far side of the Yb(1)-$(SiO_4)_4$ plane. The shortest O(2)-Cl distance is 3.165 Å. Only the O(5) oxygen atoms are completely separated from the chlorines; one of these gives the shortest Yb-O bond: Yb(1)-$O(1)_5$, 2.19 Å.

Registry No. $Yb_3(SiO_4)_2Cl$, 37291-26-2.

Acknowledgment. Support of the U. S. Atomic Energy Commission [Contract AT(11-1)-716] is acknowledged gratefully.

Contribution No. 1977 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Group VI Metal Carbonyl Phosphine Complexes. Hydrogen-Deuterium Exchange and the Crystal Structure of *cis*-Tetracarbonyldiphosphinechromium(0)

L. J. GUGGENBERGER, U. KLABUNDE,* and R. A. SCHUNN

Received September 27, 1972

Convenient, large-scale syntheses of the phosphine complexes $Cr(CO)_5PH_3$, *cis*-$M(CO)_4(PH_3)_2$, and *fac*-$M(CO)_3(PH_3)_3$ (M = Cr, Mo, W) are described and results of hydrogen-exchange experiments of some of these complexes are presented. The crystal and molecular structures of *cis*-$Cr(CO)_4(PH_3)_2$ were determined from counter data. Crystals are orthorhombic, space group $Pna2_1$, with cell dimensions of $a = 12.677$ (9), $b = 11.415$ (9), and $c = 6.759$ (6) Å. The structure was refined to a conventional R of 0.050 for 621 observed reflections. The molecular structure has an octahedrally coordinated (within 1.5°) chromium atom with two cis equatorial PH_3 ligands (Cr–P = 2.349 (2) Å), two equatorial CO ligands (Cr–C = 1.847 (4) Å, C–O = 1.162 (6) Å), and two axial CO ligands (Cr–C = 1.914 (7) Å, C–O = 1.11 (3) Å). The structural parameters are consistent with related structures and current σ–π bonding schemes.

Introduction

Phosphine complexes of chromium, molybdenum, and tungsten were among the first examples of transition metal phosphine complexes characterized.[1,2] Examples of group VI phosphine complexes include $Cr(CO)_{6-x}(PH_3)_x$ (x = 1,[1,3] 2,[2,4] 3,[5] 4[6]), $Mo(CO)_{6-x}(PH_3)_x$ (x = 1,[1,3] 2,[2,4,6] 3[7]), and $W(CO)_{6-x}(PH_3)_x$ (x = 1,[1,3] 2[2,4]).

We report here the synthesis and characterization of the new complex *fac*-$W(CO)_3(PH_3)_3$, convenient, large-scale syntheses of $Cr(CO)_5PH_3$, *cis*-$M(CO)_4(PH_3)_2$, and *fac*-$M(CO)_3(PH_3)_3$ (M = Cr, Mo), and hydrogen-exchange experiments with some of these complexes. We report also the crystal and molecular structure of *cis*-$Cr(CO)_4(PH_3)_2$; structural parameters are compared with other chromium-carbonyl complexes with phosphorus-containing ligands.[8-14]

Experimental Section

Phosphine, PH_3, is a highly toxic, spontaneously flammable gas. At low pressure, its reaction with oxygen is violent. The off-gases from a reaction mixture should be burned.

Commercially available phosphine (Matheson) contains traces of hydrogen and *biphosphine, P_2H_4, a highly toxic and spontaneously flammable liquid.* The biphosphine was removed by passing the gas through a trap at −78°.

All procedures were carried out under nitrogen in either a nitrogen drybox or equipment modified with nitrogen inlet tubes. Prior to use solvents were either distilled from CaH_2 or passed over Linde 4A molecular sieves under nitrogen.

$Cr(CO)_5PH_3$. Phosphine was bubbled slowly through a solution of 56.0 g (0.16 mol) of $[(C_2H_5)_4N][CrCl(CO)_5]$[15] in 300 ml of methanol at 0° for 2 hr. Part of the methanol was removed under reduced pressure and the solution was cooled. The pale yellow crystals of $Cr(CO)_5PH_3$ which formed were collected on a filter. The crystals, which contained 5–10% $Cr(CO)_4(PH_3)_2$ as an impurity, were dissolved in 150 ml of tetrahydrofuran and to this solution 19 g of 2,4-pentanedione and 0.5 g of NaOH in 40 ml of water were added. The solution was stirred for 1 hr at 25° and was filtered to remove a yellow solid,[16] and 100 ml of water was added to the filtrate. After part of the solvent was removed under reduced pressure, pale yellow crystals of pure $Cr(CO)_5PH_3$ were collected and sublimed at 1 μ (65°). The yield of $Cr(CO)_5PH_3$ was 26.7 g (74%). *Anal.* Calcd for $C_5H_3CrO_5P$: C, 26.4; H, 1.3; Cr, 22.9; O, 35.2; P, 14.1. Found: C, 26.9; H, 1.9; Cr, 22.4; O, 36.0; P, 13.4.

