C–F Activation

DOI: 10.1002/ange.200603972

Carbon–Fluorine Bond Activation in Fluoroolefins: Clear Documentation of Cooperative C–F Bond Activation by Adjacent Metal Centers**

*D. Jason Anderson, Robert McDonald, and Martin Cowie**

One of the most exciting developments in organometallic chemistry over the past few decades has been the activation of otherwise inert chemical bonds by transition-metal complexes.[1] In spite of substantial developments in this area, many significant challenges remain, including the activation of the very strong carbon–fluorine bond.[2] Studies on the activation of C–F bonds are being driven, not only by the fundamental challenges of effecting and understanding the processes involved, but also by the important applications of fluorocarbons in areas such as pharmaceuticals, pesticides, polymers, and refrigerants,[3] as well as by the significant challenges of converting potentially harmful chlorofluorocarbons into more environmentally benign compounds.[4]

A wide variety of transition-metal complexes have been used to activate C–F bonds,[2] but in almost all cases these approaches have been limited to the activation at a single metal center. We are aware of only two studies in which activation of C–F bonds has been observed for bridging fluorocarbyl ligands.[5,6]

Fluoroolefins bound in the bridging site between a pair of metal centers can be viewed as resulting from the addition of the dimetal unit across the olefinic bond to generate a 1,2-dimetalated fluoroalkane with concomitant rehybridization of the olefinic carbon atoms to sp^3, as confirmed in the structures of C_2F_4-bridged diiron[5] and diiridium[7] compounds. In such a geometry the bridging fluoroolefin can be viewed as analogous to two fluoroalkyl groups, for which the lability of the α-fluorine atoms towards abstraction of a fluoride ion has been demonstrated.[8] On this basis we suggest that bridging fluoroolefins should also be susceptible to abstraction of a fluoride ion by Lewis acids.

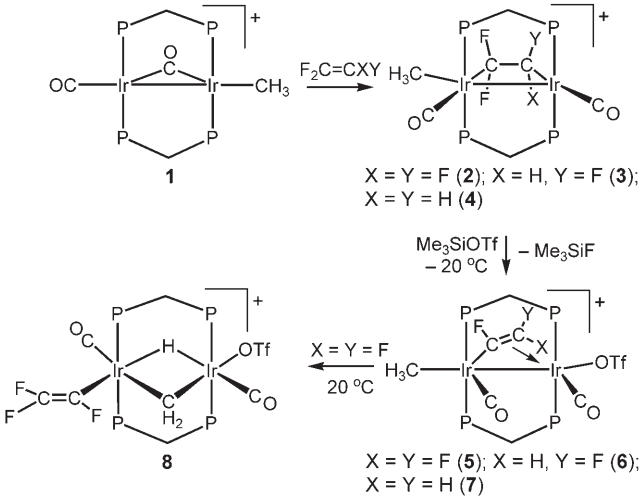
Although olefin coordination at one metal center also gives rise to some rehybridization, we suggest that it is less than when it is bridging, and set out to determine if the fluoroolefin bridging mode would result in enhanced activation of the C–F bond.

[*] D. J. Anderson, Dr. R. McDonald, Prof. M. Cowie
Department of Chemistry
University of Alberta
Edmonton, AB T6G 2G2 (Canada)
Fax: (+1) 780-492-8231
E-mail: martin.cowie@ualberta.ca

[**] This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada through grants to M.C. and a fellowship to D.J.A.; and by the University of Alberta. We wish to thank Professor Robin Perutz for an advance copy of Ref. [2e].

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

We previously established[7] that $[Ir_2(CH_3)(CO)_2(dppm)_2][CF_3SO_3]$ (**1**; dppm = μ-$Ph_2PCH_2PPh_2$) yields fluoroolefin-bridged products with olefins containing at least one pair of geminal fluorine substituents (for example, 1,1-difluoroethylene, trifluoroethylene, and tetrafluoroethylene) as shown in Scheme 1.



