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Crystal and Molecular Structures of Two Isomeric Tri(tertiary phosphine) Complexes of Manganese(I) and Chromium(0)

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The molecular and crystal structures of two isomers (α and β) of $Br(CO)_3Mn(triphos)Cr(CO)_5$ [triphos = bis(2-diphenylphosphinoethyl)phenylphosphine, $PPh(CH_2CH_2PPh_2)_2$] have been determined by single-crystal X-ray diffraction methods. The α isomer crystallizes in the orthorhombic space group *Pbcn* (No. 60), with $a = 21.260$ (6), $b = 14.451$ (3), $c = 28.338$ (9) Å, and $Z = 8$. The β isomer crystallizes in a 1:1 mole ratio with CH_2Cl_2 in the monoclinic space group *Cc* (No. 9), with $a = 24.43$ (3), $b = 10.76$ (1), $c = 17.42$ (2) Å, $\beta = 89.11$ (3)°, and $Z = 4$. Diffractometer data were collected by the θ–2θ scan method. The α isomer was refined by full-matrix least squares to a conventional final R value of 9.9% while that of the β isomer was 8.7%. Coordination of the triphos ligand to the manganese atom occurs through two adjacent phosphorus atoms and results in the formation of a five-membered chelate ring. The phenyl ring attached to the central phosphorus atom can take a position cis or trans to the bromine atom relative to the five-membered chelate ring and this gives rise to the two isomers which are formed. The conformation of the five-membered chelate ring is found to be dependent on the groups attached to both the manganese and phosphorus atoms.

Introduction

Reactions involving the substitution of CO groups in $Mn(CO)_5X$ (X = Cl, Br, I) by tertiary phosphines and phosphites (L) to give products of the type *mer-* and *fac*-Mn-$(CO)_3L_2X$ have been well documented.[2] The reactions are known to proceed by sequential substitution of the CO groups and the intermediate product, $Mn(CO)_4LX$, can in most cases be readily isolated. Further reaction of this product, $Mn(CO)_4LX$, with a different phosphine or phosphite (L′) should give products of the type *mer-* and *fac*-$Mn(CO)_3LL'X$, but as yet no known products of this type have been isolated.[3]

Reaction of $Mn(CO)_5X$ with triphos, $[PPh(CH_2CH_2PPh_2)_2]$, led to the formation of the disubstituted complexes *fac*-$Mn(CO)_3(triphos)X$[4] in which only two of the three phosphorus atoms are bonded to manganese. Since bonding through two adjacent phosphorus atoms is the most likely situation[5] and since these atoms are not equivalent, *i.e.*, the phosphorus atoms are bonded to *different* groups, the complex formed should be of the type $Mn(CO)_3LL'X$, L ≠ L′.

Furthermore, as the central phosphorus atom in the ligand should now have become optically active, more than one isomeric complex of the type *fac*-$Mn(CO)_3(triphos)X$ should have been formed. Indeed, the complex *fac*-$Mn(CO)_3$-(triphos)X was found to exist as a mixture of two isomers. These two isomers can react further, since the unbonded phosphorus atom, which is unattached to the manganese atom, should behave like a typical phosphine.[4]

We report here the crystal structures of the two isomers of $Br(CO)_3Mn(triphos)Cr(CO)_5$ obtained on reaction of *fac*-$Mn(CO)_3(triphos)Br$ and $Cr(CO)_5(THF)$ (THF = tetrahydrofuran). These results have been described, in part, in a preliminary communication.[6]

Experimental Section

The $Br(CO)_3Mn(triphos)Cr(CO)_5$ complexes were prepared as reported previously.[4] Crystallization of the α isomer[7] from CH_2Cl_2-*n*-C_6H_{14} solution afforded yellow needles which were dried *in vacuo* (0.01 mm (25°)).

The β isomer crystallized from CH_2Cl_2-*n*-C_6H_{14} solution in the form of orange plates. Attempted drying of these crystals under reduced pressure caused them to become opaque; consequently the crystals used in the X-ray study were dried under a stream of nitrogen.

Crystallographic Data. α Isomer. The space group of a crystal was determined from Weissenberg *h0l*, *h1l* and precession *hk0*, *0kl* zones as *Pbcn* (No. 60) from the systematic absences ($0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h + k = 2n$). The unit cell parameters at 20° were determined as $a = 21.260$ (6), $b = 14.451$ (3), $c = 28.338$ (9) Å, and $V = 8710$ Å^3. The density, determined by flotation in ZnI_2 solution, was $\rho_{obsd} = 1.44$ (1) g cm^{-3} (for $Z = 8$, $\rho_{calcd} = 1.44$ g cm^{-3}).

Unit cell and intensity data for the crystal structure were collected on the McGill University Picker FACS-I diffractometer using graphite-monochromated Cu Kα radiation (λ 1.5419 Å). Accurate values for 2θ, ω, and ϕ were obtained for ten Bragg reflections by an automatic centering process. Refined unit cell constants and the orientation matrix were fitted to these values by a least-squares process.[8a]

A new crystal was mounted and used for data collection in which a θ–2θ scanning process was employed, using stationary 60-sec background counts measured at the minimum and maximum 2θ values for the scan. The base scan length was 2° increasing at higher 2θ values to allow for α_1–α_2 dispersion. The scintillation counter and pulse height analyzer were adjusted to accept 100% of the Cu Kα peak.

(1) (a) Sir George Williams University. (b) Chemistry Department, McGill University. (c) Geology Department, McGill University.

(2) D. A. Brown, *Inorg. Chim. Acta Rev.*, 1, 35 (1967).

(3) A kinetic study of the reaction of $Mn(CO)_4LX$, L = phosphine, with $P(O(n\text{-}Bu))_3$ has been reported, but no products were isolated: see R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 84, 2495 (1962).

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(5) R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, 10, 1841 (1971).

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(7) The α isomer is the one which has the larger R_f value on a silica gel thin-layer chromatography plate after elution with benzene. This was referred to as the A isomer in the preliminary communication.

(8) (a) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967). Program supplied by Picker-Nuclear Co. (b) J. M. Stewart, Ed., Technical Report TR-192, University of Maryland Computer Science Center, College Park, Md., 1970.

