Fluorination

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Activation of SF_6 at Platinum Complexes: Formation of SF_3 Derivatives and their Application in Deoxyfluorination Reactions

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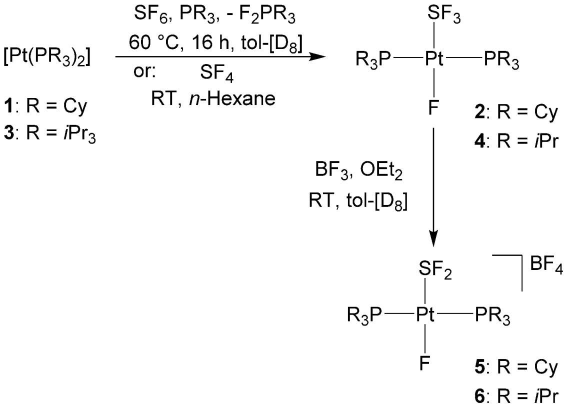
Abstract: *The activation of SF_6 at $[Pt(PR_3)_2]$ R = Cy, iPr complexes in the presence of PR_3 led selectively and in an unprecedented reaction route to the generation of the SF_3 complexes trans-$[Pt(F)(SF_3)(PR_3)_2]$. These can also be synthesized from SF_4 and the SF_2 derivative trans-$[Pt(F)(SF_2)(PCy_3)_2][BF_4]$ was characterized by X-ray crystallography. trans-$[Pt(F)(SF_3)(PR_3)_2]$ complexes are useful tools for deoxyfluorination reactions and novel fluorido complexes bearing a SOF ligand are formed. Based on these studies a process for the deoxyfluorination of ketones was developed with SF_6 as fluorinating agent.*

The development of new routes to access organic building blocks by selective fluorination is of enormous importance for the construction of new materials and bioactive compounds.[1] Among various fluorination reagents deoxyfluorinating derivatives are widely used to convert for instance alcohols into alkyl fluorides, ketones or aldehydes into *gem*-difluoroalkanes as well as carboxylic groups into trifluoromethyl groups.[1b,2] Common reagents include SF_4 and some derivatives of it, such as Fluolead, DAST or Deoxo-Fluor among others. However, they often have to be generated from SF_4 or via oxidative fluorination of sulfides.[3] An interesting alternative reagent for deoxyfluorination comprises 2-pyridinesulfonylfluorid, which can be prepared from potassium bifluoride.[4] A very exciting route to prepare sulfur-containing fluorinating agents involves SF_6 as active agent, but reported attempts are scarce.[5] This is consistent with the fact that SF_6 is an extremely inert gas, which is used as dielectric in high-voltage circuit breakers.[6] Generally, SF_6 can be activated and depleted by reduction. This activation was achieved at low-valent Ti, V, Cr, and Zr complexes as well as at Fe and at reduced Ni complexes.[7] We previously described the selective degradation of SF_6 at a binuclear rhodium complex as well as the catalytic transformation of SF_6 into fluorosilanes and phosphinesulfides with $[Rh(H)(PEt_3)_4]$ as catalytic precursor.[8] A breakthrough for using SF_6 in organic synthesis was very recently reported by McTeague and Jamison. They developed an iridium-based photoredox catalytic process leading to a deoxyfluorination of allylic alcohols to form fluorinated olefins.[9] It is speculated that in an initial step an electron-transfer to SF_6 occurs to generate a radical anion to yield via unknown steps a $(RO)SF_x$ intermediate, which further reacts by C–O cleavage and fluorination. Another report, which is covered by a patent,[10a] deals with the reduction of SF_6 to produce the SF_5^- anion.[10] This anion was shown to be a bad fluorinating agent.

Herein we present the selective and remarkable activation of SF_6 at $[Pt(PR_3)_2]$ (**1**: R = Cy, **3**: R = *i*Pr). In the presence of additional phosphine no depletion was observed, but the complexes *trans*-$[Pt(F)(SF_3)(PR_3)_2]$ (**2**: R = Cy, **4**: R = *i*Pr) are generated which contain a metal-bound SF_3 building block. These complexes can be used for fluorination reactions and are hence intermediates in deoxyfluorination reactions of ketones with SF_6 as fluorinating agent.

