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Fluorine-containing organozinc reagents

II *. The crystal structure of (1,1-dichloro-2,2,2-trifluoroethylzinc chloride) • 2(dimethylformamide)

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Abstract

The DMF complex of 1,1-dichloro-2,2,2-trifluoroethylzinc chloride, a key intermediate in the one pot synthesis of CF_3CCl_2-substituted alcohols, has been isolated and its structure determined by ^{13}C NMR spectroscopy and by X-ray diffraction. This is the first X-ray structural study of a perhalogenated alkylzinc halide and the results show the DMF complex to be monomeric.

Introduction

Several ether-type solvent complexes of CF_3CCl_2ZnCl have been known for almost twenty years. Many of them have been isolated and characterized by elemental analyses and by IR spectroscopy [2]. In contrast to those of the corresponding organolithium [3], organomagnesium [4], and organocopper [5] compounds, no C–C bond forming reactions of CF_3CCl_2ZnCl had been reported until recently, when we described the zinc-induced addition of CF_3CCl_3 to various aldehydes [1,6]. Since then, several research groups have used this approach to the preparation of CF_3-containing molecules [7].

In order to get more insight into the mechanistic aspects of this simple synthesis of CF_3CCl_2-substituted alcohols [1], we decided to look for possible reaction intermediates. We report here the structure of the dimethylformamide (DMF) complex **4**, which from its ease of formation seems to be a key intermediate in the one pot synthesis of alcohol **3** (Scheme 1).

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* For part I, see ref. 1.

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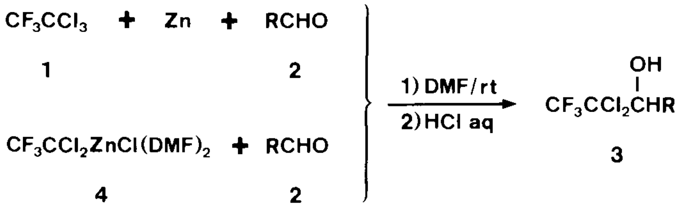


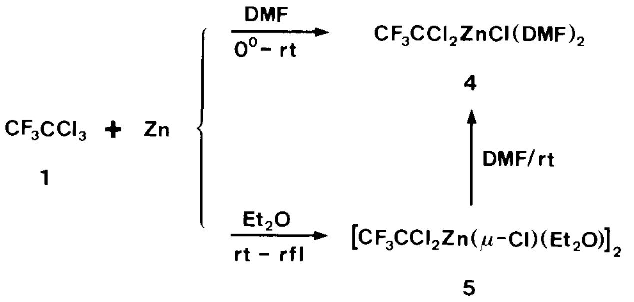
Scheme 1

Results and discussion

The DMF complex **4** can be prepared directly from **1** and zinc in DMF or by a ligand exchange reaction from an ether-type solvent complex (Scheme 2) [2,8]. It is noteworthy that direct generation of **4** from **1** proceeds almost immediately even at low temperature, whereas the formation of the ether-type solvent complexes normally requires elevated temperatures and/or prolonged reaction times [8].

The ^{13}C NMR spectrum in CD_3CN shows resonances for $CF_3CCl_2ZnCl(DMF)_2$ (**4**) at 166.1 ppm (s, CHO), 127.5 ppm (q, *J*(C–F) 274 Hz, CF_3), 76.9 ppm (q, *J*(C–F) 49 Hz, CCl_2), 38.1 and 32.6 ppm (s, each, $N(CH_3)_2$). It is evident from these data and from those for DMF in CD_3CN * that a certain amount of DMF complexation persists, but the observation of averaged resonances indicates that the ligand exchange reaction at room temperature in a strongly donating solvent such as acetonitrile is a fast reversible process. This is in contrast to what is observed in ether-type solvents, where complex **4** can be readily prepared by an irreversible ligand exchange reaction (See Experimental section).

We were able to obtain single crystals of **4** for an X-ray diffraction study, the first for a perhalogenated alkylzinc halide. The structure is shown in Fig. 1 with atomic coordinates listed in Table 1, bond lengths in Table 2, and bond angles in Table 3. The zinc atom is almost tetrahedrally surrounded by two oxygen atoms, one chlorine atom, and one carbon atom. It can be seen from Fig. 1, which shows selected bond lengths, than the monomeric unit forms a chiral complex (at least in the solid) with normal zinc–carbon, zinc–chlorine, and zinc–oxygen single bond



Scheme 2

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* The ^{13}C NMR in CD_3CN for DMF: 162.9 ppm (s, CHO), 36.4 and 31.1 ppm (s, each, $N(CH_3)_2$).