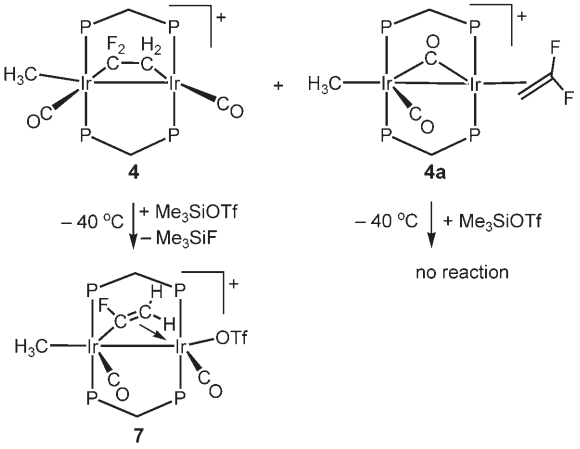
Scheme 1. Activation of C–F bonds in bridging fluoroolefins. In all the schemes the phenyl substituents on the phosphorus atoms are omitted and the triflate counterions are not shown, while coordinated triflate ions are shown as OTf.

Abstraction of a fluoride ion from compounds **2**–**4**, to give the respective fluorovinyl products **5**–**7** quantitatively, is achieved by the addition of trimethylsilyl triflate at −20 °C. Spectral data for all the compounds are given in the Experimental Section and additional characterization data are available in the Supporting Information. Although the difluorovinyl-bridged product **6** is stable upon warming to ambient temperature, the trifluorovinyl-bridged species **5** rearranges to the η^1-trifluorovinyl product **8** at this temperature, accompanied by activation of a C–H bond of the methyl group. The structure of **8** has been determined by X-ray crystallography; although it is disordered, the connectivity shown in Scheme 1 is clear (see the Supporting Information).

The differentiation between terminal and bridging fluorovinyl groups is made on the basis of the coupling patterns involving the vinyl substituents in the NMR spectra. For example, the different fluorine–fluorine coupling constants for the η^1-trifluorovinyl group in **8** ($^3J_{trans} = 115$ Hz, $^2J_{gem} =$

90 Hz, $^3J_{cis} = 40$ Hz) are consistent with previous determinations[9] and are all greater than the respective values for the bridging group in **5** (100 Hz, 85 Hz, 20 Hz). Furthermore, in **8** the lone α-fluorine atom on the vinyl group displays coupling to only the pair of adjacent ^{31}P nuclei as well as to the adjacent ^{13}CO and μ-^{13}CH$_2$ groups, while the corresponding fluorine atom in **5** displays coupling to the carbonyl groups on both metal centers and to all four ^{31}P nuclei, further supporting a bridged arrangement for the latter compound. The decrease in the coupling constants in the bridging mode has been noted for perprotiovinyl moieties.[10] We are aware of only one previous report of a bridging fluorovinyl ligand proposed on the basis of IR spectroscopy;[11] no ^{19}F NMR data were given for this species.

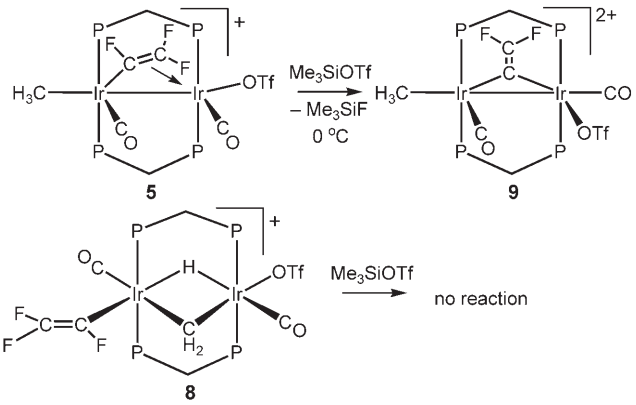
Although the tetra- and trifluoroethylene adducts **2** and **3** are the only species observed at temperatures above −60 °C, the 1,1-difluoroethylene adduct can be obtained as a mixture of two isomers (**4** and **4a**) at −20 °C (Scheme 2).[7] The



Scheme 2. Comparison of the reactivity of μ-$F_2C{=}CH_2$ versus η^2-$F_2C{=}CH_2$.

simultaneous appearance of both species with either bridging or terminal olefin arrangements allows their reactivity to be directly compared. Addition of trimethylsilyl triflate to a 2:1 mixture of **4** and **4a** at −40 °C results in an instantaneous and quantitative conversion of **4** into **7**, while **4a** remains unchanged. This observation is the first clear documentation of an enhanced reactivity of a bridging fluoroolefin over the terminal (η^2) binding mode.