Treatment of $[Pt(PCy_3)_2]$ (**1**) with SF_6 in the presence of PCy_3 led after 16 h at 60 °C to the SF_3 fluorido complex *trans*-$[Pt(F)(SF_3)(PCy_3)_2]$ (**2**) and F_2PCy_3 (Scheme 1).[11] The reaction does not take place if no additional PCy_3 is present. However, an independent experiment showed that PCy_3 does not react with SF_6. A similar activation reaction was found at $[Pt(PiPr_3)_2]$ (**3**)/$PiPr_3$ to yield *trans*-$[Pt(F)(SF_3)(PiPr_3)_2]$ (**4**) (Scheme 1). Alternatively, the complexes **2** and **4** can be synthesized by treatment of a suspension of either $[Pt(PCy_3)_2]$ (**1**) or $[Pt(PiPr_3)_2]$ (**3**) in *n*-hexane with SF_4. The conversions were complete within minutes at room temperature (Scheme 1). Comparable insertion reactions at $[Pt(PCy_3)_2]$ (**1**) into element–fluorine bonds in BF_3 or PF_5 were described by Finze and Braunschweig et al.[12]



Scheme 1. Formation and reactivity of the SF_3 complexes **2** and **4**.

The ${}^{19}F$ NMR spectrum of **2** shows two resonance signals for the SF_3 ligand and one for the fluorido ligand bound at the metal center. A doublet of doublet like pattern at $\delta = -326.3$ ppm with coupling constants of ${}^{2}J_{F,P} = 17$ Hz and

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$^2J_{\mathrm{F,P}} = 21$ Hz with ^{195}Pt satellites reveals the presence of the metal-bound fluorido ligand.[13] Two signals with ^{195}Pt satellites at $\delta = 58.0$ ppm and $\delta = -71.3$ ppm which integrate 2:1 correspond to the sulfur bound fluorides. The coupling between the two sets of fluorine atoms is 63 Hz. Note that the complexes $[\mathrm{Ir(CO)(X)(F)(PEt_3)_2(SF_3)}]$ (X = Br, Cl, I), which were synthesized from $\mathrm{SF_4}$ exhibit a nonequivalence of all three fluorine atoms bound at the $\mathrm{SF_3}$ unit.[14] The ^{31}P{^{1}H} NMR spectrum (242.9 MHz) of **2** at 263 K exhibits two resonance signals of higher order for the two nonequivalent phosphorous atoms at $\delta = 31.2$ ppm and $\delta = 22.8$ ppm. To determine the coupling constants the ^{31}P{^{1}H} NMR spectrum was simulated (Supporting Information). The pattern reveals a phosphorous–phosphorous coupling constant of 334 Hz, which is typical for phosphines in a mutually *trans* position.[15] Additional splittings are due to couplings to the four fluorine atoms. The values for the phosphorus-platinum coupling constants ($^1J_{\mathrm{Pa,Pt}} = 2745$ Hz, $^1J_{\mathrm{Pb,Pt}} = 2614$ Hz) are characteristic for a Pt$^{\mathrm{II}}$ species.[13a,b,e,j–l,16] Variable temperature ^{31}P{^{1}H} NMR spectroscopy reveals a fluxional structure rendering the phosphorous atoms to be equivalent at 348 K (121.5 MHz, see Supporting Information). Because the NMR spectroscopic data of complex **4** are very similar to those of **2**, no further discussion is given (see Supporting Information). It is likely that the non-equivalence of the two phosphorus nuclei arises from a trigonal bipyramidal arrangement of the fluorine atoms, the metal center as well as a lone electron pair at sulfur. DFT calculations on the molecular structure of **2** confirm such geometry of the $\mathrm{SF_3}$ group and the HOMO−1 is located at the sulfur atom (Figure 1, Supporting Information).

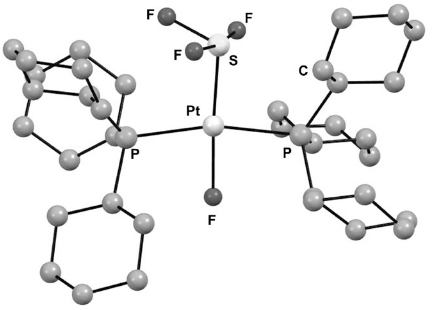


Figure 1. DFT-optimized structure of complex **2**.

