The Crystal and Molecular Structure of [1,2-Bis-(diphenylphosphino)ethane]-tetracarbonylchromium

BY M. J. BENNETT, F. A. COTTON AND M. D. LAPRADE

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, *U.S.A.*

[1,2-Bis(diphenylphosphino)ethane]tetracarbonylchromium, $Cr(CO)_4(diphos)$, where diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, prepared by the reaction of diphos with $Cr(CO)_6$ crystallizes in the orthorhombic system with unit-cell dimensions, at $24 \pm 1\,°C$, of $a = 16·73 \pm 0·06$, $b = 14·56 \pm 0·04$, $c = 22·32 \pm 0·06$ Å. Cell dimensions at $2 \pm 2\,°C$ are: $a = 16·663 \pm 0·009$, $b = 14·519 \pm 0·006$, $c = 22·277 \pm 0·009$ Å. There are eight molecules per unit cell; d_{calc} $(24°) = 1·374$ g.cm⁻³, $d_{obs} = 1·371$ g.cm⁻³. Systematic absences uniquely identify the space group as *Pbca*. Using nickel-filtered Cu $K\alpha$ radiation, 2707 independent reflections within the sphere bounded by $\sin \theta/\lambda = 0·550$ were collected using an automated counter diffractometer operated at $2 \pm 2\,°C$. Using the 2163 reflections whose intensities were deemed much greater than zero, the structure was solved by conventional Patterson and electron density functions and was refined by full-matrix least-squares procedures to final unweighted and weighted residuals of 0·066 and 0·075, respectively. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure comprises $Cr(CO)_4(diphos)$ molecules in which each chromium atom is surrounded by a distorted octahedral array of two *cis* phosphorus atoms and four carbon atoms. The Cr–P distances are equal at $2·360 \pm 0·002$ Å and the P–Cr–P angle is $83·41 \pm 0·08°$. The Cr–C bonds *trans* to Cr–P bonds have a mean length of $1·831 \pm 0·007$ Å, while the other two Cr–C bonds have a mean length of $1·884 \pm 0·007$ Å. All Cr–C–O groups are slightly but significantly bent, the angles being in the range $176·9 \pm 0·8$ to $177·8 \pm 0·8°$. The C–O bond lengths range from $1·141 \pm 0·012$ to $1·165 \pm 0·012$ Å. The molecular structure is qualitatively consistent with views on metal-to-ligand π bonding previously deduced from vibrational spectra.

Introduction

It is generally believed that metal-to-carbon monoxide bonding includes both a C → M dative σ component and an M → CO dative π component, the two components reinforcing each other in a synergic manner (Cotton & Wilkinson, 1966). The π component is thought to be comparable in strength to the σ one in most MCO systems. For ligands employing a group V atom as the donor, a similar synergic form of σ plus π bonding has also been postulated, though there has been controversy as to the importance of the π component (Plastas, Stewart & Grim, 1969; Mather & Pidcock, 1970; Keiter & Verkade, 1969). It is generally conceded that except for a few species such as PF_3, where highly electronegative groups are attached to phosphorus, ligands of the type PX_3 make a considerably smaller demand for metal $d\pi$ electrons than do those of $d\pi$ the CO group. The best evidence for this comes from the observed trends in Co stretching frequencies when the CO group is placed in competition with a PX_3 group or other ligand (Cotton, 1964; Horrocks & Taylor, 1963). Compounds derived from group VI carbonyls by replacement of one or more CO groups with other ligands are especially convenient for examining relative π-accepting tendencies, because of the occurrence of three mutually perpendicular ligand-metal-ligand axes.

A case of particular interest is the *cis*-$M(CO)_4L_2$-type complex. Here, two CO groups compete with L groups for both metal $d\pi$ orbitals with which they can interact as π acceptors and also two CO groups which compete mainly with each other for $d\pi$ electrons. The formation of stable *cis*-$M(CO)_4L_2$ compounds is especially favored when the L_2 groups are combined in a chelating bidentate ligand; indeed, such compounds afford virtually the only practical possibilities for crystallographic study. For this reason, the compound $Cr(CO)_4$ (diphos), where diphos represents $(C_6H_5)_2PCH_2CH_2P$ $(C_6H_5)_2$, was chosen. Previous studies of the infrared spectrum had shown that the *trans* and *cis* CO groups differed measurably in their π interaction with the CR atom, the former having a stretching-force constant *ca.* 0·8 md.Å⁻¹ less than the latter (Cotton, 1964). This suggests that the CO groups *trans* to phosphorus atoms have weaker C–O bonds and stronger Cr–C bonds. In the study reported here, we sought evidence of a structural nature to substantiate this conclusion.

