

- MIRTI, P., GENNARO, M. C. & VALLINOTTO, M. (1982). *Trans. Met. Chem.* **7**, 2-5.
- MUETTERTIES, E. L. & GUGGENBERGER, L. J. (1974). *J. Am. Chem. Soc.* **96**, 1748-1756.
- NEVES, D. R. & DABROWIAK, J. C. (1976). *Inorg. Chem.* **15**, 129-134.
- PAULING, L. (1947). *J. Am. Chem. Soc.* **69**, 542-553.
- RUSSEGER, P. & BRICKMANN, J. (1975). *Chem. Phys. Lett.* **30**, 276-278.
- UGI, I., MARQUARDING, D., KLUSACEK, H., GILLESPIE, P. & RAMIREZ, F. (1971). *Acc. Chem. Res.* **4**, 288-296.

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Relation between Bonding and the Substitution-Dependent Geometry of a Number of Dicobalt Hexacarbonyl Acetylene Complexes

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Abstract

The molecular structures of five dicobalt hexacarbonyl acetylene complexes, $\text{Co}_2(\text{CO})_6(\text{R}-\text{C}\equiv\text{C}-\text{R})$, are analyzed in terms of variation in their geometry as a function of increasing electronegativity of the substituent R . The crystal structures of three of the five complexes with $R = \text{COOH}$, CH_2OH and CF_3 have been determined for the first time and are reported. Crystal data are as follows: $R = \text{COOH}$: $[\text{Co}_2(\text{CO})_6(\text{C}_4\text{H}_2\text{O}_4)]$, $M_r = 400.0$, $P2_12_12_1$, $a = 7.059$ (2), $b = 11.107$ (3), $c = 17.516$ (5) Å, $Z = 4$, $V = 1373.3$ Å³, $D_m = 1.80-2.00$, $D_x = 1.93$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.7107$ Å, $T = 293$ (2) K; $R = \text{CH}_2\text{OH}$ (monohydrate): $[\text{Co}_2(\text{CO})_6(\text{C}_4\text{H}_6\text{O}_2)] \cdot \text{H}_2\text{O}$, $M_r = 390.0$, $P2_1/c$, $a = 7.974$ (3), $b = 12.591$ (5), $c = 14.551$ (6) Å, $\beta = 104.31$ (5)°, $Z = 4$, $V = 1415.6$ Å³, $D_m = 1.80-2.00$, $D_x = 1.83$ g cm⁻³, $\text{Mo K}\alpha$, $T = 293$ (2) K; $R = \text{CF}_3$: $[\text{Co}_2(\text{CO})_6(\text{C}_4\text{F}_6)]$, $M_r = 448.0$, $P2_1/c$, $a = 7.538$ (3), $b = 30.804$ (9), $c = 12.681$ (6) Å, $\beta = 100.49$ (4)°, $Z = 8$, $V = 2895.4$ Å³, $D_m = 1.95-2.10$, $D_x = 2.05$ g cm⁻³, $\text{Mo K}\alpha$, $T = 100$ (0.5) K. Final $R(F)$ factors are 2.8, 4.8 and 5.2% respectively. The two other complexes discussed here with $R = \text{Ph}$ and $R = \text{C}(\text{CH}_3)_3$ have been reported recently by Gregson & Howard [*Acta Cryst.* (1983), **C39**, 1024-1027]. The metal-acetylenic ligand distances decrease with increasing electronegativity of R , while the acetylenic C-C distance increases, indicating the strengthening of the Co-C_{ac} bonds to be due to increased back donation. The effect is attributed to a stabilization of the ligand a_2 and b_1 orbitals by the electronegative substituents. Various correlations between geometric distortion parameters are discussed.

Introduction

There is considerable interest in the study of polynuclear complexes because of their relevance as model compounds for metal-catalyzed reactions such as hydrogenation and carbonylation. As the attachment of a single molecule to more than one metal atom is related to the bonding of an organic substrate to a metal surface, the detailed study of such model compounds is of importance. Complexes of the type studied here may also be regarded simply as possible intermediates in homogeneous catalytic reactions.

The present study is part of a series of investigations on the effect of metal-ligand bonding on ligand geometry and ligand electron distribution. Studies on dicobalt octacarbonyl (Leung & Coppens, 1983) and methylidyne dicobalt nonacarbonyl (Leung, 1983) have been reported.

We report here on the geometry of three dicobalt hexacarbonyl acetylenes with general formula $\text{Co}_2(\text{CO})_6(\text{R}-\text{C}\equiv\text{C}-\text{R})$ and their comparison with two complexes of this type determined by Gregson & Howard (1983). The choice of the radical R was guided by two considerations. A range of electronegativities was desired to enable the detection of substitution-related trends in geometry and electron distribution. In addition we have avoided H atoms as much as possible to eliminate the need for neutron diffraction data in the electron density studies.

Experimental

Synthesis

All manipulations were performed in a dry nitrogen gas atmosphere.