***cis*-$Cr(CO)_4(PH_3)_2$.** An 800-ml stainless steel pressure autoclave was charged with 49.3 g (0.134 mol) of $Cr(CO)_4DTO$[17] (DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane), 450 ml of tetrahydrofuran, and 25 g (0.74 mol) of phosphine.

The autoclave was heated to 65° and kept at this temperature for 8 hr. After cooling to 25°, the autoclave was vented and twice purged with nitrogen to ensure complete removal of the phosphine. The solution was transferred in air to a 1000-ml round-bottom flask and the solvent was removed under reduced pressure. The yellow crystals were collected, washed with petroleum ether, and dissolved in 500 ml of hot diethyl ether. The solution was filtered through Celite. After removal of about 400 ml of the ether under reduced pressure, 27.0 g (89% yield) of $Cr(CO)_4(PH_3)_2$ was collected on a filter and dried at 25° (0.1 mm, 16 hr). *Anal.* Calcd for $C_5H_6CrO_4P_2$: C, 20.7; H, 2.6; Cr, 22.4; O, 27.6; P, 26.7. Found: C, 20.7; H, 2.8; Cr, 22.0; O, 27.1; P, 27.2.

***cis*-$Mo(CO)_4(PH_3)_2$.** The above procedure was used with 67.0 g

---

[1] E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 7, 136 (1968).

[2] (a) F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.*, 90, 3296 (1968); (b) F. Klanberg, U. S. Patent 3,695,853 (1972).

[3] E. O. Fischer, E. Louis, W. Bathelt, and J. Muller, *Chem. Ber.*, 102, 2547 (1969).

[4] E. O. Fischer, E. Louis, and W. Bathelt, *J. Organometal. Chem.*, 20, 147 (1969).

[5] E. O. Fischer, E. Louis, and C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, 8, 377 (1969).

[6] E. O. Fischer and E. Louis, *J. Organometal. Chem.*, 18, P26 (1969).

[7] C. G. Barlow and G. C. Holywell, *J. Organometal. Chem.*, 16, 439 (1969).

[8] M. J. Bennett, F. A. Cotton, and M. D. LaPrade, *Acta Crystallogr., Sect. B*, 27, 1899 (1971).

[9] G. Huttner and S. Schelle, *J. Organometal. Chem.*, 19, P9 (1969).

[10] G. Huttner and S. Schelle, *J. Cryst. Mol. Struct.*, 1, 69 (1971).

[11] O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, 1274 (1969).

[12] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 11, 161 (1972).

[13] H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, 91, 4326 (1969).

[14] F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 91, 7000 (1969).

[15] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).

[16] This solid is the complex $Cr(CO)_4[PH_2C(CH_3)(OH)]_2CH_3]$; U. Klabunde, U. S. Patent 3,702,336 (1972).

[17] G. R. Dobson, *Inorg. Chem.*, 8, 90 (1969).

(0.157 mol) of $Mo(CO)_4DTO$,[17] 30 g (0.9 mol) of phosphine, and 400 ml of tetrahydrofuran. The crude product was recrystallized from diethyl ether–petroleum ether and then sublimed under vacuum; yield 15 g. The ^1H nmr spectrum showed the crystals to be a mixture of 80% $Mo(CO)_4(PH_3)_2$ and 20% $Mo(CO)_5PH_3$.[18]

***cis*-$W(CO)_4(PH_3)_2$.** The above procedure was used with 60 g (0.12 mol) of $W(CO)_4DTO$,[17] 30 g (0.91 mol) of phosphine, and 400 ml of tetrahydrofuran. After removal of part of the tetrahydrofuran, the slurry was extracted with water and the crude product was collected on a filter. This off-white solid was recrystallized from diethyl ether–heptane; yield 15 g. The ^1H nmr spectrum showed it to be a mixture of 78% $W(CO)_4(PH_3)_2$ and 22% $W(CO)_5(PH_3)$.[18]