Experimental

Single crystals of 1,2-bis(diphenylphosphino)ethanetetracarbonylchromium prepared by a literature method (Chatt & Watson, 1961) were examined by Weissenberg and precession photography and found to be orthorhombic. The systematic absences $h \neq 2n$ on $hk0$, $k \neq 2n$ on $0kl$, and $l \neq 2n$ on $h0l$ uniquely identify the space group as *Pbca*. At room temperature, unit-cell dimensions as determined from various 2θ settings on the diffractometer are $a = 16·73 + 0·06$, $b = 14·56 \pm 0·04$,

$c = 22 \cdot 32 \pm 0 \cdot 06$ Å. Unit-cell constants at 2°C are $a = 16 \cdot 663 \pm 0 \cdot 009$, $b = 14 \cdot 519 \pm 0 \cdot 006$, $c = 22 \cdot 277 \pm 0 \cdot 009$ Å. The quoted uncertainty intervals are estimates of precision. Density was $1 \cdot 371 \pm 0 \cdot 005$ g.cm^{-3} as measured by flotation in aqueous potassium iodide solution; assuming eight molecules per unit cell, a density of $1 \cdot 374$ g.cm^{-3} was calculated. Thus, the entire molecule constitutes the asymmetric unit.

Intensities were collected at 2 ± 2 °C using a crystal that was approximately a rectangular parallelepiped of dimensions $0 \cdot 10 \times 0 \cdot 10 \times 0 \cdot 30$ mm. The crystal was aligned on a General Electric XRD-6 full-circle automatic diffractometer with its b^* axis coincident with the φ axis of the goniometer. The entire apparatus, except for counting and control circuitry, was operated in a cold room. Cu X radiation filtered by nickel foil was used to measure 2707 independent reflections within the sphere $\sin \theta / \lambda = 0 \cdot 550$.

The integrated intensities (I) were obtained from the total counts (P) of a coupled 2θ–ω scan and stationary background measurements (B_1, B_2) at the limits of each scan. Assuming that the background varies linearly (or gives an equivalent integrated total)

through the scan range, $I = P - B_1 - B_2$. Intensities were such that coincidence losses were negligible.

Solution and refinement of the structure

As the intensities were converted to values of $|F_o|^2$ and $|F_o|$ on a relative scale, 538 reflections had either $I \leq 0$ or $I \leq 3\sigma(I)$ where $\sigma(I) = (P + B_1 + B_2)^{\frac{1}{2}}$. Only the remaining 2163 reflections were used in solving and refining the structure.* The Cr and P atoms were located in a three-dimensional Patterson map. A three-dimensional electron-density difference synthesis, using

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* Computer programs used in this study were (a) D. P. Shoemaker, *MIXG2*, which calculates diffractometer settings; (b) W. G. Sly, D. P. Shoemaker & J. H. van den Hende, *MIFR2A*, Fourier summation for initial Patterson and Fourier maps; (c) W. C. Hamilton, *GONO9*, used for the absorption correction; (d) C. T. Prewitt, *SFLS3* and *SFLS5*, least-squares refinement of parameters minimizing $\Sigma(w||F_o| - |F_c||^2)$; (e) A. Zalkin, *FORDAP*, Fourier summation for final difference Fourier; (f) F. A. Kundell, J. M. Stewart & R. V. Chastain, *BONDLA*, which calculates distances, angles and e.s.d.'s; (g) R. C. Elder, *PUBTAB*, which prepares compact tabulation of structure factors.