This observation is consistent with calculations by B. King et al. for $[\mathrm{Ir(SF_3)(CO)_3}]$, for which the $\mathrm{SF_3}$ ligand is considered to be a one-electron donor, that is, an anionic two-electron donor.[17] However, it is in contrast to the suggested electronic structure of $[\mathrm{Pt(Cp)(SF_3)}]$ (Cp = cyclopentadienyl), for which the $\mathrm{SF_3}$ ligand is considered to be a three electron donor resulting in a tetrahedral environment at sulfur.

Mechanistically, we presume that the $\mathrm{SF_6}$ activation is initiated by an electron-transfer step from the metal to the $\mathrm{SF_6}$ molecule.[7–10,18] This might be facilitated by a precoordination of the fluorinated substrate at the platinum center followed by an inner-sphere mechanism to yield $\mathrm{SF_5}^-$ and a fluoride ion.[10] Comparable mechanistic steps have been suggested for transition-metal mediated C−F activation reactions.[1a,f,19] This gives possibly a $\mathrm{SF_5}$ fluorido platinum complex, but $\mathrm{SF_5}$ complexes have so far been elusive.[20] However, intra- or intermolecular fluoride abstraction from the $\mathrm{SF_5}$ ligand would finally lead to **2** and **4**. Note that phosphine assisted C−F bond activations which involve an addition of the carbon-fluorine bond across a metal–phosphorus bond have been reported.[13c,k,15,21] Though, when **2** was generated in the presence of P*i*Pr$_3$ instead of PCy$_3$, the generation of F$_2$P*i*Pr$_3$ was observed.

The identity of **2** was further confirmed by the generation of *trans*-$[\mathrm{Pt(F)(SF_2)(PCy_3)_2}][\mathrm{BF_4}]$ (**5**) and *trans*-$[\mathrm{Pt(F)(SF_2)}$(P*i*Pr$_3)_2][\mathrm{BF_4}]$ (**6**) on treatment of the $\mathrm{SF_3}$ complexes with a solution of $\mathrm{BF_3}$ in $\mathrm{Et_2O}$ (Scheme 1). The iridium complex $[\mathrm{Ir(CO)(Cl)(F)(PEt_3)_2(SF_3)}]$ reacts in a similar way to give $[\mathrm{Ir(CO)(Cl)(F)(PEt_3)_2(SF_2)}]$ $[\mathrm{BF_4}]$.[14]

The ^{19}F NMR spectrum of **5** shows signals at $\delta = -35.7$ ppm a triplet with a coupling constant of $^3J_{\mathrm{F,P}} = 21$ Hz with ^{195}Pt satellites, which corresponds to the $\mathrm{SF_2}$ unit. Again a triplet at $\delta = -252.7$ ppm ($^2J_{\mathrm{F,P}} = 24$ Hz) with ^{195}Pt satellites is characteristic for the fluorido ligand bound at a metal center.[12] The ^{31}P{^{1}H} NMR spectrum of **5** reveals a resonance at $\delta = 42.7$ ppm as a doublet of triplet pattern ($^3J_{\mathrm{F,P}} = 21$ Hz; $^2J_{\mathrm{F,P}} = 24$ Hz). The value for the phosphorus-platinum coupling constant ($^1J_{\mathrm{P,Pt}} = 2071$ Hz) is characteristic for a Pt$^{\mathrm{II}}$ species.[13a,b,e,j–l,16] The data of **6** are comparable to these of **5**. The structure of **5** in the solid state was determined by X-ray crystallography (Figure 2). Complex **5** exhibits an approximately square-planar coordination sphere at the platinum center. The S1−F2 and S1−F3 [1.5814(17); 1.5765(16)] bond lengths are comparable to S−F bonds in deoxyfluorination agents such as morpholinesulfurtrifluoride (MOST) and the bis(diethylamino)difluorosulfonium cation.[22] There are short contacts of S1-F′1 2.8959(18) and 2.9839(19) S1-F′3 between the $\mathrm{BF_4}^-$ ion and the metal bound sulfur atom.