Table 1. Summary of refinements

R	COOH	CH ₂ OH	CF ₃
Number of positional variables	72	87	144
Number of thermal variables	134	134	288
Number of independent reflections	2286	4427	4914
$R(F)^*$	0.028	0.048	0.052
$R_w(F)^*$ (all reflections)	—	—	0.042
Weighting scheme	Unit weight	Unit weight	$w = 1/\sigma^2(F_o)$
Number of atoms in the asymmetric unit	24	29	48
$(\Delta/\sigma)_{\max}$	0.245	0.340	0.165
$(\Delta\rho)_{\max}$ (eÅ ⁻³)	≤ 0.40	≤ 0.35	≤ 0.70

$$* R = \sum |F_o - k|F_c| / \sum F_o. R_w = (\sum w|F_o - k|F_c|^2 / \sum wF_o^2)^{1/2}.$$

(I) $R = \text{COOH}$ (Cetini, Gambino, Rossetti & Sappa, 1967). 3.8 g of dicobalt octacarbonyl was added to 1.9 g C₄H₂O₄ (acetylenedicarboxylic acid) in 50 ml of petroleum ether (35–60 °C) and placed in an Erlenmeyer flask equipped with a bubbling oil valve. Removal of the petroleum ether by evaporation in a stream of nitrogen yields crude, dark-red crystals which were purified by recrystallization.

(II) $R = \text{CH}_2\text{OH}$ (Sternberg, Greenfield, Friedel, Wotiz, Markby & Wender, 1954). 4.3 g of dicobalt octacarbonyl was added to 1.5 g of (CH₂OH)₂C₂ in 50 ml of petroleum ether (35–60 °C) using the apparatus described above. Orange-red needles were obtained after recrystallization from hexane.

(III) $R = \text{CF}_3$ (Boston, Sharp & Wilkinson, 1962). Excess hexafluoro-2-butyne was condensed onto 3 g of dicobalt octacarbonyl in 50 ml of petroleum ether (35–60 °C), contained in an ampoule immersed in liquid nitrogen. After sealing, the ampoule was placed in a thermostat bath at 323 K. A red precipitate formed, which sublimed very easily at atmospheric pressure.

Orange-red needles were obtained by sublimation at 263 K. Since they become plastic at about 279 K they must be studied at low temperature.

Data collection, structure solution and refinement

Data for dicobalt hexacarbonyl dicarboxyacetylene (I) [μ -(2-butyne-1,4-diol)-bis(tricarbonylcobalt)-(Co-Co)] and dicobalt hexacarbonyl 2-butyne-1,4-diol (II) [μ -(2-butyne-1,4-diol)-bis(tricarbonylcobalt)-(Co-Co)] monohydrate collected at room temperature on a Philips PW 1100 diffractometer. Data for dicobalt hexacarbonyl hexafluoro-2-butyne (III) [μ -(hexafluoro-2-butyne)-bis(tricarbonylcobalt)-(Co-Co)] recorded at 100 K on an Enraf-Nonius CAD-4 diffractometer. Graphite-monochromatized Mo K α radiation and a $\theta/2\theta$ scan were used in all three experiments. D_m determined by flotation in aqueous ZnCl₂ solutions for the three structures are given in the *Abstract*.

Data corrected for Lorentz and polarization effects. Absorption correction applied to the data of (III)

Table 2. $R = \text{COOH}$: atomic positional parameters ($\times 10^4$) and U_{eq} values ($\times 10^3$)

	$U_{\text{eq}} = \frac{1}{3} \sum_i U_i a_i^* a_i \cdot a_i$			U_{eq} (Å ²)
	x	y	z	
Co(1)	6155 (1)	5093 (1)	4410 (1)	35 (1)
Co(2)	7219 (1)	4047 (1)	3241 (1)	30 (1)
O(1)	6293 (4)	7785 (2)	3230 (2)	55 (3)
O(2)	9109 (4)	7073 (3)	2895 (2)	59 (3)
O(3)	12305 (4)	6187 (3)	3413 (2)	47 (4)
O(4)	2683 (4)	4873 (3)	2470 (2)	37 (3)
O(5)	8935 (6)	5083 (5)	5209 (2)	68 (6)
O(6)	2975 (9)	7855 (4)	4857 (3)	64 (8)
O(7)	3821 (8)	3187 (4)	5107 (3)	92 (7)
O(8)	4999 (6)	1811 (3)	3407 (3)	65 (5)
O(9)	7974 (7)	4242 (4)	1600 (2)	88 (5)
O(10)	11030 (5)	3325 (3)	3756 (2)	63 (4)
C(1)	5142 (5)	5153 (3)	3378 (2)	31 (3)
C(2)	6810 (5)	5741 (3)	3427 (2)	31 (3)
C(3)	7553 (5)	6915 (3)	3156 (2)	30 (3)
C(4)	3268 (5)	5370 (3)	3033 (2)	32 (3)
C(5)	8410 (7)	5082 (5)	4922 (3)	46 (5)
C(6)	5009 (9)	6360 (5)	4859 (3)	59 (6)
C(7)	4761 (8)	3909 (5)	4852 (3)	54 (6)
C(8)	2634 (4)	2634 (4)	3331 (3)	43 (5)
C(9)	7677 (7)	4143 (4)	2233 (2)	57 (5)
C(10)	9597 (6)	3606 (4)	3546 (2)	41 (4)

($\mu = 23.8 \text{ cm}^{-1}$) using the Gaussian grid integration method (Coppens, Leiserowitz & Rabinovich, 1965), transmission factors 0.83 to 0.92; no absorption corrections applied to the other two data sets. For data set (III), standard deviations obtained from $\sigma^2(I - B) = I + B + [0.02(I - B)]^2$, where I and B are respectively the intensity of the peak and the value of the background.

