Solvent Influence on Trifluoromethylation Reactions with $Cd(CF_3)_2$: One-pot Synthesis of Trifluoromethyl Iron Complexes

Wolfgang Dukat and Dieter Naumann *
Fachbereich Chemie, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50, Germany

---

Bis(trifluoromethyl)cadmium complexes $Cd(CF_3)_2{\cdot}L$ (L = $2CH_3CN$ or $CH_3OCH_2CH_2OCH_3$) react as perfluoroalkyl Grignard reagents with carbonyl-iron halides in a one-pot reaction to yield Fe–CF_3 compounds easily. A strong solvent influence is observed. The dependence of the direction of the reactions, either as a trifluoromethylation or a fluorination, is discussed. In the presence of CH_3CN a ligand-exchange reaction is observed, yielding trifluoromethyl iron acetonitrile complexes, while carbonyl complexes are obtained in ethers. The compound $[Fe(CO)_4(CF_3)_2]$ has been prepared in 65% yield, and its ^{19}F n.m.r., i.r., Raman, mass, and Mössbauer spectra recorded. The advantage of observing the ^{13}C satellites in the ^{19}F n.m.r. spectra for the analysis of trifluoromethyl metal compounds is established. If the appropriate reaction conditions are used, $Cd(CF_3)_2$ complexes react as fluorination reagents and CF_2 sources. Thus, on reaction of the trifluoromethyl cadmium reagents with tetracarbonyliron halides in CH_3CN, diamagnetic fluoroiron acetonitrile complexes are formed.

During the last decade perfluoro-organocadmium compounds have been demonstrated to be very efficient as perfluoro analogues of Grignard reagents. The trifluoromethyl cadmium derivatives have received special attention, because other trifluoromethyl metal compounds are either too unstable, like those of magnesium,[1] or show insufficient reactivity at moderate temperatures, *e.g.* $Hg(CF_3)_2$.[2,3]

Liu and Asprey[4] were the first to isolate a trifluoromethyl cadmium compound, $Cd(CF_3)_2{\cdot}2py$ (py = pyridine), and to realize its potential as a trifluoromethyl transfer reagent. Krause and Morrison[3] adapted these ideas and developed a synthetic method, yielding various trifluoromethyl cadmium complexes on a preparative scale, starting from $Cd(CH_3)_2$ and $Hg(CF_3)_2$. An easier route was established by Lange and Naumann,[5] using CF_3I as a starting material. This preparation yields purer products and is easily extended to higher homologues. An *in situ* preparation was described by Heinze and Burton,[6] involving the reaction of perfluoroiodoalkanes with cadmium metal. The disadvantage of this convenient method is that the solvent is restricted to dimethylformamide (dmf).

Krause and Morrison[3] observed that $Cd(CF_3)_2$ complexes sometimes react as CF_3^- or as a F^--transfer reagent, but made no attempt to explain this. We are working particularly on the control of the different reactivities of these complexes and have already formulated a mechanism.[7] The aim of this and subsequent work is to determine the optimum conditions for trifluoromethyl transfer to a given substrate. This information is necessary for a general application of the cadmium trifluoromethyl complexes as Grignard analogues.

This publication deals with reactions of $Cd(CF_3)_2$ complexes and carbonyliron halide complexes. The preparative routes described in the literature give either very low yields, as in the reaction of CF_3I with $[Fe(CO)_5]$ (6%),[8] or include several steps.[9,10]

Results and discussion

Reactions of $Cd(CF_3)_2$ *Complexes with Iron Halides.*—We investigated the reactions of $[Fe(CO)_4X_2]$ (X = Cl, Br, or I) and $FeCl_3$ with $Cd(CF_3)_2{\cdot}L$ (L = 2 CH_3CN or $CH_3OCH_2CH_2OCH_3$) in different solvents. All reactions were carried out under 'polar' reaction conditions. Products of both trifluoromethylation and fluorination were observed, and varied predominantly with the donor strengths of the solvents chosen, according to the Gutmann donor numbers,[11] *i.e.* dmf and py have high, acetonitrile has a medium, and ethers and CH_2Cl_2 have small donor numbers.

The reactions are discussed first with respect to $Cd(CF_3)_2$ complexes as trifluoromethylating agents. The different products resulting from $Cd(CF_3)_2$ as a fluorination reagent will be discussed subsequently.

Slow fluorination reactions in dmf and py. In the solvents dmf and py the $Cd(CF_3)_2$ complexes reacted very slowly and no Fe–CF_3 complexes were detectable by n.m.r. spectroscopy. In pyridine, however, secondary products of CF_2 have been identified for the first time.

Trifluoromethylation and ligand-exchange reactions in CH_3CN. By treating $Cd(CF_3)_2{\cdot}2CH_3CN$ with tetracarbonyliron halides, $[Fe(CO)_4X_2]$ (X = Cl, Br, or I), in acetonitrile, trifluoromethyl iron complexes and trifluoromethane were formed, and identified by ^{19}F n.m.r. spectroscopy. Except in reactions with $[Fe(CO)_4Br_2]$, two further products are observed by n.m.r. spectroscopy. In addition to the formation of chlorotrifluoromethane, reactions of $FeCl_3$ yield the same products, as shown in Figure 1.

