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THE CRYSTAL STRUCTURE OF TRIMETHYLENEMETHANECHROMIUM TRICARBONYLTRIPHENYLPHOSPHINE

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Summary

The crystal structure of trimethylenemethanechromium tricarbonyltriphenylphosphine has been determined by conventional Patterson and Fourier methods. The structural results of a full matrix least squares refinement (R_1 = 0.083, R_2 = 0.089) and those of a block-diagonal least squares refinement (R_1 = 0.088, R_2 = 0.087) are not significantly different by Cruickshank's test. The compound crystallizes in the monoclinic space group $C2/c$ with 16 molecules in a unit cell of dimensions a = 36.955(3), b = 10.789(1), c = 22.799(3) Å, β = 100.80(1)°. The experimental and calculated densities are 1.36 g/cm^3 and 1.35 g/cm^3, respectively.

Carbon—carbon bond distances within the trimethylenemethane ligand, as well as metal—ligand π-bonding distances, are equivalent with a mean value of 1.42(1) Å for the former and 2.23(1) Å for the latter. The trimethylenemethane moiety is quite non-planar with the central atom displaced 0.28 Å from the plane of the other three carbon atoms. The structure is compared to several previously-reported iron complexes which have trimethylenemethane type ligands.

The Cr—CO bond *trans* to the triphenylphosphine is short [mean = 1.83(1) Å] compared with the other two [mean = 1.86(1), 1.87(1) Å] in the structure. This is discussed in terms of a *trans* influence. The effects of the σ and π donor or acceptor properties of various ligands upon the metal—CO bond lengths and C—O stretching frequencies in numerous metal complexes are discussed.

Introduction

A subject of widespread interest in chemical research has been the isolation of heretofore unstable, unsaturated species via complexation with heavy metals. Emerson et al. [1] have reported the synthesis of trimethylenemethaneiron tri-

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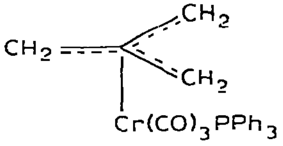
carbonyl. Derivatives of this complex have also been reported by Ehrlich and Emerson [2]. A gas-phase electron diffraction study of trimethylenemethaneiron tricarbonyl was carried out by Almenningen et al. [3]. X-ray studies of substituted trimethylenemethane ligands complexed to iron tricarbonyl have been reported by Churchill and Gold [4], Nesmeyanov et al. [5], Yasuda et al. [6] and Churchill and DeBoer [7].

Ward and Pettit [8] have reported the preparation of trimethylenemethane complexes of iron, molybdenum and chromium (I). We report here the first X-ray determination of an unsubstituted trimethylenemethane complexed to a metal and the first complex of this type which contains a metal other than iron.



(I)

Experimental

All X-ray studies were carried out using a General Electric XRD-5 diffractometer equipped with a single crystal orienter, with Cu-K_α radiation and at ambient room temperature (~ 21°C). Yellow-green crystals of $(CH_2)_3CCr(CO)_3$-$P(C_6H_5)_3$, obtained from 30% ether/Skelly B, were kindly supplied by Ward and Pettit. The crystal used for data collection, a hexagonal prism 0.54 mm long with parallel faces 0.16 mm apart, was mounted with the long direction parallel to the φ axis. Measurement of ω scans (5° take-off angle, 0.05° receiving slit) for several reflections showed the peaks to be single, symmetrical and narrow ($<$ 0.4° in width). Thus the crystal was judged to be of sufficient quality for stationary crystal—stationary counter collection of intensity data (5° take-off angle, 1° receiving slit).

Unit cell parameters, determined by a least squares refinement of 28 independent 2θ measurements with K_{α_1} (1.54050 Å) and K_{α_2} (1.54433 Å) well resolved, are as follows: a = 36.955(3), b = 10.789(1), c = 22.799(3) Å, β = 100.80(1)°. The unit cell volume is 8928.8 Å^3. The observed density (1.36 g/cm^3 measured by flotation in aqueous $ZnCl_2$) agrees well with the calculated density (1.35 g/cm^3, based on mol. wt. of 452.4 and Z = 16).

Systematic absences, shown by plots of the intensity weighted reciprocal lattice, were *hkl* for $h + k$ odd, *h0l* for *l* odd and *0k0* for *k* odd. These absences are consistent with the space groups *C2/c* (No. 15) and *Cc* (No. 9). Three dimensional single-crystal intensity data were collected to the limit 2θ = 120°, using a balanced nickel—cobalt filter pair. Of the 6629 independent reflections measured, 4731 [those with $I_{net} \geqslant 8$ counts and $I_{net} \geqslant 2\sigma(I_{net})$] were utilized in the solution and refinement of the structure. A correction for absorption (μ = 52.2 cm^{-1}) as a function of crystal shape was applied [9]; correction factors ranged from 1.81 to 3.58.