Table 1. *Final atomic positional and thermal parameters*

x, y and z are fractional coordinates. B_{ij} are in Å^2. Numbers in parentheses are the e.s.d.'s occurring in the last digit listed.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0·49425 (8)	0·10957 (9)	0·37819 (6)	3·30 (6)	2·68 (5)	3·20 (6)	−0·15 (6)	0·18 (6)	0·14 (5)
P(1)	0·53794 (13)	0·26359 (14)	0·38517 (9)	3·20 (10)	2·53 (9)	3·12 (10)	−0·23 (8)	0·03 (9)	−0·05 (8)
P(2)	0·54511 (14)	0·12080 (15)	0·27943 (10)	3·74 (11)	3·05 (10)	2·99 (9)	0·02 (10)	0·19 (9)	−0·40 (9)
C(1)	0·5979 (6)	0·0706 (6)	0·4008 (4)	5·1 (6)	2·0 (4)	3·4 (4)	0·2 (4)	0·4 (4)	−0·6 (3)
O(1)	0·6612 (4)	0·0502 (5)	0·4152 (3)	4·0 (4)	5·5 (4)	8·2 (5)	0·9 (3)	−0·2 (4)	0·8 (4)
C(2)	0·4647 (5)	0·1059 (6)	0·4573 (4)	3·4 (4)	3·2 (4)	4·0 (5)	0·3 (4)	0·1 (4)	1·2 (4)
O(2)	0·4476 (4)	0·0998 (4)	0·5076 (3)	4·9 (3)	5·7 (4)	3·7 (3)	1·0 (3)	0·9 (3)	1·4 (3)
C(3)	0·3934 (6)	0·1551 (6)	0·3546 (4)	3·7 (5)	3·1 (4)	3·2 (4)	−0·8 (4)	−0·1 (4)	−0·1 (3)
O(3)	0·3306 (4)	0·1802 (5)	0·3411 (3)	3·9 (4)	5·5 (4)	5·8 (4)	0·7 (3)	−1·0 (3)	−0·5 (3)
C(4)	0·4576 (5)	−0·0088 (7)	0·3704 (4)	3·9 (5)	3·5 (5)	4·8 (5)	0·0 (4)	−0·1 (4)	0·0 (4)
O(4)	0·4317 (4)	−0·0829 (4)	0·3650 (3)	6·0 (4)	3·5 (3)	8·2 (5)	−1·1 (3)	0·0 (3)	−0·3 (3)
C(5)	0·5640 (6)	0·3054 (6)	0·3083 (4)	6·0 (6)	3·0 (4)	3·0 (4)	−0·2 (4)	1·5 (4)	0·1 (3)
C(6)	0·6088 (5)	0·2260 (5)	0·2750 (4)	5·0 (5)	2·5 (4)	3·7 (4)	−1·5 (4)	2·0 (4)	−0·9 (4)
C(11)	0·4737 (5)	0·3553 (5)	0·4144 (3)	3·2 (4)	2·4 (4)	2·8 (4)	0·4 (3)	−0·1 (3)	−0·1 (3)
C(12)	0·4940 (6)	0·4472 (6)	0·4072 (4)	4·3 (5)	4·0 (5)	5·2 (5)	0·1 (4)	0·8 (4)	0·8 (4)
C(13)	0·4480 (7)	0·5143 (6)	0·4340 (5)	7·3 (7)	2·2 (4)	6·7 (6)	1·4 (5)	0·4 (6)	0·7 (4)
C(14)	0·3808 (7)	0·4926 (7)	0·4658 (5)	5·6 (6)	4·4 (6)	5·6 (6)	2·2 (5)	1·3 (5)	−0·4 (5)
C(15)	0·3592 (6)	0·4027 (7)	0·4729 (4)	5·1 (5)	4·0 (5)	4·6 (5)	0·5 (4)	1·9 (4)	0·6 (4)
C(16)	0·4059 (5)	0·3327 (6)	0·4472 (4)	4·4 (5)	2·5 (4)	4·5 (5)	0·0 (4)	0·7 (4)	−0·6 (4)
C(21)	0·6273 (5)	0·2844 (6)	0·4308 (4)	3·0 (4)	2·6 (4)	4·5 (5)	0·1 (3)	−0·2 (4)	−0·6 (4)
C(22)	0·6257 (5)	0·2542 (7)	0·4899 (4)	4·1 (5)	4·5 (5)	5·0 (5)	−0·5 (4)	−0·9 (4)	0·1 (4)
C(23)	0·6904 (7)	0·2728 (7)	0·5288 (5)	7·6 (7)	4·9 (6)	5·6 (6)	1·0 (6)	−3·7 (6)	−0·1 (5)
C(24)	0·7547 (7)	0·3197 (7)	0·5068 (6)	4·4 (6)	3·6 (6)	10·2 (9)	1·1 (5)	−2·6 (7)	−1·3 (6)
C(25)	0·7592 (6)	0·3495 (7)	0·4493 (6)	2·9 (5)	4·4 (6)	11·3 (9)	0·0 (4)	−1·0 (6)	−0·7 (6)
C(26)	0·6957 (6)	0·3297 (6)	0·4108 (5)	3·7 (5)	3·0 (5)	7·1 (6)	0·1 (4)	0·9 (5)	−0·7 (4)
C(31)	0·6126 (5)	0·0331 (6)	0·2495 (4)	3·4 (4)	3·7 (4)	2·8 (4)	−0·4 (4)	0·2 (4)	−0·4 (3)
C(32)	0·6628 (6)	0·0527 (7)	0·2025 (4)	5·6 (6)	4·3 (5)	4·4 (5)	0·2 (5)	1·1 (4)	−0·1 (4)
C(33)	0·7151 (6)	−0·0137 (8)	0·1794 (4)	5·7 (6)	5·6 (6)	5·0 (5)	−0·2 (5)	2·1 (5)	−0·2 (5)
C(34)	0·7175 (6)	−0·0999 (8)	0·2052 (4)	4·9 (6)	5·5 (6)	5·1 (5)	1·3 (5)	0·9 (4)	−1·0 (5)
C(35)	0·6681 (6)	−0·1209 (7)	0·2517 (5)	6·5 (7)	4·5 (5)	6·5 (6)	1·0 (5)	0·5 (5)	−0·7 (5)
C(36)	0·6161 (6)	−0·0539 (6)	0·2751 (4)	4·1 (5)	4·1 (5)	5·4 (5)	0·1 (4)	2·0 (4)	−0·2 (4)
C(41)	0·4706 (5)	0·1345 (6)	0·2197 (4)	3·7 (5)	3·4 (4)	3·0 (4)	0·6 (4)	−0·1 (4)	−0·7 (3)
C(42)	0·4754 (6)	0·1995 (7)	0·1741 (4)	6·1 (6)	5·3 (5)	4·0 (5)	1·0 (5)	0·0 (4)	0·2 (4)
C(43)	0·4140 (7)	0·2061 (8)	0·1321 (4)	7·4 (7)	7·5 (7)	3·1 (5)	2·7 (6)	−0·2 (5)	1·5 (5)
C(44)	0·3491 (7)	0·1499 (10)	0·1342 (5)	6·0 (7)	9·0 (8)	4·3 (6)	2·2 (6)	−1·2 (6)	−1·3 (6)
C(45)	0·3428 (6)	0·0848 (7)	0·1787 (5)	5·1 (6)	5·9 (6)	4·4 (5)	0·6 (5)	−0·5 (5)	−2·3 (5)
C(46)	0·4038 (6)	0·0772 (6)	0·2215 (4)	5·1 (6)	3·7 (5)	3·2 (4)	0·7 (4)	−0·8 (4)	−0·5 (4)