In each case Co atoms were located with the program *MULTAN* (Germain, Main & Woolfson, 1971). A Fourier synthesis phased by these atoms revealed the remaining non-hydrogen atoms. A difference Fourier synthesis showed the H atoms in structures (I) and (II). A water molecule of crystallization was found in the latter compound.

Refinement of atomic parameters was carried out by full-matrix least squares, minimizing the function $\sum w(|F_o| - k|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and w is defined as $1/\sigma^2(F_o)$ for (III), and taken as equal to unity for (I) and (II).

Atomic scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), and from Stewart, Davidson & Simpson (1965) for H. Anomalous-dispersion contributions for Co were included.

The refinements are summarized in Table 1. Final atomic parameters are given in Tables 2, 3 and 4, while molecular drawings with labeling of the atoms are shown in Figs. 1(a), 1(b) and 1(c). Selected bond lengths and angles are given in Tables 5 and 6, while distances from mean C-C \equiv C-C planes are listed in Table 7.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and a complete set of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39530 (81 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. $R = \text{CH}_2\text{OH}$: atomic positional parameters ($\times 10^4$) and U_{eq} values ($\times 10^3$)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq} (\AA^2)
Co(1)	8874 (1)	3907 (1)	3114 (1)	34 (1)
Co(2)	6494 (1)	3432 (1)	3838 (1)	33 (1)
O(1)	7583 (3)	4891 (3)	225 (2)	41 (2)
O(3)	5090 (3)	4325 (2)	1266 (2)	50 (2)
O(4)	9524 (3)	1242 (2)	4163 (2)	59 (3)
O(5)	11807 (4)	3781 (4)	4805 (2)	68 (4)
O(6)	10833 (4)	3631 (4)	1669 (2)	91 (4)
O(7)	7854 (4)	6158 (2)	2857 (2)	70 (4)
O(8)	4477 (5)	5418 (5)	3624 (3)	108 (5)
O(9)	3861 (5)	1901 (5)	4043 (3)	80 (5)
O(10)	8581 (4)	3382 (3)	5815 (2)	58 (3)
C(1)	6688 (4)	3184 (2)	2524 (2)	32 (2)
C(2)	7737 (4)	2525 (2)	3127 (2)	35 (2)
C(3)	5445 (4)	3255 (3)	1579 (2)	38 (3)
C(4)	8363 (5)	1410 (5)	3269 (2)	47 (3)
C(5)	10672 (4)	3836 (4)	4153 (3)	48 (3)
C(6)	10056 (5)	3734 (5)	2220 (3)	36 (4)
C(7)	8283 (5)	5307 (3)	2946 (3)	44 (3)
C(8)	5260 (5)	4665 (5)	3710 (3)	57 (4)
C(9)	4870 (5)	2497 (5)	3956 (3)	48 (4)
C(10)	7776 (4)	3402 (3)	5051 (2)	42 (3)

Table 4. $R = \text{CF}_3$: atomic positional parameters ($\times 10^4$) and U_{eq} values ($\times 10^3$)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Molecule (I)	x	y	z	U_{eq} (\AA^2)
Co(11)	6189 (1)	1377 (1)	2729 (1)	13 (1)
Co(21)	6373 (1)	2173 (1)	2591 (1)	15 (1)
F(51)	3746 (4)	2247 (1)	4630 (2)	34 (4)
F(52)	5957 (4)	1846 (1)	5321 (2)	25 (4)
F(53)	3356 (5)	1558 (1)	4681 (2)	38 (5)
F(61)	1596 (4)	2186 (1)	1873 (2)	41 (4)
F(62)	2450 (4)	1772 (1)	690 (2)	33 (4)
F(63)	1402 (4)	1495 (1)	2002 (2)	38 (5)
O(51)	9546 (5)	1213 (1)	4281 (3)	29 (5)
O(61)	7266 (5)	1151 (1)	664 (3)	27 (5)
O(71)	4000 (6)	604 (1)	3024 (3)	37 (5)
O(101)	7267 (6)	2215 (1)	407 (3)	52 (5)
O(81)	9830 (5)	2328 (1)	4084 (3)	29 (5)
O(91)	4567 (5)	3013 (1)	2711 (3)	41 (5)
C(51)	8265 (7)	1266 (1)	3681 (4)	22 (6)
C(61)	6834 (7)	1230 (1)	1461 (4)	18 (6)
C(71)	4865 (7)	896 (1)	2922 (4)	22 (6)
C(101)	6944 (8)	2210 (1)	1261 (4)	33 (7)
C(81)	8524 (8)	2275 (1)	3497 (4)	23 (6)
C(91)	5300 (7)	2697 (1)	2666 (4)	22 (6)
C(11)	5059 (7)	1821 (1)	3447 (4)	17 (6)
C(41)	4527 (7)	1865 (1)	4512 (4)	21 (6)
C(21)	4286 (6)	1800 (1)	2396 (4)	14 (6)
C(31)	2449 (7)	1814 (2)	1751 (4)	25 (7)