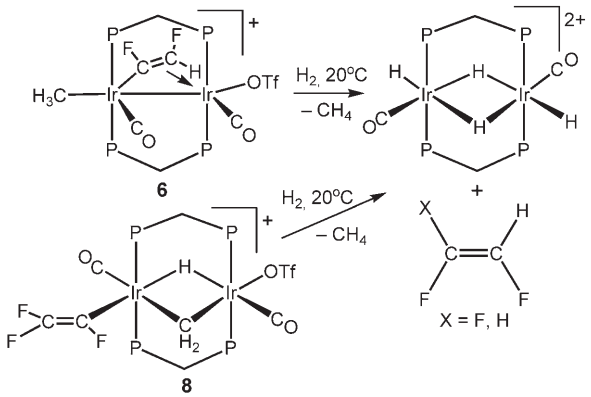
We wondered whether the unusual bridging fluorovinyl coordination mode would also give rise to greater reactivity than that of the η^1-binding mode so we set out to compare the reactivity of these groups in compounds **5** and **8**. The attempted reactions of these species with $Me_3Si(SO_3CF_3)$ are summarized in Scheme 3. Whereas Lewis acid promoted abstraction of a fluoride ion from **5** occurs readily at temperatures below 0 °C to yield the difluorovinylidene product $[Ir_2(CH_3)(CF_3SO_3)(CO)_2(\mu\text{-}C{=}CF_2)(dppm)_2][CF_3SO_3]_2$ (**9**), no reaction of **8** was observed at temperatures up to 25 °C. Again, interaction of the unsaturated fluorocarbyl unit with both metal centers gives rise to a significant



Scheme 3. Comparison of the reactivity of μ-η^1:η^2-C_2F_3 versus η^1-C_2F_3.

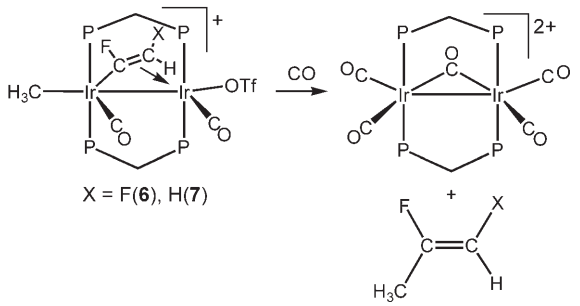
enhancement in the reactivity over that of the group bound to only one metal center. Facile removal of a fluoride ion from the *cis*-difluorovinyl- and 1-fluorovinyl-bridged species **6** and **7**, respectively, is also achieved to give the corresponding monofluorovinylidene- and vinylidene-bridged products $[Ir_2(CH_3)(CF_3SO_3)(CO)_2(\mu\text{-}C{=}CHX)(dppm)_2][CF_3SO_3]_2$ (X = F (**10**), H (**11**)).

Having converted the three fluoroolefins into the corresponding fluorovinyl groups, it was of interest to attempt the conversion of the latter into substituted fluoroolefins, thereby completing the cycle for functionalization of the starting fluoroolefins. This has been achieved in two ways: Reaction of the di- and trifluorovinyl complexes **6** and **8** with H_2 for 24 hours yields the corresponding olefins, *cis*-difluoroethylene and trifluoroethylene (Scheme 4), together with the



Scheme 4. Hydrogenolysis of fluorovinyl groups.

known dicationic tetrahydride complex.[12] No evidence of fluoroalkanes, which result from olefin hydrogenation, is observed. Although compound **8** yields trifluoroethylene quantitatively, **6** yields the expected *cis*-difluoroethylene together with *cis*-difluoropropene in a 2:1 ratio; the latter product results from a similar reductive elimination similar to that described below in Scheme 5. Furthermore, the di- and monofluorovinyl species **6** and **7** react with CO over 24 hours to give *cis*-difluoropropene and 2-fluoropropene, respectively,



Scheme 5. Formation of fluoropropenes by reductive elimination of fluorovinyl and methyl groups.

together with the known dicationic pentacarbonyl product[13] (Scheme 5). The trifluorovinyl compounds **5** and **8** do not liberate trifluoropropene upon exposure to CO.

Although, in principle, the stepwise conversions of fluoroolefins into vinylidene-bridged species, as described above, could lead to substitution of a pair of geminal fluorine atoms, we have not yet succeeded in effecting such transformations. All vinylidene species **9**–**11** are unreactive towards H_2 and react with CO to only give replacement of the coordinated triflate group.