Hence, carbonyl-containing complexes cannot be considered as products of these reactions. Due to the small linewidths in the spectra of the reaction of the diamagnetic carbonyl halides, paramagnetic products like iron(III) compounds can also be excluded. The signals in the range between δ −7 and −15 p.p.m. show ^{13}C satellites. The coupling constants $^1J(^{19}F-^{13}C)$ of about −360 Hz can be explained only by a CF_3 group attached to a metal atom like Fe. Compounds with δ −11.3 (**A**) and −9.5 p.p.m. (**B**) were formed in nearly all reactions in CH_3CN. A third signal at about −7 p.p.m. (**C**) appeared only at high concentrations of (**B**). Again, carbonyl complexes can be excluded, because the same products are formed, in the absence of CO, in reactions with $FeCl_3$ [Figure 1(*a*) and (*b*)]. Compounds of Fe–CF_3 without CO ligands such as Fe–CF_3–CH_3CN complexes are as yet unknown. However, it has been confirmed that α-CF_2 groups in n-C_3F_7 metal compounds show a similar influence on the metal and the ligands attached to the metal as CF_3 groups because they are exposed to the same strong paramagnetic shielding.[12] The $\delta(^{19}F)$ values of α-CF_2 groups in Fe–(n-C_3F_7)–CH_3CN complexes are shifted to high field by about 15 p.p.m., compared with analogous carbonyl

Table. Fluorine-19 n.m.r. data for perfluoroalkyl iron complexes

Compound	L = CO R = n-C_3F_7 δ(α-CF_2)/p.p.m.	L = CO R = CF_3 δ(CF_3)/p.p.m.	L = CH_3CN R = CF_3 δ(CF_3)/p.p.m.
cis-[FeL_4R_2]	−68.1 (in $CHCl_3$)[10]	+2.9 (in $CDCl_3$)[10] +2.88 (in CH_2Cl_2)	−11.9 (in CH_3CN)
trans-[FeL_4R_2]	−65.0 (in $CDCl_3$)[10]		
cis-[FeL_4R(I)]	−54.9 (in CH_2Cl_2)[12]	+7.1 (in CH_2Cl_2)[9]	−9.5 (in CH_3CN)
trans-[FeL_4R(I)]		+14.5 (in CH_2Cl_2)[9]	
cis-[FeL_4R(Br)]	−55.0 (in $CDCl_3$)*	+4.5 (in Et_2O)	−9.5 (in CH_3CN)
trans-[FeL_4R(Br)]		+10.3 (in Et_2O)	[−7.3 (in CH_3CN)]
cis-[FeL_4R(Cl)]	−55.4 (in $CDCl_3$)*	+4.2 (in Et_2O)	−9.3 (in CH_3CN)
trans-[FeL_4R(Cl)]		+10.5 (in Et_2O)	[−7.0 (in CH_3CN)]
[$Fe(CO)_2(CH_3CN)_2R$(I)]	−81.5 (in CH_2Cl_2)[27]		
[$Fe(CO)_2(CH_3CN)_3R]^+$	−76.9 (in CH_2Cl_2)[27]		

* I. I. Gerus and Yu. L. Yagupol'skii, *Zh. Org. Khim.*, 1985, **21**, 1850.

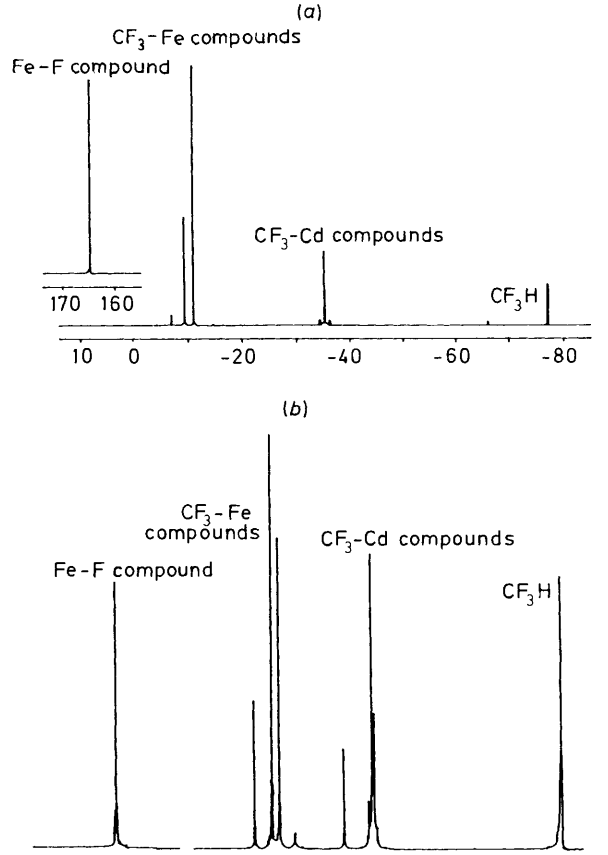


Figure 1. Fluorine-19 n.m.r. spectra of a reacting solution of (*a*) [$Fe(CO)_4I_2$] with $Cd(CF_3)_2{\cdot}2CH_3CN$ in CH_3CN and (*b*) $FeCl_3$ with $Cd(CF_3)_2{\cdot}2CH_3CN$ in CH_3CN

complexes, as shown in the Table. Hence, a chemical shift range between −5 and −15 p.p.m. can be estimated for Fe–CF_3–CH_3CN complexes.

The n.m.r. parameters (Table) allow the assignment of [$Fe(CH_3CN)_4(CF_3)_2$] to (**A**) and [$Fe(CH_3CN)_4(CF_3)X$] (X = Cl, Br, or I) to (**B**).