Molecule (II)	x	y	z	U_{eq} (\AA^2)
Co(12)	1690 (1)	4098 (1)	1076 (1)	13 (1)
Co(22)	163 (1)	4225 (1)	3616 (1)	13 (1)
F(71)	2987 (4)	5162 (1)	3184 (2)	24 (4)
F(72)	1351 (5)	5246 (1)	1621 (2)	36 (4)
F(73)	209 (4)	5344 (1)	3041 (2)	33 (4)
F(81)	-3157 (4)	4036 (1)	1156 (2)	20 (3)
F(82)	-2123 (4)	4592 (1)	427 (2)	34 (4)
F(83)	-3480 (4)	4677 (1)	1773 (2)	29 (3)
O(52)	435 (5)	3211 (1)	1418 (3)	27 (5)
O(62)	2676 (5)	4446 (1)	95 (3)	33 (5)
O(72)	5319 (5)	3967 (1)	3384 (3)	26 (5)
O(102)	-1283 (5)	3334 (1)	3711 (3)	31 (5)
O(82)	3284 (5)	4266 (1)	5419 (3)	27 (5)
O(92)	-2470 (5)	4760 (1)	4501 (3)	36 (5)
C(52)	954 (7)	3550 (1)	1660 (4)	21 (6)
C(62)	2309 (7)	4303 (1)	829 (4)	17 (6)
C(72)	3950 (7)	4013 (2)	2855 (4)	22 (6)
C(102)	-742 (7)	3675 (2)	3710 (4)	23 (6)
C(82)	2071 (7)	4242 (2)	4747 (4)	24 (6)
C(92)	-1480 (8)	4550 (1)	4189 (4)	17 (6)
C(12)	805 (7)	4633 (1)	2591 (4)	13 (6)
C(42)	1336 (7)	5089 (1)	2609 (4)	21 (6)
C(22)	-588 (7)	4377 (1)	2122 (4)	16 (5)
C(32)	-2338 (7)	4419 (1)	1381 (4)	19 (6)

Discussion

Thorn & Hoffmann (1978) have discussed the bonding scheme in $M_2(\text{CO})_6$ ligand complexes as obtained with extended Hückel type calculations (Fig. 2). In the dicobalt hexacarbonyl acetylene complexes the acetylene π orbitals of a_1 and b_2 symmetry, which are filled in the isolated ligand, are donor orbitals with respect to the metal-ligand interaction, while the originally empty π^* orbitals of a_2 and b_1 symmetry accept electrons from the metal d orbitals. The four acetylene orbitals interact with orbitals of the same symmetry from the 'sawhorse' shaped $\text{Co}_2(\text{CO})_6$ group to give four low-lying orbitals which together with the a_1 σ orbital of $\text{Co}_2(\text{CO})_6$ accommodate the six Co valence electrons and the four acetylene electrons.

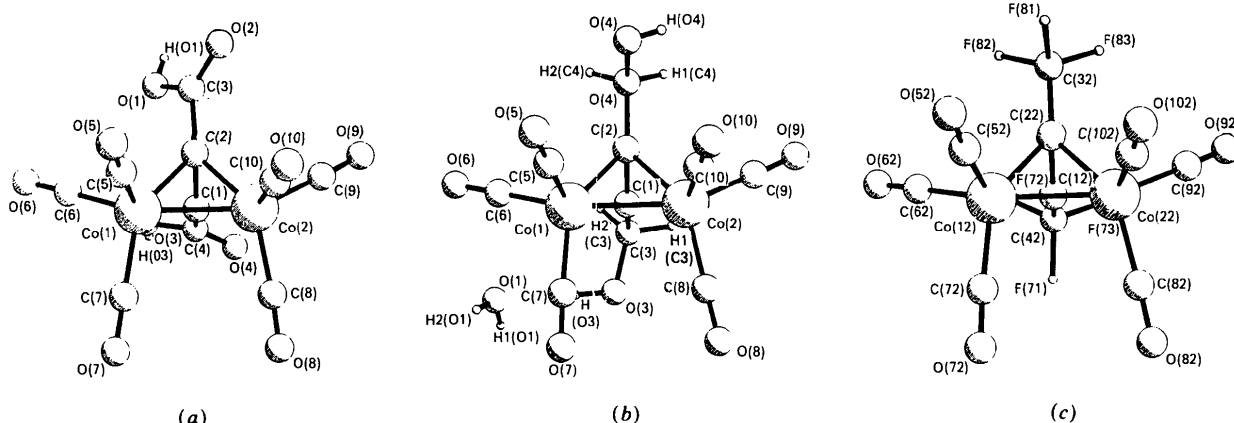


Fig. 1. Molecular drawings indicating labeling of atoms. (a) $R = \text{COOH}$, (b) $R = \text{CH}_2\text{OH}$, (c) $R = \text{CF}_3$, [F(72) and F(73) are hidden].

