Journal of Organometallic Chemistry, 461 (1993) 95–97

JOM 23731

A novel approach to the preparation of pentacarbonyl(dialkylaminofluorocarbene)chromium compounds. Confirmation of structure by single crystal X-ray diffraction *

John T. Welch, Erno M. Keskeny and Paul J. Toscano

Department of Chemistry, State University of New York at Albany, Washington Avenue, Albany, NY 12222 (USA)

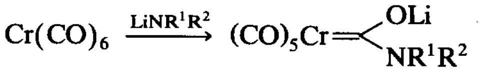
(Received January 20, 1993; in revised form March 16, 1993)

Abstract

A new method for the preparation of monofluorocarbene complexes with sulfur tetrafluoride, such as pentacarbonyl(dialkylaminofluorocarbene)chromium compounds, facilitated establishment of the carbene character of these materials by single crystal X-ray diffraction studies.

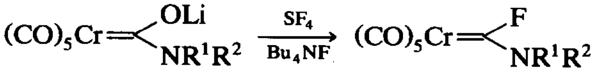
Pentacarbonyl(dialkylaminofluorocarbene)chromium compounds are potentially valuable building blocks [1] for the construction of selectively fluorinated materials that possess interesting biological activity or unique physical properties. Very few transition metal carbonyl monofluorinated carbene complexes are known [2]. We have prepared a variety of pentacarbonyl(dialkylaminofluorocarbene)chromium compounds by a novel strategy. Although these fluorinated Fischer type carbenes demonstrate remarkable stability in sharp contrast to other pentacarbonyl(dialkylaminohalocarbene)chromium species, single crystal X-ray diffraction studies have confirmed the carbene character of these materials.

The stability of *N,N*-disubstituted-aminofluorocarbene complexes has so far frustrated our use of these compounds as building blocks for the synthesis of selectively fluorinated organic substances. Not only do the pentacarbonyl(dialkylaminofluorocarbene)chromium complexes have remarkable stability in comparison with pentacarbonyl(diethylaminohalocarbene)chromium complexes [2a,3] but also relative to aryl- or alkylfluorocarbene complexes [2a–c]. We were therefore interested to confirm the structure of this type of compound, since an early report of the existence of pentacarbonyl(diethylaminofluorocarbene)chromium relied solely upon spectroscopic evidence [2a]. To facilitate our investigation, a general synthesis of pentacarbonyl (*N,N*-disubstituted-aminofluorocarbene)chromium complexes of the Fischer type was developed. Chromium hexacarbonyl was allowed to react with lithium dialkylamides to form the lithium acylates **1a–e** according to known procedures. These salts **1a–e** can be easily fluorinated with sulfur tetrafluoride in the presence of a stoichiometric amount of tetrabutylammonium fluoride to form the fluorocarbene complexes **2a—e** [4*,5*].



$$\mathrm{Cr(CO)_6} \xrightarrow{\mathrm{LiNR^1R^2}} \mathrm{(CO)_5Cr{=}C}\begin{smallmatrix}\mathrm{OLi}\\ \mathrm{NR^1R^2}\end{smallmatrix}$$

(1a–e)



$$\mathrm{(CO)_5Cr{=}C}\begin{smallmatrix}\mathrm{OLi}\\ \mathrm{NR^1R^2}\end{smallmatrix} \xrightarrow[\mathrm{Bu_4NF}]{\mathrm{SF_4}} \mathrm{(CO)_5Cr{=}C}\begin{smallmatrix}\mathrm{F}\\ \mathrm{NR^1R^2}\end{smallmatrix}$$

(2a–e)

Correspondence to: Dr. J.T. Welch

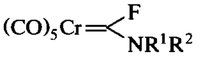
* Dedicated to Professor G.A. Olah on the occasion of his 65th birthday.

* Reference number with asterisk indicates a note in the list of references.