Table I. Final Parameters

Positions and Isotropic Thermal Parameters[a] with Esd's[b]

Atom	α isomer				β isomer			
	x	y	z	B, Å^2	x	y	z	B, Å^2
Br	0.2582 (2)	0.1075 (3)	−0.0373 (2)	c	0.5000	0.3009 (2)	0.5000	c
Mn	0.3647 (4)	0.1589 (4)	−0.0680 (2)	c	0.56250 (15)	0.1147 (3)	0.5151 (2)	c
Cr	0.3882 (3)	−0.0173 (5)	0.1684 (3)	c	0.75173 (16)	0.0338 (3)	0.8289 (2)	c
P1	0.3097 (5)	0.2823 (7)	−0.1009 (4)	c	0.5113 (3)	0.0518 (6)	0.6249 (4)	c
P2	0.3762 (5)	0.2569 (7)	−0.0046 (4)	c	0.6095 (2)	0.2390 (5)	0.6029 (4)	c
P3	0.3423 (5)	0.1205 (7)	0.1350 (4)	c	0.7656 (2)	0.1931 (6)	0.7361 (3)	c
O1	0.344 (1)	0.048 (2)	−0.152 (1)	10.3 (8)	0.4973 (6)	−0.0352 (15)	0.4085 (9)	4.7 (4)
O2	0.488 (1)	0.209 (2)	−0.100 (1)	10.8 (9)	0.6413 (6)	−0.0855 (14)	0.5334 (8)	4.9 (4)
O3	0.416 (1)	−0.001 (2)	−0.017 (1)	11.7 (9)	0.6217 (6)	0.2097 (15)	0.377 (1)	5.8 (4)
O4	0.334 (1)	−0.120 (2)	0.087 (1)	14.6 (11)	0.7787 (6)	0.2128 (17)	0.957 (1)	6.5 (4)
O5	0.506 (1)	0.023 (2)	0.118 (1)	10.5 (8)	0.8711 (7)	−0.0341 (16)	0.815 (1)	6.5 (5)
O6	0.453 (2)	−0.186 (2)	0.209 (1)	13.9 (11)	0.7377 (7)	−0.1612 (16)	0.948 (1)	6.5 (5)
O7	0.431 (1)	0.075 (2)	0.254 (2)	10.6 (9)	0.7156 (7)	−0.1569 (17)	0.716 (1)	7.6 (5)
O8	0.276 (2)	−0.061 (2)	0.229 (1)	15.3 (12)	0.6344 (7)	0.1137 (14)	0.849 (1)	5.5 (4)
C1	0.354 (2)	0.095 (3)	−0.116 (1)	9 (1)	0.5211 (9)	0.022 (2)	0.446 (1)	4.8 (6)
C2	0.433 (2)	−0.088 (3)	−0.088 (1)	10 (1)	0.6077 (8)	−0.008 (2)	0.525 (1)	2.9 (5)
C3	0.395 (2)	0.068 (3)	−0.038 (2)	11 (1)	0.6015 (9)	0.175 (2)	0.429 (1)	4.0 (6)
C4	0.360 (2)	−0.081 (3)	0.120 (2)	12 (2)	0.7712 (10)	0.145 (3)	0.907 (2)	6.6 (8)
C5	0.456 (2)	0.002 (3)	0.137 (1)	9 (1)	0.8240 (10)	−0.006 (2)	0.818 (1)	5.0 (6)
C6	0.428 (2)	−0.128 (4)	0.195 (2)	15 (2)	0.7440 (10)	−0.082 (2)	0.900 (2)	5.9 (7)
C7	0.410 (2)	0.034 (3)	0.222 (1)	8 (1)	0.7287 (10)	−0.082 (3)	0.761 (2)	6.1 (7)
C8	0.317 (3)	−0.046 (4)	0.205 (2)	15 (2)	0.6787 (9)	0.080 (2)	0.838 (1)	4.0 (5)
C9	0.286 (1)	0.353 (2)	−0.050 (1)	5.0 (9)	0.5442 (8)	0.120 (2)	0.708 (1)	3.6 (5)
C10	0.336 (2)	0.372 (2)	−0.019 (1)	6 (1)	0.5653 (7)	0.257 (2)	0.687 (1)	2.4 (4)
C11	0.338 (2)	0.232 (2)	0.051 (1)	5.5 (9)	0.6736 (8)	0.165 (2)	0.640 (1)	2.8 (5)
C12	0.359 (2)	0.135 (2)	0.073 (1)	5.1 (8)	0.7005 (8)	0.259 (2)	0.696 (1)	2.9 (5)
C13	0.357 (2)	0.360 (2)	−0.139 (1)	5.7 (9)	0.5067 (8)	−0.114 (2)	0.649 (1)	3.3 (5)
C14	0.396 (2)	0.322 (3)	−0.172 (1)	8 (1)	0.4967 (9)	−0.200 (2)	0.593 (1)	4.1 (5)
C15	0.430 (2)	0.381 (3)	−0.205 (1)	8 (1)	0.4884 (9)	−0.328 (2)	0.612 (1)	4.9 (6)
C16	0.420 (2)	0.477 (3)	−0.202 (1)	10 (1)	0.4876 (9)	−0.361 (2)	0.688 (2)	5.6 (6)
C17	0.384 (2)	0.513 (3)	−0.168 (2)	13 (1)	0.4949 (10)	−0.276 (2)	0.745 (2)	6.1 (7)
C18	0.345 (2)	0.457 (3)	−0.134 (2)	10 (1)	0.5065 (10)	−0.144 (2)	0.726 (2)	5.9 (7)
C19	0.238 (2)	0.268 (2)	−0.138 (1)	5.8 (9)	0.4395 (7)	0.101 (2)	0.628 (1)	2.5 (4)
C20	0.184 (2)	0.303 (3)	−0.123 (2)	10 (1)	0.4055 (9)	0.064 (2)	0.565 (1)	4.0 (5)
C21	0.129 (2)	0.296 (3)	−0.156 (2)	10 (1)	0.3508 (10)	0.098 (2)	0.567 (2)	5.2 (6)
C22	0.141 (2)	0.257 (3)	−0.200 (1)	9 (1)	0.3265 (9)	0.166 (2)	0.627 (2)	4.9 (6)
C23	0.194 (2)	0.216 (3)	−0.215 (2)	10 (1)	0.4198 (9)	0.172 (2)	0.687 (1)	4.0 (5)
C24	0.248 (2)	0.223 (3)	−0.182 (1)	8 (1)	0.3617 (11)	0.198 (2)	0.686 (2)	6.9 (7)
C25	0.453 (2)	0.290 (3)	0.014 (1)	8 (1)	0.6312 (7)	0.392 (2)	0.578 (1)	2.4 (4)
C26	0.504 (2)	0.230 (3)	0.011 (2)	10 (1)	0.6725 (8)	0.409 (2)	0.522 (1)	3.8 (5)
C27	0.569 (2)	0.254 (3)	0.029 (2)	12 (2)	0.6945 (9)	0.531 (2)	0.508 (1)	4.7 (6)
C28	0.575 (2)	0.342 (4)	0.047 (2)	14 (2)	0.6774 (9)	0.632 (2)	0.555 (1)	4.6 (6)
C29	0.529 (2)	0.396 (3)	0.054 (2)	12 (2)	0.6364 (10)	0.617 (2)	0.608 (1)	5.2 (1)
C30	0.463 (2)	0.375 (3)	0.040 (2)	11 (1)	0.6123 (9)	0.500 (2)	0.624 (1)	4.9 (6)
C31	0.254 (2)	0.130 (2)	0.140 (1)	6.0 (9)	0.8098 (8)	0.155 (2)	0.644 (1)	3.0 (5)
C32	0.231 (2)	0.150 (2)	0.183 (1)	7 (1)	0.8232 (9)	0.034 (2)	0.627 (1)	4.5 (6)
C33	0.165 (2)	0.156 (3)	0.192 (1)	9 (1)	0.8560 (10)	0.012 (3)	0.561 (2)	6.4 (7)
C34	0.135 (2)	0.148 (3)	0.151 (1)	8 (1)	0.8705 (9)	0.109 (3)	0.517 (1)	5.2 (6)
C35	0.150 (2)	0.122 (3)	0.106 (1)	9 (1)	0.8552 (11)	0.222 (3)	0.538 (2)	6.5 (7)
C36	0.222 (2)	0.115 (3)	0.098 (1)	7 (1)	0.8231 (9)	0.262 (2)	0.605 (1)	3.9 (5)
C37	0.367 (2)	0.235 (3)	0.156 (1)	8 (1)	0.7981 (8)	0.334 (2)	0.776 (1)	2.9 (5)
C38	0.433 (2)	0.240 (3)	0.166 (1)	8 (1)	0.8537 (11)	0.319 (3)	0.793 (2)	6.7 (7)
C39	0.464 (2)	0.326 (3)	0.176 (1)	9 (1)	0.8787 (12)	0.421 (3)	0.836 (2)	8.2 (9)
C40	0.426 (2)	0.403 (3)	0.181 (1)	8 (1)	0.8497 (11)	0.520 (3)	0.854 (2)	5.7 (6)
C41	0.361 (2)	0.400 (3)	0.174 (1)	7 (1)	0.7931 (11)	0.534 (3)	0.836 (2)	7.6 (8)
C42	0.331 (2)	0.316 (2)	0.163 (1)	7 (1)	0.7677 (9)	0.432 (2)	0.799 (1)	4.7 (6)
Cl1					0.6084 (4)	0.4768 (9)	0.8405 (5)	c
Cl2					0.5029 (4)	0.3640 (11)	0.8757 (5)	c
C43					0.5577 (17)	0.406 (4)	0.906 (1)	c

