

# The 2,2,2-Trifluoroethyl Ligand: A Structural "Reporter" Group for Its Carbanion Character in Organometallic Compounds

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Received August 22, 1984

The crystal and molecular structures of the complexes *trans*-bis(dimethylglyoximate)(trifluoroethyl)(L)cobalt(III) [L = 4-cyanopyridine (4-CNpy) (I), triphenylphosphine (PPh<sub>3</sub>) (II), trimethyl phosphite (III)] are reported. Crystal data for I:  $P2_1/c$ ,  $a = 14.03$  (1) Å,  $b = 8.518$  (7) Å,  $c = 17.73$  (1) Å,  $\beta = 113.0$  (1)°,  $Z = 4$ ,  $R = 0.032$  for 2468 independent reflections. Crystal data for II:  $P2_1/n$ ,  $a = 19.801$  (1) Å,  $b = 13.295$  (7) Å,  $c = 14.494$  (8) Å,  $\beta = 131.0$  (4)°,  $Z = 4$ ,  $R = 0.029$  for 2685 independent reflections. Crystal data for III:  $P\bar{1}$ ,  $a = 10.020$  (8) Å,  $b = 15.65$  (1) Å,  $c = 16.06$  (1) Å,  $\alpha = 86.3$  (1)°,  $\beta = 76.0$  (1)°,  $\gamma = 116.8$  (1)°,  $Z = 4$ ,  $R = 0.041$  for 3915 independent reflections. In all cases, the CH<sub>2</sub>CF<sub>3</sub> group has a geometry that departs significantly from that expected for sp<sup>3</sup> hybridization at the C bearing the F substituents. This departure was such that the C-C-F angles were much larger and the F-C-F angles were much smaller than expected. The values of the experimental angles were compared with those obtained from MNDO calculations (using several different initial assumptions) on CH<sub>3</sub>CF<sub>3</sub>, CH<sub>2</sub>CF<sub>3</sub>, and CH<sub>2</sub>CF<sub>3</sub><sup>-</sup> species. A plot of the average F-C-F angle vs. the average C-C-F angle for each determination in both the theoretical and experimental studies conformed to the expected geometric relationship, and the position of the point for each determination appears to be indicative of the carbanion character of each compound. Compound II occurs at a position even more "carbanionic" in character than does the calculated carbanion. Compounds I and III are less carbanionic in geometry, but III occurs as two crystallographically independent species which differ somewhat in carbanion character, possibly due to lattice effects. One view of this deviation from sp<sup>3</sup> geometry is that the hybridization favors p character in the C-F bonds and s character in the C-C bonds of the CH<sub>2</sub>CF<sub>3</sub> groups. This view is supported by "hybridization indexes" calculated according to methods developed by others. It is suggested that the geometry of the -CH<sub>2</sub>CF<sub>3</sub> group indirectly furnishes some clue as to the electron donation by the alkyl group to the metal. The group thus is a structural reporter group for carbanion character of the alkyl.

## Introduction

As a first approximation, organometallic compounds can be formally viewed as having carbanionic ligands and positively charged metal species.<sup>1</sup> However, although qualitatively useful, the concept must depart considerably from a true picture of the electron distribution of organometallic compounds. For some time, we have been interested in comparisons of the properties of organometallic B<sub>12</sub> model complexes with those of nonorganometallic compounds containing acido ligands which can exist as stable anionic species, e.g., Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc.<sup>2</sup> For example, cobaloximes, LCo(DH)<sub>2</sub>X (where L = neutral ligand and DH = monoanion of dimethylglyoxime), are among the most thoroughly studied classes of compounds and have been well characterized both as organometallic species LCo(DH)<sub>2</sub>R and as coordination compounds LCo(DH)<sub>2</sub>X.<sup>2</sup> Spectral, structural and rate comparisons frequently indicate a continuous trend between organometallic and non-organometallic compounds<sup>2-8</sup> and furthermore suggest that the changes in properties between the compounds primarily reflect the greater ability of most R groups to donate electron density to Co, in comparison

to typical X ligands. Frequently, however, where R contains electronegative groups, it is claimed that R withdraws electron density from the metal moiety.<sup>9</sup> A better view of the bonding is that such R groups are not as good electron donors as those lacking electron-attracting substituents.

A structural means of evaluating carbanionic character of an alkyl group presented itself when we observed unusual bond lengths and angles in the -CH<sub>2</sub>CF<sub>3</sub> group of PPh<sub>3</sub>Co(DH)<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>. We, therefore, have prepared and structurally characterized two related complexes and carried out some MNDO calculations on relevant species containing the CH<sub>2</sub>CF<sub>3</sub> moiety.

We propose that the -CH<sub>2</sub>CF<sub>3</sub> groups may prove to be a useful structural "reporter" group for evaluating M-C bonding in a broad range of metal complexes. In addition, the preparation and structural characterization of complexes of CH<sub>2</sub>CF<sub>3</sub> with several transition-metal centers may be helpful in the development of more complete theoretical treatments of organometallic complexes.

## Experimental Section

**Preparations.** The complexes were prepared by standard methods.<sup>2-8</sup>

**Crystal Data.** Crystals of I and II were obtained by slow crystallization from acetone/H<sub>2</sub>O. Crystals of III were obtained from dichloromethane/ligroin. Cell dimensions were determined from Weissenberg and precession photographs and refined on a SIEMENS AED single crystal diffractometer. Crystal data are given in Table I. One check-reflection intensity was measured

(1) Hoffman, R. *Science (Washington, DC)* **1981**, *211*, and references therein.

(2) Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. *J. Coord. Chem. Rev.*, in press, and references therein.

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

(4) Stewart, R. C.; Marzilli, L. G. *Inorg. Chem.* **1977**, *16*, 424.

(5) Stewart, R. C.; Marzilli, L. G. *J. Am. Chem. Soc.* **1978**, *100*, 817.

(6) Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1979**, *18*, 421.

(7) Bresciani-Pahor, N.; Randaccio, L.; Summers, M.; Toscano, P. J. *Inorg. Chim. Acta* **1983**, *68*, 69.

(8) Randaccio, L.; Bresciani-Pahor, N.; Orbell, J. D.; Calligaris, M.; Summers, M. F.; Snyder, B.; Toscano, P. J.; Marzilli, L. G. *Organometallics*, in press.

(9) See, for example: Bied-Charreton, C.; Septe, B.; Gaudemer, A. *Org. Magn. Reson.* **1975**, *7*, 116. Dodd, D.; Johnson, M. D.; Fong, C. W. *J. Chem. Soc., Dalton Trans.* **1974**, 58. Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338. Brown, K. L.; Lu, L.-Y. *Inorg. Chem.* **1981**, *20*, 4178.