Similar to [$Fe(CO)_4(n\text{-}C_3F_7)X$], where the influence of the halogen X on δ(α-CF_2) is rather small, no influence can be observed in [$Fe(CH_3CN)_4(CF_3)X$].

An excess of $Cd(CF_3)_2{\cdot}2CH_3CN$ and an increase of the temperature or the reaction time results in the formation of [$Fe(CH_3CN)_4(CF_3)_2$] in the reaction of [$Fe(CH_3CN)_4(CF_3)X$] with the cadmium reagent. The appearance of ^{13}C satellites in the ^{19}F n.m.r. spectra gives further support to this assignment. The satellites of (**B**), [$Fe(CH_3CN)_4(CF_3)X$], always appeared as sharp singlets, whereas the satellites of (**A**), [$Fe(CH_3CN)_4(CF_3)_2$], were observed only in the presence of paramagnetic impurities, causing linewidths larger than 10 Hz. This is strong evidence for the presence of several, magnetically equivalent, CF_3 groups in (**A**). The splitting due to $^4J(^{19}F–^{19}F)$ decreases the signal intensities, probably causes second-order spectra, and prevents their detection. Similarly, the detection of (**A**) and (**B**) by ^{13}C n.m.r. spectroscopy failed without isolation or ^{19}F decoupling facilities.

In the reaction of $Cd(CF_3)_2{\cdot}2CH_3CN$ with [$Fe(CO)_4Br_2$] in CH_3CN only [$Fe(CH_3CN)_4(CF_3)Br$] is formed at −30 °C. There is no evidence for any other Fe–CF_3 compound. A coupled ^{13}C n.m.r. spectrum, besides solvent signals and signals for the CF_3 groups in $Cd(CF_3)Br{\cdot}2CH_3CN$, $Cd(CF_3)_2{\cdot}2CH_3CN$, and [$Fe(CH_3CN)_4(CF_3)Br$], shows two quartets at δ 132.9 and 126.7 p.p.m. [$^1J(^{13}C\text{-}^1H)$ = 10.4 Hz] in a 1:1 integration ratio, the latter peak being slightly broadened. They are due to CH_3CN firmly attached to Fe. The downfield shift, compared with 'free' CH_3CN [δ(CN) 116.8 pm, $^2J(^{13}C\text{-}^1H)$ = 9.8 Hz], is similar to that of δ(CO) in *cis*-[$Fe(CO)_4(CF_3)_2$][10] [δ(equatorial CO) 195.9, δ(axial CO) = 197.8 p.p.m.] compared with uncomplexed CO (δ = 183.2 p.p.m.[13]). These CH_3CN signals have not been detected in the ^{13}C n.m.r. spectra of $Cd(CF_3)_2{\cdot}2CH_3CN$ or in reactions of [$Fe(CO)_4X_2$] (X = Br or I) with CH_3CN, forming Fe–CH_3CN halogen complexes while liberating CO.

The presence of two different CH_3CN ligands confirms the *cis* structure of this complex. The similar electronic properties of CF_3 and Br ligands are responsible for the equivalence of the two theoretically different equatorial CH_3CN ligands in *cis*-[$Fe(CH_3CN)_4(CF_3)Br$]. The signal (**C**) [δ −7.0 (X = Cl), −7.3 p.p.m. (X = Br)] probably belongs to *trans*-[$Fe(CH_3CN)_4(CF_3)X$], but besides δ(^{19}F) there is no further evidence for this assignment.

Trifluoromethylation and fluorination reactions in ethers. In the reaction of $Cd(CF_3)_2{\cdot}CH_3OCH_2CH_2OCH_3$ with [$Fe(CO)_4Br_2$] in diethyl ether no ligand exchange was observed. Two main products are formed. Besides the trifluoromethylated product, [$Fe(CO)_4(CF_3)_2$], the CF_2 secondary product

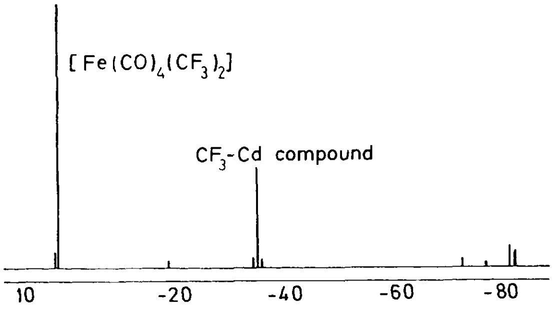


Figure 2. Fluorine-19 n.m.r. spectrum of a reacting solution of $[Fe(CO)_4Br_2]$ and $Cd(CF_3)_2{\cdot}CH_3OCH_2CH_2OCH_3$ in $CH_3OCH_2CH_2OCH_3$

CF_2H-O-CF_2H has also been detected (Figure 2) [equation (1)]. The ratio between the two products can be controlled by

$$Cd(CF_3)_2{\cdot}CH_3OCH_2CH_2OCH_3 + [Fe(CO)_4Br_2] \xrightarrow{Et_2O} CF_2H\text{-}O\text{-}CF_2H + [Fe(CO)_4(CF_3)_2] \quad (1)$$