Anisotropic Thermal Parameters[d] (×10^4)

	α isomer						β isomer					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	47 (2)	66 (2)	28 (1)	−11 (2)	0 (1)	−1 (2)	20.0 (6)	103 (3)	44 (1)	8 (1)	0.4 (7)	14 (2)
Mn	35 (2)	67 (4)	22 (1)	6 (3)	2 (1)	1 (2)	12.8 (7)	76 (4)	23 (1)	0 (2)	−1.4 (8)	0 (2)
Cr	47 (2)	82 (5)	28 (2)	1 (3)	−4 (2)	7 (2)	14.3 (8)	98 (5)	21 (2)	−6 (1)	−1.1 (9)	9 (3)
P1	39 (4)	44 (6)	21 (2)	3 (4)	3 (2)	−3 (3)	17.6 (13)	103 (8)	32 (3)	−8 (3)	0.3 (15)	0 (4)
P2	26 (2)	73 (7)	24 (2)	−3 (4)	3 (2)	−2 (3)	16.8 (13)	93 (8)	28 (3)	−2 (3)	−1.1 (14)	4 (4)
P3	40 (4)	50 (7)	29 (2)	−8 (4)	0 (2)	2 (3)	18.7 (15)	93 (8)	32 (3)	−4 (3)	−0.6 (16)	−2 (4)
Cl1							40 (2)	193 (13)	46 (4)	−26 (5)	6 (3)	−41 (6)
Cl2							29 (2)	319 (19)	53 (5)	−31 (6)	4 (3)	−44 (8)
C43							82 (14)	360 (70)	15 (12)	90 (27)	−2.5 (11)	−25 (25)

[a] Isotropic thermal parameters in Å^2. [b] Esd's are shown in parentheses. These are right justified to the least significant digit in the preceding number. [c] Atoms refined anisotropically. [d] Of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

An asymmetric set of 3789 diffraction intensities to $2\theta_{max} = 90°$ was collected. Instrumental and crystal instabilities were checked by remeasuring three standards every 50 reflections. The intensity of these reflections fell by 36% during data collection. The data were corrected for decomposition by locally written computer programs. Although $\mu = 73.0$ cm^{-1} and the crystal measured approximately $0.10 \times 0.10 \times 0.15$ mm, the third dimension being along the rotation axis, it was felt that the poor quality of the data did not warrant the time and effort involved in making an absorption correction.

Data reduction, as well as structure solution and refinement, was performed with the aid of the "X-RAY 70" program package[8b] adapted for use on the McGill University IBM 360/75 computer. Scattering factors for the atoms were taken from Cromer.[9a] Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) were made for the six heavy atoms (Mn, Br, Cr, 3 P).[9b] For data reduction, intensity $I = [N - (B_1 + B_2)t_s/2t_b]$ and $\sigma(I) = [N + (B_1 + B_2)(t_s/2t_b)^2]^{1/2}$ where N and B are the counts accumulated during the scan time t_s and background time t_b, respectively. All data with $I < 2\sigma(I)$ were rejected and the remaining data (1324 reflections) were corrected for Lorentz and polarization effects [$1/Lp = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample crystal and monochromator respectively].