Table I. Crystallographic Data for Compounds I, II, and III<sup>a</sup>

|   | I  | II  | III   |
|---|--|---|---|
| formula   | CoF <sub>3</sub> O <sub>4</sub> N <sub>6</sub> C <sub>16</sub> H <sub>20</sub> | CoPF <sub>3</sub> O <sub>4</sub> N <sub>4</sub> C <sub>28</sub> H <sub>31</sub> | CoPF <sub>3</sub> O <sub>7</sub> N <sub>4</sub> C <sub>13</sub> H <sub>25</sub> |
| mol wt  | 476.4  | 634.5   | 496.3   |
| <i>a</i> , Å  | 14.03 (1)  | 19.801 (1)  | 10.020 (8)  |
| <i>b</i> , Å  | 8.518 (7)  | 13.295 (7)  | 15.65 (1)   |
| <i>c</i> , Å  | 17.73 (1)  | 14.494 (8)  | 16.06 (1)   |
| $\alpha$ , deg  |  |   | 86.3 (1)  |
| $\beta$ , deg   | 113.0 (1)  | 131.0 (4)   | 76.0 (1)  |
| $\gamma$ , deg  |  |   | 116.8 (1)   |
| <i>D</i> <sub>measd</sub> , g cm <sup>-3</sup>              | 1.53 (1)   | 1.41 (1)  | 1.54 (1)  |
| <i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>              | 1.53   | 1.42  | 1.54  |
| <i>Z</i>  | 4  | 4   | 4   |
| space group   | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>n</i>  | <i>P</i> $\bar{1}$  |
| $\mu$ , cm <sup>-1</sup>                                    | 9.3  | 7.2   | 9.0   |
| cryst dims, cm <sup>3</sup>                                 | 0.04 × 0.04 × 0.06   | 0.04 × 0.04 × 0.07  | 0.06 × 0.04 × 0.09  |
| no. of reflects measd                                       | 5464   | 6742  | 12 016  |
| no. of indep reflects ( <i>I</i> ≥ 3 $\sigma$ ( <i>I</i> )) | 2468   | 2685  | 3915  |
| max 2 $\theta$ , deg (Mo K $\alpha$ )                       | 56   | 56  | 56  |
| <i>R</i>  | 0.032  | 0.029   | 0.041   |
| <i>R</i> <sub>w</sub>                                       | 0.042  | 0.038   | 0.053   |

<sup>a</sup> Esd's are given in parentheses.

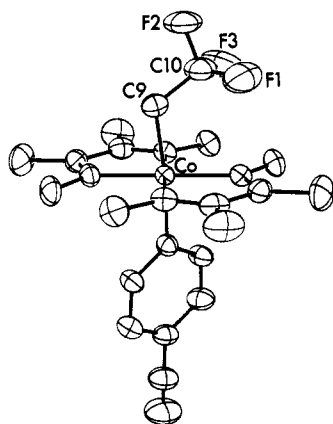


Figure 1. SHELXTL drawing and atom numbering scheme for I.

every hundred reflections during data collections. There was no systematic variation throughout the data recording.

**Solution and Refinement of Structures.** The structures of the three compounds were solved by conventional Patterson and Fourier methods and refined by the block-diagonal anisotropic least-squares methods to final *R* values of 0.032 (I), 0.029 (II), and 0.041 (III). The contribution of hydrogen atoms, at calculated positions, was held constant ( $B = 5 \text{ \AA}^2$ ) in all the structures. In the final refinement the weighting scheme was  $w = 1/(A_1 + F_{o1} + B/F_{o1})$  where  $A = 17.5$  (I), 20.7 (II), and 14.0 (III) and  $B = 0.01$  for all the structures were chosen so as to maintain  $w(|F_o| - |F_c|)^2$  essentially constant over all ranges of  $F_o$  and  $(\sin \theta)/\lambda$ . Atomic scattering factors were those given in ref 10. Final non-hydrogen positional parameters are collected in Table II and III. Hydrogen atom coordinates, anisotropic thermal parameters, and a list of final calculated and observed structure factors are given in the supplementary material. All calculations were done by using the computer programs from X-Ray 70.<sup>11</sup> No correction for absorption was applied because of the small values of the absorption coefficient and the small size of the crystals used (Table I).

**Theoretical Calculations.** Theoretical results were obtained by using MNDO, the approximations and parameterizations of which are fully described by Dewar and Thiel.<sup>12</sup> Calculations were done on both partially and fully optimized neutral and anionic molecules. The partially optimized anion geometries obtained are based upon X-ray crystallographic data. In one series of these calculations, the bond lengths, bond angles, and dihedral angles were initially set to the X-ray values, but only the bond

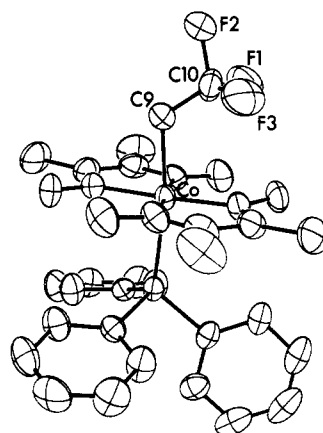


Figure 2. SHELXTL drawing and atom numbering scheme for II.

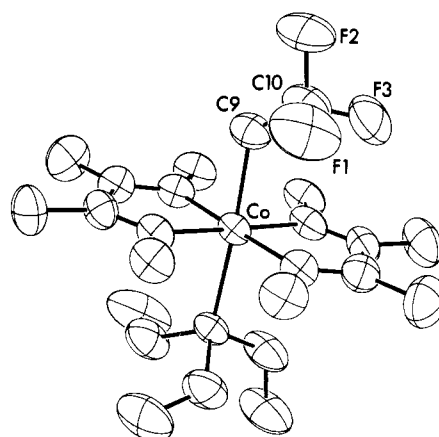


Figure 3. SHELXTL drawing and atom numbering scheme for IIIA.

angles and dihedral angles were allowed to optimize. In another series, only the bond lengths and dihedral angles were allowed to optimize. In this way, the deviations of the observed bond lengths and angles from the theoretically optimized ones can be studied along with the effect of these deviations on the rest of the molecule. The fully optimized molecules (both the neutral and the anion) were calculated disregarding X-ray data completely and allowing for complete optimization.

### X-ray Results

**Structure.** SHELXTL drawings of the crystallographically independent molecule of I with the atom numbering scheme is depicted in Figure 1. The corresponding

(10) Moore, F. H. *Acta Crystallogr.* 1963, 16, 1169.

(11) Stewart, J. M.; Kundal, F. A.; Baldwin, J. C. "The X-Ray System"; University of Maryland: College Park, MD 1970.

(12) Dewar, M. J. S.; Thiel, W. J. *Am. Chem. Soc.* 1977, 99, 4899.

Table II. Positional Parameters ( $\times 10^4$ ) for Non-Hydrogen Atoms of I and II