Table 5. Characteristic bond lengths (Å)

R Temperature	COOH 293 K	CH ₂ OH 293 K	CF ₃ 100 K	C(CH ₃) ₃ * 200 K	C ₆ H ₅ * 293 K	
C(1)-C(4)	1.474 (5)	1.489 (5)	1.483 (7)	1.460 (5)	1.516 (4)	1.471 (13)
C(1)-C(2)	1.350 (5)	1.338 (4)	1.355 (7)	1.360 (7)	1.341 (3)	1.359 (13)
C(2)-C(3)	1.483 (5)	1.489 (4)	1.475 (7)	1.479 (7)	1.515 (5)	1.458 (14)
C(1)-Co(1)	1.946 (4)	1.963 (3)	1.925 (5)	1.935 (5)	1.988 (2)	2.021 (10)
C(1)-Co(2)	1.927 (4)	1.978 (3)	1.930 (5)	1.932 (5)	1.982 (2)	1.948 (5)
C(2)-Co(1)	1.923 (4)	1.962 (3)	1.927 (5)	1.931 (5)	1.991 (2)	1.960 (10)
C(2)-Co(2)	1.931 (3)	1.963 (3)	1.927 (5)	1.934 (5)	1.985 (2)	1.953 (10)
Co(1)-Co(2)	2.471 (1)	2.461 (1)	2.464 (4)	2.472 (2)	2.460 (1)	2.476 (2)

* Gregson & Howard (1983).

Table 6. Comparison of bond angles (°)

R	COOH	CH ₂ OH	CF ₃	C(CH ₃) ₃ *	C ₆ H ₅ *	
C(2)-C(1)-Co(1)	68.7 (2)	70.0 (2)	69.5 (3)	69.2 (3)	70.4 (1)	67.6 (5)
Co(1)-C(1)-Co(2)	79.3 (1)	77.3 (1)	79.4 (2)	79.5 (2)	76.6 (1)	77.2 (3)
C(2)-C(1)-Co(2)	69.7 (2)	69.6 (2)	69.3 (3)	69.5 (3)	70.4 (1)	69.8 (5)
C(1)-C(2)-Co(2)	69.4 (2)	70.1 (2)	69.6 (3)	69.3 (3)	70.1 (1)	69.4 (5)
Co(1)-C(2)-Co(2)	79.7 (1)	77.7 (1)	79.5 (2)	79.5 (2)	76.4 (1)	78.5 (4)
C(1)-C(2)-Co(1)	70.5 (2)	70.8 (2)	69.4 (3)	69.6 (3)	70.1 (1)	72.5 (5)
C(1)-Co(1)-Co(2)	50.0 (1)	51.6 (1)	50.4 (2)	50.2 (2)	51.6 (1)	50.1 (2)
C(1)-Co(1)-C(2)	40.8 (2)	39.9 (1)	41.2 (2)	41.2 (2)	39.4 (1)	39.9 (4)
C(2)-Co(1)-Co(2)	50.3 (1)	51.2 (1)	50.3 (2)	50.3 (2)	51.6 (1)	50.6 (3)
C(2)-Co(2)-Co(1)	50.0 (1)	51.1 (1)	50.3 (2)	50.2 (2)	51.9 (1)	50.8 (3)
C(2)-Co(2)-C(1)	41.0 (2)	39.7 (1)	41.1 (2)	41.2 (2)	39.5 (1)	40.8 (4)
Co(1)-Co(2)-C(1)	50.7 (1)	51.1 (1)	50.2 (2)	50.3 (2)	51.8 (1)	52.7 (2)
C(4)-C(1)-C(2)	136.9 (3)	143.9 (3)	139.5 (4)	138.8 (4)	144.0 (2)	140.4 (8)
C(1)-C(2)-C(3)	135.6 (3)	143.9 (3)	137.4 (4)	139.0 (4)	144.5 (2)	140.0 (9)
θ†	30.05	30.60	29.95	29.53	32.48	29.40

* Gregson & Howard (1983).

† As defined by Thorn & Hoffmann (1978); angle between Co-Co and local threefold axis through Co relating the three carbonyl groups.

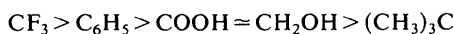
Table 7. Distance (Å) from mean plane through C-C≡C-C groups

R	COOH	CH ₂ OH	CF ₃
C(1)*	-0.002 (3)	-0.002 (3)	-0.002 (5)
C(2)*	0.002 (3)	0.002 (3)	0.001 (5)
C(3)*	-0.001 (3)	0.001 (3)	0.002 (5)
C(4)*	0.001 (3)	-0.002 (4)	-0.001 (5)
Co(1)	-1.286 (2)	-1.203 (1)	-1.236 (1)
Co(2)	1.183 (2)	1.258 (1)	1.236 (1)
O(5)	-1.673 (4)	-1.695 (3)	-1.819 (4)
O(6)	-2.607 (5)	-2.769 (4)	-3.688 (4)
O(7)	-1.907 (5)	-1.919 (4)	-1.821 (4)
O(8)	1.534 (5)	1.335 (4)	1.516 (3)
O(9)	3.688 (4)	3.809 (3)	3.718 (4)
O(10)	1.456 (4)	1.597 (3)	-1.574 (4)

* Atoms included in the calculation of the mean plane.

