Inorganica Chimica Acta, 166 (1989) 163–165

A Convenient Preparation and the Molecular Structure of *trans*-Bis(dimethylglyoximato)(trifluoromethyl)(pyridine)cobalt(III): a Cobaloxime with a Very Short Co–C(sp^3) Bond

PAUL J. TOSCANO*, LINDA KONIECZNY,
SHUNCHENG LIU and JON ZUBIETA

Department of Chemistry, State University of New York at Albany, Albany, NY 12222 (U.S.A.)

(Received August 25, 1989)

Relatively few direct molecular structure comparisons between isostructural alkyl and fluoroalkyl transition metal complexes, containing M–C(sp^3) σ-bonds, exist [1, 2]. This is probably in part due to the relative difficulty in preparing the fluoroalkyl complexes and in the identification of suitable systems in which stable, well-formed crystals of both fluorinated and non-fluorinated alkyl compounds may readily be obtained [3].

In this letter, we describe an efficient synthesis of [pyCo(DH)$_2$CF$_3$] (1) (where py = pyridine and DH = the monoanion of dimethylglyoxime), utilizing Co(I) methodology. In addition, the molecular structure of 1 was determined; over one hundred cobaloxime structures can be found in the literature [4, 5], including that for the structurally analogous [pyCo(DH)$_2$CH$_3$] (2) [6]. This sufficiently broad data-base permits meaningful comparisons to be drawn between the isostructural complexes, 1 and 2, as well as interpretation of the bonding differences.

Experimental

In general, reagents were purchased from standard sources and used as received. CF$_3$Br was obtained from PCR Incorporated and used without further purification. ^{1}H (299.943 MHz), ^{13}C (75.429 MHz) and ^{19}F (282.203 MHz) NMR spectra were obtained on a Varian XL-300 spectrometer. The first two nuclei were referenced to internal (CH$_3$)$_4$Si, while ^{19}F chemical shifts were referenced upfield from internal CFCl$_3$.

Synthesis of Compound 1

To a solution of [pyCo(DH)$_2$Cl] [7] (2.01 g, 5.0 mmol) and NaOH (0.40 g, 10 mmol) in degassed methanol (100 ml) under nitrogen was added an aqueous NaBH$_4$ solution (0.05 g, 1.32 mmol in 3–5 ml). The mixture was stirred for 15 min and then CF$_3$Br was bubbled briefly through the solution, causing an immediate color change from dark greenish black to deep reddish brown, accompanied by the deposition of a small amount of solid. After several brief additions of CF$_3$Br, the mixture was stirred for 4 h. The reaction was then opened to the air, acetone (5 ml) and H$_2$O (10 ml) were added, and the solution was concentrated to give a golden yellow precipitate of 1 in 40% yield (0.88 g). ^{1}H NMR (CDCl$_3$): 8.54 (d, 2H, α-H py); 7.78 (t, 1H, γ-H py); 7.35 (t, 2H, β-H py); 2.20 (s, 12H, DH–CH$_3$). ^{13}C NMR (CDCl$_3$): 151.38 (C=N); 149.82 (α-C py); 138.44 (γ-C py); 125.54 (β-C py); 12.24 (DH–CH$_3$). ^{19}F NMR (CDCl$_3$): −32.34 (s, CF$_3$).

If larger molar quantities of NaBH$_4$ were used, significant amounts of [pyCo(DH)$_2$CHF$_2$] (3) were also formed: ^{1}H NMR (CDCl$_3$): 8.57 (d, 2H, α-H py); 7.78 (t, 1H, γ-H py); 7.35 (t, 2H, β-H py), 5.95 (t, 1H, CHF$_2$, ^2J(H–F) = 53.0 Hz), 2.17 (s, 12H, DH–CH$_3$). ^{19}F NMR (CDCl$_3$): −96.24 (d, CHF$_2$, ^2J(H–F) = 55.0 Hz).