|       | x         | y         | z         |
|-------|-----------|-----------|-----------|
| I     |           |           |           |
| Co    | 2791 (0)  | 1063 (0)  | 290 (0)   |
| F(1)  | 2855 (2)  | -867 (5)  | 1986 (2)  |
| F(2)  | 4423 (2)  | -1082 (3) | 2345 (1)  |
| F(3)  | 3741 (3)  | 1165 (4)  | 2304 (2)  |
| O(1)  | 4368 (2)  | 2876 (3)  | -14 (1)   |
| O(2)  | 1502 (2)  | 1801 (3)  | 1279 (1)  |
| O(3)  | 1222 (2)  | -780 (3)  | 599 (1)   |
| O(4)  | 4039 (2)  | 360 (3)   | -736 (1)  |
| N(1)  | 3649 (2)  | 2795 (3)  | 376 (2)   |
| N(2)  | 2285 (2)  | 2269 (3)  | 1004 (1)  |
| N(3)  | 1953 (2)  | -693 (3)  | 218 (1)   |
| N(4)  | 3293 (2)  | -143 (3)  | -431 (1)  |
| N(5)  | 1850 (2)  | 2124 (3)  | -612 (1)  |
| N(6)  | -731 (3)  | 4323 (5)  | -3089 (2) |
| C(1)  | 4147 (3)  | 5372 (5)  | 978 (3)   |
| C(2)  | 3522 (2)  | 3924 (4)  | 841 (2)   |
| C(3)  | 2699 (3)  | 3610 (4)  | 1205 (2)  |
| C(4)  | 2398 (4)  | 4706 (5)  | 1773 (3)  |
| C(5)  | 1444 (3)  | -3251 (5) | -385 (3)  |
| C(6)  | 2069 (2)  | -1814 (4) | -256 (2)  |
| C(7)  | 2876 (2)  | -1497 (4) | -636 (2)  |
| C(8)  | 3176 (3)  | -2572 (5) | -1206 (2) |
| C(9)  | 3794 (2)  | -38 (4)   | 1107 (2)  |
| C(10) | 3707 (3)  | -163 (5)  | 1915 (2)  |
| C(11) | 2160 (2)  | 2717 (4)  | -1221 (2) |
| C(12) | 1534 (3)  | 3330 (4)  | -1873 (2) |
| C(13) | 540 (2)   | 3348 (4)  | -1890 (2) |
| C(14) | 208 (2)   | 2771 (5)  | -1264 (2) |
| C(15) | 879 (2)   | 2169 (4)  | -642 (2)  |
| C(16) | -155 (3)  | 3902 (5)  | -2566 (2) |
| II    |           |           |           |
| Co    | 2818 (0)  | 756 (0)   | 271 (0)   |
| P     | 1246 (1)  | 982 (1)   | -1274 (1) |
| F(1)  | 4657 (2)  | -753 (2)  | 1469 (3)  |
| F(2)  | 5614 (1)  | 106 (2)   | 3035 (2)  |
| F(3)  | 4540 (2)  | -624 (3)  | 2775 (3)  |
| O(1)  | 2761 (2)  | 1842 (2)  | 1864 (2)  |
| O(2)  | 2788 (2)  | -1362 (2) | -13 (2)   |
| O(3)  | 2956 (2)  | -334 (2)  | -1256 (2) |
| O(4)  | 2979 (2)  | 2870 (2)  | 683 (3)   |
| N(1)  | 2700 (2)  | 932 (2)   | 1410 (3)  |
| N(2)  | 2721 (2)  | -603 (2)  | 524 (3)   |
| N(3)  | 2984 (2)  | 578 (2)   | -824 (3)  |
| N(4)  | 2968 (2)  | 2122 (2)  | 72 (3)    |
| C(1)  | 2448 (4)  | 155 (5)   | 2666 (5)  |
| C(2)  | 2566 (3)  | 126 (3)   | 1766 (3)  |
| C(3)  | 2570 (2)  | -782 (3)  | 1236 (3)  |
| C(4)  | 2456 (3)  | -1831 (3) | 1507 (5)  |
| C(5)  | 3271 (3)  | 1363 (4)  | -2047 (4) |
| C(6)  | 3124 (2)  | 1382 (3)  | -1176 (3) |
| C(7)  | 3121 (2)  | 2292 (3)  | -641 (3)  |
| C(8)  | 3291 (3)  | 3330 (3)  | -862 (5)  |
| C(9)  | 4171 (2)  | 806 (3)   | 1606 (3)  |
| C(10) | 4675 (3)  | -79 (3)   | 2142 (4)  |
| C(11) | 999 (2)   | 1592 (2)  | -2560 (3) |
| C(12) | 905 (3)   | 968 *3)   | -3384 (3) |
| C(13) | 789 (3)   | 1364 (3)  | -4336 (4) |
| C(14) | 758 (3)   | 2390 (3)  | -4487 (4) |
| C(15) | 850 (3)   | 3013 (3)  | -3692 (4) |
| C(16) | 975 (3)   | 2624 (3)  | -2721 (4) |
| C(17) | 432 (2)   | -57 (2)   | -2038 (3) |
| C(18) | 700 (3)   | -1054 (3) | -1872 (3) |
| C(19) | 39 (3)    | -1808 (3) | -2527 (4) |
| C(20) | -852 (3)  | -1563 (4) | -3330 (4) |
| C(21) | -1115 (3) | -558 (4)  | -3502 (4) |
| C(22) | -476 (3)  | 198 (3)   | -2862 (3) |
| C(23) | 792 (2)   | 1719 (2)  | -732 (3)  |
| C(24) | 895 (3)   | 2752 (3)  | -556 (3)  |
| C(25) | 562 (3)   | 3245 (3)  | -84 (4)   |
| C(26) | 163 (3)   | 2711 (4)  | 256 (4)   |
| C(27) | 99 (4)    | 1692 (4)  | 139 (5)   |
| C(28) | 400 (3)   | 1195 (3)  | -364 (4)  |

SHELXTL drawing for II is shown in Figure 2. The atom numbering scheme for the  $\text{Co}(\text{DH})_2\text{CH}_2\text{CF}_3$  unit is the same as I. The SHELXTL drawing and the atom numbering scheme for one of the two crystallographically independent molecules of III are depicted in Figure 3.

In all the compounds, cobalt exhibits a distorted octahedral stereochemistry and the  $(\text{DH})_2$  ligands occupy the four equatorial positions. Selected bond lengths and angles are reported in Tables IV and V. The  $\text{Co}(\text{DH})_2$  units are similar within the experimental errors in all the compounds, and complete bond lengths and angles are reported in the supplementary material.

Some relevant geometrical parameters, namely  $d$ , the displacement of cobalt out of the 4N donor plane,  $\alpha$ , the interplanar angle between the two DH units, and the geometry of the  $\text{L-Co-CH}_2\text{CF}_3$  fragment are reported in Tables VI and VII for all the three compounds.

## Discussion

This section is organized as follows: (a) first we present structural data revealing that the effects of the  $\text{CH}_2\text{CF}_3$  group on the  $\text{LCo}(\text{DH})_2$  moiety and its bonding to Co are representative of typical alkyl groups; (b) we will then describe the unusual structural features of the complexes; (c) we next consider a simple model for the binding, and (d) finally, we carry out some more elaborate calculations on the alkyl group itself.