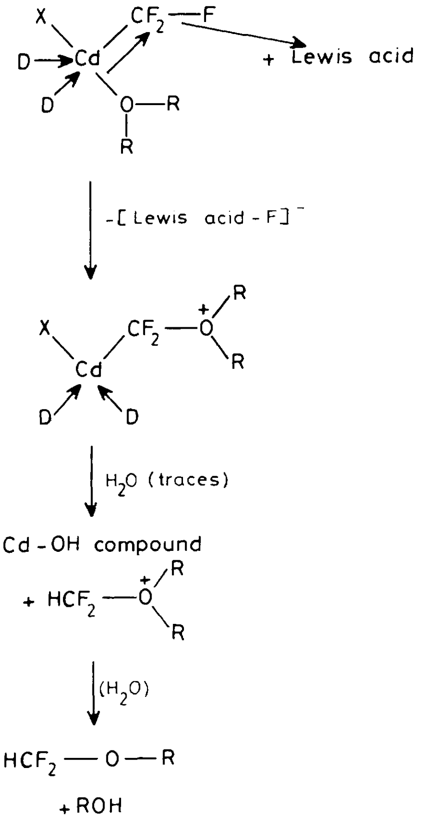
the temperature. At −30 °C difluorocarbene products are formed exclusively, while at 37 °C only the trifluoromethylation reaction occurred. The latter was complete after 21 h. The main product is $[Fe(CO)_4(CF_3)_2]$ (70% yield). A second Fe–CF_3 compound (13%) could not be characterized due to its complex n.m.r. pattern.

The corresponding reaction in $CH_3OCH_2CH_2OCH_3$ is faster. At 20 °C, the trifluoromethylation reaction occurred predominantly. The reacting solutions contained two further Fe-CF_3 compounds in small concentration, appearing as singlets in the ^{19}F n.m.r. spectra, which can be assigned to the expected intermediates *cis*- and *trans*-$[Fe(CO)_4(CF_3)Br]$ by comparison with the chemical shifts of the iodine derivatives, described in the literature (see Table).

The reaction of $[Fe(CO)_4Cl_2]$ with $Cd(CF_3)_2{\cdot}CH_3OCH_2CH_2OCH_3$ in ether yields, besides $(CF_2H)_2O$, *cis*- and *trans*-$[Fe(CO)_4(CF_3)Cl]$ and $[Fe(CO)_4(CF_3)_2]$ even at −30 °C. A reaction at 20 °C was complete after 3 d, yielding $[Fe(CO)_4(CF_3)_2]$ as the only CF_3-containing compound.

Fluorination products of $Cd(CF_3)_2$ *complexes and secondary products of difluorocarbene, the formation of pentafluoroethyl and fluoro metal compounds in dmf and py.* In the solvents dmf and py the $Cd(CF_3)_2$ complexes reacted very slowly. After several weeks in py, $[Fe(CO)_4I_2]$ yielded C_2F_5-containing compounds with >50% selectivity, indicating the intermediate formation of difluorocarbene. This species has been observed during $Cd(CF_3)_2$ reactions in the solvent pyridine for the first time. Iron fluorides or fluoroiron pyridine complexes could not be observed by ^{19}F n.m.r. spectroscopy, due to their paramagnetism. Such paramagnetic products are responsible for the huge linewidths observed in the ^{19}F n.m.r. spectra of solutions of both reactions in dmf (400 Hz) and py (50 Hz).

The formation of diamagnetic fluoroiron solvent complexes in CH_3CN. The ^{19}F n.m.r. spectra of all iron halide reactions except those of $[Fe(CO)_4Br_2]$ contain a singlet at δ +164 p.p.m., occasionally accompanied by a second signal of low intensity at δ +166 p.p.m. (see Figure 1). Carbon–fluorine compounds can be excluded by the absence of ^{13}C satellites and the huge downfield shift that is typical of transition-metal fluorides, *e.g.* WF_6[14] and MoF_6.[14] However, iron fluoride complexes like $[FeF_6]^{4-}$ are expected to be paramagnetic[15] and cannot be taken into account according to the observed linewidth in some n.m.r. spectra. Thus, these signals are interpreted as due to fluoroiron(II) acetonitrile complexes like *cis*- and *trans*-$[Fe(CH_3CN)_4F_2]$ or $[Fe(CH_3CN)_2F_4]^{2-}$. These compounds are unknown, but the analogous iron(III) complexes $[Fe(dmso)_2F_4]^-$ and $[Fe(dmso)_4F_2]^+$ (dmso = dimethyl sulphoxide) have been reported.[11]



Scheme.

Despite the possibility of the formation of iron fluoride complexes with other solvents, for instance ethers, such paramagnetic complexes cannot be detected directly by n.m.r. spectroscopy due to paramagnetic line broadening. Only ligands with both good donor and π-acceptor properties like CO, CN^-, or CH_3CN cause ligand-field splittings suitable for low-spin complexes and, assuming a +2 oxidation state for iron, easily detectable diamagnetic products. No attempts were made to isolate these iron fluoride species.

Secondary products of difluorocarbene in ethers. By treating $Cd(CF_3)_2$ complexes with $FeCl_3$ or $[Fe(CO)_4X_2]$ (X = I, Br, or Cl) in ethers (diethyl ether or $CH_3OCH_2CH_2OCH_3$), difluoromethyl ethers (*i.e.* CF_2H–O–R) could easily be detected in the ^{19}F n.m.r. spectra, due to their chemical shift and characteristic doublet pattern with a coupling constant $^2J(^{19}F-^1H)$ = 70 Hz.[16] Various difluoromethyl ethers have been observed previously as by-products of the reactions of $Cd(CF_3)_2$ complexes with Lewis acids when the trifluoromethylation reaction was very slow, *e.g.* in reactions of $Cd(CF_3)_2{\cdot}CH_3OCH_2CH_2OCH_2CH_2OCH_3$ with $SOCl_2$ in $CH_3(OCH_2CH_2)_2OCH_3$.[17] These are secondary products of CF_2, liberated during the fluorination of the Lewis acid by the cadmium complex. The mechanism of their formation is not yet fully understood. There are no indications of C_2F_4 or cyclo-C_3F_6, the oligomerisation products of CF_2. We thus believe that no free CF_2 is formed in these reactions. An intramolecular insertion into the Cd–O bond seems likely, with transfer of a F^- to the Lewis acid. The loss of an alkyl group in the second step yields a Cd–CF_2–OR compound, which can hydrolyse to CF_2H–O–R ethers (Scheme).