Introduction of electronegative substituents on the acetylene will lead to electron withdrawal and therefore stabilization of both π and π^* orbitals. The relative position of the acetylene and 'sawhorse' orbitals indicates that this stabilization will increase π^* back donation, but reduce the donating interaction between the π and the metal σ orbitals.

According to tables given by Huheey (1965, 1978), the sequence of electronegativities for the substituents studied here is



with (approximate) numerical values of 3.46, 3.00, 2.85, 2.74 and 2.29 respectively. With the exception of the $R = \text{C}_6\text{H}_5$ complex, the average length of the Co-C_{acetylene} distance mimics this trend rather closely

(Table 5, Fig. 3), thus confirming the dominant effect of the increase in back donation to the ligand over any decrease in ligand to metal donation. (For $R = \text{C}_6\text{H}_5$ one of the four Co-C_{acetylene} distances is much longer than the other three.)

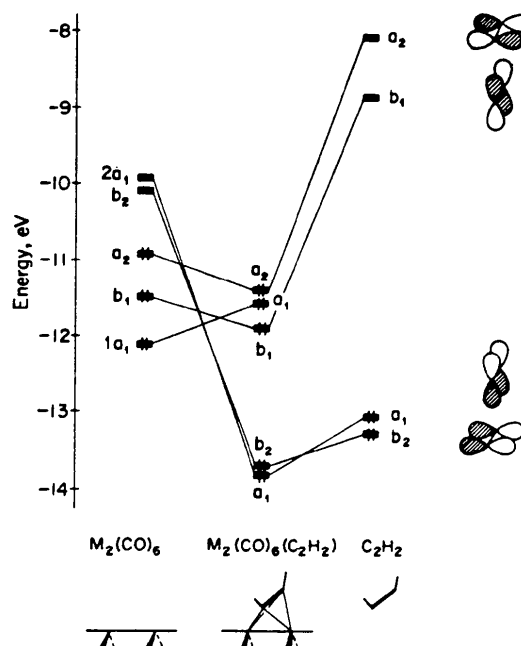


Fig. 2. Orbital interaction diagram for $M_2(\text{CO})_6(\text{acetylene})$ according to Thorn & Hoffmann (1978). Orbital occupation of $M = \text{Co}$ is indicated. (1 eV = 1.6×10^{-19} J.)

This interpretation is confirmed by the lengthening of the acetylenic C-C bond which accompanies the shortening of $\langle\text{Co}-\text{C}_{\text{ac}}\rangle$ (Fig. 3). The exception is again the phenyl complex in which C-C appears longer than in the other compounds, perhaps as a result of partial conjugation with the phenyl π electrons. The C-C bond length correlates equally well with the distortion of the acetylene ligand from linearity (Fig. 4), an effect not evident in a number of structures surveyed by Ittel & Ibers (1976). The distortion is more severe the stronger the π^* back donation, as may be expected.

Correlation with $\text{C}\equiv\text{C}$ bond length is somewhat hampered by the fact that the distance in the uncomplexed ligands is mostly unavailable, so the change in bond length upon complex formation is not known.

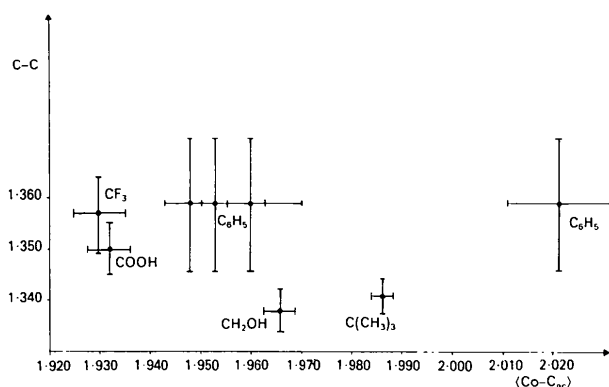


Fig. 3. Relation between acetylenic C-C bond length (Å) and average $\text{Co}-\text{C}_{\text{acetylene}}$ distance (Å). For $R = \text{C}_6\text{H}_5$ individual values are plotted. Bars indicate experimental standard deviations.