(a) **Effect of  $\text{CH}_2\text{CF}_3$  on the  $\text{LCo}(\text{DH})_2$  Moiety.** In the compound I, the  $\text{Co-N}(\text{py})$  bond length of 2.041 (2) Å is in agreement with our suggestion<sup>13</sup> that in the series  $\text{pyCo}(\text{DH})_2\text{CH}_2\text{R}'$ , the  $\text{Co-N}(\text{py})$  bond length increases with the expected increasing  $\sigma$ -donor power of  $\text{R}'$ . In fact, the present value is very close to that found when  $\text{R}' = \text{COOEt}$  (2.040 (6) Å)<sup>14</sup> but significantly shorter than those reported for  $\text{R}' = \text{CMe}_3$ ,  $\text{SiMe}_3$ , and  $\text{H}$  and longer than the value of 2.028 (3) Å reported for  $\text{R}' = \text{NO}_2$ .<sup>15</sup> The  $\text{Co-C}$  bond of 2.010 (3) Å in I is slightly longer than that of 1.998 (5) Å reported for  $\text{pyCo}(\text{DH})_2\text{Me}$ <sup>16</sup> but slightly shorter than that of 2.028 (3) Å reported for  $\text{pyCo}(\text{DH})_2\text{CH}_2\text{NO}_2$ .<sup>15</sup> On the other hand, even longer values have been reported for  $\text{pyCo}(\text{DH})_2\text{CH}_2\text{R}'$ <sup>13</sup> where  $\text{R}' = \text{SiMe}_3$  (2.031 (6) Å) and  $\text{R}' = \text{CMe}_3$  (2.060 (6) Å). The influence of substituents on py on these values is not known, however.<sup>2</sup>

The  $\text{Co-P}$  bond length of 2.383 (1) Å in II fits well into the trend observed in the series  $\text{Ph}_3\text{PCo}(\text{DH})_2\text{CH}_2\text{R}'$ ,<sup>7,8</sup> being the shortest  $\text{Co-PPh}_3$  distance so far reported for a  $\text{Ph}_3\text{PCo}(\text{DH})_2\text{R}$  compound. Analogously, the  $\text{Co-C}$  bond of 2.036 (3) Å in II is very close to that of 2.026 (6) Å reported for  $\text{PPh}_3\text{Co}(\text{DH})_2\text{Me}$ <sup>17</sup> but shorter than those reported for  $\text{PPh}_3\text{Co}(\text{DH})_2\text{CH}_2\text{CMe}_3$  (2.117 (9) Å).<sup>18</sup>

Although fewer data are available for comparison, the  $\text{Co-P}$  and  $\text{Co-C}$  bond lengths in III are very close to the expected values.<sup>2</sup>

In all three compounds the orientation of the  $\text{CH}_2\text{CF}_3$  group with respect to the equatorial  $(\text{DH})_2$  ligands is very similar. The  $\text{CH}_2\text{-CF}_3$  bond lies almost over one of the equatorial  $\text{Co-N}$  bonds. Such an orientation, very similar to those found in all but one ( $\text{R}' = \text{Br}$ )  $\text{LCo}(\text{DH})_2\text{CH}_2\text{R}'$

(13) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347.

(14) Lenhart, P. J. *J. Chem. Soc., Chem. Commun.* **1967**, 980.

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

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

(17) Bresciani-Pahor, N.; Calligaris, M.; Randaccio, L.; Marzilli, L. G. *Inorg. Chim. Acta* **1979**, *32*, 181.

(18) Bresciani-Pahor, N.; Randaccio, L.; Toscano, P. J.; Marzilli, L. G. *J. Chem. Soc., Dalton Trans.* **1982**, 567.

Table III. Positional Parameters ( $\times 10^4$ ) for Non-Hydrogen Atoms of III

|       | molecule A |          |           | molecule B |          |          |
|-------|------------|----------|-----------|------------|----------|----------|
|       | x          | y        | z         | x          | y        | z        |
| Co    | 24 (1)     | 7353 (0) | 1402 (0)  | 83 (1)     | 2571 (0) | 3705 (0) |
| P     | 1724 (2)   | 7128 (1) | 352 (1)   | 1622 (2)   | 1867 (1) | 3374 (1) |
| F(1)  | -1411 (6)  | 8970 (3) | 1969 (3)  | -3310 (5)  | 2374 (3) | 5082 (3) |
| F(2)  | -3257 (5)  | 8018 (3) | 3118 (3)  | -3312 (5)  | 3567 (3) | 4363 (3) |
| F(3)  | -3341 (5)  | 7672 (4) | 1857 (3)  | -3620 (5)  | 2302 (3) | 3816 (4) |
| O(1)  | -1047 (5)  | 5516 (2) | 2483 (3)  | 2291 (5)   | 4183 (3) | 2329 (3) |
| O(2)  | 2527 (4)   | 9208 (2) | 1392 (3)  | -107 (4)   | 2313 (3) | 5514 (2) |
| O(3)  | 1055 (5)   | 9207 (3) | 334 (3)   | -2126 (4)  | 931 (2)  | 5077 (2) |
| O(4)  | -2552 (4)  | 5514 (3) | 1461 (3)  | 207 (5)    | 2844 (3) | 1905 (3) |
| O(5)  | 2810 (5)   | 6734 (3) | 604 (3)   | 2886 (6)   | 2014 (4) | 3819 (4) |
| O(6)  | 3051 (5)   | 8082 (3) | -327 (3)  | 2798 (6)   | 2300 (4) | 2369 (4) |
| O(7)  | 877 (5)    | 6487 (3) | -262 (3)  | 702 (6)    | 787 (4)  | 3291 (4) |
| N(1)  | 25 (5)     | 6477 (3) | 2265 (3)  | 1865 (5)   | 3798 (3) | 3181 (3) |
| N(2)  | 1725 (5)   | 8253 (3) | 1742 (3)  | 685 (5)    | 2890 (3) | 4715 (3) |
| N(3)  | -9 (5)     | 8233 (3) | 556 (3)   | -1691 (4)  | 1342 (3) | 4220 (3) |
| N(4)  | -1720 (5)  | 6471 (3) | 1079 (3)  | -558 (5)   | 2242 (3) | 2701 (3) |
| C(1)  | 1270 (9)   | 6235 (5) | 3346 (5)  | 4166 (7)   | 5211 (5) | 3378 (5) |
| C(2)  | 1085 (7)   | 6836 (4) | 2659 (4)  | 2659 (6)   | 4244 (4) | 3700 (4) |
| C(3)  | 2115 (6)   | 7888 (4) | 2341 (4)  | 1988 (6)   | 3710 (4) | 4596 (4) |
| C(4)  | 3457 (7)   | 8489 (5) | 2669 (5)  | 2676 (8)   | 4046 (5) | 5314 (5) |
| C(5)  | -1336 (10) | 8486 (6) | -482 (5)  | -3832 (6)  | -144 (4) | 3991 (4) |
| C(6)  | -1081 (7)  | 7881 (4) | 168 (4)   | -2454 (6)  | 861 (4)  | 3703 (4) |
| C(7)  | -2097 (6)  | 6834 (4) | 483 (4)   | -1787 (6)  | 1398 (4) | 2803 (4) |
| C(8)  | -3469 (8)  | 6231 (6) | 170 (6)   | -2479 (9)  | 1019 (6) | 2086 (5) |
| C(9)  | -1497 (7)  | 7480 (4) | 2419 (4)  | -1088 (6)  | 3349 (4) | 3886 (4) |
| C(10) | -2354 (8)  | 8018 (5) | 2333 (5)  | -2751 (7)  | 2928 (4) | 4244 (5) |
| C(11) | 2211 (11)  | 5732 (6) | 1015 (7)  | 2280 (12)  | 1444 (7) | 4787 (6) |
| C(12) | 4574 (8)   | 8683 (5) | -299 (6)  | 4397 (10)  | 3039 (9) | 2164 (9) |
| C(13) | 1717 (9)   | 6310 (7) | -1045 (6) | 1457 (11)  | 215 (6)  | 2983 (7) |