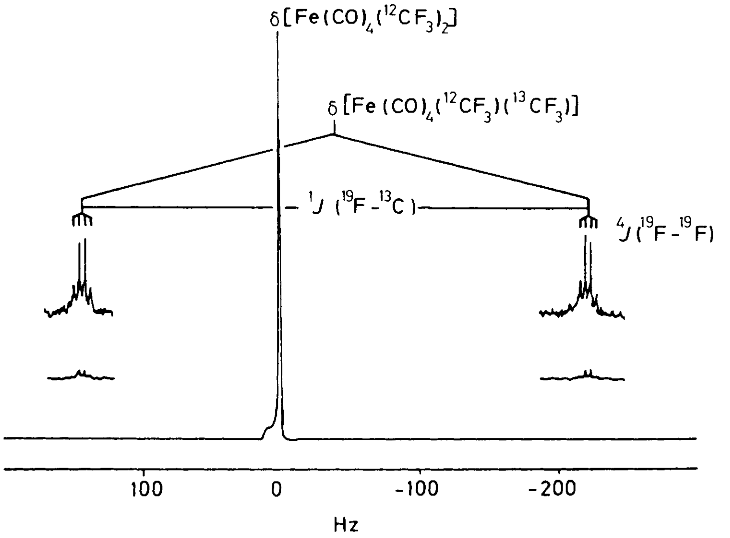


Figure 3. Fluorine-19 n.m.r. spectrum of $[Fe(CO)_4(CF_3)_2]$

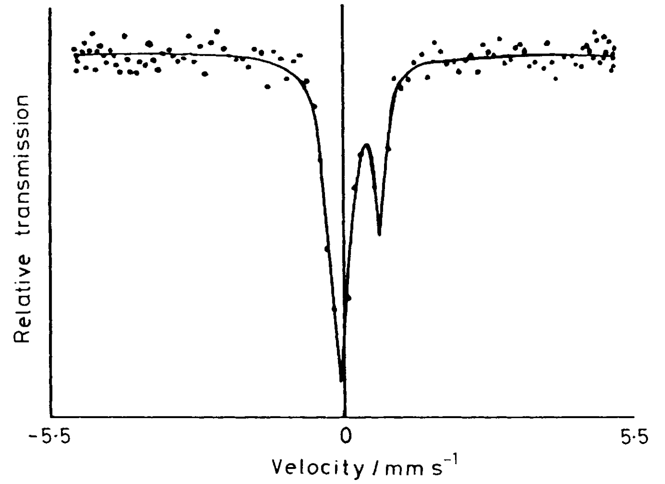


Figure 4. Iron-57 Mössbauer spectrum of $[Fe(CO)_4(CF_3)_2]$

The formation of tetrafluoroethene and perfluorocyclopropene in CH_2Cl_2. The compound $Cd(CF_3)_2{\cdot}2CH_3CN$ was treated with $[Fe(CO)_4I_2]$ in CH_2Cl_2. At −30 °C Fe–CF_3–CH_3CN complexes were the main products, while at 20 °C secondary products of CF_2 appeared. Compounds of C_2F_5 are formed as well as C_2F_4 and cyclo-C_3F_6 which are the oligomerisation products of difluorocarbene. **CAUTION**: This reaction was much faster with $[Fe(CO)_4Br_2]$, leading to an explosion during the first few seconds of stirring the solution, which is an indication of the rapid formation of a gaseous compound like C_2F_4.

One-pot preparation, isolation, and characterisation of cis-$[Fe(CO)_4(CF_3)_2]$. It is more convenient to use $[Fe(CO)_4Br_2]$ rather than its chlorine analogue to prepare $[Fe(CO)_4(CF_3)_2]$, as it is more simple to prepare and easier to handle. In a one-pot reaction, $[Fe(CO)_4Br_2]$ and $Cd(CF_3)_2{\cdot}CH_3OCH_2CH_2OCH_3$ (10% excess) were refluxed in diethyl ether for 21 h. The compound $[Fe(CO)_4(CF_3)_2]$ can be separated from the non-volatile by-products, after distillation of the ether, by distillation in the presence of n-heptane. The product can be frozen out of the heptane solution quantitatively. The yield is 65%. This method of isolation cannot be used with $CH_3OCH_2CH_2OCH_3$ as the solvent as the complex cannot be recovered from the $CH_3OCH_2CH_2OCH_3$–heptane solution after distillation.

The compound *cis*-$[Fe(CO)_4(CF_3)_2]$ is a slightly yellow, almost colourless crystalline substance, which shows a remarkable stability for an iron carbonyl as well as for a trifluoromethyl metal compound. It sublimes at ambient pressure even at room temperature, far below its melting (80 °C) or decomposition point (120 °C). No decomposition occurred in the presence of moisture or light, even after months.