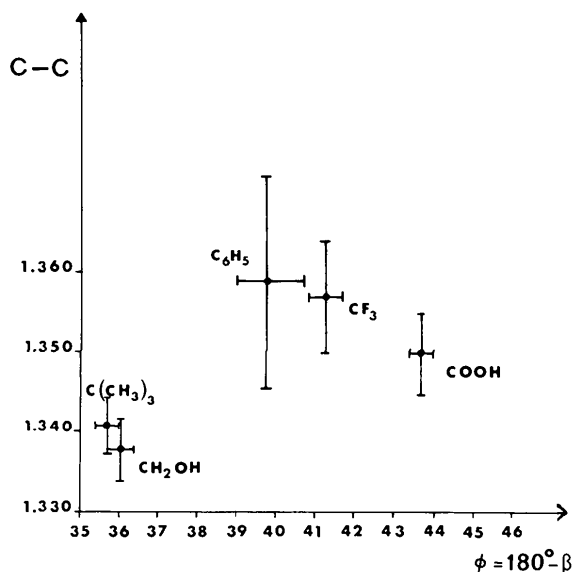


Fig. 4. Relation between acetylenic C-C bond length (Å) and deviation from linearity ($^\circ$) of the acetylene ligand. β is the average $\text{C}\equiv\text{C}-\text{C}$ angle. Bars indicate experimental standard deviations.

An alternative comparison is between the average $\langle\text{Co}-\text{C}_{\text{ac}}\rangle$ distance and the ligand angular distortion $180-\beta$ for which this ambiguity does not occur. Excluding the complex with $R = \text{C}_6\text{H}_5$, the range of these two variables is $\approx 0.06 \text{ \AA}$ and $\approx 8^\circ$, respectively, which far exceeds the experimental standard deviations (see Fig. 5). The complexes with more electronegative substituents ($R = \text{CF}_3$, $R = \text{COOH}$) have $\langle\text{Co}-\text{C}_{\text{ac}}\rangle = 1.93 \text{ \AA}$, and $180-\beta = 36^\circ$, while for the other two compounds [$R = \text{CH}_2\text{OH}$, $R = \text{C}(\text{CH}_3)_3$] the values are $1.97-1.99 \text{ \AA}$, and $41-44^\circ$ respectively. This indicates a clear and unambiguous correlation between metal-ligand distance and ligand distortion.

Thorn & Hoffmann (1978) have defined the distortion of the $\text{Co}_2(\text{CO})_6$ group from threefold symmetry in terms of θ , the angle between the pseudo-threefold axis of the $\text{Co}(\text{CO})_3$ group and the $\text{Co}-\text{Co}$ bond. A decrease in this angle from the 'linear spine' value of 58.3° is believed to reduce repulsion between the a_1 σ orbital of $\text{Co}_2(\text{CO})_6$ and the acetylene a_1 orbital. For a given value of θ we expect this repulsion to be larger for the more electron-withdrawing acetylene complex, which has a larger acetylene a_1 population because of reduced σ donation. Experimental values of θ , listed in Table 6, are indeed smallest for the more electronegative and largest for the least electronegative substituent [*i.e.* 29.95° , 29.53° for $R = \text{CF}_3$; 32.48° for $\text{C}(\text{CH}_3)_3$], and thus in agreement with the theoretical interpretation.

Finally we note that the $\text{Co}-\text{Co}$ distances vary only between $2.476(2)$ and $2.460(1) \text{ \AA}$. They are shorter than those observed in $\text{Co}_2(\text{CO})_8$ [$2.530(1)$ and $2.528(1) \text{ \AA}$] (Leung & Coppens, 1983).

The above thus shows a correlation between ligand distortion parameters, metal-ligand distance and electron-withdrawing power of the substituent, which can be interpreted in terms of existing bonding schemes. The extent to which these changes are accompanied by measurable shifts in the electron density distribution of the complexes will be the subject of further studies.

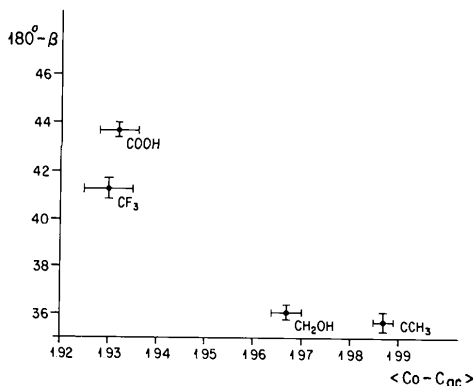


Fig. 5. Relation between average $\text{Co}-\text{C}_{\text{acetylene}}$ distance (Å) and deviation from linearity ($^\circ$) of the acetylene ligand. Bars indicate experimental standard deviations.

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References

- BOSTON, J. L., SHARP, D. W. A. & WILKINSON, G. (1962). *J. Chem. Soc.* pp. 3488-3494.
 CETINI, G., GAMBINO, O., ROSSETTI, R. & SAPPA, E. (1967). *J. Organomet. Chem.* pp. 149-154.
 COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035-1038.

- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 390-397.
 GREGSON, D. & HOWARD, J. (1983). *Acta Cryst.* **C39**, 1024-1027.
 HUHEEY, J. E. (1965). *J. Phys. Chem.* **69**, 3284-3291.
 HUHEEY, J. E. (1978). *Principles of Structure and Reactivity*, pp. 563-671. New York: Harper International Edition.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 ITTEL, J. E. & IBERS, J. A. (1976). *Adv. Organomet. Chem.* **14**, 33-35.
 LEUNG, P. C. W. (1983). Thesis, State Univ. of New York at Buffalo.
 LEUNG, P. C. W. & COPPENS, P. (1983). *Acta Cryst.* **B39**, 535-542.
 STERNBERG, H. W., GREENFIELD, H., FRIEDEL, R. A., WOTIZ, J., MARKBY, R. & WENDER, I. (1954). *J. Am. Chem. Soc.* **76**, 1457-1458.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
 THORN, D. L. & HOFFMANN, R. (1978). *Inorg. Chem.* **17**, 126-140.