As noted in the most recent review on the subject,[2e] "There are remarkably few examples of C–F activation of coordinated fluoroalkenes or fluorovinyl complexes." Herein we have demonstrated facile activation of a C–F bond involving both types of fluorocarbyl groups in what we believe to be the first such study involving a closely related series of fluoroolefins and their derived fluorovinyl groups. One pivotal finding in this study is the greatly enhanced reactivity of these groups when bridging a pair of metal centers instead of being bound to a single metal center. As such, this study also represents one of the few clear demonstrations of metal–metal cooperativity in substrate activation.

Although selective activation of a single C–F bond and subsequent functionalization has been observed with fluoroarenes,[14] it has not previously been observed with fluoroolefins. Unlike recent studies[15] in which multiple hydrodefluorinations of fluoroolefins has occurred, our system allows regioselective replacement of a single fluorine atom by a hydrogen atom to give trifluoroethylene from tetrafluoroethylene, as well as *cis*-difluoroethylene from trifluoroethylene. It is also believed to be the first report of the regioselective transformation of fluoroethylene molecules into the respective fluoropropenes by replacement of a fluorine atom by a methyl group.

Experimental Section

All solvents were dried, distilled, and stored under dinitrogen. Reactions were carried out under argon using standard Schlenk techniques. 1,1-Difluoroethylene was supplied by Lancaster Synthesis; trifluoroethylene was supplied by SynQuest Fluorochemicals, or prepared by a literature method.[16] Tetrafluoroethylene was prepared as reported.[17] NMR experiments were carried out on Bruker AM400, Varian Unity 400, 500, or 600 spectrometers. The NMR data reported below were recorded at 25 °C in CD_2Cl_2, except where noted. In all cases, ^{31}P and ^{13}C NMR spectra are reported with broadband ^1H decoupling.

In a typical C–F bond activation experiment, the fluoroolefin-bridged complex (**2**, **3**, or **4**; 50 mg) was prepared in CH_2Cl_2 as previously reported.[7] One equivalent of $Me_3Si(SO_3CF_3)$ was added dropwise and the mixture stirred for 30 min. The resulting fluorovinyl-bridged species (**5**, **6**, or **7**) was treated with an additional equivalent of $Me_3Si(SO_3CF_3)$ to produce the vinylidene complexes (**9**, **10**, or **11**).

In a typical hydrogenation experiment, hydrogen gas (1–5 equiv) was added slowly by a gas-tight syringe to a solution of **6** or **8** (50 mg) in CD_2Cl_2 (0.7 mL) in an NMR tube at −78 °C. In the carbonylation experiments, excess carbon monoxide gas was added slowly by a gas-tight syringe to a solution of **6** or **7** (50 mg) in CD_2Cl_2 (0.7 mL) in an NMR tube at −78 °C. NMR spectra (^1H, ^{31}P, ^{19}F, and ^{13}C) were recorded from −80 °C to ambient temperature at 20 °C intervals. Identification of the fluoroolefin products was established by comparison of the spectra to those of the known compounds.[18] A more complete description is given in the Supporting Information.

5: ^{31}P NMR: $\delta = 13.0$ (t, $^2J_{PP} = 24$ Hz, 2P), −8.0 ppm (t, $^2J_{PP} = 24$ Hz, 2P); ^1H NMR: $\delta = 4.5$ (brs, 2H), 3.6 (brs, 2H), 1.4 ppm (dt, $^3J_{HP} = 5.6$, $^5J_{HF} = 6.0$ Hz, 3H); ^{13}C NMR: $\delta = 161$ (m), 178 (m), −19 ppm (d, $^4J_{CF} = 13$ Hz,); ^{19}F NMR: $\delta = -80$ (brdd, $^2J_{FF} = 85$, $^3J_{FF} = 20$ Hz, 1F), −120 (dd, $^2J_{FF} = 85$, $^3J_{FF} = 100$ Hz, 1F), −131 (dd, $^3J_{FF} = 20$, $^3J_{FF} = 100$ Hz, 1F), −76 ppm (s, 3F). Spectra were recorded at −20 °C.