At frequent intervals (every 150-175 reflections) throughout the data collection, the crystal was aligned under fine conditions (1° take-off angle, 0.05° slit) and the intensities of six standard reflections were monitored. On this basis it was determined that the crystal had suffered neither serious radiation damage nor misalignment during data collection. An analysis of the standard reflections was carried out according to the following scheme: the intensity, y_j, of each standard, j, was plotted versus X-ray exposure hours, x_j, and the best straight line (defined by $y = a_j + b_j x$) through these points was extrapolated to zero exposure time, yielding an I_{0j} value for this standard. Each point in this plot was divided by the I_{0j} value, giving a set of normalized y_i values for this standard, j. This procedure was followed for each of six different standard reflections. A weighted ($w_j = 1/\sigma^2 (I_{0j})$) average of the six normalized values was computed for each value of exposure hours. The best linear correction factor (defined by $K = 1 + dx$) was determined through these averaged points. The total fall in this composite curve was less than 5% (± 2.5% of the intensity at the midpoint of data collection) with only one composite point out of 57 deviating more than 3σ from the best straight line through these points. Therefore, no decay correction was made.

Lorentz and polarization corrections were applied, as well as a correction for α_1—α_2 splitting [10]. Standard deviations in the observed structure factor amplitudes, σ ($|F_o|$), based on counting statistics, were calculated according to Evans [11].

The space group $C2/c$ was assumed in the solution of the Patterson map because a populated plane at v = 0 and a populated line at u = 0, w = $\frac{1}{2}$ could be interpreted as the Harker section and Harker line in $C2/c$ and because the density required 16 molecules per unit cell which called for an unlikely four molecules per asymmetric unit in the space group Cc. This assumption proved well-founded when the coordinates for two chromium and two phosphorus atoms were determined from the Patterson map. These four positions were used to phase a heavy atom map which showed the positions of all remaining non-hydrogen atoms.

The structure was refined anisotropically by block-diagonal least squares methods (single atom blocks, 9 × 9 anisotropic) to a final R_1 value of 0.088 (R_2 = 0.087). Trimethylenemethane hydrogens and phenyl carbons were refined isotropically. At the insistence of two referees a full matrix refinement was carried out at an additional cost of over $700 in computer funds. This resulted in an R_1 value of 0.083 and an R_2 value of 0.089. With the exception of the phenyl rings, which were treated as rigid bodies, only one bond distance average (Cr—C6; Δ/σ = 1.76) and one bond angle average (C6—C4—Cr; Δ/σ = 1.70) changed to a possibly significant degree, judged by the Cruickshank test [12]. All other changes in the average values of bond distances and bond angles are not significant by this test. This virtual identity of structural results obtained by the block-diagonal and by the full matrix least squares treatments is consistent with our experience for numerous other structures. The difference in R_1 values for the two refinements may be due to the fact that 30 phenyl hydrogens were not included in the block-diagonal refinement but were part of the rigid bodies in the full matrix treatment. In addition, a variable extinction parameter [13, 14] (extinction coefficient = 1.9×10^{-7}) was used in the second refinement. Final difference Fourier syntheses at the end of each refinement showed one large peak on the 2-fold axis (1.0 $e^-/\text{Å}^3$ for block-diagonal and 1.3 $e^-/\text{Å}^3$ for full matrix). All other regions of residual electron density were less than $\approx 0.6 e^-/\text{Å}^3$.

TABLE 1a

FINAL POSITIONAL ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^4$) OF THE NON-HYDROGEN ATOMS FROM THE FULL MATRIX REFINEMENT