Table IV. Selected Bond Lengths (Å) and Angles (deg) for Compounds I and II

|                  | I         | II         |
|------------------|-----------|------------|
| Co-N(5) [P]      | 2.041 (2) | 2.383 (1)  |
| Co-C(9)          | 2.010 (3) | 2.036 (3)  |
| C(9)-C(10)       | 1.469 (5) | 1.405 (5)  |
| C(10)-F(1)       | 1.368 (6) | 1.330 (7)  |
| C(10)-F(2)       | 1.363 (5) | 1.429 (4)  |
| C(10)-F(3)       | 1.321 (5) | 1.351 (8)  |
| C(9)-Co-N(5) [P] | 174.6 (1) | 170.9 (1)  |
| N(1)-Co-N(5) [P] | 90.3 (1)  | 90.32 (9)  |
| N(1)-Co-C(9)     | 88.6 (1)  | 88.5 (2)   |
| N(2)-Co-N(5) [P] | 90.6 (1)  | 94.32 (9)  |
| N(2)-Co-C(9)     | 94.5 (1)  | 94.4 (1)   |
| N(3)-Co-N(5) [P] | 90.9 (1)  | 92.00 (9)  |
| N(3)-Co-C(9)     | 90.2 (1)  | 89.4 (2)   |
| N(4)-Co-N(5) [P] | 89.1 (1)  | 88.09 (8)  |
| N(4)-Co-C(9)     | 85.8 (1)  | 83.2 (1)   |
| Co-C(9)-C(10)    | 122.6 (3) | 121.1 (3)  |
| C(9)-C(10)-F(1)  | 112.8 (3) | 118.4 (4)  |
| C(9)-C(10)-F(2)  | 112.0 (4) | 113.0 (3)  |
| C(9)-C(10)-F(3)  | 116.5 (4) | 117.2 (6)  |
| F(1)-C(10)-F(2)  | 104.2 (3) | 101.3 (4)  |
| F(1)-C(10)-F(3)  | 104.9 (4) | 104.4 (4)  |
| F(2)-C(10)-F(3)  | 105.3 (3) | 99.9 (3)   |
| Co-P-C(11)       |           | 110.7 (1)  |
| Co-P-C(17)       |           | 124.2 (1)  |
| Co-P-C(23)       |           | 110.18 (9) |
| C(11)-P-C(17)    |           | 99.1 (2)   |
| C(11)-P-C(23)    |           | 110.9 (2)  |
| C(17)-P-C(23)    |           | 101.0 (2)  |

compounds,<sup>7</sup> is shown in Figure 4 in the case of II. As a consequence, the C(9)-Co-N(2) angle is significantly larger and the C(9)-Co-N(4) angle is smaller than 90°, the other two C-Co-N(eq) angles being nearly 90° (see Table IV). The numbering scheme used above refers to that of compounds I and II, while for compound III N(2) and N(4) must be interchanged with N(3) and N(1), respectively (see Table V).

In summary, the CH<sub>2</sub>CF<sub>3</sub> group is a typical alkyl group with respect to its influence on the LCo(DH)<sub>2</sub> moiety.

Table V. Selected Bond Lengths (Å) and Angles (deg) for Compound III

|                 | molecule A | molecule B |
|-----------------|------------|------------|
| Co-P            | 2.257 (2)  | 2.255 (2)  |
| Co-C(9)         | 2.035 (6)  | 2.028 (7)  |
| C(9)-C(10)      | 1.469 (12) | 1.428 (8)  |
| C(10)-F(1)      | 1.344 (7)  | 1.388 (9)  |
| C(10)-F(2)      | 1.362 (8)  | 1.353 (10) |
| C(10)-F(3)      | 1.339 (9)  | 1.340 (9)  |
| C(9)-Co-P       | 175.3 (2)  | 172.8 (1)  |
| N(1)-Co-P       | 91.5 (2)   | 88.8 (2)   |
| N(1)-Co-C(9)    | 83.8 (3)   | 84.5 (2)   |
| N(2)-Co-P       | 89.5 (2)   | 91.8 (2)   |
| N(2)-Co-C(9)    | 89.7 (2)   | 89.7 (3)   |
| N(3)-Co-P       | 89.7 (2)   | 90.9 (2)   |
| N(3)-Co-C(9)    | 95.0 (3)   | 95.9 (2)   |
| N(4)-Co-P       | 92.3 (2)   | 88.9 (2)   |
| N(4)-Co-C(9)    | 88.6 (2)   | 89.8 (3)   |
| Co-C(9)-C(10)   | 124.7 (5)  | 124.4 (5)  |
| C(9)-C(10)-F(1) | 113.5 (6)  | 112.3 (7)  |
| C(9)-C(10)-F(2) | 113.0 (6)  | 115.9 (5)  |
| C(9)-C(10)-F(3) | 114.7 (7)  | 116.6 (7)  |
| F(1)-C(10)-F(2) | 104.1 (6)  | 102.1 (6)  |
| F(1)-C(10)-F(3) | 105.7 (7)  | 102.8 (5)  |
| F(2)-C(10)-F(3) | 104.8 (6)  | 105.4 (7)  |

Table VI. Some Relevant Geometrical Parameters for LCo(DH)<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub> Compounds

| L                   | Co-C, Å   | Co-L, Å   | L-Co-C, Å | α, deg | d, <sup>a</sup> Å |
|---------------------|-----------|-----------|-----------|--------|-------------------|
| P(OMe) <sub>3</sub> | 2.035 (6) | 2.257 (2) | 175.3 (2) | 0.9    | 0.02              |
|                     | 2.028 (7) | 2.255 (2) | 172.8 (1) | 4.5    | ~0.0              |
| 4-NCpy              | 2.010 (3) | 2.041 (2) | 174.6 (1) | 1.0    | 0.01              |
| PPH <sub>3</sub>    | 2.036 (3) | 2.383 (1) | 170.9 (1) | 1.7    | 0.04              |

<sup>a</sup> A positive d indicates displacement toward L.

(b) Unusual Structural Features of CH<sub>2</sub>CF<sub>3</sub>. The most interesting feature of the present structural determinations is the geometry of the Co-CH<sub>2</sub>-CF<sub>3</sub> grouping. Some geometrical parameters are reported in Table VII together with the relative parameters for neopentyl and

Table VII. Comparison of Some Geometrical Parameters of the Co-CH<sub>2</sub>R' Group in LCo(DH)<sub>2</sub>CH<sub>2</sub>CX<sub>3</sub> Complexes Having C-C Bond Length (Esd's = 0.01 Å)