Furthermore, the reactivity of the complexes **2** and **4** were tested towards organic substrates. Thus, a reaction of **2** with ethanol led to the generation of *trans*-$[\mathrm{Pt(F)(SOF)(PCy_3)_2}]$

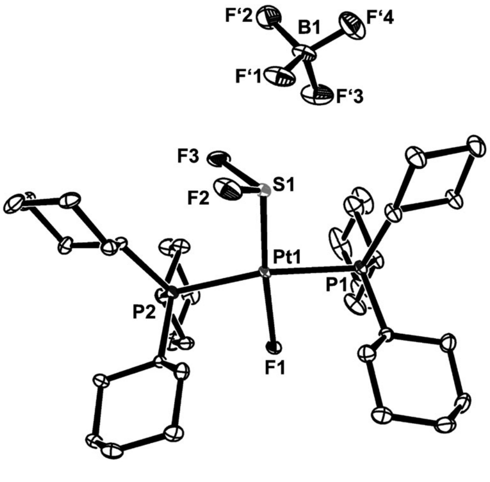
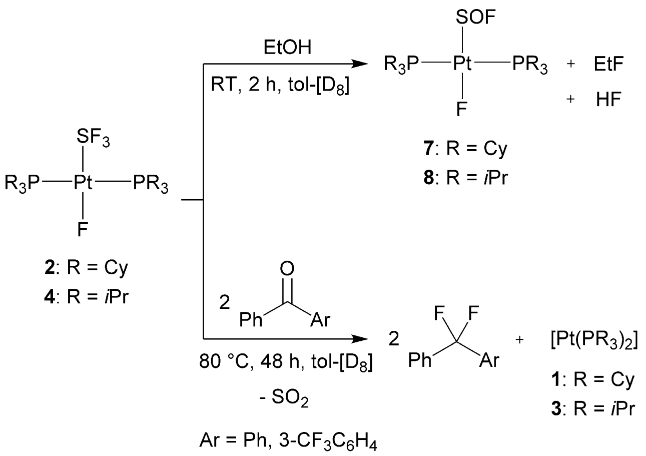


Figure 2. ORTEP diagram of **5**·toluene. Ellipsoids are set at 50% probability. Hydrogen atoms and a toluene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–S1 2.1108(6), Pt1–F1 1.9810(13), Pt1–P1 2.3720(7), Pt1–P2 2.3731(6), S1–F2 1.5814(17), S1–F3 1.5765(16), B1–F′1 1.386(4); F1-Pt1-S1 174.52(4), F1-Pt1-P1 85.34(4).

(**7**) as well as of EtF and HF by deoxyfluorination (Scheme 2). To our knowledge **7** represents a unique example of a transition metal SOF complex. The ^{19}F NMR spectrum of **7** exhibits at $\delta = -5.0$ ppm a triplet with a coupling constant of $^{3}J_{\mathrm{F,P}} = 12$ Hz with ^{195}Pt satellites and a triplet at $\delta = -285$ ppm ($^{2}J_{\mathrm{F,P}} = 15$ Hz) with ^{195}Pt satellites for the fluorido ligand.[13] The ^{31}P{^{1}H} NMR spectrum of **7** depicts a doublet of doublet with $^{3}J_{\mathrm{P,SOF}} = 12$ Hz and $^{2}J_{\mathrm{P,PtF}} = 15$ Hz with ^{195}Pt satellites ($^{1}J_{\mathrm{P,Pt}} = 2650$ Hz). The molecular structure of **7** was also determined by X-ray crystallography. Although the structure reveals a positional disorder of the oxygen and fluorine atoms about the sulfur atom, and the oxygen and fluorine atoms were only refined isotropically, the data are consistent with the proposed structure (Figure 3, and Supporting Information).



Scheme 2. Reactivity of **2** and **4** towards organic substrates.

Complex **2** can also be applied for the fluorination of non-enolizable ketones. Thus, a reaction with two equivalents of benzophenone or 3-(trifluoromethyl)benzophenone led to the regeneration of **1** and produced bis-(phenyl)difluoromethane derivativesand SO_2 (Scheme 2). The SO_2 was identified by GC/MS. Note that a catalytic deoxyfluorination of the benzophenones with SF_6 as fluorinating agent was also tested. On using 20 mol% of **2** 44% conversion of benzophenone to the corresponding deoxyfluorinated product was observed according to the NMR spectra after 5 days at 80°C. Though, slightly more than two equivalents of the fluorinated product are generated based on one equivalent SF_6.