Crystal Structure Analysis and Refinement

A Nicolet R3m diffractometer in the $\theta/2\theta$ mode with variable scan speed (3.0 to 20.0 deg min^{-1}) and graphite monochromated Mo Kα radiation was used to measure 3193 reflections with $0° \leq 2\theta \leq 50°$. Of these, there were 2670 unique reflections with $|F_o| > 6|(F_o)|$. Data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion, but not for absorption [8]. The structure was refined to $R = 0.0452$ and $R_w = 0.0452$. Crystal data are summarized in Table 1 and final atomic positional parameters are provided in Table 2.

TABLE 1. Crystallographic data for compound 1

Formula	C$_{14}$H$_{19}$F$_3$N$_5$O$_4$Co
Molecular weight	437.26
Space group	$P\bar{1}$
a (Å)	8.842(3)
b (Å)	9.199(2)
c (Å)	12.012(4)
α (°)	90.77(2)
β (°)	92.14(3)
γ (°)	111.45(3)
V (Å^3)	908.27(10)
Z	2
D_{calc} (g cm^{-3})	1.60
λ(Mo Kα) (Å)	0.71073
μMo Kα) (cm^{-1})	10.0
Temperature (K)	298
Crystal dimensions (cm)	0.02 × 0.04 × 0.02

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Co	1247(1)	2782(1)	2273(1)	33(1)
F(1)	454(5)	−352(4)	1655(4)	115(2)
F(2)	−1278(5)	518(4)	1074(3)	108(2)
F(3)	−1224(5)	−64(4)	2729(3)	95(2)
O(1)	332(4)	3703(4)	172(3)	56(2)
O(2)	3807(4)	1661(4)	2757(3)	55(1)
O(3)	2212(5)	1850(4)	4341(3)	58(2)
O(4)	−1356(4)	3787(5)	1778(3)	60(2)
N(1)	1386(5)	3177(4)	731(3)	40(1)
N(2)	3074(4)	2249(4)	1972(3)	40(1)
N(3)	1152(5)	2386(4)	3809(3)	42(1)
N(4)	−578(4)	3293(5)	2567(3)	43(1)
N(5)	2719(4)	5055(4)	2604(3)	38(1)
C(1)	4058(6)	5428(6)	3266(4)	48(2)
C(2)	5074(7)	6967(7)	3506(5)	65(2)
C(3)	4668(8)	8151(7)	3047(6)	74(3)
C(4)	3306(8)	7780(6)	2379(5)	65(3)
C(5)	2347(6)	6238(6)	2162(4)	50(2)
C(6)	4919(7)	1978(7)	575(5)	66(3)
C(7)	3570(5)	2417(5)	967(4)	42(2)
C(8)	2589(6)	3027(5)	230(4)	40(2)
C(9)	2950(7)	3431(6)	−949(4)	57(2)
C(10)	−291(8)	2285(8)	5528(4)	73(3)
C(11)	2(6)	2611(6)	4326(4)	47(2)
C(12)	−1018(6)	3172(6)	3597(4)	48(2)
C(13)	−2438(7)	3522(8)	3965(6)	75(3)
C(14)	−230(6)	646(6)	1926(4)	47(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