structure factors with phases calculated from the chromium and phosphorus positions only, gave the coordinates of other non-hydrogen atoms.

All non-hydrogen atoms were refined by full-matrix least-squares methods to a conventional R index of $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.103$. Scattering factors were those of Cromer & Waber (1965). The data were then corrected for absorption ($\mu = 50.45$ cm^{-1}). Phenyl-hydrogen atoms were fixed at positions 1.00 Å beyond the carbon atoms, along lines directed from the phenyl ring centers through the carbon atoms; each hydrogen atom was assigned an isotropic temperature factor 1.1 times that of the carbon atom to which it was attached. Scattering factors for hydrogen atoms were those determined experimentally by Mason & Robertson (1966). The other atoms were refined with anisotropic temperature factors of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Anomalous dispersion corrections (Cromer, 1965) for chromium and phosphorus were included in the calculated structure factors. Core space in the computer was limited. Consequently, the inclusion of anisotropic temperature factors forced further refinement to be done in sections, with cycles in which parameters for C(11)–C(26) were held constant, alternating with cycles in which parameters for C(31)–C(46) were held constant. Weights $w = \sigma^{-1/2}$ where $\sigma = \text{LP}^{-1}(P + B_1 + B_2)^{1/2}/2F_o$ (LP = the Lorentz and polarization corrections), were assigned. This weighting scheme gave no significant variation of $w(\Delta F)^2$ as a function of F_o or sin θ/λ.