In conclusion, we have developed transition-metal mediated fluorination reactions with SF_6 as the fluorinating agent. The unprecedented conversions reveal an initial activation at Pt^0 complexes to yield the SF_3 complexes *trans*-[Pt(F)(SF_3)-(PR_3)$_2$]. Remarkably, the SF_6 molecule is not depleted, but transformed into a SF_3 group and a metal fluoride ligand. The generation of a stable sulfur fluoride species in a lower oxidation state from SF_6 is extraordinary and the conversions are in strong contrast to other reactions at transition-metal complexes, which result in a depletion of SF_6.[7,8] Note that even decomposition reactions of SF_5 groups bound at organic molecules are rare.[23] The SF_3 complexes can then be applied in deoxyfluorination reactions of ketones and all four fluorine atoms are transferred to the organic substrate. Future studies aim for catalytic deoxyfluorination on using the greenhouse gas SF_6 as fluorinating agent.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: fluorination · fluorine · platinum · S–F activation · sulfurhexafluoride

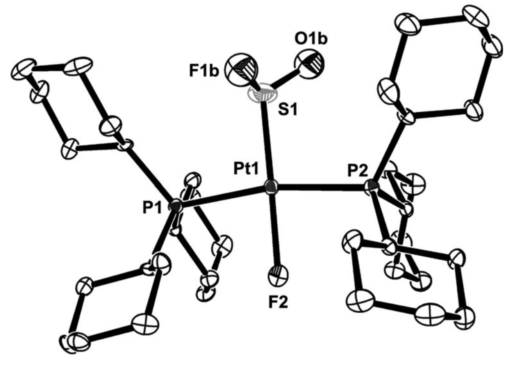

Figure 3. ORTEP diagram of **7**. Ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–S1 2.1927(16), Pt1–F2 2.048(3), Pt1–P1 2.3306(13), Pt1–P2 2.3267(13); F2-Pt1-S1 177.47(11), P1-Pt1-S1 89.67(2), P1-Pt1-F2 84.50(9).

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[1] a) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749–2757; b) M. G. Campbell, T. Ritter, *Chem. Rev.* **2015**, *115*, 612–633; c) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183; d) Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J. L. Aceña, V. A. Soloshonok, K. Izawa, H. Liu, *Chem. Rev.* **2016**, *116*, 422–518; e) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; f) T. Ahrens, J. Kohlmann, M. Ahrens, T. Braun, *Chem. Rev.* **2014**, *114*, 931–972; g) J. Wang, M. Sanchez-Rosello, J. L. Acena, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev.* **2014**, *114*, 2432–2506; h) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; i) D. Le Bars, *J. Fluorine Chem.* **2006**, *127*, 1488–1493; j) D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308–319; k) P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis Reactivity, Applications*, Wiley-VCH, Weinheim, **2004**; l) T. Hiyama, *Organofluorine Compounds: Chemistry and Applications*, Springer, Berlin, **2000**; m) J. P. B. a. D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, Wiley, Hoboken, **2008**.

[2] a) C. F. Ni, M. Y. Hu, J. B. Hu, *Chem. Rev.* **2015**, *115*, 765 – 825; b) M. R. C. Gerstenberger, A. Haas, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 647 – 667; *Angew. Chem.* **1981**, *93*, 659 – 680; c) N. Al-Maharik, D. O'Hagan, *Aldrichimica Acta* **2011**, *44*, 65 – 75; d) R. P. Singh, J. M. Shreeve, *Synthesis* **2002**, 2561 – 2578.

[3] a) W. Xu, H. Martinez, W. R. Dolbier, *J. Fluorine Chem.* **2011**, *132*, 482 – 488; b) T. Umemoto, R. P. Singh, Y. Xu, N. Saito, *J. Am. Chem. Soc.* **2010**, *132*, 18199 – 18205; c) W. J. Middleton, *J. Org. Chem.* **1975**, *40*, 574 – 578; d) A. L'Heureux, F. Beaulieu, C. Bennett, D. R. Bill, S. Clayton, F. LaFlamme, M. Mirmehrabi, S. Tadayon, D. Tovell, M. Couturier, *J. Org. Chem.* **2010**, *75*, 3401 – 3411; e) G. S. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic, H. S. Cheng, *J. Org. Chem.* **1999**, *64*, 7048 – 7054; f) M. Kosobokov, B. Cui, A. Balia, K. Matsuzaki, E. Tokunaga, N. Saito, N. Shibata, *Angew. Chem. Int. Ed.* **2016**, *55*, 10781 – 10785; *Angew. Chem.* **2016**, *128*, 10939 – 10943.