Estimated standard deviations are in parentheses. The temperature factor expression was $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
CrA	4243(1)	1279(2)	3297(1)	6(1)	71(2)	18(1)	−3(1)	0(1)	−6(1)
CrB	1915(1)	1154(2)	3224(1)	7(1)	57(2)	15(1)	1(1)	1(1)	3(1)
PA	4556(1)	2729(2)	4024(1)	4(1)	57(3)	17(1)	−1(1)	0(1)	−1(1)
PB	2164(1)	−0366(2)	3955(1)	4(1)	48(3)	13(1)	−1(1)	0(1)	1(1)
CA1	4385(3)	0227(11)	3940(5)	7(1)	76(14)	28(3)	−4(3)	−3(2)	−7(5)
CB1	2013(3)	2172(10)	3903(5)	9(1)	65(13)	22(3)	−1(3)	1(1)	3(5)
CA2	3848(3)	0257(11)	3167(5)	10(1)	111(16)	24(3)	−11(4)	0(2)	−5(6)
CB2	1406(3)	2118(10)	3120(5)	10(1)	69(13)	25(3)	2(3)	1(2)	−7(5)
CA3	3854(3)	2380(11)	3273(5)	6(1)	117(16)	22(3)	1(3)	−1(1)	−12(6)
CB3	1531(3)	−0024(10)	3085(5)	8(1)	83(14)	21(3)	6(3)	0(1)	13(5)
CA4	4509(3)	1032(13)	2604(5)	8(1)	145(18)	21(3)	−9(4)	5(2)	−28(6)
CB4	2219(4)	1530(12)	2593(5)	12(1)	81(15)	22(3)	2(4)	7(2)	9(5)
CA5	4715(4)	0236(13)	3042(6)	10(1)	140(18)	23(3)	14(4)	3(2)	2(7)
CB5	2407(4)	2231(14)	3083(6)	13(2)	127(19)	30(4)	−8(5)	7(2)	3(7)
CA6	4148(4)	0571(13)	2373(6)	15(2)	136(19)	29(4)	−9(5)	6(2)	−17(7)
CB6	1874(5)	2019(14)	2332(7)	16(2)	135(23)	30(4)	15(5)	5(2)	19(8)
CA7	4526(4)	2336(14)	2664(6)	12(2)	102(19)	22(4)	−2(4)	5(2)	6(6)
CB7	2250(3)	0240(13)	2629(6)	12(1)	116(17)	26(4)	−1(4)	5(2)	1(6)
OA1	4468(2)	−0459(7)	4323(4)	13(1)	90(10)	31(2)	0(2)	−1(1)	12(4)
OB1	2067(2)	2820(7)	4289(3)	17(1)	79(10)	27(2)	−4(3)	1(1)	−17(4)
OA2	3589(2)	−0367(8)	3103(4)	12(1)	164(13)	36(3)	−25(3)	−2(1)	3(5)
OB2	1236(2)	2703(8)	3063(4)	10(1)	103(11)	47(3)	13(3)	0(1)	−4(5)
OA3	3599(2)	2986(8)	3266(4)	9(1)	163(13)	36(3)	13(3)	−1(1)	−19(5)
OB3	1292(2)	−0693(7)	3002(4)	8(1)	111(11)	34(2)	−9(2)	−3(1)	0(4)

The atomic scattering factors used in both refinements were those of Stewart, Davidson and Simpson [15] for hydrogen and those of Cromer and Waber [16] for carbon, oxygen, phosphorus and chromium. The real parts of the anomalous dispersion corrections for phosphorus and chromium were included [17].

Calculations were carried out on a Control Data 6600/6400 computer system. Structure factor and block-diagonal least squares calculations were carried out utilizing a local modification of the Sparks and Trueblood program (modified by Kartha) [18]. Ibers' modification of the Busing, Martin and Levy [19] program was used in the full matrix refinement. All Fourier calculations were performed using a program by Rao [20]. Various other data processing programs of local origin were also used *.

Discussion

Final positional and anisotropic thermal parameters from the full matrix refinement are shown in Table 1a for non-hydrogen, non-group atoms. Positional and isotropic temperature factors are given in Table 1b for the six rigid phenyl rings and Table 1c for the trimethylenemethane hydrogens. Because two molecules per asymmetric unit were present (related such that $x_A \simeq \frac{1}{4} + x_B$, $y_A \simeq \frac{1}{4} - y_B$, $z_A \simeq z_B$), it was possible to obtain two determinations of all distances and angles. Values shown in Fig. 1 and cited in this discussion are in all cases the averages for the two molecules. All values tabulated and discussed are those resulting from the full matrix refinement. Individual bond distances and bond angles for molecules A and B appear in Tables 2 and 3. The geometry of the molecule is shown by the stereoscopic drawings [21] in Figs. 2a and 2b. Selected intramolecular non-bonded contacts are shown in Table 4. No intermolecular non-bonded contacts less than the sum of the van der Waals radii occur.

The π-bonded chromium atom is positioned directly beneath C4 [2.03(1)Å] of the trimethylenemethane ligand and is approximately equidistant from C5, C6 and C7 [2.24(1), 2.21(1) and 2.24(1) Å, respectively]. The average carbon—carbon bond distances in the trimethylenemethane structure are equivalent within one standard deviation with a mean distance of 1.42(1) Å for all such bonds. Thus, no tendency toward bond localization is seen.