The refinement was considered complete when, in one cycle, no parameter changed by as much as $\frac{1}{5}$ its estimated standard deviation. After the final cycle of refinement, $R_1 = 0.066$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.075$. In the final electron-density differ-ence map the standard deviation in the electron density (Cruickshank, 1949) was 0.074 e.Å^{-3}. The highest peak in the difference map was in the vicinity of the Cr and contained 0.32 e.Å^{-3}. The final standard deviation of an observation of unit weight was 1.335, indicating a slight underestimation in the standard deviations. Of the 538 F_{calc} values corresponding to reflections not included in the refinement, 44 were found to lie between 1.5 F_{min} and 2.0 F_{min}, where F_{min} is the small-est F_{obs} included in the refinement, and 4 were be-tween 2.0 F_{min} and 2.5 F_{min}. None was higher than 2.5 F_{min}.

Results

Final atomic positional parameters and anisotropic thermal parameters are given in Table 1. The molecular structure, viewed down [100], is displayed in Fig. 1. Fig. 1 defines the numbering scheme used in the Tables. Table 2 lists bonding distances; e.s.d.'s include all parameter correlations greater than 0.25. Table 3 gives bond angles. The e.s.d. on averages listed in Tables 2 and 3 are root-mean-square deviations. Table 4 lists all nonbonded contacts less than 2.90 Å. Calcu-lated and observed structure factors are given in Table 5.

Table 2. *Bond distances* (Å)

Cr—P(1)	2.357 (2)	C(11)–C(12)	1.386 (12)
Cr—P(2)	2.363 (3)	C(12)–C(13)	1.376 (14)
Cr—C(1)	1.886 (10)	C(13)–C(14)	1.361 (15)
Cr—C(3)	1.881 (10)	C(14)–C(15)	1.364 (14)
Cr—C(2)	1.830 (9)	C(15)–C(16)	1.402 (13)
Cr—C(4)	1.832 (10)	C(16)–C(11)	1.385 (12)
C(1)–O(1)	1.141 (12)	C(21)–C(22)	1.388 (13)
C(3)–O(3)	1.148 (11)	C(22)–C(23)	1.410 (15)
C(2)–O(2)	1.161 (11)	C(23)–C(24)	1.361 (10)
C(4)–O(4)	1.165 (12)	C(24)–C(25)	1.355 (20)
P(1)–C(11)	1.828 (8)	C(25)–C(26)	1.392 (16)
P(1)–C(21)	1.829 (9)	C(26)–C(21)	1.389 (12)
P(1)–C(5)	1.869 (9)	C(31)–C(32)	1.370 (13)
P(2)–C(6)	1.863 (9)	C(32)–C(33)	1.398 (14)
P(2)–C(31)	1.826 (9)	C(33)–C(34)	1.378 (15)
P(2)–C(41)	1.830 (8)	C(34)–C(35)	1.358 (15)
C(5)–C(6)	1.559 (12)	C(35)–C(36)	1.403 (14)
		C(36)–C(31)	1.387 (13)
		C(41)–C(42)	1.391 (13)
		C(42)–C(43)	1.389 (15)
		C(43)–C(44)	1.356 (18)
		C(44)–C(45)	1.375 (16)
		C(45)–C(46)	1.398 (14)
		C(46)–C(41)	1.390 (12)
		Average	1.382 (15)