[4] M. K. Nielsen, C. R. Ugaz, W. Li, A. G. Doyle, *J. Am. Chem. Soc.* **2015**, *137*, 9571 – 9574.

[5] a) A. P. Hagen, B. W. Callaway, *Inorg. Chem.* **1975**, *14*, 2825 – 2827; b) L. Batt, F. R. Cruickshank, *J. Phys. Chem.* **1966**, *70*, 723 – 727.

[6] a) J. Vondrak, M. Sedlarikova, K. Liedermann, *Chem. Listy* **2001**, *95*, 791 – 795; b) K. Seppelt, *Chem. Rev.* **2015**, *115*, 1296 – 1306; c) S. E. Quiñones-Cisneros, M. L. Huber, U. K. Deiters, *J. Phys. Chem. Ref. Data* **2012**, *41*, 023102; d) L. G. Christophorou, J. K. Olthoff, R. J. VanBrunt, *IEEE Elect. Insul. Mag.* **1997**, *13*, 20 – 24.

[7] a) P. Holze, B. Horn, C. Limberg, C. Matlachowski, S. Mebs, *Angew. Chem. Int. Ed.* **2014**, *53*, 2750 – 2753; *Angew. Chem.* **2014**, *126*, 2788 – 2791; b) R. Basta, B. G. Harvey, A. M. Arif, R. D. Ernst, *J. Am. Chem. Soc.* **2005**, *127*, 11924 – 11925; c) H. L. Roberts, *Q. Rev. Chem. Soc.* **1961**, *15*, 30 – 55; d) B. G. Harvey, A. M. Arif, A. Glockner, R. D. Ernst, *Organometallics* **2007**, *26*, 2872 – 2879; e) J. R. Case, F. Nyman, *Nature* **1962**, *193*, 473.

[8] a) L. Zámostná, T. Braun, B. Braun, *Angew. Chem. Int. Ed.* **2014**, *53*, 2745 – 2749; *Angew. Chem.* **2014**, *126*, 2783 – 2787; b) L. Zámostná, T. Braun, *Angew. Chem. Int. Ed.* **2015**, *54*, 10652 – 10656; *Angew. Chem.* **2015**, *127*, 10798 – 10802.

[9] T. A. McTeague, T. F. Jamison, *Angew. Chem. Int. Ed.* **2016**, *55*, 15072 – 15075; *Angew. Chem.* **2016**, *128*, 15296 – 15299.

[10] a) P. K. D. Sevenard, A. A. Kolomeitsev, G.-V. Röschenthaler, DE 10220901, **2004**; b) C. W. Tullock, D. D. Coffman, E. L. Muetterties, *J. Am. Chem. Soc.* **1964**, *86*, 357 – 361; c) W. Heilemann, R. Mews, S. Pohl, W. Saak, *Chem. Ber.* **1989**, *122*, 427 – 432; d) M. Clark, C. J. Kellenyuen, K. D. Robinson, H. Zhang, Z. Y. Yang, K. V. Madappat, J. W. Fuller, J. L. Atwood, J. S. Thrasher, *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 809 – 833; e) R. Tunder, B. Siegel, *J. Inorg. Nucl. Chem.* **1963**, *25*, 1097 – 1098; f) J. Bittner, J. Fuchs, K. Seppelt, *Z. Anorg. Allg. Chem.* **1988**, *557*, 182 – 190; g) J. T. Goettel, N. Kostiuk, M. Gerken, *Angew. Chem. Int. Ed.* **2013**, *52*, 8037 – 8040; *Angew. Chem.* **2013**, *125*, 8195 – 8198.

[11] Small amounts of *trans* [Pt(F)(SOF)(P*i*Pr$_3$)$_2$] (**7**), which are also present in the reaction solution, are a result of adventitious water.

[12] a) N. Arnold, R. Bertermann, F. M. Bickelhaupt, H. Braunschweig, M. Drisch, M. Finze, F. Hupp, J. Poater, J. A. P. Sprenger, *Chem. Eur. J.* **2016**, DOI: 10.1002/chem.201604997; b) J. Bauer, H. Braunschweig, R. D. Dewhurst, K. Radacki, *Chem. Eur. J.* **2013**, *19*, 8797 – 8805; c) J. Bauer, H. Braunschweig, K. Kraft, K. Radacki, *Angew. Chem. Int. Ed.* **2011**, *50*, 10457 – 10460; *Angew. Chem.* **2011**, *123*, 10641 – 10644.