Structure Solution and Refinement. α Isomer. Three-dimensional Patterson and sharpened Patterson maps did not prove helpful in the structure determination, owing to severe overlap of peaks. Therefore direct methods were employed and the six heavy atoms were located on the E map computed after phasing 380 reflections.[10] The remaining nonhydrogen atoms were found from successive difference Fourier maps.

Least-squares refinement using isotropic temperature and positional parameters gave $R = 15.4\%$ ($R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$). Three reflections were considered extinct (104, 106, 304) and were thus rejected. Anisotropic thermal parameters for the six heavy atoms were then included and block-diagonal least-squares refinement gave $R = 9.9\%$. The weighting scheme $\sqrt{w} = F_o/A$ for $F_o \leq A$ and $\sqrt{w} = A/F_o$ for $F_o > A$ ($A = 120$) was employed during the latter cycles of refinement. This gave a reasonably uniform distribution of $\Sigma w||F_o| - |F_c||^2$ with varying θ and I. A final difference Fourier map showed no peak higher than 0.9 e/Å^3. Final atomic parameters are given in Table I.[11]

Crystallographic Data. β Isomer. A preliminary photographic survey of Weissenberg $h0l$ and precession $0kl$, $hk0$, $hk1$ zones gave two possible space groups, Cc (No. 9) and $C2/c$ (No. 15), consistent with the observed systematic absences of X-ray diffractions (hkl, $h + k = 2n$; $h0l$, $k = 2n$). The refined unit cell parameters, $a = 24.41$ (3), $b = 10.76$ (1), $c = 17.42$ (2) Å, $\beta = 89.11$ (3)°, and $V = 4575$ Å^3, at 20°, were obtained after transferring the crystal to the diffractometer.

The density of the complex, found by flotation in ZnI$_2$ solution, was $\rho_{obsd} = 1.50$ (1) g cm^{-3} [for $Z = 4$, $\rho_{calcd} = 1.50$ g cm^{-3} for the monosolvate, Br(CO)$_3$Mn(triphos)Cr(CO)$_5$·CH$_2$Cl$_2$]. In $C2/c$, with $Z = 4$, the molecules lie on special positions. As the molecule has no symmetry, this space group was ruled out. Successful structure solution confirmed Cc as the appropriate space group.

Data were collected on the Sir George Williams University Picker FACS-I fully automated diffractometer, using monochromatic Mo Kα radiation (λ 0.71069 Å).[12]

Refined cell constants and the orientation matrix were obtained as described above, but in this case, twelve reflections centered at both positive and negative 2θ values were used, after averaging.

A quarter sphere of intensities in the range $2° < 2\theta < 45°$ was collected by a θ-2θ scanning procedure. The base scan width was 2° and the background counting time 40 sec. One hundred per cent of the Mo Kα peak was accepted by the pulse height analyzer. Instrumental and crystal instabilities were checked by monitoring three standards every 50 reflections. The intensity of the three standard reflections decreased by 2% during data collection; they were used to scale the observed data.

(9) (a) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); (b) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(10) F. R. Ahmed, Ed., "Proceedings of the 1969 International Summer School of Crystallographic Computing," Munksgaard, Copenhagen, 1970, p 71.

(11) See paragraph at end of paper regarding supplementary material.

(12) For a more detailed description of the experimental procedure see A. D. Adley, P. H. Bird, A. R. Fraser, and M. Onyszchuk, *Inorg. Chem.*, **11**, 1402 (1972).
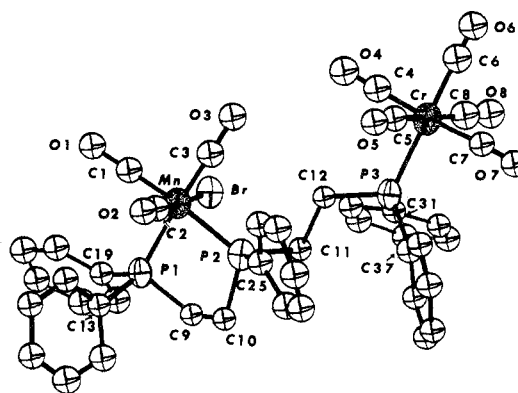

Figure 1. Molecular structure of the α isomer projected approximately down [010].

Of the 3265 reflections collected, 2278 reflections ($I > 3\sigma(I)$) were corrected for Lorentz and polarization effects, using locally written programs for the Sir George Williams University CDC 6400 computer. The formula for the intensity, I, is given above and $\sigma(I) = [N + (B_1 + B_2)(t_s/t_b)^2 + (0.02N)^2]^{1/2}$. During refinement the weighting factor $w = [\sigma(I)]^{-2}$ was used. No absorption correction was made ($\mu = 11.8$ cm^{-1}). (The crystal used, a parallelepiped of *ca.* $0.1 \times 0.07 \times 0.1$ mm, would lead to transmission factors of approximately 89–94%.)

Structure Solution and Refinement. β Isomer. Inspection of the sharpened three-dimensional Patterson synthesis suggested several possibilities for the positions of the heavy atoms (Br, Mn, Cr). These possibilities were tested in trial structure factor calculations; a Fourier synthesis based on the best of these gave the positions of the three phosphorus atoms. Subsequent syntheses yielded the positions of the remaining atoms. Owing to computer memory restrictions, least-squares refinement of positional and isotropic thermal parameters necessitated dividing the parameters into two matrices. The discrepancy index, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, at this stage dropped to 9.6%. During refinement both real and imaginary parts of the anomalous dispersion were applied to the scattering factors. Since the noncentrosymmetric space group Cc specifies an absolute configuration for the molecule, least-squares refinement was also carried out on the inverse structure and gave a final $R = 9.9\%$. The significance of the difference between the two R values was supported by application of the Hamilton R test.[13] The λ isomer,[14] with the lower R value, was thus chosen as the correct isomer. A further four cycles of refinement including anisotropic temperature refinement on atoms other than carbon, hydrogen, and oxygen gave a final R value of 8.7% and R_w of 6.7% ($R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$, where $w = [\sigma(F_o)]^{-2}$). The "goodness of fit" index, defined by $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where n and m are numbers of observations and variables, respectively, was 2.01.

The final atomic parameters are given in Table I.