0022-328X/93/$6.00

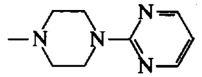
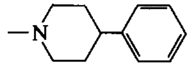
© 1993 – Elsevier Sequoia S.A. All rights reserved

TABLE 1. Pentacarbonyl(dialkylaminofluorocarbene)chromium complexes



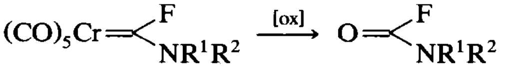
$$\mathrm{(CO)_5Cr{=}C}\begin{smallmatrix}\mathrm{F}\\ \mathrm{NR^1R^2}\end{smallmatrix}$$

2a–2e

Entry	-NR^{1}R^2	Yield (%)
2a	-NEt$_2$	62.0
2b	-NBn$_2$	35.8
2c	-NBnEt	31.5
2d		32.3
2e		26.1

In the absence of either tetrabutylammonium fluoride or sulfur tetrafluoride, the fluorination reaction fails to proceed. The pale yellow crystalline carbene complexes **2a–e** can be heated at 110°C or irradiated by a medium pressure mercury vapor lamp for several hours without noticeable changes, although the solid materials slowly decompose on exposure to air.

Reaction with oxidizing agents such as dimethylsulfoxide or simply prolonged exposure to air results in the formation of *N,N*-disubstituted carbamyl fluorides.



$$\mathrm{(CO)_5Cr{=}C}\begin{smallmatrix}\mathrm{F}\\ \mathrm{NR^1R^2}\end{smallmatrix} \xrightarrow{[ox]} \mathrm{O{=}C}\begin{smallmatrix}\mathrm{F}\\ \mathrm{NR^1R^2}\end{smallmatrix}$$

These compounds were typically identified by their IR and ^{19}F NMR spectra, and in the case of diethyl carbamyl fluoride, by comparison with an authentic sample [6]. The spectroscopic characteristics of **2a** prepared by this method were in agreement with published data [1a]. Although crystals of **2a** suitable for X-ray studies could be grown from pentane by slow cooling to −50°C, it was not possible to solve the structure as a result of symmetry constraints in the crystal. On the other hand, **2e** yielded crystals whose structure was successfully solved (Fig. 1).

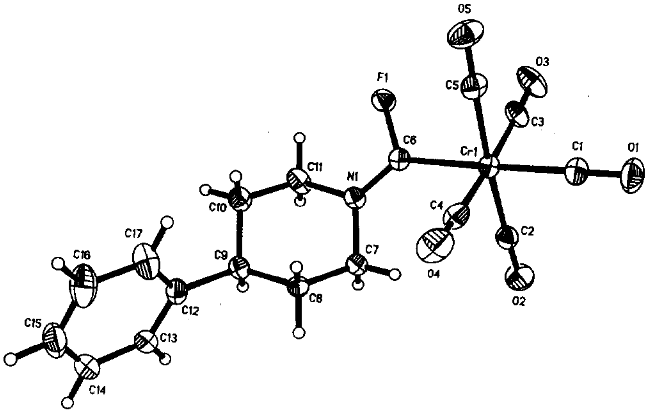


Fig. 1. Molecular structure of **2e**. Selected bond lengths (Å) and angles (°): Cr–C(1) 1.864(5), Cr–C(2) 1.888(4), Cr–C(3) 1.896(4), Cr–C(4) 1.886(4), Cr–C(5) 1.878(4), Cr–C(6) 2.059(4), N–C(6) 1.309(5), F–C(6) 1.353(4); Cr–C(6)–F 115.1(2), Cr–C(6)–N 136.1(3), N–C(6)–F 108.8(3), C(1)–Cr–C(2) 88.3(2), C(1)–Cr–C(3) 91.2(2), C(1)–Cr–C(4) 89.5(2), C(1)–Cr–C(5) 90.2(2), C(2)–Cr–C(3) 89.5(2), C(2)–Cr–C(4) 95.3(2), C(2)–Cr–C(5) 176.9(2), C(3)–Cr–C(4) 175.1(2), C(3)–Cr–C(5) 87.8(2), C(3)–Cr–C(6) 87.7(2), C(4)–Cr–C(5) 87.4(2), C(4)–Cr–C(6) 91.5(2), C(5)–Cr–C(6) 89.0(2).