[13] a) H. C. S. Clark, J. Fawcett, J. H. Holloway, E. G. Hope, L. A. Peck, D. R. Russell, *J. Chem. Soc. Dalton Trans.* **1998**, 1249 – 1252; b) T. Wang, L. Keyes, B. O. Patrick, J. A. Love, *Organometallics* **2012**, *31*, 1397 – 1407; c) V. V. Grushin, *Acc. Chem. Res.* **2010**, *43*, 160 – 171; d) C. Berg, T. Braun, R. Laubenstein, B. Braun, *Chem. Commun.* **2016**, *52*, 3931 – 3934; e) J. Berger, T. Braun, R. Herrmann, B. Braun, *Dalton Trans.* **2015**, *44*, 19553 – 19565; f) A. Vigalok, *Acc. Chem. Res.* **2015**, *48*, 238 – 247; g) T. Beweries, L. Brammer, N. A. Jasim, J. E. McGrady, R. N. Perutz, A. C. Whitwood, *J. Am. Chem. Soc.* **2011**, *133*, 14338 – 14348; h) N. D. Ball, J. W. Kampf, M. S. Sanford, *Dalton Trans.* **2010**, *39*, 632 – 640; i) V. V. Grushin, W. J. Marshall, *Angew. Chem. Int. Ed.* **2002**, *41*, 4476 – 4479; *Angew. Chem.* **2002**, *114*, 4656 – 4659; j) A. Yahav, I. Goldberg, A. Vigalok, *J. Am. Chem. Soc.* **2003**, *125*, 13634 – 13635; k) E. Clot, O. Eisenstein, N. Jasim, S. A. Macgregor, J. E. McGrady, R. N. Perutz, *Acc. Chem. Res.* **2011**, *44*, 333 – 348; l) A. Yahav, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2005**, *44*, 1547 – 1553.

[14] R. W. Cockman, E. A. V. Ebsworth, J. H. Holloway, *J. Am. Chem. Soc.* **1987**, *109*, 2194 – 2195.

[15] N. A. Jasim, R. N. Perutz, A. C. Whitwood, T. Braun, J. Izundu, B. Neumann, S. Rothfeld, H.-G. Stammler, *Organometallics* **2004**, *23*, 6140 – 6149.

[16] A. D. Sun, J. A. Love, *Dalton Trans.* **2010**, *39*, 10362 – 10374.

[17] a) X. Gao, N. Li, R. B. King, *Inorg. Chem.* **2014**, *53*, 12635 – 12642; b) X. Z. Gao, S. D. Gong, N. Li, R. B. King, *New J. Chem.* **2015**, *39*, 4939 – 4947; c) J. Deng, C. Wang, Q.-s. Li, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.* **2011**, *50*, 2824 – 2835.

[18] a) L. Zámostná, T. Braun, *Nachr. Chem.* **2016**, *64*, 829 – 835; b) R. E. Weston, *J. Phys. Chem.* **1995**, *99*, 13150 – 13155.

[19] a) W. D. Jones, *Dalton Trans.* **2003**, 3991 – 3995; b) M. Aizenberg, D. Milstein, *Science* **1994**, *265*, 359 – 361; c) M. F. Kuehnel, D. Lentz, T. Braun, *Angew. Chem. Int. Ed.* **2013**, *52*, 3328 – 3348; *Angew. Chem.* **2013**, *125*, 3412 – 3433; M. K. Whittlesey, R. N. Perutz, M. H. Moore, *Chem. Commun.* **1996**, 787 – 788; d) T. Braun, F. Wehmeier, *Eur. J. Inorg. Chem.* **2011**, 613 – 625; e) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber.* **1997**, *130*, 145 – 154; f) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373 – 431; g) H. Torrens, *Coord. Chem. Rev.* **2005**, *249*, 1957 – 1985; h) J. Weaver, S. Senaweera, *Tetrahedron* **2014**, *70*, 7413 – 7428; i) R. P. Hughes, *Eur. J. Inorg. Chem.* **2009**, 4591 – 4606; j) J. A. Hatnean, S. A. Johnson, *Organometallics* **2012**, *31*, 1361 – 1373; k) J.-Y. Hu, J.-L. Zhang, *Top. Organomet. Chem.* **2015**, *52*, 143 – 196.