Results

The molecular structures of the two isomers are shown in Figures 1 and 2. The packing diagram for the β isomer is given in Figure 3. Tables II and III list bond lengths and bond angles, respectively. The average bond lengths and angles for the ten phenyl rings are collected together in Table IV while the least-squares planes through these ten rings are given in Table V. No intermolecular contacts less than 3.0 Å were found.

Discussion

The overall geometry of both isomers consists of two metal atoms linked together by the triphos ligand. The coordination around the Mn atom in both structures is essentially octahedral with three CO groups cis to each other (facial configuration). The coordination around the Cr atom is also octahedral.

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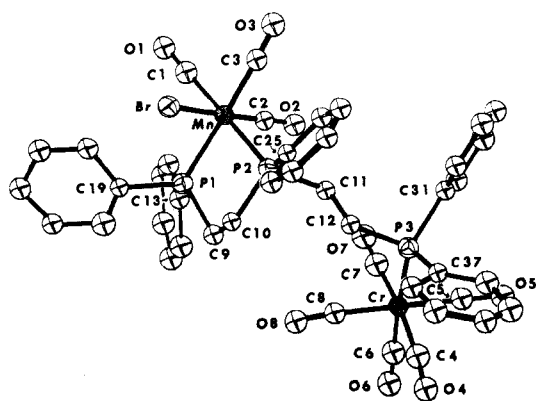(14) This is in accordance with the IUPAC convention: see *Inorg. Chem.*, **9**, 1 (1970).

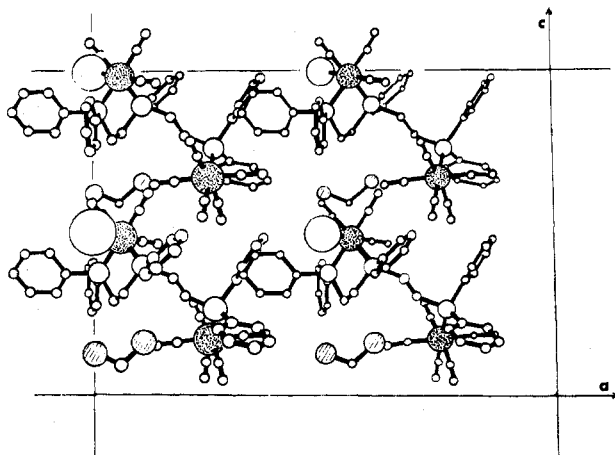**Figure 2.** Molecular structure of the β isomer projected down [010].

Figure 3. Projection of the contents of the unit cell on [010] for the β isomer.

Table II. Principal Intermolecular Bond Distances (Å)[a]

	α isomer	β isomer		α isomer	β isomer
Br–Mn	2.537 (8)	2.534 (4)	C6–O6	1.07 (6)	1.20 (3)
Mn–P1	2.328 (12)	2.369 (7)	C7–O7	1.18 (5)	1.18 (3)
Mn–P2	2.301 (13)	2.346 (7)	C8–O8	1.12 (6)	1.16 (3)
Mn–C1	1.65 (4)	1.86 (2)	P1–C9	1.83 (3)	1.83 (2)
Mn–C2	1.61 (4)	1.73 (2)	P1–C13	1.86 (3)	1.84 (2)
Mn–C3	1.70 (5)	1.87 (2)	P1–C19	1.87 (4)	1.83 (2)
C1–O1	1.26 (5)	1.08 (3)	P2–C10	1.91 (3)	1.82 (2)
C2–O2	1.26 (5)	1.19 (3)	P2–C11	1.82 (3)	1.89 (2)
C3–O3	1.22 (5)	1.10 (3)	P2–C25	1.78 (4)	1.78 (2)
Cr–P3	2.41 (1)	2.376 (7)	P3–C12	1.82 (3)	1.88 (2)
Cr–C4	1.77 (5)	1.88 (3)	P3–C31	1.89 (4)	1.96 (2)
Cr–C5	1.71 (4)	1.82 (2)	P3–C37	1.83 (4)	1.85 (2)
Cr–C6	1.96 (5)	1.77 (3)	C9–C10	1.43 (4)	1.60 (3)
Cr–C7	1.75 (4)	1.81 (3)	C11–C12	1.59 (4)	1.56 (3)
Cr–C8	1.88 (5)	1.86 (3)	C11–C43		1.84 (4)
C4–O4	1.23 (6)	1.16 (3)	C12–C43		1.52 (4)
C5–O5	1.24 (5)	1.19 (3)			

[a] The esd's shown in parentheses are right adjusted.

The β isomer crystallizes as the mono-CH₂Cl₂ solvate Br-(CO)₃Mn(triphos)Cr(CO)₅·CH₂Cl₂. Structures containing CH₂Cl₂ have been reported previously, *e.g.*, [(PPh₃)₂Rh-(CO)₂]·2CH₂Cl₂,[15] in which the possibility of bonding between one of the Cl atoms of the CH₂Cl₂ molecule and a carbonyl group seemed probable. For the β isomer, no contacts less than 3.5 Å were found between either Cl atom and a CO group. The shortest distance between Br and a hydrogen atom in a computed position on methylene chloride

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Table III. Principal Bond Angles (deg)[a]