Discussion

The structure of Cr(CO)$_4$(diphos) is qualitatively as expected, with the phosphorus atoms of the diphos ligand, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$, occupying *cis* posi-tions in the octahedron about the chromium atom. The five-membered chelate ring is puckered in the manner typical of such rings, with C(5) and C(6) lying on opposite sides of the plane defined by the P(1)–Cr–P(2) atoms.
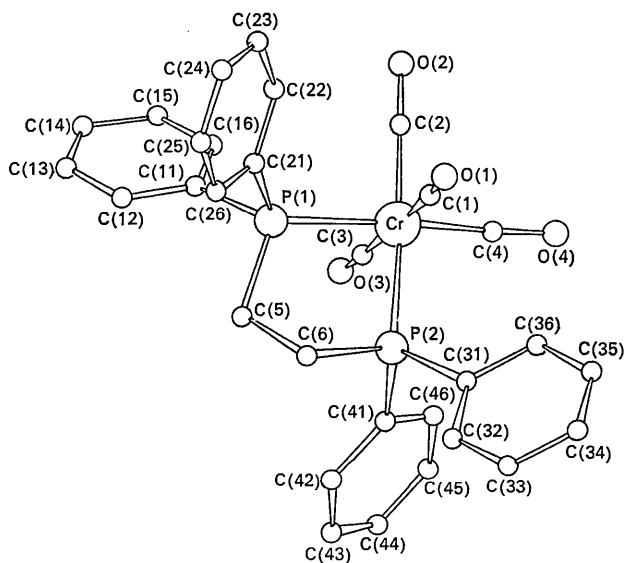

Fig. 1. The Cr(CO)$_4$(diphos) molecule viewed in the [100] direction. The atom numbering scheme used in the Tables is shown.

Table 3. *Bond angles* (°)

P(1)-Cr—P(2)	83·41 (8)	C(11)-P(1)—C(21)	99·1 (4)	C(11)-C(12)-C(13)	119·7 (8)
C(1)-Cr—P(1)	89·1 (3)	C(11)-P(1)—C(5)	103·1 (4)	C(12)-C(13)-C(14)	121·4 (9)
C(1)-Cr—P(2)	86·6 (3)	C(21)-P(1)—C(5)	105·5 (4)	C(13)-C(14)-C(15)	120·0 (9)
C(1)-Cr—C(2)	88·9 (4)	Cr—P(1)—C(11)	122·3 (3)	C(14)-C(15)-C(16)	119·9 (9)
C(1)-Cr—C(3)	176·7 (4)	Cr—P(1)—C(21)	116·4 (3)	C(15)-C(16)-C(11)	119·8 (8)
C(1)-Cr—C(4)	92·9 (4)	Cr—P(1)—C(5)	108·6 (3)	C(16)-C(11)-C(12)	119·3 (7)
C(2)-Cr—P(1)	92·7 (3)	C(31)-P(2)—C(41)	103·2 (4)	C(21)-C(22)-C(23)	120·5 (9)
C(2)-Cr—P(2)	174·1 (2)	C(31)-P(2)—C(6)	101·7 (4)	C(22)-C(23)-C(24)	118·4 (1·0)
C(2)-Cr—C(3)	92·2 (4)	C(41)-P(2)—C(6)	105·0 (4)	C(23)-C(24)-C(25)	123·0 (1·1)
C(2)-Cr—C(4)	88·6 (4)	Cr—P(2)—C(31)	120·9 (3)	C(24)-C(25)-C(26)	118·3 (1·0)
C(3)-Cr—P(1)	87·8 (3)	Cr—P(2)—C(41)	116·2 (3)	C(25)-C(26)-C(21)	121·6 (1·0)
C(3)-Cr—P(2)	92·1 (3)	Cr—P(2)—C(6)	108·1 (3)	C(26)-C(21)-C(22)	118·0 (8)
C(3)-Cr—C(4)	90·3 (4)	P(1)—C(5)—C(6)	107·9 (5)	C(31)-C(32)-C(33)	121·2 (9)
C(4)-Cr—P(1)	177·7 (5)	C(5)—C(6)—P(2)	108·0 (6)	C(32)-C(33)-C(34)	119·4 (9)
C(4)-Cr—P(2)	95·5 (3)			C(33)-C(34)-C(35)	120·4 (1·0)
Cr—C(1)-O(1)	177·6 (8)	P(1)—C(11)-C(12)	121·1 (6)	C(34)-C(35)-C(36)	120·1 (9)
Cr—C(2)-O(2)	176·9 (8)	P(1)—C(11)-C(16)	119·5 (6)	C(35)-C(36)-C(31)	120·3 (9)
Cr—C(3)-O(3)	177·7 (8)	P(1)—C(21)-C(22)	117·4 (6)	C(36)-C(31)-C(32)	118·6 (8)
Cr—C(4)-O(4)	177·8 (8)	P(1)—C(21)-C(26)	124·6 (7)	C(41)-C(42)-C(43)	119·8 (9)
		P(2)—C(31)-C(32)	120·7 (7)	C(42)-C(43)-C(44)	121·5 (1·0)
		P(2)—C(31)-C(36)	120·7 (7)	C(43)-C(44)-C(45)	120·0 (1·1)
		P(2)—C(41)-C(46)	117·2 (6)	C(44)-C(45)-C(46)	119·4 (1·0)
		P(2)—C(41)-C(42)	124·5 (7)	C(45)-C(46)-C(41)	121·1 (8)
				C(46)-C(41)-C(42)	118·3 (8)
				Average	120·0 (9)