The trimethylenemethane moiety is quite non-planar with the central atom (C4) displaced 0.28 Å from the plane through C5, C6 and C7 (in a direction away from the Cr atom). This was also found to be the case with phenyltrimethylenemethaneiron tricarbonyl [4], in which the corresponding displacement was 0.32 Å. This effect is reflected by the acute $C_{term.}$—$C_{cent.}$—M bond angles for the two compounds. A significant difference between the two structures is discernible in the relative orientations of the ligands about the central metal atom. The staggered configuration of the trimethylenemethane ligand and the metal carbonyls adopted in the iron compounds is impossible in the chromium

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* The table of structure factors has been deposited as NAPS Document No. 02472, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1b

FINAL POSITIONAL PARAMETERS (X 10^4) AND TEMPERATURE FACTORS FOR RIGID GROUP ATOMS (FULL MATRIX REFINEMENT)

Molecule A	*x*	*y*	*z*	*B*
C8	5055(1)	2812(7)	4081(3)	3.5
C9	5225(2)	3894(6)	3941(3)	4.5
C10	5601(2)	3897(6)	3934(3)	6.1
C11	5807(1)	2818(7)	4067(3)	5.2
C12	5636(2)	1736(6)	4208(3)	5.4
C13	5261(2)	1733(6)	4214(3)	4.3
H9	5078(3)	4670(7)	3845(4)	3.4
H10	5724(3)	4675(7)	3833(4)	7.6
H11	6077(1)	2820(11)	4063(4)	8.0
H12	5784(3)	0960(7)	4303(4)	5.6
H13	5138(3)	0955(7)	4315(4)	3.4
Molecule B				
C8	2668(1)	−0412(7)	4160(3)	3.7
C9	2866(2)	−1490(6)	4105(3)	3.9
C10	3249(2)	−1483(6)	4254(3)	5.2
C11	3434(1)	−0397(7)	4460(3)	5.0
C12	3236(2)	0681(6)	4515(3)	4.7
C13	2853(2)	0673(6)	4365(3)	4.6
H9	2733(3)	−2270(7)	3957(4)	2.9
H10	3391(3)	−2257(7)	4214(4)	6.3
H11	3709(1)	−0392(10)	4567(4)	9.7
H12	3370(3)	1460(7)	4662(4)	6.9
H13	2711(3)	1448(7)	4405(4)	5.3
Molecule A				
C14	4507(2)	2436(6)	4798(2)	3.4
C15	4805(1)	2487(6)	5274(3)	5.2
C16	4750(2)	2297(6)	5855(3)	6.3
C17	4398(2)	2057(7)	5959(2)	6.1
C18	4100(2)	2006(6)	5484(3)	5.8
C19	4155(2)	2196(6)	4903(3)	4.4
H15	5058(2)	2660(10)	5198(5)	6.9
H16	4964(2)	2334(10)	6196(3)	10.3
H17	4358(3)	1921(10)	6377(3)	9.3
H18	3847(2)	1833(10)	5559(5)	5.9
H19	3941(2)	2159(10)	4561(3)	8.7
Molecule B				
C14	2024(2)	−0148(6)	4672(2)	2.9
C15	2274(1)	−0226(6)	5210(3)	3.8
C16	2156(2)	−0041(6)	5748(2)	4.9
C17	1787(2)	0222(7)	5747(2)	5.7
C18	1537(1)	0300(6)	5209(3)	5.9
C19	1655(2)	0115(6)	4672(2)	4.2
H15	2539(1)	−0415(9)	5210(5)	5.1
H16	2336(2)	−0097(10)	6134(3)	7.4
H17	1702(3)	0355(10)	6134(3)	5.2
H18	1272(2)	0489(10)	5209(5)	7.7
H19	1475(2)	0171(9)	4285(3)	3.5
Molecule A				
C20	4415(2)	4357(5)	3931(3)	3.4
C21	4396(2)	5095(7)	4425(2)	4.4
C22	4271(2)	6312(6)	4345(3)	5.9
C23	4164(2)	6789(5)	3771(4)	5.6

(continued)

TABLE 1b (continued)

Molecule A	*x*	*y*	*z*	*B*
C24	4183(2)	6051(7)	3277(2)	7.2
C25	4308(2)	4835(7)	3357(3)	6.7
H21	4473(3)	4752(10)	4837(3)	6.0
H22	4257(3)	6842(9)	4700(4)	8.8
H23	4074(3)	7663(6)	3714(5)	8.4
H24	4106(3)	6394(10)	2865(3)	9.3
H25	4322(3)	4304(9)	3002(4)	6.5
Molecule B				
C20	2035(2)	−1996(5)	3784(3)	2.7
C21	1897(2)	−2738(6)	4190(2)	3.7
C22	1785(2)	−3947(6)	4036(3)	4.4
C23	1812(2)	−4413(5)	3477(3)	4.9
C24	1951(2)	−3671(7)	3071(2)	4.6
C25	2062(2)	−2463(6)	3225(3)	4.2
H21	1877(3)	−2403(9)	4592(3)	3.1
H22	1686(2)	−4480(8)	4328(4)	7.0
H23	1732(3)	−5282(5)	3367(5)	7.6
H24	1970(3)	−4007(9)	2670(3)	5.5
H25	2162(2)	−1930(9)	2933(4)	5.2

structure which possesses a triphenylphosphine in addition to three carbonyls. As is seen in Fig. 2b, C5 and C6 lie approximately over carbonyls 1 and 2 respectively, while C7 lies approximately midway between the phosphorus atom and the third carbonyl.