| X <sub>J</sub> | L                                | Co-C, Å   | Co-CH <sub>2</sub> CX <sub>3</sub> ,<br>deg | H <sub>2</sub> C-CX <sub>3</sub> ,<br>Å | HI(C-C) <sup>a</sup> | C-X <sub>J</sub> , Å | HI(C-I) <sup>a</sup> | Σ, <sup>b</sup> deg  |
|----------------|----------------------------------|-----------|---|---|----------------------|----------------------|----------------------|----------------------|
| F              | P(OMe) <sub>3</sub> <sup>c</sup> | 2.035 (6) | 124.7 (5)                                   | 1.47 (1)                                | 1.6                  | 1.344 (7), 1.339 (9) | 3.9                  | 323.3 (6), 325.9 (6) |
|                |                                  | 2.028 (7) | 124.4 (5)                                   | 1.428 (8)                               | 1.3                  | 1.362 (8)            | 3.8                  | 321.2 (7)            |
|                |                                  |           |   |   |                      | 1.35 (1), 1.340 (9)  | 3.8                  | 323.4 (6), 324.8 (6) |
| F              | 4-CNpy <sup>c</sup>              | 2.010 (3) | 122.6 (3)                                   | 1.469 (5)                               | 1.7                  | 1.388 (9)            | 5.6                  | 317.2 (6)            |
|                |                                  |           |   |   |                      | 1.368 (6), 1.363 (5) | 4.1                  | 321.9 (4), 321.5 (3) |
| F              | PPh <sub>3</sub> <sup>c</sup>    | 2.036 (3) | 121.1 (3)                                   | 1.405 (5)                               | 1.1                  | 1.321 (5)            | 3.5                  | 326.7 (4)            |
|                |                                  |           |   |   |                      | 1.330 (7), 1.351 (8) | 4.0                  | 324.1 (4), 321.4 (4) |
| H              | 4-MeOC(NH)py <sup>d</sup>        | 2.035 (5) | 117.8 (4)                                   | 1.519 (8)                               |                      | 1.429 (4)            | 6.9                  | 314.2 (4)            |
|                |                                  | Me        | H <sub>2</sub> O <sup>e</sup>               | 2.044 (7)                               | 126.9 (5)            | 1.531 (10)           | 1.55 (1), 1.56 (1)   |                      |
| Me             | py <sup>f</sup>                  | 2.060 (6) | 130.3 (4)                                   | 1.529 (7)                               |                      | 1.52 (1)             |                      | 333.0 (7)            |
|                |                                  |           |   |   |                      | 1.53 (1), 1.54 (1)   |                      | 330.1 (5), 319.6 (5) |
| Me             | PMe <sub>3</sub> <sup>g</sup>    | 2.084 (3) | 130.2 (2)                                   | 1.523 (5)                               |                      | 1.521 (8)            |                      | 331.0 (5)            |
|                |                                  |           |   |   |                      | 1.543 (6), 1.53 (8)  |                      | 324.9 (4), 322.7 (4) |
|                |                                  |           |   |   |                      | 1.489 (6)            |                      | 332.0 (4)            |

<sup>a</sup> Hybridization index. <sup>b</sup> Sum of the angles around C involving the C-X<sub>J</sub> bond. <sup>c</sup> Present work. <sup>d</sup> Reference 24. <sup>e</sup> Reference 18. <sup>f</sup> Reference 13. <sup>g</sup> Reference 23.

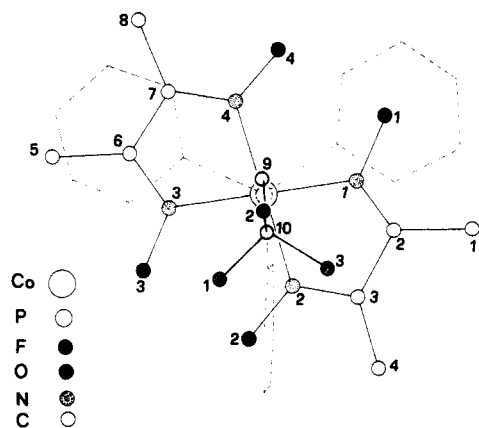


Figure 4. The orientation of the CH<sub>2</sub>-CF<sub>3</sub> bond with respect to one of the Co-N bonds of the equatorial ligand set.

ethyl derivatives. As already observed, the Co-CH<sub>2</sub>-CF<sub>3</sub> angle is significantly distorted from the tetrahedral value. Furthermore it is larger than that observed for the Co-C-H<sub>2</sub>-CH<sub>3</sub> fragment but smaller than those reported for the Co-CH<sub>2</sub>CMe<sub>3</sub> fragment. This trend is that expected from steric considerations. Examination of the corresponding Co-C bond lengths does not show any simple relation between these and the above angles. No evidence appears that the different amount of hybridization of the C atom bonded to cobalt due to the large variation of the Co-CH<sub>2</sub>-R' angle influences the Co-C bond length in a straightforward way. In contrast, the hybridization of both the carbon atoms of the CH<sub>2</sub>CF<sub>3</sub> group appears to strongly influence the C-C bond lengths. Thus, this bond, which ranges from 1.41 to 1.47 Å, appears shortened as compared with the values (>1.50 Å) reported for organic compounds containing CF<sub>3</sub> groups.<sup>19</sup> Such a shortening may be interpreted as a consequence of the increased s character in the hybrid orbitals of both the C atoms forming the bond. The increase is due to the opening of the Co-CH<sub>2</sub>CF<sub>3</sub> angle for the C bonded to cobalt and to the strong compression (vide infra) undergone by the CF<sub>3</sub> group (Tables IV and V). It is noteworthy that in the PPh<sub>3</sub>Co(DH)<sub>2</sub>CH<sub>2</sub>CN complex,<sup>7</sup> where the Co-CH<sub>2</sub>-CN angle is 116.5 (3)° and the C atom of CN has sp hybridization, the H<sub>2</sub>C-CN bond length is 1.424 (5) Å. The compression of the CF<sub>3</sub> group is clearly shown by the values of the F-C-F angles which

range in the three structures from 99.9 to 105.7°. These values are significantly smaller than those reported for CF<sub>3</sub> groups in organic compounds. For example, in tris(trifluoromethyl)methane<sup>20</sup> the FCF angle is 108.0 (2)°. Such angular distortions parallel the C-F bond length distortions. In fact, for XCF<sub>3</sub> compounds, C-F bond lengths of 1.33–1.34 Å are expected, while in the present structures they range from 1.321 (5) to 1.429 (4) Å. In Table VII, for each C-F bond length, the sum of the angles, Σ, around C of the CF<sub>3</sub> group involving this bond is also reported. Note that longer C-F distances correspond to smaller values of Σ. This trend is easily explained, since the p character in the C-F bond is expected to decrease when Σ decreases. When allowance is made for the larger esds of their bond lengths and angles, a similar trend is also found for the neopentyl derivatives (Table VII), but the effect, as expected, is less pronounced compared to that in the CH<sub>2</sub>CF<sub>3</sub> complexes.

Finally, the longest C-C distances correspond to two short and one long C-F bond lengths. Vice versa, the shortest C-C distances correspond to one short and two long C-F bond lengths.

Bond angles around C(10) are consistent with a local, approximately mirror, symmetry for the C-CF<sub>3</sub> group. The C-C and the short (or long) C-F bond are in the pseudo-mirror plane.

(c) **A Simple Bonding Model.** For all the above bond lengths and angles, distortions of the C-CF<sub>3</sub> grouping may be rationalized in terms of changes of the s and p character in the hybrid orbitals of C(10). Following the method of Dewar et al.,<sup>21</sup> Gilli and Bertolazzi<sup>22</sup> have derived the hybridization index for AX<sub>2</sub>YZ systems with a mirror symmetry as a function of the bond angles around A. The hybridization index (HI) is the ratio of the sum of the squared coefficients of the p AO's to the squared coefficient of the s AO. For example, in exactly tetrahedral molecules (AX<sub>4</sub>), HI = 3. As expected, the mean calculated values for the present fluoroalkyl complexes, reported in Table VII, increase with the increasing values of the observed C-C and C-F distances.

(d) **MNDO Calculations.** As discussed in the Experimental Section, we performed a series of calculations

(19) "Molecular Structure by Diffraction Methods - Specialist Periodical Reports", The Chemical Society, London, vols. 1-5.