Figure 3 shows the ^{19}F n.m.r. spectrum of the substance. The ^{13}C satellites which are due to the compound $[Fe(CO)_4(^{12}CF_3)(^{13}CF_3)]$ are of particular importance. Because of the magnetic inequivalence of the CF_3 groups, a further coupling, besides $^1J(^{19}F-^{13}C)$, due to $^4J(^{19}F-^{19}F)$ is observable. The quartet pattern indicates the presence of two equivalent CF_3 groups in the all-^{12}C compound. The coupling constant of 4.2 Hz is strong evidence for a *cis* arrangement of the CF_3 groups. The $^4J(^{19}F-^{19}F)$ coupling is known to be much smaller between *trans* CF_3 groups.[18] The i.r. spectrum is consistent with spectra previously published.[9,10] It indicates a *cis* structure. The Raman spectrum exhibits frequencies for CF_3 and two carbonyl vibrations of CO.

Figure 4 shows the ^{57}Fe Mössbauer spectrum of *cis*-$[Fe(CO)_4(CF_3)_2]$ at 20 °C. It contains an asymmetric doublet with an isomeric shift of δ +0.367(8) mm s^{-1}. The quadrupolar splitting is Δ = 0.735(6) mm s^{-1}. The asymmetry of the doublet is due to the crystalline structure of the substance, platelets (0.3 × 0.3 × 0.18 mm) orientated in the same direction. Because of its vapour pressure, grinding in a mortar was impossible. Collins and Pettit[19] found a linear relationship between the isomeric shift $\delta(^{57}Fe)$ and the quadrupolar splitting of $Fe(CO)_4$ donor complexes. The compound $[Fe(CO)_4I_2]$ also obeys this linear relationship. ^{129}I Mössbauer investigations confirmed its formulation as a complex containing iodine.[20] The compound *cis*-$[Fe(CO)_4(CF_3)_2]$ does not fit this relationship, however. As shown by n.m.r. spectroscopy [$^4J(^{19}F-^{19}F)$], it contains two CF_3 groups which are separately attached to the iron. This could be the reason for the difference in the thermal and chemical stability and in the colour.

The mass spectrum of *cis*-$[Fe(CO)_4(CF_3)_2]$ shows a small M^+ peak, but no other $Fe(CO)_4$ species. It is stabilised primarily by cleavage of a CO group, probably *trans* to another

CO, using the same orbitals for the (d_π-σ^*) back bonding in octahedral complexes. A perfluoroalkyl group *trans* to a CO has a stabilising electronic effect. In a metal carbonyl complex the transfer of electron density to the metal *via* a σ bond is partially compensated by the reverse transfer *via* (d_π-σ^*) back bonding. Perfluoroalkyl groups behave in the opposite manner. Due to their high group electronegativities (3.3[21]), they accept electron density *via* the σ bond, while fluorine atoms in an α position undergo intramolecular donor interactions with unoccupied metal π orbitals. Such a 'back donation' has been previously thought to be responsible for the relatively higher thermal stability of perfluoroalkyl metal compounds when compared with the non-fluorinated homologues. Exceptions to this are $Cd(CF_3)_2$ or $Zn(CF_3)_2$ complexes, where this 'back donation' simply promotes the liberation of CF_2 at moderate temperatures.

Thus, perfluoroalkyl and carbonyl ligands in the *trans* position electronically complement each other perfectly. We believe this to be the reason why no *trans*-$[Fe(CO)_4(CF_3)_2]$ could be synthesised, although several attempts have been made.[22]

Conclusions

The Reactivity of $Cd(CF_3)_2$ *Complexes as Grignard Reagents.*—Even Krause and Morrison[3] noticed that $Cd(CF_3)_2$ complexes react with some compounds, *e.g.* $SnBr_4$, in solvents like CH_2Cl_2 exclusively as trifluoromethylating agents, while carboxylic acid halides yield only the corresponding acid fluorides besides the intermediate formation of difluorocarbene, CF_2.

We have shown earlier[17] that the reactivity, as a trifluoromethylating or a fluorinating agent, can be directed by appropriate choice of the solvent. Solvents like py or dmf with high donor abilities, as classified by Gutmann's donor numbers, DN,[11] favoured the trifluoromethylation of the reacted Lewis acids. These solvents are understood to complex the Lewis acid reversibly, decreasing their hardness, thus favouring the transfer of the softer CF_3^- anion rather than attack of the harder fluoride anion, and simultaneously liberating CF_2.

In the case of the iron halides and iron carbonyl halides the reactivity was inverted. While in ether and acetonitrile trifluoromethylation reactions occurred, the reaction in pyridine was found to be very slow yielding mainly CF_3H and secondary products of CF_2. These results can be also understood by the donor activities of the solvents. According to Hieber and Bader,[23] solvents like pyridine (DN = 33) replace the carbonyl groups and the iodide in $[Fe(CO)_4I_2]$ [equations (2)—(4)]. The

$$[Fe(CO)_4I_2] + 2py \longrightarrow [Fe(CO)_2(py)_2I_2] + 2CO \quad (2)$$

$$[Fe(CO)_2(py)_2I_2] + 2py \longrightarrow [Fe(py)_4I_2] + 2CO \quad (3)$$

$$[Fe(py)_4I_2] + 2py \longrightarrow [Fe(py)_6]^{2+} + 2I^- \quad (4)$$

same mechanism is expected with dmf (DN = 26.6). Similarly $FeCl_3$ reacts with dmso (DN = 29.8) forming $[Fe(dmso)_6]^{3+}$ and solvated chloride anions. The formation of these octahedral solvent complexes of Fe^{2+} and Fe^{3+} is irreversible, preventing the trifluoromethylation of the metal. The 'free' halides in the solution can catalyse the formation of CF_2 from the $Cd(CF_3)_2$ complexes, as reported earlier for trifluoromethyl tin[24,25] and mercury[26] compounds. In solvents having smaller donor numbers, like acetonitrile, ethers, or CH_2Cl_2, trifluoromethylation is observed, even at −30 °C.