The chromium–carbonyl carbon bond lengths are approximately the same and the carbonyl carbon–chromium–carbonyl carbon bond angles are close to 90°, as would be expected from an octahedral coordination environment around the chromium. The bond angles around the carbene carbon atom are those of a distorted sp^2 hybridized carbon atom. The distance between the carbene carbon atom and the chromium atom (2.059(4) Å) is significantly shorter than that found in the case of other chromium complexes; *e.g.* in pentacarbonyl(dimethylaminoethoxycarbene)chromium [7], the bond length is 2.132(4) Å. However, the carbon–fluorine bond length (1.352(4) Å) is quite comparable to that known for fluorine bound to an sp^2 hybridized carbon atom [8]. The limited ability of fluorine to stabilize the carbene is reflected in the concomitant shortening of the carbon–nitrogen bond to 1.309(5) Å. A similar effect on the carbon–nitrogen bond has primarily been seen in the structures of pentacarbonyl(diethylaminomethylcarbene)chromium [9] (1.310(1) Å) and pentacarbonyl(diethylaminochlorocarbene)chromium [10] (1.299(8) Å) where neither the methyl group nor the chlorine contribute significantly to stabilizing the complex.

Acknowledgement

This work was supported by the National Science Foundation (CHE-8901986) and the Defense Advanced Research Projects Agency (Contract DAAL 0398K0198).

References and notes

1 (a) U. Schubert (ed.), *Advances in Metal Carbene Chemistry*, Kluwer, Dordrecht, 1989; (b) D. Seyferth (ed.), *Transition Metal Carbene Complexes*, Verlag Chemie, Deerfield Beach, FL, 1983; (c) F.J. Brown, in S.J. Lippard (ed.), *Progress in Inorganic Chemistry*, Vol. 27, Wiley, New York, 1980; (d) K.H. Dötz, *Angew. Chem., 96* (1984) 573; *Angew. Chem., Int. Ed. Engl., 23* (1984) 587.

2 (a) E.O. Fischer, W. Kleine and F.A. Kreissl, *Angew. Chem., 88* (1976) 646; *Angew. Chem., Int. Ed. Engl.*, 15 (1976) 616; (b) E.O. Fischer, W. Kleine, W. Schambeck and U. Schubert, *Z. Naturforsch., 36b* (1981) 1575; (c) E.O. Fischer and J. Chen, *Z. Naturforsch., 38b* (1983) 580; (d) E.O. Fischer and J. Chen, *J. Organomet. Chem., 253* (1983) 231.

3 (a) E.O. Fischer, W. Kleine and F.A. Kreissl, *J. Organomet. Chem.*, *107* (1976) C23; (b) E.O. Fischer, W. Kleine, F.A. Kreissl, H. Fischer, P. Friedrich and G. Huttner, *J. Organomet. Chem.*, *128* (1977) C49–C53.

4 The preparation of **2e** was as follows: 4-phenylpiperazine, 0.81 g (5 mmol), was dissolved in 15 ml of THF. The solution was cooled to 0°C and 3.63 ml (6 mmol, 1.5 M solution in diethyl ether) of methyllithium was added dropwise. After 20 min stirring, the solution was slowly added to a suspension of 0.88 g (4 mmol) of hexacarbonyl chromium in 30 ml of THF at 0°C via a cannula. The resultant yellow solution was stirred at ambient temperature for an additional hour then 1.05 g (4 mmol) of tetrabutylammonium-fluoride (dried under vacuum at 50°C for 6 h) in 10 ml of THF was added. After cooling to −100°C, sulfur tetrafluoride was bubbled slowly through the solution for 3 min. The mixture was allowed to warm to ambient temperature and stirred overnight. After concentrating to 5 ml, followed by the addition of 30 ml of pentane, the solution was clarified by filtration. The orange-red oil, isolated by evaporation of the pentane (1.5 g) was deposited on 3.0 g of silica gel by concentration of a fresh pentane solution and then was layered onto a column of 40 g of silica gel. Elution with hexane/diethyl ether (9:1) yielded a fraction which was concentrated *in vacuo*. The crude product was dissolved in 5 ml of diethyl ether and was then filtered through a short Celite column. Concentration of this solution under argon yielded crystals (0.4 g, 26.1%) suitable for X-ray analysis [11*]. Anal. Found: C, 53.47; H, 3.70; N, 3.73; F, 5.12. $C_{17}H_{14}FNO_5Cr$ calc.: C, 53.27; H, 3.68; N, 3.65; F, 4.96%.