	α isomer	β isomer
Br–Mn–P1	85.0 (3)	89.9 (2)
Br–Mn–P2	90.4 (3)	85.3 (2)
Br–Mn–C1	90 (1)	91.5 (8)
Br–Mn–C2	178 (2)	177.4 (7)
Br–Mn–C3	87 (2)	86.6 (7)
P1–Mn–P2	83.9 (4)	83.9 (3)
P1–Mn–C1	92 (2)	94.4 (8)
P1–Mn–C2	96 (2)	91.6 (7)
P1–Mn–C3	171 (2)	176.2 (7)
P2–Mn–C1	176 (2)	176.3 (8)
P2–Mn–C2	92 (2)	92.7 (7)
P2–Mn–C3	93 (2)	94.2 (7)
C1–Mn–C2	89 (2)	91 (1)
C1–Mn–C3	91 (2)	87 (1)
C2–Mn–C3	92 (2)	92 (1)
Mn–C1–O1	177 (3)	178 (2)
Mn–C2–O2	175 (4)	176 (2)
Mn–C3–O3	177 (4)	176 (2)
P3–Cr–C4	89 (2)	89.9 (9)
P3–Cr–C5	90 (1)	88.2 (8)
P3–Cr–C6	179 (1)	177.3 (9)
P3–Cr–C7	96 (1)	95.5 (9)
P3–Cr–C8	94 (2)	89.5 (7)
C4–Cr–C5	87 (2)	88 (1)
C4–Cr–C6	92 (2)	88 (1)
C4–Cr–C7	172 (2)	174 (1)
C4–Cr–C8	93 (2)	91 (1)
C5–Cr–C6	89 (2)	90 (1)
C5–Cr–C7	99 (2)	95 (1)
C5–Cr–C8	176 (2)	178 (1)
C6–Cr–C7	84 (2)	87 (1)
C6–Cr–C8	87 (2)	92 (1)
C7–Cr–C8	80 (2)	86 (1)
Mn–P1–C9	105 (1)	107.2 (7)
Mn–P1–C13	114 (1)	119.7 (7)
Mn–P1–C19	123 (1)	116.1 (7)
C9–P1–C13	106 (2)	103.4 (9)
C9–P1–C19	106 (2)	106.5 (10)
C13–P1–C19	101 (2)	102.6 (9)
Mn–P2–C25	119 (1)	122.5 (7)
C10–P2–C11	99 (2)	104.4 (9)
C10–P2–C25	104 (2)	105.1 (9)
C11–P2–C25	102 (2)	103.2 (9)
Mn–P2–C10	109 (1)	107.5 (6)
Mn–P2–C11	121 (1)	113.7 (7)
C12–P3–C31	105 (1)	103.8 (9)
C12–P3–C37	99 (2)	101.5 (9)
Cr–P3–C12	113 (1)	114.1 (7)
Cr–P3–C31	116 (1)	118.5 (7)
Cr–P3–C37	120 (1)	112.7 (7)
C31–P3–C37	101 (2)	104.3 (9)
Cr–C4–O4	172 (4)	174 (2)
Cr–C5–O5	172 (4)	176 (2)
Cr–C6–O6	175 (5)	179 (2)
Cr–C7–O7	170 (3)	178 (2)
Cr–C8–O8	175 (5)	174 (2)
Cl1–C43–Cl2		119 (2)

[a] The esd's shown in parentheses are right adjusted.

Table IV

	Distance, Å		Angle, deg	
	α	β	α	β
Ring 1 (C13–C18)	1.41	1.41	120	120
Ring 2 (C19–C24)	1.43	1.40	120	120
Ring 3 (C25–C30)	1.43	1.43	120	120
Ring 4 (C31–C36)	1.40	1.38	119	120
Ring 5 (C37–C42)	1.43	1.40	119	120
Av[a]	1.42 (3)	1.40 (2)	120 (2)	120 (1)

[a] Average values for bond distances and angles of the 10 phenyl rings in the α and β isomers.

(2.88 Å) is only slightly less than the sum of the van der Waals radii (3.15 Å).

In the α isomer, the plane around the Mn atom, defined

Table V[a]

	A	B	C	D	$\chi^{2\ c}$	σ^c
Ring 1:[b] C13 (0.003), C14 (0.008), C15 (0.003), C16 (−0.028), C17 (0.038), C18 (−0.024)	0.7646	0.0540	0.6422	3.5525	1.71	0.024
Ring 2: C19 (0.017), C20 (−0.005), C21 (−0.026), C22 (0.044), C23 (−0.030), C24 (−0.001)	0.2621	0.8789	−0.3992	6.2666	2.36	0.028
Ring 3: C25 (−0.064), C26 (0.022), C27 (0.035), C28 (−0.052), C29 (0.006), C30 (0.052)	−0.2001	−0.4092	0.8902	−3.2348	5.10	0.047
Ring 4: C31 (0.010), C32 (−0.001), C33 (−0.027), C34 (0.046), C35 (−0.030), C36 (0.002)	0.0561	0.9768	−0.2066	1.3130	2.67	0.028
Ring 5: C37 (0.034), C38 (0.040), C39 (−0.021), C40 (−0.005), C41 (0.108), C42 (0.008)	−0.1311	−0.1995	−0.9711	2.6294	2.21	0.026
Ring 6: C13 (−0.019), C14 (0.000), C15 (0.009), C16 (0.002), C17 (−0.020), C18 (0.029)	0.2111	0.8485	−0.4852	−2.0697	1.63	0.018
Ring 7: C19 (0.010), C20 (−0.023), C21 (0.015), C22 (0.007), C23 (−0.021), C24 (0.012)	0.9818	−0.1816	−0.0549	11.9104	1.38	0.018
Ring 8: C25 (0.002), C26 (0.012), C27 (−0.027), C28 (0.030), C29 (−0.018), C30 (0.002)	0.7127	−0.1908	0.6750	17.0927	1.75	0.021
Ring 9: C31 (−0.002), C32 (−0.006), C33 (0.008), C34 (−0.003), C35 (−0.005), C36 (0.007)	0.8418	0.0942	0.5315	22.9124	0.13	0.006
Ring 10: C37 (−0.016), C38 (−0.007), C39 (0.018), C40 (−0.006), C41 (−0.018), C42 (0.029)	−0.2298	−0.4380	0.8702	5.6974	1.09	0.019

[a] Equations of best least-squares planes in the form $Ax + By + Cz = D$ where x, y, z are coordinates in Å with deviations (Å) of atoms from the plane are given in parentheses. [b] α isomer, rings 1–5; β isomer, rings 6–10. [c] χ^2 is defined by $\Sigma d_i^2/\sigma_i^2$ where d_i is the deviation of the atom from the plane and σ_i is the atom's positional standard deviation.

by P1–P2–C3–C1, is almost coplanar with the P3–C7–C6–C4 plane around Cr and this no doubt arises from packing effects. In the β isomer these planes are not coplanar.

In both structures, the triphos ligand is linked to the Mn atom through two adjacent P atoms with the remaining P atom bonding to Cr. The difference between the two isomers is found to reside on P2 only. This difference can be more readily seen if one considers the position of the phenyl ring (C25–C30) and the Br atom relative to the Mn–P1–C9–C10–P2 plane (see Figure 4). In the α isomer the Br atom is trans to the phenyl ring while in the β isomer it lies cis to the phenyl ring.