The geometry of the five ligands about the central metal is approximately square pyramidal with the trimethylenemethane ligand in the apical position. The four atoms P, C1, C2, C3 are all within 0.12 and 0.04 Å of the basal planes

(continued on p. 399)

TABLE 1c

FINAL POSITIONAL PARAMETERS ($\times 10^3$) FOR TRIMETHYLENEMETHANE HYDROGEN ATOMS (FULL MATRIX REFINEMENT)

The temperature factors were fixed at 5.0.

	x	*y*	*z*
Molecule A			
H5A	479(2)	−078(8)	297(4)
H5B	496(2)	071(8)	316(4)
H6A	408(3)	126(9)	208(4)
H6B	415(3)	−042(8)	229(4)
H7A	482(2)	299(7)	265(3)
H7B	444(3)	278(10)	247(4)
Molecule B			
H5A	232(3)	317(9)	322(4)
H5B	261(2)	176(8)	340(4)
H6A	174(3)	147(10)	204(4)
H6B	178(3)	273(9)	231(4)
H7A	246(2)	−027(8)	296(4)
H7B	206(2)	−016(8)	240(4)

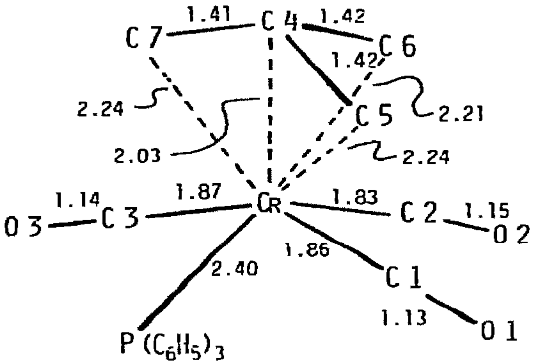


Fig. 1. Numbering scheme of the molecule with average bond distances shown (full matrix refinement).

TABLE 2

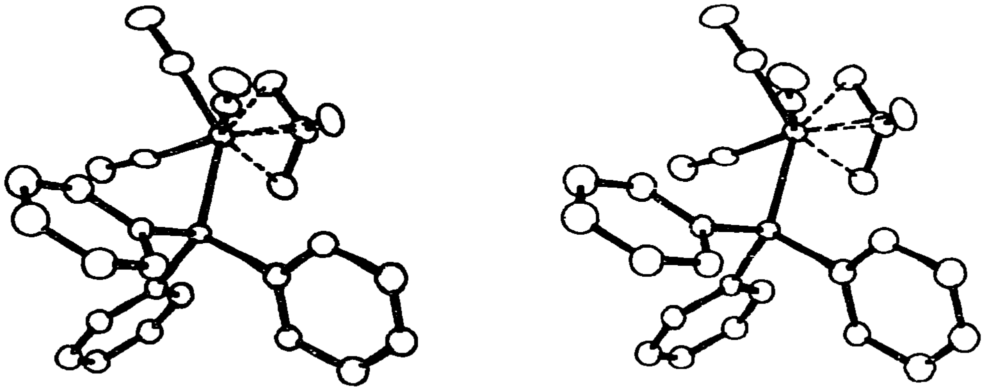
BOND DISTANCES (FULL MATRIX REFINEMENT)

	Molecule A	Molecule B
Cr—P	2.410(3) Å	2.395(3) Å
Cr—C4	2.030(12)	2.028(12)
Cr—C5	2.242(13)	2.234(14)
Cr—C6	2.207(14)	2.218(15)
Cr—C7	2.247(14)	2.231(13)
C4—C5	1.424(18)	1.418(19)
C4—C6	1.429(19)	1.405(21)
C4—C7	1.414(20)	1.398(19)
Cr—C1	1.851(12)	1.876(11)
Cr—C2	1.811(12)	1.843(12)
Cr—C3	1.860(11)	1.888(11)
C1—O1	1.141(14)	1.114(13)
C2—O2	1.156(15)	1.136(14)
C3—O3	1.145(14)	1.129(13)
P—C8	1.828(5)	1.836(5)
P—C14	1.837(6)	1.822(6)
P—C20	1.832(6)	1.843(5)