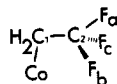
(20) Stolevik, R.; Thom, E. *Acta Chem. Scand.* 1971, 25, 3205.  
 (21) Dewar, J. S.; Kollmar, H.; Li, W. K. *J. Chem. Educ.* 1975, 52, 305.  
 (22) Gilli, G.; Bertolazzi, V. *J. Chem. Educ.* 1983, 60, 630.  
 (23) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1982, 2549.  
 (24) Marzilli, L. G.; Summers, M. F.; Ramsden, J. H., Jr.; Bresciani-Pahor, N.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1984, 511.

Table VIII. Geometric Data for the Observed and Fully Optimized CH<sub>2</sub>CF<sub>3</sub> Group<sup>a</sup>

|  | X-ray data       |                             |                                 |       | fully optimized MNDO data                |  |                                 |
|--|------------------|-----------------------------|---------------------------------|-------|--|--|---------------------------------|
|  | I,<br>L = 4-CNpy | II,<br>L = PPh <sub>3</sub> | IIIa<br>L = P(OMe) <sub>3</sub> | IIIb  | CH <sub>2</sub> CF <sub>3</sub><br>anion | CH <sub>2</sub> CF <sub>3</sub><br>radical | CH <sub>3</sub> CF <sub>3</sub> |
| C <sub>2</sub> -F <sub>a</sub>                 | 1.363            | 1.429                       | 1.362                           | 1.353 | 1.390                                    | 1.358                                      | 1.358                           |
| C <sub>2</sub> -F <sub>b</sub>                 | 1.368            | 1.330                       | 1.339                           | 1.388 | 1.377                                    | 1.358                                      | 1.358                           |
| C <sub>2</sub> -F <sub>c</sub>                 | 1.321            | 1.351                       | 1.344                           | 1.340 | 1.377                                    | 1.358                                      | 1.358                           |
| C <sub>1</sub> -C <sub>2</sub>                 | 1.469            | 1.405                       | 1.469                           | 1.428 | 1.467                                    | 1.540                                      | 1.587                           |
| C <sub>1</sub> -C <sub>2</sub> -F <sub>a</sub> | 112.0            | 113.0                       | 113.0                           | 115.9 | 116.6                                    | 112.1                                      | 112.6                           |
| C <sub>1</sub> -C <sub>2</sub> -F <sub>b</sub> | 112.8            | 118.4                       | 113.5                           | 112.3 | 115.3                                    | 112.8                                      | 112.6                           |
| C <sub>1</sub> -C <sub>2</sub> -F <sub>c</sub> | 116.5            | 117.2                       | 114.7                           | 116.6 | 115.3                                    | 112.8                                      | 112.6                           |
| mean C-C-F                                     | 113.8            | 116.2                       | 113.7                           | 114.9 | 115.7                                    | 112.6                                      | 112.6                           |
| F <sub>a</sub> -C <sub>2</sub> -F <sub>b</sub> | 104.2            | 101.3                       | 104.8                           | 102.1 | 101.9                                    | 106.2                                      | 106.1                           |
| F <sub>a</sub> -C <sub>2</sub> -F <sub>c</sub> | 104.9            | 99.9                        | 104.1                           | 102.8 | 101.9                                    | 106.2                                      | 106.1                           |
| F <sub>b</sub> -C <sub>2</sub> -F <sub>c</sub> | 105.3            | 104.4                       | 105.7                           | 105.4 | 103.9                                    | 106.1                                      | 106.2                           |
| mean F-C-F                                     | 104.8            | 101.9                       | 104.9                           | 103.4 | 102.6                                    | 106.2                                      | 106.1                           |
| C <sub>1</sub> -H <sub>1</sub>                 |                  |                             |                                 |       | 1.076                                    | 1.080                                      | 1.062                           |
| C <sub>1</sub> -H <sub>2</sub>                 |                  |                             |                                 |       | 1.076                                    | 1.080                                      | 1.062                           |
| C <sub>1</sub> -H <sub>3</sub>                 |                  |                             |                                 |       |  |  | 1.073                           |

<sup>a</sup> Atoms are defined in Scheme I. Distances in angstroms and angles in degrees.

using some of the experimentally determined distances and angles for the CH<sub>2</sub>CF<sub>3</sub> group as well as some calculations where relevant distances and angles were fully optimized. In all cases, the results differed in minor details only, and the fully optimized data are presented in Table VIII along with a summary of the related experimental values.



Both in the experimental data and in the theoretical calculations, either one long and two short or two long and one short CF bonds were found but there appeared to be no definitive pattern. In contrast to the clear relationships between C-C bond length and bond angles as well as carbanionic character in the experimental data (vide infra), the calculations showed no clear relationship. The C-C distance of the experimental data are typically shorter than the theoretical calculations. Bond angles, on the other hand, give a more consistent picture both in internal comparison and cross comparison of experimental and theoretical results.

The mean of the theoretically calculated bond angles proved to be the most useful value for comparison of the results. A large mean C-C-F angle and a small mean F-C-F angle corresponded to greater carbanionic character in the CH<sub>2</sub>CF<sub>3</sub> groups. Thus, the theoretical results indicate increasing carbanionic character as follows: CH<sub>2</sub>CF<sub>3</sub> ≈ CH<sub>3</sub>CF<sub>3</sub> < CH<sub>2</sub>CF<sub>3</sub><sup>-</sup>. The experimental results follow the pattern IIIa < Ia < IIIb < II. A plot of mean F-C-F vs. mean C-C-F bond angles for the data in Table VIII is slightly curved (Figure 5). Assuming C<sub>3v</sub> symmetry, the geometric relationship between the angle (γ) involving the principal axis (in this case along the C-C bond) and the substituents at C (F, in this case) is related to the angle (δ) between the substituents as follows:

$$\gamma = 180^\circ - \sin^{-1} [(2/(3)^{1/2}) \sin (\delta/2)]$$

Thus for an unhybridized C, γ = 125.3° and δ = 90°. The points in Figure 5 fall on the curve determined by this relationship. We suggest that the position of a point on this curve is indicative of the carbanionic character of the CH<sub>2</sub>CF<sub>3</sub> group. It is interesting that the molecule HC(C-F)<sub>3</sub> falls closest to the fully hybridized position on the curve (the y intercept, 109.5°) whereas PPh<sub>3</sub>Co(DH)<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub> falls closest to the unhybridized position (the x intercept, 125.3°).

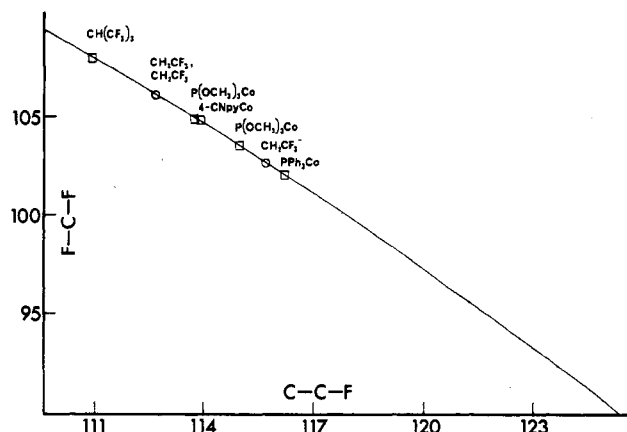


Figure 5. Mean F-C-F angle (deg) vs. mean C-C-F angle (deg) for observed (□) and calculated (○) C-CF<sub>3</sub> groups. The curve was derived as described in the text; the y intercept represents pure sp<sup>3</sup> hybridization and the X intercept represents no hybridization.