A further complication appeared in CH_3CN, due to the exchange of CO with CH_3CN ligands, when carbonyliron halides were treated with the trifluoromethyl cadmium reagent. The compounds $[Fe(CO)_4X_2]$ (X = Br or I) are stable to ligand exchange at −30 °C in CH_3CN, as confirmed by i.r. and ^{13}C n.m.r. spectroscopy. At 20 °C, however, they are decomposed, liberating CO and forming complexes with acetonitrile. The ^{13}C n.m.r. signals of the nitrile carbon in CH_3CN became broad, and, in contrast to $[Fe(CH_3CN)_4(CF_3)_2]$ in CH_3CN, no separate signals for CH_3CN molecules bound to the metal appeared, indicating a dynamic solvent ligand exchange.

In the presence of $Cd(CF_3)_2 \cdot 2CH_3CN$ the formation of Fe–CF_3–CH_3CN complexes has been observed, even at −30 °C, while $[Fe(CO)_4(CF_3)_2]$ is stable in CH_3CN at 20 °C. Thus, we assume that the ligand exchange reaction occurs preferably with the intermediate $[Fe(CO)_4(CF_3)X]$ (X = Cl, Br, or I). Similar reactions have been reported with the n-C_3F_7 homologues[27] [equation (5)]. The iodide can be exchanged by CH_3CN by the means of $AgPF_6$ [equation (6)]. In dmf,

$$[Fe(CO)_4(n\text{-}C_3F_7)I] + 2CH_3CN \longrightarrow [Fe(CO)_2(CH_3CN)_2(n\text{-}C_3F_7)I] + 2CO \quad (5)$$

$$[Fe(CO)_2(CH_3CN)_2(n\text{-}C_3F_7)I] + AgPF_6 \longrightarrow [Fe(CO)_2(CH_3CN)_3(n\text{-}C_3F_7)]^+PF_6^- + AgI \quad (6)$$

however, both CO and I^- ligands are substituted by the solvent without silver salts present, yielding stepwise $[Fe(dmf)_5R]^+I^-$ (R = CF_3, n-C_3F_7, or n-C_6F_{13}).[28] In solvents like ether, $CH_3OCH_2CH_2OCH_3$, CH_2Cl_2, and n-hexane the carbonyl halides $[Fe(CO)_4X_2]$ (X = Br or I) proved to be stable at ambient temperatures, due to the lower donor strength of these solvents, which explains the formation of trifluoromethyl iron carbonyl complexes.

Thus, it is now possible to predict the reactivity of $Cd(CF_3)_2$ complexes with Lewis acids and to choose the appropriate solvent, if the interaction between the solvent and the Lewis acid is monitored beforehand.

Experimental

The $Cd(CF_3)_2$ complexes were prepared from $Cd(CH_3)_2$ and CF_3I according to our method published previously.[5] Anhydrous $FeCl_3$ is commercially available. The compound $[Fe(CO)_5]$ was synthesised from iron powder and CO at 250 bar (2.5×10^7 Pa) and 180 °C and purified by vacuum distillation; $[Fe(CO)_4X_2]$ (X = I, Br, or Cl) were prepared from $[Fe(CO)_5]$ and the halogens according to ref. 24.

N.m.r. spectra were obtained on a Bruker FT AM 300 spectrometer (^{19}F, 282.4; ^{13}C, 75.47 MHz). Chemical shifts are referred to CCl_3F and $SiMe_4$, positive values indicating low-field shifts. I.r. spectra were recorded on a Perkin-Elmer grating spectrograph 580B; laser Raman spectra were obtained on a Coderg HPO with a He–Ne laser from Spectra-Physics. Cobalt-57 in a rhodium matrix was used as a source for the Mössbauer spectra.

The solvents were dried and purified by standard laboratory methods. All reactions were carried out under dry nitrogen. The reactants were dissolved in the solvents, stirred at −30 °C, and then warmed to the reaction temperature. Samples were taken continuously for n.m.r. and i.r. spectroscopy.

Preparation, Isolation and Characterisation of $[Fe(CO)_4(CF_3)_2]$.—The compound $Cd(CF_3)_2 \cdot CH_3OCH_2CH_2OCH_3$ (2.9 g, 8.5 mmol) was added to $[Fe(CO)_4Br_2]$ (2.5 g, 7.6 mmol) in diethyl ether (20 cm^3) at −30 °C and refluxed for 21 h at 37 °C. After cooling to 20 °C, heptane was added. The condenser was substituted for a distillation apparatus. After distillation of ether, $[Fe(CO)_4(CF_3)_2]$ was removed from the residue by distillation. The obtained product in heptane solution was cooled to −78 °C and the solvent removed by a pipette. The compound was dried at −196 °C in high vacuum, yielding 1.5 g (65.4%) of $[Fe(CO)_4(CF_3)_2]$. No impurities could be detected by ^{19}F n.m.r. spectroscopy. The compound is identical with an authentic sample.[10]