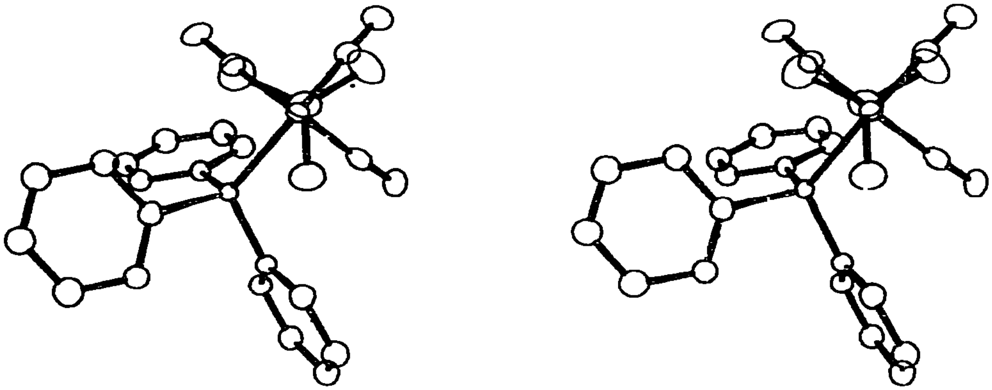
TABLE 3

BOND ANGLES (FULL MATRIX REFINEMENT)

	Molecule A	Molecule B		Molecule A	Molecule B
C5—C4—C6	112.7(12)°	113.9(12)°	C3—Cr—C7	96.3(5)°	95.0(5)°
C5—C4—C7	121.5(11)	117.5(11)	P—Cr—C7	83.8(4)	86.3(3)
C6—C4—C7	113.9(12)	117.1(12)	P—Cr—C5	102.1(3)	103.9(4)
C5—C4—Cr	78.8(7)	78.6(8)	C1—Cr—C2	81.6(5)	78.5(5)
C6—C4—Cr	77.1(8)	78.2(9)	C1—Cr—P	80.0(4)	80.7(3)
C7—C4—Cr	79.2(8)	78.9(8)	C2—Cr—C3	77.7(5)	76.8(5)
C4—Cr—C5	38.5(5)	38.5(5)	C3—Cr—P	82.7(4)	80.4(3)
C4—Cr—C6	39.1(5)	38.3(6)	C1—Cr—C3	121.1(5)	123.7(5)
C4—Cr—C7	38.2(5)	37.9(5)	C2—Cr—P	140.8(4)	132.8(4)
C5—Cr—C6	64.5(5)	64.2(6)	Cr—C1—O1	177.4(10)	176.9(10)
C5—Cr—C7	67.0(5)	65.3(5)	Cr—C2—O2	177.0(10)	179.0(10)
C6—Cr—C7	64.7(5)	65.0(5)	Cr—C3—O3	175.0(10)	177.4(10)
C1—Cr—C4	115.5(5)	114.9(5)	Cr—P—C8	115.2(2)	115.8(2)
C2—Cr—C4	106.7(5)	111.1(5)	Cr—P—C14	115.4(2)	113.5(2)
C3—Cr—C4	123.2(5)	121.1(5)	Cr—P—C20	117.0(2)	116.9(2)
P—Cr—C4	112.4(4)	116.0(4)	C8—P—C14	102.9(3)	102.9(3)
C1—Cr—C5	77.3(5)	77.2(5)	C8—P—C20	102.8(3)	103.9(3)
C2—Cr—C6	69.8(5)	74.6(6)	C14—P—C20	101.5(3)	102.0(3)



(a)



(b)

Fig. 2a. Stereo pair of molecule B. Note the non-planar character of the trimethylenemethane ligand.

Fig. 2b. Stereo pair of molecule B showing the relative orientations of the ligands.

TABLE 4

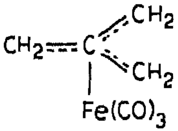
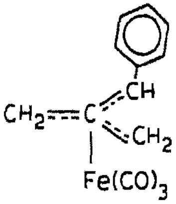
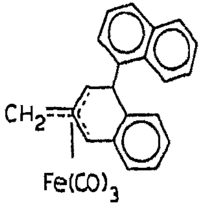
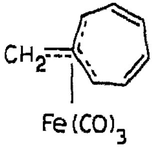
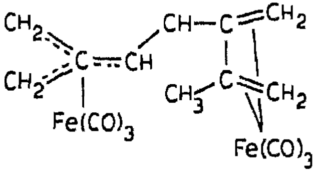
SELECTED INTRAMOLECULAR NON-BONDED CONTACTS (FULL MATRIX REFINEMENT)

		Molecule A	Molecule B
P	C1	2.77(1) Å	2.79(1) Å
P	C3	2.85(1)	2.79(1)
P	C5	3.62(1)	3.64(2)
P	C7	3.11(1)	3.17(1)
P	O1	3.53(1)	3.55(1)
P	O3	3.64(1)	3.55(1)
C1	C5	2.57(2)	2.58(2)
C2	C6	2.32(2)	2.48(2)
C3	C6	3.17(2)	3.20(2)
C3	C7	3.07(2)	3.04(2)
C8	C7	3.48(2)	3.61(1)
C14	C1	3.06(1)	3.05(1)
C20	C3	3.15(1)	3.06(1)

TABLE 5

TRIMETHYLENEMETHANEIRON STRUCTURES

Asterisks denote terminal carbon atoms which are bonded to another group.