5 Selected spectroscopic data for pentacarbonyl(dialkylaminofluoro carbene) chromium complexes **2**. **2a**: ^{1}H NMR ($CDCl_3$): δ 3.92 (q, $J = 7.3$, 2H, CH_2 (E)); 3.53 (dq, $J = 7.3$ Hz, J(H–F) = 3 Hz, 2H, CH_2(Z)); 1.40 (t, $J = 7.3$ Hz, 3H, CH_3 (E)); 1.27 (t, $J = 7.3$ Hz, 3H, CH_3 (Z)). ^{19}F NMR: δ 76.45 (s, 1 F). ^{13}C NMR: $\delta = 247.98$ (d, J(C–F) = 395.8 Hz, Cr=C); 220.76 (d, J(C–F) = 6.3 Hz, CO (*trans*)); 216.18 (d, J(C–F) = 9.0 Hz, CO (*cis*)); 48.83 (s, CH_2 (E)); 43.35 (d, J(C–F) = 18 Hz, CH_2 (Z)); 14.21 (s, CH_3 (E)); 13.65 (s, CH_3 (Z)). IR (CH_2Cl_2): 2066, 1989, 1914. **2b**: ^{1}H NMR ($CDCl_3$): δ 7.45–7.05 (m, 10 H; Ar); 5.04 (s, 2H; CH_2 (E)); 4.57 (d, J(H–F) = 2.5 Hz, 2H; CH_2 (Z)). ^{19}F NMR: δ 79.65 (s, 1 F). ^{13}C NMR: δ 250.39 (d, J(C–F) = 398.3 Hz, Cr=C); 220.90 (s, CO (*trans*)); 216.26 (d, J(C–F) = 9.4 Hz, CO (*cis*)); 133.95 (s; C−1); 129.74 (s; C−2, C−6); 129.38 (s; C−3, C−5); 129.05 (s; C−6); 56.89 (s; CH_2 (E)); 50.78 (d, J(C–F) = 16.1 Hz, CH_2 (Z)). IR (CH_2Cl_2): 2066, 1985, 1933. **2c**: ^{1}H NMR ($CDCl_3$): δ 7.47–7.12 (m, 10H, Ar); 5.11 (s, 2H, CH_2Ph (E)); 4.74 (d, J(H–F) = 3 Hz, 2H, CH_2Ph (Z)); 3.89 (q, $J = 7.3$ Hz, 2H, CH_2CH_3 (E)); 3.43 (dq, $J = 7.3$ Hz, J(H–F) = 3.0 Hz, 2H, CH_2CH_3 (Z)); 1.39 (t, $J = 7.3$ Hz, 3H, CH_3 (E)); 1.14 (t, $J = 7.3$ Hz, 3H, CH_3 (Z)). ^{19}F NMR: δ 78.59 (s; 1F). ^{13}C NMR: δ 249.82 (d, J(C–F) = 397.6 Hz, Cr=C), 220.56 (d, J(C–F) = 6.5, CO (*trans*)); 216.02 (d, J(C–F) = 9.7, CO (*cis*)); 133.41, 132.95, 129.30, 129.20, 128.91, 128.50, 127.72, 127.25 (Ar); 57.21 (CH_2Ph (E)); 50.52 (d, J(C–F) = 20.5 Hz, CH_2Ph (Z)); 48.31 (CH_2CH_3 (E)), 13.33 (CH_3 (Z)). IR (CH_2Cl_2): 2066, 1988, 1924. **2d**: ^{1}H NMR ($CDCl_3$): δ 8.31 (d, $J = 4.9$ Hz, 2H, 4′H, 5′H); 6.55 (t, $J = 4.9$ Hz, 1H, 3′H); 4.15–3.35 (m; 8H, 2−CH_2, 3−CH_2, 5−CH_2, 6−CH_2). ^{19}F NMR: δ 73.57 (s; 1F). ^{13}C NMR: δ 247.27 (d, J(C–F) = 397.2, Cr=C); 220.43 (d, J(C–F) = 6.1 Hz, CO (*trans*)); 216.01 (d, $J = 9.7$ Hz, CO (*cis*)); 157.84 (2′C); 111.39 (5′C); 110.85 (4′C, 6′C); 51.98 (5C); 44.56 (d, J(C–F) = 11.0 Hz, 6C); 43.94 (3C); 43.12 (d, J(C–F) = 17.1 Hz, 2C). IR (CH_2Cl_2): 2066, 1986, 1938. **2e**: ^{1}H NMR ($CDCl_3$): δ 7.39–7.20 (m, 5H, Ar); 4.81 (m, 2H, 6CH_2), 3.54 (tt, $J = 13.1$, $J = 3.2$ Hz, 1H, 4−CH); 3.04–2.84 (m, 2H, 2CH_2); 2.28–1.66 (m, 4H, 3−CH_2, 5−CH_2). ^{19}F NMR: δ 71.60 (s, 1F). ^{13}C NMR: δ 245.05 (d, J(C–F) = 400.4 Hz, Cr=C); 220.72 (d, J(C–F) = 3.11 Hz, CO (*trans*)); 216.17 (d, J(C–F) = 9.2 Hz, CO (*cis*)); 143.24 (1′C); 128.81 (4′C); 127.07 (2′C, 6′C); 126.61 (3′C, 5′C); 63.93 (4C); 53.19 (5C); 46.39 (d, J(C–F) = 20.0 Hz, 6C); 42.04 (3C); 33.47 (d, J(C–F) = 23.3 Hz, 2C). IR (CH_2Cl_2): 2064, 1980, 1918.