6: ^{31}P NMR: $\delta = 9.0$ (m, 1P), −2.5 (m, 2P), −19.0 ppm (m, 1P); ^1H NMR: $\delta = 6.0$ (dd, $^2J_{HF} = 65$, $^3J_{HF} = 10$ Hz, 1H), 6.1 (brs, 1H), 5.6 (brs, 1H), 5.5 (m, 1H), 4.7 (m, 1H), 1.2 ppm (t, $^3J_{HP} = 6.0$ Hz, 3H); ^{13}C NMR: $\delta = 165$ (brm), 172 (brm), −23 ppm (brs); ^{19}F NMR: $\delta = -23$ (dd, $^3J_{FF} = 35$, $^3J_{FH} = 10$ Hz, 1F), −171 (dd, $^3J_{FF} = 35$, $^2J_{FH} = 65$ Hz, 1F), −77 ppm (s, 3F).

7: ^{31}P NMR: $\delta = 1.6$ (dt, $^2J_{PP} = 18.5$ Hz, $^3J_{PF} = 45$ Hz, 2P), −5.5 ppm (t, $^2J_{PP} = 18.5$ Hz, 2P); ^1H NMR: $\delta = 6.0$ (d, $^2J_{HH} = 6$ Hz, 1H), 5.4 (dd, $^2J_{HH} = 6$, $^3J_{HF} = 14$ Hz, 1H), 3.1 (m, 2H), 4.3 (m, 2H), 0.2 ppm (t, $^3J_{HP} = 5.6$ Hz, 3H); ^{13}C NMR: $\delta = 164$ (brd, $^3J_{CF} = 58$ Hz), 172 (t, $^2J_{CP} = 11$ Hz), 5 ppm (s); ^{19}F NMR: $\delta = -211$ (brt, $^3J_{FP} = 45$ Hz, 1F), −77 ppm (s, 3F). Spectra were recorded at −20 °C.

8: ^{31}P NMR: $\delta = -0.5$ (t, $^2J_{PP} = 26$ Hz, 2P), −28.5 ppm (t, $^2J_{PP} = 26$ Hz, 2P); ^1H NMR: $\delta = 6.4$ (q, $^3J_{HP} = 6.0$ Hz, 2H), 5.0 (m, 4H), −12.2 ppm (brs, 1H); ^{13}C NMR: $\delta = 164$ (dt, $^2J_{CP} = 11$ Hz, $^4J_{CF} = 22$ Hz), 166 (brm), 38 ppm (brs); ^{19}F NMR: $\delta = -92$ (dd, $^2J_{FF} = 90$, $^3J_{FF} = 40$ Hz, 1F), −121 (dd, $^2J_{FF} = 90$, $^3J_{FF} = 115$ Hz, 1F), −123 (dd, $^3J_{FF} = 40$, $^3J_{FF} = 115$ Hz, 1F), −76 ppm (s, 3F).

9: ^{31}P NMR: $\delta = -6.2$ (t, $^2J_{PP} = 21$ Hz, 2P), −20.6 ppm (m, $^2J_{PP} = 21$ Hz, 2P); ^1H NMR: $\delta = 4.1$ (m, 2H), 2.8 (m, 2H), 1.9 ppm (t, $^3J_{HP} = 9.0$ Hz, 3H); ^{13}C NMR: $\delta = 151$ (brs), 174 (brs), 38 ppm (s); ^{19}F NMR: $\delta = -69$ (d, $^2J_{FF} = 97$ Hz), −86 (d, $^2J_{FF} = 97$ Hz), −76 ppm (s, 3F).

10: ^{31}P NMR: $\delta = -5.0$ (t, $^2J_{PP} = 23$ Hz, 2P), −21.0 ppm (t, $^2J_{PP} = 23$ Hz, 2P); ^1H NMR: $\delta = 8.6$ (d, $^2J_{HF} = 85$ Hz, 1H), 4.3 (m, 2H), 2.8 (m, 2H), 2.15 ppm (t, $^3J_{HP} = 9.0$ Hz, 3H); ^{13}C NMR: $\delta = 153$ (t, $^2J_{CP} = 12.5$ Hz), 176 (brs), 41 ppm (s); ^{19}F NMR: $\delta = -107$ (d, $^2J_{FH} = 85$ Hz), −76 ppm (s, 3F).