Compound	$C_{cent.}$–$C_{term.}$	$C_{cent.}$–Metal	$C_{term.}$–Metal	$C_{term.}$–$C_{cent.}$–$C_{term.}$	$C_{term.}$–$C_{cent.}$–Metal	Method
	1.437(3) Å	1.938(5)	2.123(5)	114.6(2)°	76.4(2)	Electron diffraction [3]
	1.405(13) 1.406(13) 1.436(12)*	1.932(10)	2.098(11) 2.118(10) 2.162(9)*	116.2(9) 114.4(8) 115.0(8)	76.1(6) 77.0(6) 78.3(5)*	X-ray [4]
	1.41(4) 1.37(4)* 1.42(4)*	1.95(2)	2.10(2) 2.11(2)* 2.11(2)*	116(3) 108(3) 119(3)		X-ray [5]
	1.428(5) 1.405(4)* 1.412(4)*	1.946(2)	2.120(3) 2.192(3)* 2.175(3)*	113.4(3) 114.9(3) 119.9(2)	76.1(2) 79.9(2)* 79.0(1)*	X-ray [7]
	1.42(2) 1.45(2) 1.43(1)*	1.94(1)	2.12(1) 2.12(1) 2.17(1)*			X-ray [6]

for molecules A and B respectively. The displacements of the chromium atoms from these planes are 0.80 and 0.86 Å for molecules A and B respectively. Typically, the phenyl rings of the triphenylphosphine ligand lie in approximately mutually perpendicular planes.

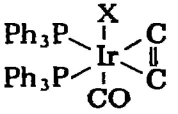
The average values of molecule A and B for $C_{cent.}$—$C_{term.}$, $C_{term.}$—$C_{cent.}$—$C_{term.}$ and $C_{term.}$—$C_{cent.}$—M agree well with the analogous bond lengths and bond angles for the five trimethylenemethaneiron tricarbonyl structures summarized in Table 5. The carbon—iron π-bond distances are shorter than the carbon—chromium π-bond distances by about 0.10 Å. This is approximately the amount which would be expected on the basis of differences in the covalent radii of iron and chromium (0.12 Å) estimated from π-cyclopentadienyl complexes [22]. A smaller effect is noticeable by comparing the average Cr—O carbonyl distances in the present work (2.99 Å), benzocyclobutadienechromium tricarbonyltriphenylphosphine [23] (3.01 Å) and various arenechromium tricarbonyls [24-26] (2.98-2.99 Å) with the average Fe—O carbonyl distances in 4-carbomethoxybenzocyclobutadieneiron tricarbonyl [23] (2.92 Å), *o*-xylyleneiron dicarbonyltriphenylphosphine [23] (2.91 Å), 1,6,7,8-*tetrahapto*-heptafulveneiron tricarbonyl [7] (2.92 Å) and phenyltrimethylenemethaneiron tricarbonyl [4] (2.91 Å). The greatest effect, however, seems to occur in the metal—phosphorus bond which has a value of about 2.25 Å in iron triphenylphosphines [23, 27] and about 2.40 Å in chromium triphenylphosphines [23, 28].

It is interesting to note that in this work the shortest Cr—CO distance in each molecule is *trans* to the triphenylphosphine (see Fig. 1). Other workers [24, 25] have noted that the average Cr—CO bond length in arenechromium complexes shortens as electron releasing substituents are added to the π-complexed ring. This effect has been attributed to an increased back-bonding of electrons from the filled *d* orbitals of the metal into the π* antibonding orbitals of the carbonyls as electron releasing groups are added to the ring. Although the differences are small, it may be significant that in the above arenechromium structures which are unsymmetrically substituted, it is the Cr—CO bond which is most *trans* to the electron releasing group which is consistently the shortest.

The shortest Cr—CO bond in this work occurs *trans* to phosphorus which is a good forward σ-donor, as well as a poor π-acceptor, compared with CO. An even larger difference is seen in benzocyclobutadienechromium tricarbonyltriphenylphosphine [23] in which the Cr—CO bond *trans* to phosphorus (as well as *trans* to the benzo ring) is 1.81(1) Å, compared with 1.89(1) and 1.90(1) Å for the other two carbonyls. Short Mn—CO bond distances are observed in $Mn(CO)_4(PPh_3)Cl$ for carbonyls which are *trans* to PPh_3 or Cl [1.75(1), 1.75(1) Å] vs. carbonyls which are *trans* to another carbonyl [1.82(2), 1.86(1) Å] [29]. In $(CH_3CO_2)Mn(CO)_2(PPh_3)_2$ both Mn—CO bonds [mean value = 1.73(1) Å] occur *trans* to the acetate oxygens. This short Mn—CO distance compared with 1.80(2) Å for $C_5H_5Mn(CO)_3$ [30] is attributed to a considerable σ-donation to the metal by the acetate group with relatively little involvement of the oxygen atoms as either π-acceptors or π-donors [29].