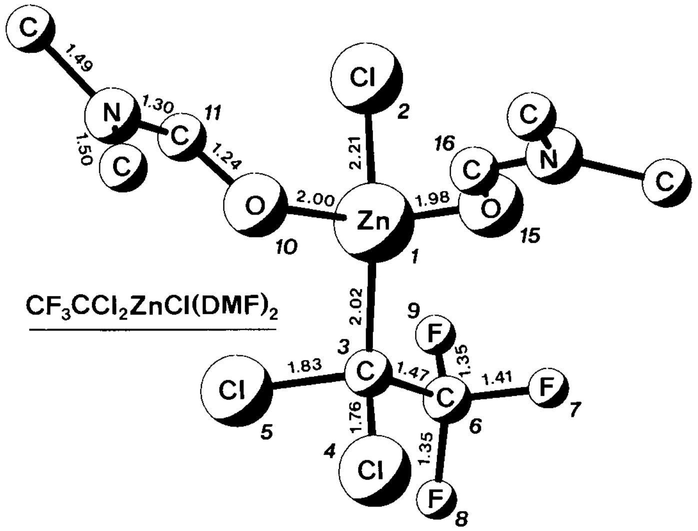

Fig. 1. Molecular structure of the DMF complex **4** with selected bond lengths in Å.

distances *. However, the C(6)–F(7) bond is significantly longer than the other two C–F bonds, and exactly antiperiplanar to the appreciably elongated C(3)–Cl(5) bond. The angles F(7)–C(6)–C(3) and C(6)–C(3)–Cl(5) are markedly less than the

Table 1

Positional parameters for $CF_3CCl_2ZnCl(DMF)_2$ (**4**)

Atom	x	y	z
Zn(1)	0.7917(1)	0.32306(8)	0.68104(7)
Cl(2)	0.8285(3)	0.4377(2)	0.5495(2)
C(3)	1.005(1)	0.1672(9)	0.7815(7)
Cl(4)	0.9348(3)	0.0949(3)	0.8775(2)
Cl(5)	1.0977(4)	0.0090(3)	0.6684(2)
C(6)	1.163(1)	0.210(2)	0.8582(9)
F(7)	1.0913(8)	0.3288(6)	0.9464(5)
F(8)	1.3072(8)	0.0995(7)	0.9186(6)
F(9)	1.2379(7)	0.2478(7)	0.7851(6)
O(10)	0.6010(7)	0.2343(6)	0.5794(5)
C(11)	0.549(1)	0.2233(7)	0.4618(7)
N(12)	0.4102(8)	0.1836(7)	0.3957(6)
C(13)	0.350(1)	0.182(1)	0.2551(8)
C(14)	0.292(1)	0.1598(9)	0.4610(9)
O(15)	0.6309(9)	0.4710(6)	0.7877(5)
C(16)	0.460(1)	0.4991(8)	0.7619(7)
N(17)	0.3522(9)	0.6028(7)	0.8315(6)
C(18)	0.156(1)	0.631(1)	0.7991(9)
C(19)	0.428(1)	0.686(1)	0.9473(8)

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* For comparison of bond lengths, see (a) $CH_2{=}CHCH{=}CHCH_2ZnCl$ [9], and (b) $BrZnCH_2COO\text{-}t\text{-}Bu$ [10].

Table 2

Bond distances (Å) for $CF_3CCl_2ZnCl(DMF)_2$ (**4**)

Atom 1-Atom 2	Distance	Atom 1-Atom 2	Distance
Zn(1)-Cl(2)	2.209(3)	O(10)-C(11)	1.242(9)
Zn(1)-C(3)	2.021(7)	C(11)-N(12)	1.30(2)
Zn(1)-O(10)	2.002(6)	N(12)-C(13)	1.49(2)
Zn(1)-O(15)	1.983(6)	N(12)-C(14)	1.50(1)
C(3)-Cl(4)	1.76(2)	O(15)-C(16)	1.27(2)
C(3)-Cl(5)	1.829(8)	C(16)-N(17)	1.33(1)
C(3)-C(6)	1.47(1)	N(17)-C(18)	1.46(2)
C(6)-F(7)	1.41(1)	N(17)-C(19)	1.46(2)
C(6)-F(8)	1.354(9)		
C(6)-F(9)	1.35(1)		

Table 3

Bond angles (°) for $CF_3CCl_2ZnCl(DMF)_2$ (**4**)