11: ^{31}P NMR: $\delta = -10.0$ (t, $^2J_{PP} = 17$ Hz, 2P), −20.0 ppm (t, $^2J_{PP} = 17$ Hz, 2P); ^1H NMR: $\delta = 6.01$ (s, 1H), 5.99 (s, 1H), 4.1 (m, 2H), 2.9 (m, 2H), 1.25 ppm (brt, $^3J_{HP} = 4.9$ Hz, 3H); ^{13}C NMR: $\delta = 164$ (brs), 170 (brs), 0.2 ppm (s); ^{19}F NMR: $\delta = -77$ ppm (s, 3F). Spectra were recorded at 0 °C.

Received: September 27, 2006
Revised: February 24, 2007
Published online: April 5, 2007

Keywords: bond activation · bridging ligands · cooperative phenomena · fluorinated ligands · iridium

[1] R. A. Gossage, G. van Koten, *Top. Organomet. Chem.* **1999**, *3*, 1.
[2] Relevant reviews: a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373; b) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber.* **1997**, *130*, 145; c) T. G. Richmond, *Top. Organomet. Chem.* **1999**, *3*, 243; d) H. Torrens, *Coord. Chem. Rev.* **2005**, *249*, 1957; e) R. N. Perutz, T. Braun, *Comprehensive Organometallic Chemistry III* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Dordrecht, chap. 1.26 in press.
[3] T. Hiyama, *Organofluorine Compounds*, Springer, Berlin, **2000**; *Organofluorine Chemistry: Principles and Commercial Applications* (Eds.: R. E. Banks, B. E. Smart, J. C. Tatlow), Plenum, New York, **1994**.
[4] A. R. Ravishankara, S. Solomon, A. A. Turnipseed, R. F. Warren, *Science* **1993**, *259*, 194.
[5] J. J. Bonnet, R. Mathieu, R. Poilblanc, J. A. Ibers, *J. Am. Chem. Soc.* **1979**, *101*, 7487.
[6] R. Rumin, F. Y. Pétillon, L. Manojlovic-Muir, K. W. Muir, D. S. Yufit, *J. Chem. Soc. Chem. Commun.* **1995**, 1431.
[7] D. Ristic-Petrovic, D. J. Anderson, J. R. Torkelson, R. McDonald, M. Cowie, *Organometallics* **2003**, *22*, 4647.
[8] See for example: a) A. K. Burrell, G. R. Clark, C. E. F. Rickard, W. R. Roper, *J. Organomet. Chem.* **1994**, *482*, 261; b) T. G. Richmond, A. M. Crespi, D. F. Shriver, *Organometallics* **1984**, *3*, 314; c) D. L. Reger, M. D. Dukes, *J. Organomet. Chem.* **1978**, *153*, 67; d) S. A. Garratt, R. P. Hughes, I. Kovacik, A. J. Ward, S. Willemsen, D. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 15585.
[9] D. Ristic-Petrovic, M. Wang, R. McDonald, M. Cowie, *Organometallics* **2002**, *21*, 5172; and references therein.
[10] A. N. Nesmeyanov, M. I. Rybinskaya, L. V. Rybin, V. S. Kaganovich, P. V. Petrovskii, *J. Organomet. Chem.* **1971**, *31*, 257.
[11] H. C. Clark, J. H. Tsai, *Inorg. Chem.* **1966**, *5*, 1407.
[12] R. McDonald, B. R. Sutherland, M. Cowie, *Inorg. Chem.* **1987**, *26*, 3333.
[13] B. R. Sutherland, M. Cowie, *Organometallics* **1985**, *4*, 1637.
[14] M. Aizenberg, D. Milstein, *J. Am. Chem. Soc.* **1995**, *117*, 8674.
[15] See for example: a) B. M. Kraft, W. D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 8681; b) D. Noveski, T. Braun, M. Schulte, B. Neumannn, H.-G. Stammler, *Dalton Trans.* **2003**, 4075.
[16] R. N. Haszeldine, B. R. Steele, *J. Chem. Soc.* **1957**, 2800.
[17] J. D. Lazerte, L. J. Hals, T. S. Reid, G. H. Smith, *J. Am. Chem. Soc.* **1953**, *75*, 4525.
[18] C. H. Dungan, J. R. Van Wazer, *Compilation of reported ^{19}F NMR chemical shifts, 1951 to mid-1967*, Wiley-Interscience, New York, **1970**.