In conclusion, the structural parameters of the CH<sub>2</sub>CF<sub>3</sub> group in the complexes investigated here appear to resemble those expected for a CH<sub>2</sub>CF<sub>3</sub> carbanion. The factors favoring increased carbanionic character are not completely clear. The greater apparent carbanionic character of II may be partly the result of a steric compression since the Co-C-C bond angle is small. However, lattice forces may play some role as evidenced by the differences between IIIa and IIIb. Clearly more structural work on organometallic CH<sub>2</sub>CF<sub>3</sub> compounds as well as more extensive and sophisticated theoretical work is needed.<sup>25</sup> However, the present results support the usefulness of the simple picture of the alkyl ligand as being a coordinated carbanion in organometallic complexes related to B<sub>12</sub> coenzymes.

**Acknowledgment.** This work was supported by NIH grant 29225 (L.G.M.) and by a grant (to L.R.) from CNR, Rome, Italy. We are grateful to these organizations. L.

(25) One reviewer felt that the carbanionic character of the CH<sub>2</sub>CF<sub>3</sub> group should be influenced by electronic character of the trans ligand. However, there is no clear evidence for such a structural relationship.<sup>2</sup> Since lattice and steric effects cannot be fully evaluated, the average position of the four experimental determinations should be taken as an indication of carbanionic character of the CH<sub>2</sub>CF<sub>3</sub> group in cobaloximes.

G.M. thanks the Alexander von Humboldt Foundation for a Senior U.S. Scientist Award which aided in the preparation of the manuscript.

Registry No. I, 86942-05-4; II, 17567-52-1; III, 88887-03-0.

**Supplementary Material Available:** A listing of observed and calculated structure factors and tables of anisotropic thermal parameters, complete bond angles and bond lengths, and hydrogen atom coordinates (49 pages). Ordering information is given on any current masthead page.

## Electronic Structure of Group 14 ( $\eta^4$ -Metallole)tricarbonyliron Complexes<sup>†,‡</sup>

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Received July 19, 1984

Some methyl derivatives of metalloles  $R_2XC_4H_4$  ( $X = C, Si, Ge$ ) and their tricarbonyliron complexes have been prepared in order to study the influence of both the group 14 elements and complexation effects on the electronic structure of the diene ring using photoelectron spectroscopy (UPS, He I, He II). Strong electron donation from iron to the metallole ligand has been demonstrated. This transfer, which is the result of participation of the lowest vacant orbital of the ring ( $3b_1$ ) in the highest occupied orbital (HOMO) of the complex, shows that these compounds have a certain aromatic character.

A few of the numerous studies on the electronic structures of metal-diene complexes are devoted to tricarbonyliron compounds. Most of the research has been limited to the butadiene ligand itself and to its substituted derivatives,<sup>1-5</sup> to cyclobutadiene,<sup>5-7</sup> 1,3-cyclohexadiene,<sup>4,5</sup> and *trans*-1,3-pentadiene.<sup>1,5,8</sup> As far as we know, no systematic studies have been undertaken on tricarbonyliron complexes of cyclopentadienes and, a fortiori, on silicon and germanium analogues.

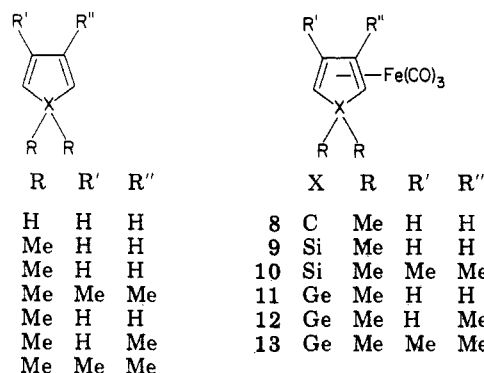
A comprehensive analysis of the electronic features of (5,5-dimethylcyclopentadiene)tricarbonyliron and those of several (methylsilole) and (methylgermole)tricarbonyliron complexes is presented in this paper. We have extended the synthesis used for methylsiloles<sup>9,10</sup> to methylgermoles. Photoelectron spectroscopy is a very suitable technique to evaluate metal-ligand interactions or electronic modifications arising from the substitution of a carbon atom by a silicon or a germanium atom.

### Synthesis and Identification of Group 14 ( $\eta^4$ -Metalloles)tricarbonyliron Complexes

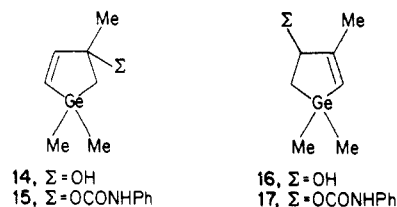
5,5-Dimethylcyclopentadiene (**2**) was prepared from  $\beta,\beta$ -dimethylglutaric acid by the method of Rouse and Tyler.<sup>11</sup> Reaction of **2** with  $Fe_2(CO)_9$  led to the corresponding tricarbonyliron complex **8**.<sup>12-14</sup> Preparation of complexes **9-11** has been described previously.<sup>9</sup> The method of synthesis of 1,1,3,4-tetramethylsilole (**4**)<sup>9b</sup> was applied to the two methylgermole derivatives **6** and **7**, which were obtained pure and were uncontaminated with the transoid isomer.<sup>15</sup>

<sup>†</sup>The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

<sup>‡</sup>Part 22 of "Application of Photoelectron Spectroscopy to Molecular Properties". Part 21: C. Guimon, G. Pfister-Guillouzo, P. Meunier, B. Gautheron, G. Tainturier, and S. Pouly, to be submitted for publication.



The *N*-phenylcarbamates corresponding to alcohols **14** and **16** (prepared by photooxygenation-reduction of



- (1) Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 654.
- (2) Worley, S. D. *J. Chem. Soc., Chem. Commun.* **1970**, 980.
- (3) Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1974**, *28*, 1193.
- (4) Green, J. C.; Powell, P.; Van Tilborg, J. *J. Chem. Soc., Dalton Trans.* **1976**, 1974.
- (5) Worley, S. D.; Webb, T. R.; Gibson, D. H.; Ong, T. S. *J. Electron Spectrosc.* **1980**, *18*, 189. Worley, S. D.; Webb, T. R.; You, T. *Ibid.* **1982**, *28*, 129.
- (6) Hall, M. B.; Hillier, I. H.; Connor, J. A.; Guest, M. F.; Lloyd, D. R. *Mol. Phys.* **1975**, *30*, 839.
- (7) Bursten, E. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760. Kostic, N. M.; Fenske, R. F. *Chem. Phys. Lett.* **1982**, *90*, 306.
- (8) (a) Derrick, P. J.; Asbrink, L.; Edquist, O.; Jonsson, B. O.; Lindholm, E. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *6*, 203. (b) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.
- (9) (a) Laporterie, A.; Iloughmane, H.; Dubac, J. *J. Organomet. Chem.* **1983**, *244*, C12. (b) *Tetrahedron Lett.* **1983**, 3521.