Atom 1-1Atom 2-Atom 3	Angle	Atom 1-Atom 2-Atom 3	Angle
Cl(2)-Zn(1)-C(3)	122.2(3)	Zn(1)-O(10)-C(11)	123.5(7)
Cl(2)-Zn(1)-O(10)	106.1(2)	Zn(1)-O(10)-N(12)	151.5(4)
Cl(2)-Zn(1)-O(15)	109.8(3)	O(10)-C(11)-N(12)	124.3(9)
C(3)-Zn(1)-O(10)	109.0(4)	C(11)-N(12)-C(13)	120.6(8)
C(3)-Zn(1)-O(15)	112.1(3)	C(11)-N(12)-C(14)	120.1(7)
O(10)-Zn(1)-O(15)	94.1(3)	C(13)-N(12)-C(14)	118.7(7)
Zn(1)-C(3)-Cl(4)	112.0(4)	Zn(1)-O(15)-C(16)	123.2(5)
Zn(1)-C(3)-Cl(5)	107.6(4)	O(15)-C(16)-N(17)	122.7(7)
Zn(1)-C(3)-C(6)	116.9(7)	C(16)-N(17)-C(18)	121.0(7)
Cl(4)-C(3)-Cl(5)	105.5(5)	C(16)-N(17)-C(19)	121.4(7)
Cl(4)-C(3)-C(6)	109.0(6)	C(18)-N(17)-C(19)	117.5(6)
Cl(5)-C(3)-C(6)	104.9(6)		
C(3)-C(6)-F(7)	104.3(6)		
C(3)-C(6)-F(8)	114.9(8)		
C(3)-C(6)-F(9)	111.2(8)		
F(7)-C(6)-F(8)	110.5(7)		
F(7)-C(6)-F(9)	112.9(8)		
F(8)-C(6)-F(9)	103.4(7)		

tetrahedral value, indicating a tendency for the remaining substituents to come into a plane. Furthermore, the average bond lengths of the complexed DMF molecules have slightly elongated C=O bonds and consequently shortened C-N bonds *, confirming that the mode of coordination of the DMF is as expected.

Any mechanism for the reductive addition of CF_3CCl_3 to a carbonyl compound in DMF (Scheme 1) must take into account the monomeric structure of the reagent **4**. The first step after the formation of **4** will undoubtedly be the displacement of a coordinated DMF molecule by another carbonyl compound. The second step will then depend on whether the CF_3CCl_2 unit can be transferred to the activated

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* For DMF the average C=O bond length is 1.23 Å, and the C-N bond length 1.33 Å (Interatomic Distances, Special Publication, The Chemical Society, London 1965).

carbonyl group before any side reaction can interfere. This seems to be the case for aldehydes (Scheme 1) [1,6], and CO_2 [8], but not for ketones. Detailed studies on the use of isolated complexes of type **4** for the synthesis of new CF_3-containing molecules are under investigation and will be the subject of a subsequent publication.

Experimental

All operations were performed under purified argon by Schlenk techniques. Solvents and reagents were dried over a suitable dehydrating agent and then distilled. Zn powder (Riedel de Haen, p.a.) was activated as described by Fieser & Fieser [11]. Melting points were determined with a Tottoli capillary melting-point apparatus, and are uncorrected. ^{13}C NMR spectra were recorded with a Bruker WM 360 spectrometer. Elemental analyses were carried out by Malissa & Reuter, Analytische Laboratorien, D-5270 Gummersbach 1, Elbach.

Synthesis of $[CF_3CCl_2Zn(\mu\text{-}Cl)(Et_2O)]_2$ *(5)*

The ether complex **5** was prepared as described previously [2b], and recrystallized from ether, to give an 80% yield of colourless needles; m.p. 105 °C ^{13}C NMR (CD_3CN): 127.5 ppm (q, *J*(C–F) 274 Hz, CF_3); 76.0 ppm (q, *J*(C–F) 48 Hz, CCl_2); 66.1 ppm (s, CH_2); 15.6 ppm (s, CH_3). Anal. Found: C, 21.93; H, 3.10; Cl, 32.34; F, 17.25; Zn, 20.15. $C_{12}H_{20}Cl_6F_6O_2Zn_2$ (653.75) calcd.: C, 22.05; H, 3.08; Cl, 32.54; F, 17.44; Zn, 20.00%.

Synthesis of $CF_3CCl_2ZnCl(DMF)_2$ *(4)*

Method A: DMF (2.5 ml, 32 mmol) was added dropwise to a solution of 4.8 g (7.3 mmol) of **5** in 50 ml ether at room temperature. After a few minutes the DMF complex **4** began to crystallize. Removal of the solvent, washing of the solid with ether and pentane, and recrystallization from DMF/ether yielded 79% of colourless needles; m.p. 67 °C.