Although an extensive review article on the *trans* influence with an X-ray bibliography has recently appeared [31], very little attention was given to crystal structure data of Cr, Mn and Fe (no carbonyls were cited). In addition to the structures discussed in this paper, many other structures which we believe are examples of a *trans* influence have appeared [32-43]. We note that comparisons based on axial vs. equatorial bond lengths (in cases where such designations are meaningful) lead to apparent contradictions. Thus, for a large number of crystal structures it seems that the presence of a good σ-donor and/or a poor π-acceptor shortens the metal—CO bond *trans* to it. One apparent exception to this *trans* influence is tetracarbonylirondiphenylphosphine in which all Fe—CO bonds are equal [44].

With an increase in the metal—CO bond order, one would expect a decrease in C—O bond order, leading to a decrease in CO stretching frequency. Infrared studies of substituted arenechromium tricarbonyls have shown this to be the case [45]. Evidence of this influence in complexes of type II has been compiled by



(II) X = Cl or I

Hartley [46] who points out that when an olefin complexes to [IrCl(CO)(PPh_3)$_2$] there is an increase in CO stretching frequency and this increase is greatest for olefins which are poor σ-donors but good π-acceptors. Furthermore, an expected increase in CO frequency (which accompanies a reduction in back-donation from the metal to the carbonyl) upon oxidation of the metal is observed [46]. In addition, Cotton [47] has shown that in many octahedral $M(CO)_6$ complexes the CO stretching frequency decreases when carbonyls are replaced with alkyl- or arylphosphine ligands and the effect is greatest on the CO *trans* to the phosphine. This is attributed to increased d_π(metal)—p_π(CO) overlap due to the relatively poor π-acceptor ability of phosphines compared with CO.

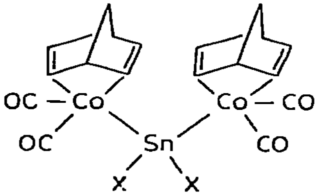
A relative scale of effects of σ and π donor or acceptor character for a number of ligands has been derived by Graham [48]. He suggests that the force constants of all carbonyl groups in $LMn(CO)_5$ and $LMo(CO)_5$ complexes will change by the same amount due to the change in inductive effect of one ligand vs. another, while the differences in π-bonding between two ligands will affect the *trans* CO force constant twice as much as the *cis*. Others [49, 50] have related CO force constants to Taft polarity constants.

Discussions correlating changes in the CN stretching frequency of isocyanides upon complexation, as well as *trans* influences on Pt—Cl stretching frequencies in several complexes [51, 52], have likewise been based on back-bonding arguments.

Tsang et al. [53], have shown that complexes of the type $M(CO)_3I_3PPh_3^-$ (M = Mo or W) have lower CO frequencies than those of the analogous neutral complexes. The inference drawn is that the higher electron density present in the anion is partially distributed by increased back-donation from the metal to the carbonyls.

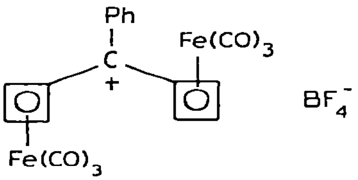
Evidence that an electron-withdrawing group may increase metal—CO bond lengths through depletion of electrons available for back-bonding is afforded [54] by the distances and IR data in Table 6. In studies of related compounds [$X_3GeCo(CO)_4$, X_3 = halogens, methyls, phenyls or combinations of these] a strikingly linear relationship was found between CO stretching frequency and the sum of the halogen electronegativities in the complex [55].

TABLE 6



	Co—CO mean (Å)	C—O frequencies (cm^{-1})			
X = Cl	1.78(1)	2034	2005	1984	1970
X = C_6H_5	1.71(2)	2011	1991	1960	1951

Another structure in which unusual M—CO distances can be rationalized in these terms is the cationic complex III [56]. The average Fe—Co distance in this complex [1.84(1) Å] is considerably longer than the average values of 1.75(1) Å in tetraphenylcyclobutadiene — $Fe(CO)_3$ [57] or 1.77(1) Å in carbomethoxybenzocyclobutadiene — $Fe(CO)_3$ [23]. For III the greatly enhanced stability of the cation was explained in terms of the release of π-electron density from $Fe(CO)_3$ through the π-system [58]. The C—O bond distances are extremely short [range 1.09-1.12 Å, mean 1.11(1) Å], consistent with an increased C—O bond order.



(III)

In conclusion, it appears that a large body of crystal structure data is in agreement with the conclusions reached from spectral evidence. Metal—CO bond lengths are quite sensitive to the σ and π donor or acceptor properties of other ligands in the complex. However, meaningful quantitative relationships between X-ray bond lengths and these donor—acceptor properties must await additional structural data in which bond lengths are known more reliably (possibly obtained at low temperatures).

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