6 V. Wray, *Annu. Rep. NMR Spectrosc.*, *10B* (1980) 188.

7 G. Huttner and B. Krieg, *Chem. Ber.*, *105* (1972) 67.

8 J.L. Carlos, A.A. Karl and S.H. Bauer, *J. Chem. Soc.*, *Faraday Trans. 2*, *70* (1974) 177.

9 J.A. Connor and O.S. Mills, *J. Chem. Soc. A*, (1969) 334.

10 G. Huttner, A. Frank, E.O. Fischer and W. Kleine, *J. Organomet. Chem.*, 141 (1977) C17.

11 Crystal data for **2e**: $C_{17}H_{14}FNO_5Cr$, $M = 383.299$, monoclinic $P2_1/c$, $a = 13.098(4)$ Å, $b = 11.206(4)$ Å, $c = 12.217(4)$ Å, $\beta = 97.07(3)°$, $V = 1779.5(11)$ Å^3, $D_c = 1.431$ g.cm^{-3}, $\mu = 6.6$ cm^{-1}, $Z = 4$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), $T = 298$K. Nicolet R3m/V was used to collect 4557 reflections ($3° < 2\theta < 55°$) on a colorless crystal, 0.40×0.60×0.60 mm^3. Of these, 4107 were unique and 2296 observed ($|F_o| > 6\sigma|F_o|$). Lorentz and polarization corrections were applied to the data. The structure was solved by Patterson method. The hydrogen atoms were included at their idealized positions. $R = 0.0470$, $R_w = 0.0464$, GOF = 1.717.