Such isomerism is well documented in the case of the reactions of ethylenediamine and its derivatives with Co(III) and Cu(II) salts.[16] Recently, the reactions of metal complexes with bridging arsine ligands have also been shown to produce isomers of this type.[17,18] Reaction of the tertiary diphosphine PPh(Me)CH$_2$CH$_2$P(Me)Ph (meso or racemic form) with RuCl$_3$ also yields similar complexes.[19]

The conformation of the five-membered ring (Mn–P1–C9–C10–P2) would be expected to be influenced by the groups attached to the P atoms. An attempt was thus made to try to determine the factors responsible for the observed conformations.

An analysis of the chelate rings involving substituted ethylenediamine has shown that a series of energetically equivalent "minimum energy" conformations can exist.[15] These depend on, among other factors, the relative positions of the groups attached to the N atoms. This analysis has been extended to phosphine type ligands.[20] The results show that in all cases (using symmetrical bridging phosphine ligands), the conformation of the ring is largely determined by steric interaction of the phenyl rings on the phosphine phosphorus atoms. However, in the present work, this does not seem to be the only factor responsible for the conformational changes.

Using the P–Mn–P plane as the reference plane,[21] a comparison of the angles between the normal to this plane and the substituent attached to the P atoms, for both the α and β isomers, is shown in Figure 4. The α isomer can have either ring conformation depending on which enantiomer is chosen. Consider the λ conformation, as shown in Figure 4a; C9 and C10 are on opposite sides of, though not equidistant from, the P–Mn–P plane. Since the phenyl ring (C19–C24) is much bulkier than the methylene group (C11), it will move as far away as possible from the large Br atom. It does this by "buckling" the chelate ring, thus giving rise to the conformation observed. Although the C2–O2 group remains normal (within experimental error) to the P–Mn–P plane, the Br–Mn–P1 angle is less than 90°. The nonbonded interaction is thus relieved by distortion of the groups attached to the phosphorus atoms with concomitant distortion of the chelate ring.

In the β isomer, which has the λ conformation, atoms C9 and C10 are on opposite sides and are nonequidistant from the P–Mn–P plane (Figure 4b). The phenyl ring (C25–C30) tends to move as far away from the Br atom as possible, "buckling" the ring in the opposite direction, with the methylene group (C11) moving in toward C2–O2. The phenyl ring (C19–C24), on P1, is blocked from moving further away from the Br atom by interaction of ring C13–C18 with C2–O2. The C2–O2 group remains normal to the P–Mn–P plane but in this isomer the Br–Mn–P2 angle is reduced to less than 90°. The steric interaction is again relieved by the distortion of the chelate ring and the groups attached to the P atoms.

The structures of numerous tertiary phosphine and phosphite derivatives containing manganese carbonyl and chromium carbonyl moieties have been reported.[22-34] The

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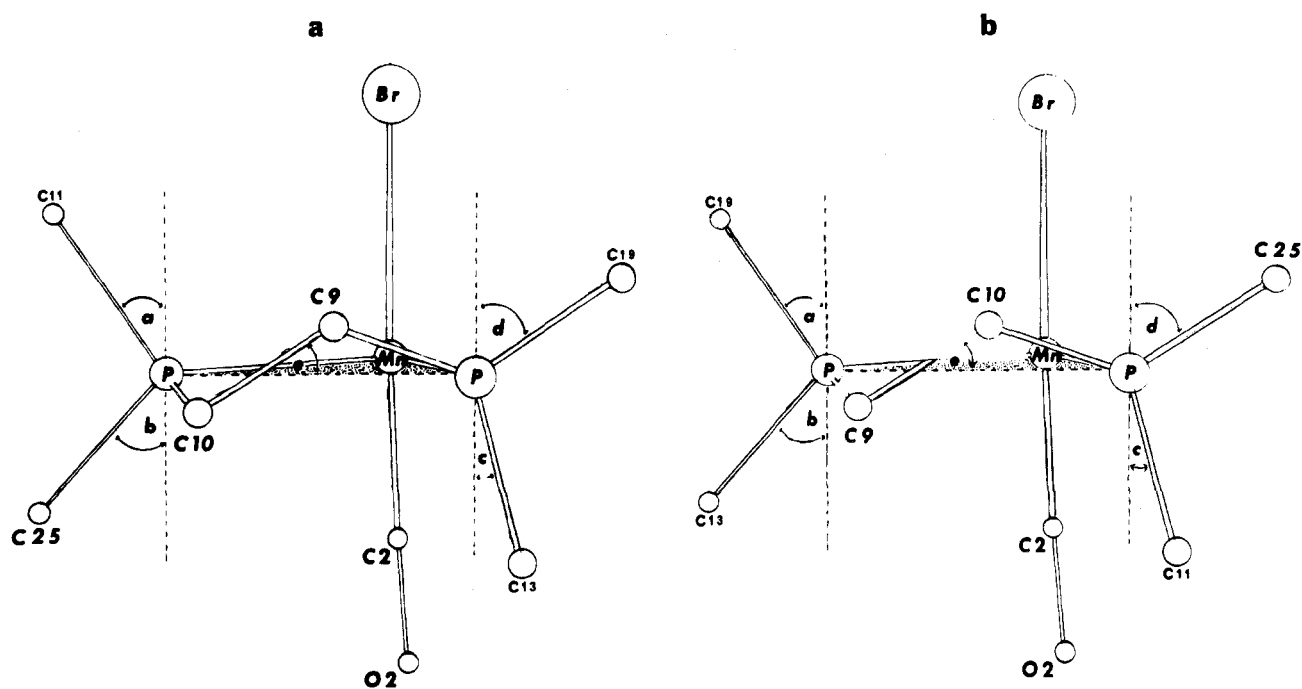
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a   **b**

Figure 4. Projection of the molecule showing the conformation of the chelate ring: (a) α isomer; (b) β isomer. The angles are in terms of the P–Mn–P plane.

Angle	α isomer		β isomer	
	Bond	Value, deg	Bond	Value, deg
a	P2–C11[a]	41	P1–C19	34
b	P2–C25	38	P1–C13	44
c	P1–C13	25	P2–C11	24
d	P1–C19	59	P2–C25	58
e[b]		28		31

[a] *E.g.*, *a* is the angle between the normal to the plane and the *bond* joining P with a carbon atom. [b] *e* is the angle between the P–Mn–P plane and the bond joining C9–C10.

present results for the various metal carbonyl bond lengths correlate well with those obtained previously. [The following discussion will be confined to the more accurately determined β isomer, unless otherwise stated.]