^{19}F N.m.r. (saturated in CH_2Cl_2, 20 °C): δ +2.88 p.p.m. $^1J(^{19}F-^{13}C) = 364.4$, $^4J(^{19}F-^{19}F) = 4.2$ Hz. i.r. (saturated in heptane); 2 158m, 2 098vs, and 2 084m cm^{-1} [ν(CO)]. Raman (solid): 124vs, 253vw, 260m, 283w, 300m, 391m, 525vw, 615vw, 710vs [$\delta(CF_3)$], 1 060s [$\nu(CF_3)$], 2 120vs [ν(CO)], and 2 170vs cm^{-1} [ν(CO)]. Mass spectrum (−50 °C, 10^{-8} Torr, *ca.* 1.33×10^{-6} Pa): m/e = 306 (M^+, 2); 278 [$Fe(CO)_3(CF_3)_2{}^+$, 49]; 259 [$Fe(CO)_3(CF_2)(CF_3)^+$, 65]; 250 [$Fe(CO)_2(CF_3)_2{}^+$, 12]; 231 [$Fe(CO)_2(CF_2)(CF_3)^+$, 34]; 222 [$Fe(CO)(CF_3)_2{}^+$, 2]; 203 [$Fe(CO)(CF_2)(CF_3)^+$, 2]; 175 [$Fe(CF_2)(CF_3)^+$, 4]; 162 [$Fe(CO)_2(CF_2)^+$, 2], 153 [$Fe(CO)(CF_3)^+$, 35]; 131 [$Fe(CO)_2F^+$, 19]; 125 [$Fe(CF_3)^+$, 100]; 112 [$Fe(CO)_2{}^+$, 12]; 106 [$Fe(CF_2)^+$, 11]; 103 [$Fe(CO)F^+$, 20]; 84 [$Fe(CO)^+$, 48]; 75 (FeF^+, 44); and 56 (Fe^+, 57%). Melting point (differential thermal analysis, d.t.a.) 80 °C; decomposition point (d.t.a.) 120 °C.

Acknowledgements

We thank Gerd Varbelow for his assistance in the experimental work. Financial support by the Fond der Chemischen Industrie and the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen is gratefully acknowledged. One of us (W. D.) thanks the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen for a grant.

References

1 R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1748.
2 I. L. Knunyants, Y. F. Kommissarov, B. L. Dyatkin, and L. T. Lantseva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, **4**, 943.
3. L. J. Krause and J. A. Morrison, *J. Am. Chem. Soc.*, 1981, **103**, 2995.
4 E. K. S. Liu and L. B. Asprey, *J. Organomet. Chem.*, 1979, **169**, 249.
5 H. Lange and D. Naumann, *J. Fluorine Chem.*, 1984, **26**, 1.
6 P. L. Heinze and D. J. Burton, *J. Fluorine Chem.*, 1985, **29**, 359.
7 D. Naumann, W. Tyrra, and F. Leifeld, *J. Organomet. Chem.*, 1987, **333**, 193.
8 R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, 1961, **83**, 3604.
9 I. I. Gerus, Y. L. Yagupol'skii, and N. D. Volkov, *Zh. Org. Khim.*, 1982, **18**, 1186.
10 D. W. Hensley, W. L. Wurster, and R. P. Stewart, jun., *Inorg. Chem.*, 1981, **20**, 645.
11 V. Gutmann, 'Coordination Chemistry in Non-Aqueous Solutions,' Springer, Wien, New York, 1968.
12 E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.
13 H. O. Kalinowski, S. Berger, and S. Braun, '^{13}C-NMR-Spektroskopie,' Georg Thieme, Stuttgart, New York, 1984.
14 C. H. Dungan and J. R. van Wazer, 'Compilation of Reported ^{19}F-NMR Chemical Shifts,' Wiley-Interscience, New York, 1970.
15 G. C. Allan and D. W. Clack, *J. Chem. Soc. A*, 1970, 2668.
16 V. V. Berenblit, Yu.P. Dolnakov, V. P. Sass, L. N. Sengushov, and S. V. Sokolov, *J. Org. Chem. USSR*, 1973, **10**, 2048.
17 W. Dukat and D. Naumann, 11th International Symposium on Fluorine Chemistry, Berlin, 1985, Abstract A 7; *J. Fluorine Chem.*, 1985, **29**, 29.
18 W. Dukat and D. Naumann, *Rev. Chim. Miner.*, 1986, **23**, 589.
19 R. L. Collins and R. Pettit, *J. Chem. Phys.*, 1963, **39**, 3433.
20 P. Vasudev and C. H. W. Jones, *Can. J. Chem.*, 1973, **51**, 405.
21 P. R. Wells, *Prog. Phys. Org. Chem.*, 1968, **6**, 111.
22 S. I. Udovenko, I. I. Gerus, and Yu.L. Yagupol'skii, *J. Organomet. Chem.*, 1986, **301**, 195.
23 W. Hieber and G. Bader, *Chem. Ber.*, 1928, **61**, 1717.
24 D. J. Burton and J. L. Hahnfeld, *Fluorine Chem. Rev.*, 1976, **8**, 119.
25 D. Seyferth, H. Dertonzos, R. Suzuki, and J. Yick Pui Mui, *Org. Chem.*, 1967, **32**, 2980.
26 H. Koroniak, *J. Fluorine Chem.*, 1984, **24**, 503.
27 D. W. Hensley and R. P. Stewart, jun., *Inorg. Chem.*, 1976, **15**, 2418.
28 K. v. Werner and H. Blank, *J. Organomet. Chem.*, 1980, **195**, C25.

Received 7th June 1988; *Paper* 8/02272K