Acta Cryst. (1984). **B40**, 595-606

Effect of Crystal Packing on Linkage Isomerism in the [Pd(1,1,7,7-tetraethyldiethylenetriamine)(thiocyanato)]⁺ Cation: Structures of the Hexafluorophosphate Salt and of Four Crystal Forms of the Tetraphenylborate Salt

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Abstract

The influence of the counterion and crystal environment on the bonding mode of the ambidentate thiocyanate ion in the [Pd(Et₄dien)CNS]⁺ cation (where Et₄dien is the 1,1,7,7-tetraethyldiethylenetriamine moiety, Et₂NCH₂CH₂NHCH₂CH₂NEt₂) has been investigated. It had been reported previously that the thiocyanate is N-bonded in the PF₆⁻ salt but that it undergoes an N- to S-bonded isomerization in the BPh₄⁻ salt. In crystals of the PF₆⁻ salt {[Pd(NCS)(C₁₂H₂₉N₃)]PF₆, *M_r* = 524.8, orthorhombic, *P*2₁2₁2₁, *a* = 11.824 (3), *b* = 11.838 (2), *c* = 15.626 (3) Å, *T* = 296 K, *Z* = 4, *V* = 2187.2 Å³, *D_x* = 1.594 g cm⁻³, *μ* = 10.34 cm⁻¹, Mo *Kα*, λ = 0.71069 Å, *F*(000) = 1060.10, 2500 observations with *I* > 3σ(*I*), 300 variables, final *R* index on *F_o* of 0.033} the thiocyanate is N-bonded as expected. It is, however, also N-bonded in two stable crystal forms of the BPh₄⁻ salt {acetone solvate: [Pd(NCS)(C₁₂H₂₉N₃)]·[B(C₆H₅)₄]·C₃H₆O, *M_r* = 757.2, monoclinic, *P*2₁/*c*, *a* = 11.927 (2), *b* = 19.250 (3), *c* = 17.252 (3) Å, β = 100.33 (2)°, *T* = 143 K, *Z* = 4, *V* = 3896.8 Å³, *D_x* = 1.291 g cm⁻³, *μ* (Mo *Kα*) = 5.54 cm⁻¹, *F*(000) =

1587.74, 5221 observations with *I* > 3σ(*I*), 265 variables, final *R* on *F_o* of 0.044} {unsolvated: [Pd(NCS)(C₁₂H₂₉N₃)]·[B(C₆H₅)₄], *M_r* = 699.1, orthorhombic, *P*2₁2₁2₁, *a* = 9.566 (2), *b* = 14.745 (5), *c* = 24.419 (7) Å, *T* = 150 K, *Z* = 4, *V* = 3444.3 Å³, *D_x* = 1.348 g cm⁻³, *μ* (Mo *Kα*) = 6.19 cm⁻¹, *F*(000) = 1459.74, 5144 observations with *I* > 3σ(*I*), 229 variables, final *R* on *F_o* of 0.045}. A third crystal form {CH₂BrCl solvate: [Pd(NCS)(C₁₂H₂₉N₃)]·[B(C₆H₅)₄]·CH₂BrCl, *M_r* = 828.5, monoclinic, *P*2₁/*n*, *a* = 11.058 (3), *b* = 20.833 (10), *c* = 16.955 (5) Å, β = 100.72 (3)°, *T* = 150 K, *Z* = 4, *V* = 3837.8 Å³, *D_x* = 1.434 g cm⁻³, *μ* (Mo *Kα*) = 16.62 cm⁻¹, *F*(000) = 1698.83, 4940 observations with *I* > 3σ(*I*), 256 variables, final *R* on *F_o* of 0.045} loses solvent but does not isomerize. A fourth crystal form of the BPh₄⁻ salt is S-bonded but unstable {CH₃OH solvate: [Pd(SCN)(C₁₂H₂₉N₃)]·[B(C₆H₅)₄]·CH₃O, *M_r* = 731.1, monoclinic, *P*2₁/*n* or *P*2₁, *a* = 12.748 (5), *b* = 9.929 (3), *c* = 29.112 (18) Å, β = 97.39 (6)°, *T* = 137 K, *Z* = 4, *V* = 3654.2 Å³, *D_x* = 1.329 g cm⁻³, *μ* (Mo *Kα*) = 5.88 cm⁻¹, *F*(000) = 1531.74, 1346 observations with *I* > 3σ(*I*), 174 variables, final *R* on *F_o* of 0.050}. In this last crystal form the N end of the S-bonded ligand is hydrogen-bonded to the incorporated solvent. Other crystal forms were discovered but not investigated in detail. Some packing

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