The Mn–C bond length with CO groups trans to the tertiary phosphines (1.86, 1.87 Å) are longer than the Mn–C bond length for the CO trans to Br (1.73 Å). A related but opposite effect should be observable[35] in the corresponding C–O bond lengths. Although the trend in the CO bond lengths is in the right direction, the effect is small.

Mention of the structure determination of Mn(CO)₅Br has been made,[36] but as yet no results have been published. Mn–Br bond lengths have been reported for the complexes Mn(CO)₄(C=C=PPh₃)Br (2.507 (8) Å)[37a] and Mn(CO)₃-(CNCH₃)₂Br (2.537 (2) Å)[37b] and are similar to the values found in this work (2.534 (4) Å) (for the α isomer, 2.537

(8) Å). The Mn–Br bond length reported for the Br-bridged complex [Mn(CO)₄Br]₂ is 2.526 (5) Å.[38]

Bond length data are available for the Cr–P bond in Cr-(CO)₅PPh₃ (2.442 (1) Å) and Cr(CO)₅P(OPh)₃ (2.309 (1) Å).[24] If the phosphine ligand attached to Cr in the β isomer is regarded as a PEtPh₂ type ligand, comparisons with these other Cr–P bond lengths can be made. Since the PEtPh₂ type ligand is not as good a π-bonding ligand as P(OPh)₃, but is thought to be a better σ-donating ligand than PPh₃, a Cr–PEtPh₂ bond length intermediate between the Cr–P-(OPh)₃ and Cr–PPh₃ bond lengths is expected. Indeed, the value obtained (2.376 (7) Å) lies between these two values.

According to current σ-π-bonding theory, as the CO groups in Cr(CO)₆ are replaced by phosphines, the remaining CO groups become more strongly bound to the Cr atom. So, replacement of two CO's is more difficult to achieve than replacement of one CO group. Since structural parameters for Cr(CO)₄diphos[33] and Cr(CO)₃(PNP)[23] (PNP = [PPh₂-CH₂CH₂]₂NEt) are available, it is possible to draw some tentative conclusions concerning the effect of the substitution of more than one CO group in a metal carbonyl by the same ligand, *viz.*, PEtPh₂. The average Cr–C bond length (trans to phosphine), for instance, in Cr(CO)₄diphos (1.83 (1) Å) is apparently slightly *longer* than the equivalent bond length in the β isomer (1.77 (3) Å) being considered here, contrary to what is expected. This result must be due to some special effect of the chelate ring which causes a bond strengthening in the Cr–C bonds strongly suggesting that

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CO substitution reactions of metal carbonyls containing chelating phosphines (*e.g.*, diphos) will depend on both steric and *electronic* effects.

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Crystal and Molecular Structure of μ-Hydroxo-μ-di(p-tolyl)phosphido-hexacarbonyldiiron, Fe₂(CO)₆[P(p-C₆H₄CH₃)₂]OH

P. M. TREICHEL,* W. K. DEAN, and J. C. CALABRESE

An X-ray crystal structure determination has shown that the compound previously characterized as Fe₂(CO)₆[P(p-C₆H₄-CH₃)₂]H, and as containing a bridging hydride ligand, is in fact Fe₂(CO)₆[P(p-C₆H₄CH₃)₂]OH, having a bridging hydroxide ligand. The compound crystallizes in the monoclinic space group C2/c with eight molecules in a unit cell with dimensions a = 10.534 (6) Å, b = 17.231 (8) Å, c = 23.810 (15) Å, and β = 100.72 (5)°. Full-matrix isotropic–anisotropic least-squares refinement of 1219 independent counter data yielded a final unweighted R factor of 4.6%. The molecular configuration of approximate Cₛ-m symmetry consists of two Fe(CO)₃ units linked by bridging bis(p-tolyl)phosphido and hydroxide groups and by an iron–iron bond. The properties and structural features of this molecule are discussed and compared with those of other related complexes.

Introduction

Studies of reactions of various secondary phosphines with metal carbonyls have recently been reported[1-4] by several groups including ours. With some variation in chosen reaction conditions a number of different products have been isolated. For example, the room temperature reaction of several phosphines PR₂H (R = CH₃, C₂H₅, C₆H₅, p-C₆H₄CH₃) and Fe₂(CO)₉ gave three complexes: yellow solid or liquid Fe(CO)₄PR₂H, always the primary product under these conditions, and two solid yellow to orange complexes in yields generally under 10%. The first of these latter species belonged to the well-known group of complexes having the general formula Fe₂(CO)₆(PR₂)₂[1,2,4,5] and as such were not of particular interest. The second complex was initially characterized by analyses as having the formula Fe₂(CO)₆(PR₂)H. Infrared data (ν_CO) suggested that the overall geometry of these species was similar to the Fe₂(CO)₆(PR₂)₂ complexes, and the pmr spectrum showed a high-field peak in the range τ 12.20–12.60 which was consistent with the bridging hydride formulation, although this value was a little lower than might have been expected.

Many metal carbonyl complexes containing bridging hydrides are known, of course, so another compound with this functionality would not be considered unusual. However, this particular type of complex was of significance from another point of view, namely that it could have provided unique information with respect to an interesting controversy concerning the bonding in these species.[6] The question has been posed as to whether one should view a metal–hydrogen–metal linkage as having only a three-center two-electron bridging bond, or whether it has such a linkage in addition to a formal metal–metal bond. A satisfactory answer to the question of which bonding representation best fits these systems has not been obtained unequivocally from bond length data alone.

Whereas earlier examples of complexes with bridging hydride ligands were of such a nature that the M–H–M unit and the M–M bond (if present) were required to lie in one plane, this would not necessarily have been the case with a complex Fe₂(CO)₆(PR₂)H. If the structure of such a species conformed to the structures of other Fe₂(CO)₆X₂ species (wherein X represents a bridging group such as PR₂[7]) then the planes for the Fe–H–Fe unit and for a *bent* Fe–Fe bond would not be coincident. By virtue of this fact, there would be present unambiguous evidence for the existence of both Fe–H–Fe and Fe–Fe bonds. This would in turn allow assessment of the structural parameters (bond lengths and bond angles) for the Fe–H–Fe unit in this structure which need not be qualified for lack of the knowledge of the correct bonding representation.

If, on the other hand, there was no Fe–Fe bond (a postulate which seemed unlikely considering the electron count), then

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