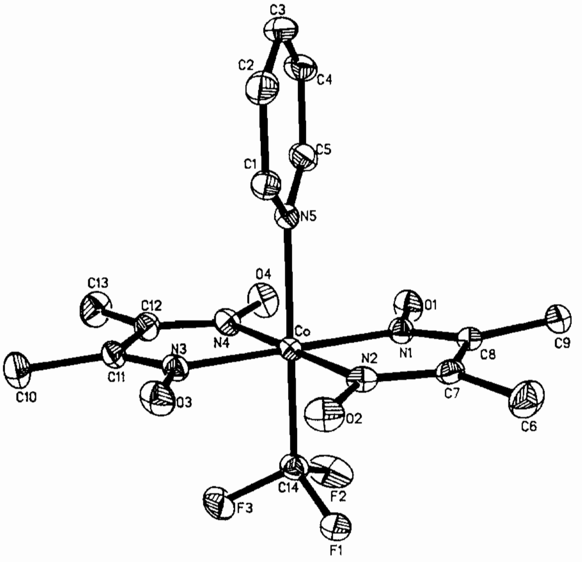

Fig. 1. ORTEP view of the structure of $pyCo(DH)_2CF_3$ (1) showing the atom-labelling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (see Table 1 for other pertinent data): C(14)–F(1), 1.314(7); C(14)–F(2), 1.329(7); C(14)–F(3), 1.339(6); Co–C(14)–F(1), 116.1(3); Co–C(14)–F(2), 114.0(4); Co–C(14)–F(3), 115.9(3); F(1)–C(14)–F(2), 103.4(4); F(1)–C(14)–F(3), 103.8(4); F(2)–C(14)–F(3), 101.7(4).

TABLE 3. Selected structural comparisons for $[pyCo(DH)_2CX_3]$, X = F (1) and H (2)

	1 [a]	2 [b]
Co–C (Å)	1.949(4)	1.998(5)
Co–N(py) (Å)	2.043(3)	2.068(3)
C–Co–N(py) (°)	177.4(2)	178.0(2)
α (°) [c]	+3.0	+3.2
d (Å) [d]	+0.002	+0.04

[a] This work. [b] Ref. 6. [c] Interplanar angle between DH ligands; positive values indicate bending away from the py ligand. [d] Displacement of the Co atom out of the N_4-donor plane; positive values indicate bending towards the py ligand.

Results and Discussion

The title complex has been previously prepared via Co(I) techniques, as reported by Schrauzer *et al.* [9, 10]. However, it was subsequently shown [11] that the usual reductive alkylation procedures can lead to partial replacement of F with H. At this time, it is not clear why this occurrence was not detected in earlier preparations [9, 12, 13]. In our hands, under the 'usual conditions' of two times molar excess of $NaBH_4$ (based upon Co(III) complex) [7, 14], reductive defluorination of the coordinated CF_3 ligand in **1** to give some $pyCo(DH)_2CHF_2$ was also observed. The CF_3:CHF_2 ratio in the isolated product was *c.* 7.5:1, as judged by integrated intensities for the DH–CH_3 resonances in the ^1H NMR spectrum. Even when the $NaBH_4$ reagent was reduced to as little as 0.50 molar equivalents, the CF_3:CHF_2 ration was improved only to 11:1.

On the other hand, if just 0.25 molar equivalents of $NaBH_4$ are employed in the synthesis (see Experimental), then complex **1**, free from **3**, is obtained in essentially one step. Thus, undesirable reductive defluorination is avoided in the new preparation via the usage of a minimum amount of reducing agent. The new, modified procedure is also superior to the previously reported Co(II) method [11], in that time-consuming reaction and chromatographic procedures are not necessary to obtain pure **1** and that the less costly CF_3Br may be substituted for CF_3I.

Yellow–orange crystals of **1** suitable for a single-crystal X-ray diffraction study were obtained by slow evaporation of an acetone/water solution at 0–5 °C. The crystals consist of discrete $[pyCo(DH)CF_3]$ units (see Fig. 1). Structural comparisons to **2** [6] of interest are presented in Table 3. The slightly, but significantly, shorter Co–N(py) distance in **1** suggests that the CF_3 group has a somewhat weaker *trans* influence compared to CH_3. However, the γ-^{13}C(py) chemical shift, which is a very sensitive indicator of the electron-donating ability of the *trans* ligand in this system [4], reveals that the CF_3 group (δ 138.44) is a much poorer electron-donor than CH_3 (δ 137.48).

