ ^[27a] or $[\text{IrCl}_3(\text{CCl}_2)(\text{PPh}_3)_2]$.^[27b] To the best of our knowledge, our metal-tailored synthesis of a NHC ligand with a CF_3 group acting as a pre-carbenic unit is unprecedented in the vast NHC chemistry.^[28] This method is particularly suited for non-isolable NHC ligands (Wanzlick carbenes)^[29] and provides a convenient alternative to the classical dimer (enetetramine) method.^[30] We note that in the NHC ligands of compounds **9–13**, the N atoms bear either the small substituent methyl or bare H with little or no steric shielding.^[31]

It is also worth noting that compound **12** is a ring-chain tautomer of **4**. The intermediacy of the latter in the synthesis of the former has been confirmed experimentally. Compound **4**, which arises by reaction of **1** with *o*-phenylenediamine (Scheme 3a), further reacts with NEt_3 to afford **12** as the result of an intramolecular cyclization process. Here, the NEt_3 base has a catalytic role, acting merely as a proton-carrier. We therefore provide both the intermediate and the final product in the frequently suggested intramolecular nucleophilic attack by a pendant amino function at an isocyanide carbon atom.^[32]

In the ^{13}C NMR spectra of **9–13**, the carbene-C signal appears in the range 210–185 ppm (see Supporting Information). The ^{19}F NMR spectra show the typical pattern of the



Scheme 4. Metal-template, one-pot synthesis of NHC ligands by cyclization of diamines using a CF_3 group as a pre-carbene unit.

(CF₃)₃ML moiety with a π -acceptor ligand (Figures S7–S12). The crystal structures of **9–11** were established by sc-XRD methods (Figure 3).^[12,33] In all three cases (Table 1), the Pd–C^{carbene} bond length (*ca.* 203 pm) is slightly longer than that found in the fluoroaminocarbene complex **6** (199.5 (2) pm). Since the metal frame is identical in all cases, we take this elongation as evidence for diminished π Pd–C^{carbene} interaction, which we consider negligible in the NHC complexes **9–11**. Steady elongation of the Pd–C^{carbene} bond is also observed in the optimized structures of the [(CF₃)₃Pd(carbene)][–] anions: CF₂ < C(F)NPh₂ < SiMe₃ (Figure S17). Crystals of **11** contain the equimolar amount of cocrystallized [PPh₄][FHF], which evidence the fate of the leaving fluoride ions in the preceding reactions. The strong H-bonding interactions of the NH unit with the [FHF][–] anion (Figure S15) may well explain the cocrystal.^[34]

In summary, the low fluoride-ion affinity of the difluorocarbene complex [(CF₃)₃Pt(CF₂)][–] (**B**-Pd) seems to underlie the unusually high C–F activity observed in the homoleptic complex [Pd(CF₃)₄]^{2–} (**1**). Straightforward C–F functionalization is described involving selective single, double and triple CF₃-defluorination. Facile amination takes place under very mild conditions without the need of any prior acidic activation. This enhanced activity uproots an otherwise hard reagent-compatibility issue (acid/base). Rare fluoroaminocarbene complexes [(CF₃)₃Pd(CFNR₂)][–] are readily obtained by reaction with secondary amines R₂NH. An unprecedented NHC-synthesis by direct reaction of a [M]CF₃ unit and a diamine is also described and demonstrated to apply to various NHC topologies. Given the ease with which the NH unit in protic NHC carbenes can be *N*-alkylated,^[35] the method opens the door to an even wider variety of species.

Acknowledgements

This work was supported by the Spanish MCIU/FEDER (Project PID2021-122869NB-I00) and the Gobierno de Aragón (E17_23R, E47_23R). BIFI (Instituto de Biocomputación y Física de Sistemas Complejos) and CESGA (Centro de Supercomputación de Galicia) are acknowledged for allocation of computational resources. D. J.-S. thanks the Spanish MCIU for a grant (BES-2016-078732).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: amination · C–F activation · difluorocarbene · fluoroaminocarbene · organopalladium

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Manuscript received: February 13, 2024

Accepted manuscript online: April 12, 2024

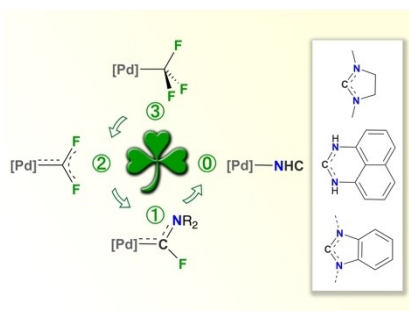
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Communications

Mechanistic Investigations

D. Joven-Sancho, M. Baya, A. Martín,
J. Orduna, B. Menjón* — e202403108

The CF_3 Group as a Synthon of the CF^+
Unit in Palladium Chemistry



Pulling fluorine off: The unusually high activity of the C–F bond found in the homoleptic trifluoromethyl-palladium(II) complex $[\text{Pd}(\text{CF}_3)_4]^{2-}$ is correlated to the very low fluoride-ion affinity of the conjugate difluorocarbene complex $[(\text{CF}_3)_3\text{Pd}(\text{CF}_2)]^-$, which is experimentally detected. Selective single, double or triple defluorination of a CF_3 group is achieved under very mild conditions.