Method B: CF_3CCl_3 (**1**) (9.3 g, 50 mmol) was added to a suspension of 3.3 g (50 mmol) of Zn in 25 ml of DMF at such a rate that the temperature of the mixture did not rise above 35 °C. After 1 h stirring at r.t., the brown reaction mixture was filtered and ether added to precipitate brownish crystals of **4**. Recrystallization from DMF/ether yielded 85% of colourless needles; m.p. 67 °C. ^{13}C NMR (CD_3CN): 166.1 ppm (s, CHO); 127.5 ppm (q, *J*(C–F) 274 Hz, CF_3); 76.9 ppm (q, *J*(C–F) 49 Hz, CCl_2); 38.1 and 32.6 ppm (s, each, $N(CH_3)_2$). Anal. Found: C, 24.27; H, 3.51; N, 6.95; Cl, 26.82; F, 14.19; Zn, 16.25%. $C_8H_{14}Cl_3F_3N_2O_2Zn$ (398.94) calcd.: C, 24.09; H, 3.54; N, 7.02; Cl, 26.66; F, 14.29; Zn, 16.39%.

X-ray crystallography

Crystal data. $CF_3CCl_2ZnCl(DMF)_2$ (**4**), $M = 398.94$, triclinic, a 8.201(3), b 9.855(3), c 11.207(4) Å, α 103.55, β 108.55, γ 66.26 °, space group $P\bar{1}$ (No. 2), $Z = 2$; D_c 1.698 g cm^{-3}; U 780 $Å^3$. The linear absorption coefficient was not determined.

A single crystal of dimensions 0.6 × 0.5 × 0.1 mm was used for data collection on a Philips PW 1100 four-circle diffractometer at -83 ± 3 °C using graphite-monochromated Mo-K_α radiation (λ Mo-K_{α_1} 0.70926 Å) and liquid nitrogen cooling. A total of 2462 reflections with $3° < \theta < 24°$ were measured in the $\omega/2\theta$ scan mode. Of these, 2414, observed reflections meeting the criterion $I > 2\sigma(I)$ were used. No crystal decay was observed from three reference reflections measured every 60 min.

The structure was solved by direct methods (MULTAN 78), and refined by full-matrix least squares. Final refinements were carried out with anisotropic thermal parameters for all the non-hydrogen atoms. The refinement converged at $R = 0.082$. Hydrogens could not be located. The final atomic coordinates are listed in Table 1. Lists of structure factors and thermal parameters are available from the authors.

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References

1 R.W. Lang, Helv. Chim. Acta, 69 (1986) 881.
2 (a) A.H. Fainberg and M. Hauptschein (Pennsalt Chemicals Corp.), US Pat. 3 290 333 (prior. 9.9.1963); Chem. Abstr., 66 (1969) 65633r; (b) A. Pošta and O. Paleta, Collect. Czech. Chem. Commun., 37 (1972) 3946.
3 D. Seyferth, D.C. Müller and F.M. Armbrecht, Jr., Organomet. Chem. Syn., 1 (1970/71) 3.
4 I. Hemer, A. Pošta and V. Dědek, J. Fluorine Chem., 26 (1984) 467.
5 (a) J.F. Engel (FMC Corp), US Pat. 4 332 815 (prior. 10.5.1979); Chem. Abstr., 98 (1983) 72491g; (b) P. Martin, J. Streith, G. Rihs, T. Winkler and D. Belluš, Tetrahedron Lett., 26 (1985) 3947; (c) P. Martin, E. Steiner, J. Streith, T. Winkler and D. Belluš, Tetrahedron, 41 (1985) 4057.
6 R.W. Lang (CIBA-GEIGY AG), Eur. Pat. appl 157 739 (prior. 29.3.1984); Chem. Abstr., 105 (1985) 79366s.
7 (a) M. Fujita, T. Morita and T. Hiyama, Tetrahedron Lett., 27 (1986) 2135; (b) M. Fujita and T. Hiyama, ibid., 27 (1986) 3655; (c) J. Hemer, A. Pošta and V. Dědek, J. Fluorine Chem., 29 (1985) 86; (d) J. Hemer, J. Havlíček and V. Dědek, ibid., 34 (1986) 241; (e) P. Massardo, F. Bettarini, P. Piccardi and F. Rama (Istituto Guido Donegani S.p.A.), Eur. Pat. appl. 187 674 (prior. 11.1.1985).
8 R.W. Lang and B. Klingert (CIBA-GEIGY AG), Eur. Pat. appl. 195 744 (prior. 11.3.1985); Chem. Abstr., 106 (1986) 18833r.
9 H. Yasuda, Y. Ohnuma, A. Nakamura, Y. Kai, N. Yasuoka and N. Kasai, Bull. Chem. Soc. Japan, 53 (1980) 1101.
10 J. Dekker, J. Boersma and G.J.M. van der Kerk, J. Chem. Soc., Chem. Commun., (1983) 553.
11 L.F. Fieser and M. Fieser, Reagents for Organic Synthesis, J. Wiley & Sons, New York, 1967, p. 1276.