Perhaps the most striking structural feature of **1** is the extremely short Co–C(sp^3) bond distance that is significantly shorter than that found in **2** [6] and other pyCo(DH)$_2$R molecules (Co–C, Å (R): 1.995(2) ($CHCl_2$) [15]; 2.002(3) (CH_2NO_2) [16]; 2.002(7) (CH_2CH_2CN) [17]) and which is, in fact, in the range normally observed for Co–C(sp^2) bond lengths of 1.95–1.97 Å [4, 5]. Such a diminution in bond length has previously been observed for fluoroalkyl complexes [1–3, 18, 19] and has been interpreted in terms of a combination of electrostatic and hybridization changes brought about by the electronegative F atoms [1, 2], rather than M–CF_3 double bonding character. In the present instance, we observe an elongation of the tetrahedron at C(14) (summation of F–C–F angles = 308.9°; summation of Co–C–F angles = 346.0°). Interestingly, the C(14)–F bond distances (1.327 Å ave.) are normal [20]; in general, elongation of the CF_3 tetrahedron has been accompanied by C–F bond lengthening in previous structural determinations of trifluoromethyl complexes [1, 2, 18]. This last result may imply that the short Co–C(14) bond length might best be ascribed for the most part to electrostatic (i.e., ionic/covalent resonance), rather than rehybridization effects. Further work is in progress to crystallize other trifluoromethyl cobaloximes in order to make a more definitive assessment.

Supplementary Material

Complete tables of bond lengths, bond angles, temperature factors, hydrogen atom positions and structure factors for **1** are available from the authors.

Acknowledgements

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the State University of New York Faculty Research Award Program for their generous support.

References

1 M. A. Bennett, H.-K. Chee and G. B. Robertson, *Inorg. Chem., 18* (1979) 1061, and refs. therein.

2 M. A. Bennett, H.-K. Chee, J. C. Jeffery and G. B. Robertson, *Inorg. Chem., 18* (1979) 1071, and refs. therein.

3 M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A,* (1970) 161, and refs. therein.

4 N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summers and P. J. Toscano, *Coord. Chem. Rev., 63* (1985) 1.

5 L. Randaccio, N. Bresciani-Pahor, E. Zangrando and L. G. Marzilli, *Chem. Soc. Rev., 18* (1989) 225.

6 A. Bigotto, E. Zangrando and L. Randaccio, *J. Chem. Soc., Dalton Trans.,* (1976) 96.

7 W. C. Trogler, R. C. Stewart, L. A. Epps and L. G. Marzilli, *Inorg. Chem., 13* (1974) 1564.

8 A. Bruce, J. L. Corbin, P. L. Dahlstrom, J. R. Hyde, M. Minelli, E. I. Stiefel, J. T. Spence and J. Zubieta, *Inorg. Chem., 21* (1982) 917.

9 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc., 88* (1966) 3738.

10 G. N. Schrauzer, A. Ribeiro, L. P. Lee and R. K. Y. Ho, *Angew. Chem., Int. Ed. Engl., 10* (1971) 807.

11 K. L. Brown and T.-F. Yang, *Inorg. Chem., 26* (1987) 3007, and refs. therein.

12 R. J. Guschl, R. S. Stewart and T. L. Brown, *Inorg. Chem., 13* (1974) 417.

13 P. L. Gaus and A. L. Crumbliss, *Inorg. Chem., 15* (1976) 2080.

14 J. Bulkowski, A. Cutler, D. Dolphin and B. Silverman, *Inorg. Synth., 20* (1980) 131.

15 Q. Chen, L. G. Marzilli, N. Bresciani-Pahor, L. Randaccio and E. Zangrando, *Inorg. Chim. Acta, 144* (1988) 241.

16 L. Randaccio, N. Bresciani-Pahor, P. J. Toscano and L. G. Marzilli, *Inorg. Chem., 20* (1981) 2722.

17 E. Zangrando, N. Bresciani-Pahor, L. Randaccio, J.-P. Charland and L. G. Marzilli, *Organometallics, 5* (1986) 1938.

18 R. A. Michelin, R. Ros, G. Guadalupi, G. Bombieri, F. Benetollo and G. Chapuis, *Inorg. Chem., 28* (1989) 840.

19 R. Mason and D. R. Russell, *J. Chem. Soc., Chem. Commun.,* (1965) 182.

20 *Molecular Structure by Diffraction Methods – Specialist Periodical Reports,* The Chemical Society, London, Vols. 1–6.