Table 4. *Close nonbonded contacts*

Atom 1	Atom 2	Atom 2 location	Distance (Å)
H(24)	H(16)	$x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$	2·11
H(15)	H(44)	$x , -y+\frac{1}{2}, z+\frac{1}{2}$	2·47
O(1)	H(25)	$-x+\frac{3}{2}, y-\frac{1}{2}, z$	2·51
C(2)	C(4)	x , y , z	2·56
H(36)	C(4)	x , y , z	2·58
C(1)	C(2)	x , y , z	2·60
C(3)	C(4)	x , y , z	2·63
H(14)	C(24)	$-x+1, -y+1, -z+1$	2·65
H(25)	O(2)	$x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$	2·65
C(2)	C(3)	x , y , z	2·67
C(1)	C(4)	x , y , z	2·69
H(16)	C(24)	$x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$	2·76
H(14)	C(23)	$-x+1, -y+1, -z+1$	2·77
C(11)	C(21)	x , y , z	2·78
H(14)	C(25)	$-x+1, -y+1, -z+1$	2·80
C(31)	C(41)	x , y , z	2·87

Ligand-metal-ligand angles differ in varying degrees from the ideal octahedral angle of 90°. The most pronounced deviation, presumably attributable to the constraints inherent in the chelate ring, is found in the P(1)–Cr–P(2) angle, which has the value 83·4°. Comparable effects have been found in the related species Cr(CO)₃ (dien) (Cotton & Richardson, 1966) and in Cr(CO)₃[(C₆H₅)₂PCH₂–CH₂N(C₂H₅)CH₂CH₂P(C₆H₅)₂] (Cotton & LaPrade, 1969). The opposite C(2)–Cr–C(4) angle (88·6°) is more nearly regular and the remaining C–Cr–C angles are all in the range 88·9 to 92·9°.

Structural parameters show variations consistent with generally accepted notions about metal-ligand π interactions in such compounds (Cotton & Wilkinson, 1966). Relative values of various bond distances are all qualitatively as would be expected, though quantitative correlations might be more difficult to formulate.

The π-accepting ability (π acidity) of the phosphorus atoms in alkyl and aryl phosphines is much less than that of CO, but more than that of amine nitrogen; the latter has essentially nil π acidity because of the absence of empty valence shell π orbitals. Infrared evidence supporting these statements has been presented (Cotton, 1964; Horrocks & Taylor, 1963). The parameters of this structure provide independent support. Thus, the Cr–C bonds *cis* to Cr–P bonds should be longer than those *trans*, since the *cis* CO groups are mainly competing with each other for metal $d\pi$ electrons, while those *trans* are mainly competing with the inferior π acidity of the phosphorus atoms. The mean Cr–C(*cis*) bond length is 1·884 (7) Å; the Cr–C (*trans*) bonds have a mean length of 1·831 (7) Å. A difference in CO distances, such that $d_{CO}(cis)/d_{CO}(trans) < 1$, should be directly correlated with this difference in the two types of Cr–C distance. Though the difference cannot be considered significant, the mean $d_{CO}(cis)$ and d_{CO} (*trans*) values, 1·145(8) and 1·163(8) Å, do not disobey this inequality. For reasons discussed previously (Cotton & Wing, 1965), the CO bond lengths are expected to show much smaller variations than the corresponding M–C distances.