[20] A SF$_5$ Pt complex has been proposed, but the compound was only characterized by IR spectroscopy; R. D. W. Kemmitt, R. D. Peacock, J. Stocks, *Chem. Commun.* **1969**, 554a.

[21] a) A. Nova, S. Erhardt, N. A. Jasim, R. N. Perutz, S. A. Macgregor, J. E. McGrady, A. C. Whitwood, *J. Am. Chem. Soc.* **2008**, *130*, 15499 – 15511; b) A. Nova, M. Reinhold, R. N. Perutz, S. A. Macgregor, J. E. McGrady, *Organometallics* **2010**, *29*, 1824 – 1831; c) J. Goodman, S. A. Macgregor, *Coord. Chem. Rev.* **2010**, *254*, 1295 – 1306; d) S. Erhardt, S. A. Macgregor, *J. Am. Chem. Soc.* **2008**, *130*, 15490 – 15498; e) O. Blum, F. Frolow, D. Milstein, *J. Chem. Soc. Chem. Commun.* **1991**, 258 – 259; f) A. L. Raza, J. Panetier, M. Teltewskoi, S. Macgregor, T. Braun, *Organometallics* **2013**, *32*, 3795 – 3807; g) M. Teltewskoi, J. A. Panetier, S. A. Macgregor, T. Braun, *Angew. Chem. Int. Ed.* **2010**, *49*, 3947 – 3951; *Angew. Chem.* **2010**, *122*, 4039 – 4043.

[22] a) P. S. Barber, A. de Bettencourt-Dias, *J. Chem. Crystallogr.* **2011**, *41*, 902 – 907; b) A. Flores Antognini, N. L. Robles, E. H. Cutin, E. Bernhardt, M. Hirschberg, X. Q. Zeng, H. Willner, H. Oberhammer, *J. Fluorine Chem.* **2012**, *144*, 59 – 64.

[23] a) D. S. Lim, J. S. Choi, C. S. Pak, J. T. Welch, *J. Pestic. Sci.* **2007**, *32*, 255 – 259; b) R. Winter, G. L. Gard, *J. Fluorine Chem.* **2000**, *102*, 79 – 87; c) D. A. Jackson, S. A. Mabury, *Environ. Toxicol. Chem.* **2009**, *28*, 1866 – 1873; d) E. Falkowska, M. Y. Laurent, V. Tognetti, L. Joubert, P. Jubault, J. P. Bouillon, X. Pannecoucke, *Tetrahedron* **2015**, *71*, 8067 – 8076; e) P. Dudziński, A. V. Matsnev, J. S. Thrasher, G. Haufe, *J. Org. Chem.* **2016**, *81*, 4454 – 4463; f) A. Budinská, J. Václavík, V. Matoušek, P. Beier, *Org. Lett.* **2016**, *18*, 5844 – 5847; g) G. Kleemann, K. Seppelt, *Angew. Chem.*

Int. Ed. Engl.Angew. Chem. Int. Ed. **1978**, *17*, 516–518; *Angew. Chem.* **1978**, *90*, 547–549; h) P. Kirsch, M. Bremer, M. Heckmeier, K. Tarumi, *Angew. Chem. Int. Ed.* **1999**, *38*, 1989–1992; *Angew. Chem.* **1999**, *111*, 2174–2178; i) Y. Huang, G. L. Gard, J. N. M. Shreeve, *Tetrahedron Lett.* **2010**, *51*, 6951–6954.

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Communications

Fluorination

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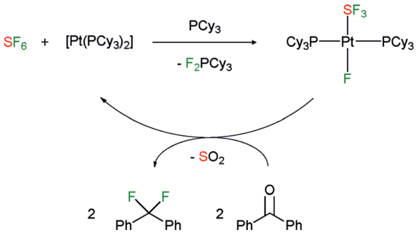
Activation of SF_6 at Platinum Complexes: Formation of SF_3 Derivatives and their Application in Deoxyfluorination Reactions



Special eFFects: The activation of SF_6 at Pt complexes yields SF_3 fluorido complexes which can be used for the fluorination of ketones.