The mean of all Cr–C distances in Cr(CO)₄ (diphos), 1·86 A, is greater than that in Cr(CO)₃(dien), 1·82 Å, but less than that in Cr(CO)₆, 1·91 Å, reflecting the intermediate π acidity of the phosphorus atoms of diphos.

The mean Cr–P distance, 2·36 Å, exceeds the mean Cr–N distance in Cr(CO)₃(dien), 2·19 Å, by only 0·17 Å, whereas the P and N atoms differ in their normal covalent radii by 0·36 Å. This can be attributed, at least in part, to the effect of a Cr($d\pi$)–P($d\pi$) bonding component which has no counterpart in the Cr–N bonds. However, it is also possible that some of this shortening may be due to high s character in the orbital used by phosphorus to form the Cr–P bond. Both free phosphines and coordinated ones generally have

C–P–C angles much less than the tetrahedral value, whereas amines have angles much closer to 109°. This means that for a coordinated amine, R_3NM, the s and p character of the orbital used for the N–M bond will be much the same as in the orbitals used for the N–C bonds, and the latter can justifiably be used to form an estimate of the N bond radius in the direction of the N–M bond. With phosphines, however, the P–C bonds

Table 5. *Calculated and observed structure factors, in units of one tenth of an electron*

must be assumed to have greater than the tetrahedral proportion of p character; hence, the lone pair or P–M orbital must have a larger share of s character. Since the s and p orbitals of the phosphorus atom have distinctly different radii (Coulson & Gianturco, 1968) with the s orbital smaller by a value on the order of perhaps 0·3 Å, there will be an apparent shortening of the P–M bond, if the length of the latter is predicted directly from a 'radius' derived from the P–C bonds themselves.

In Cr(CO)$_4$(diphos), the Cr–P–C angles have an average value of 115°, so an effect of the kind just described is to be expected. We do not, however, consider it worthwhile to attempt a quantitative estimate of its magnitude, because of the marked irregularity of the set of C–P–C angles, which range from 122 to 108°.

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A Refinement of the Crystal Structure of Bis(triphenylphosphine)(ethylene)nickel

BY P.-T. CHENG, C. D. COOK, CHUNG HOE KOO,* S. C. NYBURG AND M. T. SHIOMI

Lash Miller Chemical Laboratories, University of Toronto, Toronto 181, Ontario, Canada

Dreissig & Dietrich (*Acta Cryst.* (1968). B24, 108) published the result of a crystal structure determination of bis(triphenylphosphine) (ethylene) nickel at a time when the authors' analysis was unrefined. The fully refined results are reported. The transformation from Dreissig & Dietrich's triclinic axes is given and normal probability plot analyses used to compare the estimated standard deviations of the two sets of atomic parameters. These analyses indicate that the e.s.d.'s of Dreissig & Dietrich's parameters are about three times as large as the present e.s.d.'s.

Some time ago we published a short note on the unrefined X-ray crystal-structure analysis of bis(triphenylphosphine)(ethylene)nickel. (Cook, Koo, Nyburg & Shiomi, 1967). We gave the approximate atomic geometry for the nickel environment and stated that the ethylene-carbon atoms were not coplanar with the P(1)–Ni–P(2) plane; they were twisted by about 12°.

While the data were being refined, another structure analysis was published independently by Dreissig & Dietrich (1968), (hereafter D & D). This analysis, although more refined than ours at that time, involved fewer intensity measurements (2112 observed as against 4050) and although the authors did not give the angle of twist of ethylene from the P(1)–Ni–P(2) plane, their listed coordinates give a twist of 8·4°.

* Present address: Dept. of Chemistry, College of Liberal Arts & Science, Seoul National University, Korea.

The triclinic axial system used by us was different from that used by D & D and, because our cell dimensions were unrefined, did not give quite the same cell volume. This has led to the identity of the two substances being questioned (McGinnety & Mays, 1968). As we now show, the substances are certainly identical.

Refinement

The cell dimensions were carefully remeasured by calibrating Weissenberg photographs at 25 °C with aluminum wire. Parameters are given in the first column of Table 1. The transformation to the axes used by D & D is **b**, **a**+**c**, −**a**. This transformation yields the parameters given in the second column of Table 1, which are compared with those given by D & D in the third column. There are some significant discrepancies but not sufficient to throw any doubt on the identity