***fac*-$Cr(CO)_3(PH_3)_3$.** Phosphine was bubbled through a yellow slurry of 6.8 g (0.0262 mol) of $Cr(CO)_3(CH_3CN)_3$[19] in 120 ml of tetrahydrofuran at 0° for 15 min and then at 25° for 0.5 hr to give a dark yellow solution. The solution was filtered, the filtrate was concentrated to *ca.* 50 ml (rotary evaporator), and 100 ml of *n*-heptane was added. Additional concentration to *ca.* 75 ml gave yellow crystals which were collected and washed with *n*-heptane. The crude product was purified by dissolution in 150 ml of benzene and precipitated by addition of 400 ml of *n*-hexane to the yellow extract. The yellow crystalline precipitate was collected, washed with *n*-hexane, and dried at 25° (0.1 μ, 16 hr) to give 2.6 g of *fac*-$Cr(CO)_3(PH_3)_3$, dec pt 130°. *Anal.* Calcd for $C_3H_9CrO_3P_3$: C, 15.1; H, 3.8; Cr, 21.9; O, 20.2; P, 39.0. Found: C, 15.3; H, 3.7; Cr, 21.2; O, 20.4; P, 39.7.

Concentration of the filtrate to *ca.* 75 ml followed by addition of 200 ml of *n*-hexane precipitated an additional 1.1 g with identical melting point and infrared spectrum for a total yield of 3.7 g (60%).

***fac*-$Mo(CO)_3(PH_3)_3$.** The molybdenum compound was made in 64% yield by a procedure analogous to that used for chromium complex. *Anal.* Calcd for $C_3H_9MoO_3P_3$: C, 12.8; H, 3.2; Mo, 34.1; O, 17.0; P, 32.8. Found: C, 13.0; H, 3.2; Mo, 33.8; O, 17.1; P, 33.8.

***fac*-$W(CO)_3(PH_3)_3$.** A 400-ml stainless steel bomb was charged with 5.0 g (0.0128 mol) of $W(CO)_3(CH_3CN)_3$[19] and 100 ml of tetrahydrofuran. The bomb was closed, cooled to −78°, and evacuated and 15.0 g (0.44 mol) of PH_3 was condensed therein under pressure. The bomb was closed and agitated at 50° for 12 hr. After the excess pressure was vented, the bomb was flushed with nitrogen and the pale blue slurry was discharged and filtered in a nitrogen atmosphere. The yellow filtrate was mixed with 100 ml of *n*-heptane and the mixture was concentrated (rotary evaporator) to *ca.* 100 ml. After addition of 100 ml of *n*-heptane and concentration of the mixture, a pale green crystalline solid was collected. Additional purification from benzene–heptane and then tetrahydrofuran–heptane utilizing the rotary evaporator gave, after drying at 25° (0.1 μ, 16 hr), 2.4 g of pale yellow crystalline *fac*-$W(CO)_3(PH_3)_3$, dec pt 150°. *Anal.* Calcd for $C_3H_9O_3P_3W$: C, 9.7; H, 2.5; P, 25.1. Found: C, 10.0; H, 2.5; P, 24.9.

The solid compound decomposes in air over a period of weeks; solutions decompose in several hours. It is moderately soluble in benzene, tetrahydrofuran, and chloroform, very slightly soluble in hexane, and insoluble in diethyl ether.

The infrared spectrum (Nujol) shows ν_{PH} at 2364 (sh) and 2283 (s) cm^{-1}, ν_{CO} at 1934 (s) and 1815 (vs) cm^{-1}, and δ_{PH} at 1028 (s) and 1004 (s) cm^{-1}; solutions show ν_{CO} at 1950 (w), 1898 (w) cm^{-1} (hexane) and 1961 (s), 1873 (vs) cm^{-1} ($CHCl_3$). The ^1H nmr spectrum (C_6D_6) shows the PH_3 resonances centered at τ 7.08 as a doublet of complex multiplets similar to those observed for the chromium and molybdenum complexes[20] with a splitting of 349 Hz between the strongest lines and *ca.* 11 Hz between the lines of the multiplets. The weakest lines of the multiplets were not observed because of the low solubility of the complex.

$Cr(CO)_5PD_3$. A 10-ml benzene solution containing 2.2 g (10 mmol) of $Cr(CO)_5PH_3$ was chromatographed on a 12 × 3 cm column filled with 60 g of acid-washed Merck alumina which had been deactivated with 8% D_2O. The complex was eluted with 40 ml of heptane, followed by 60 ml of benzene. After removal of the solvent under reduced pressure, the infrared spectrum of the residual $Cr(CO)_5PD_3$ showed that total exchange had occurred.

The *cis*-$Cr(CO)_4(PD_3)_2$ and *fac*-$Cr(CO)_3(PD_3)_3$ compounds were prepared by an analogous procedure. Some infrared spectral data of the deuterated complexes and of the starting compounds are given in Table I.

Table I. Infrared P–H(D) Frequencies of $Cr(CO)_{6-x}(PH_3 \text{ or } PD_3)_x$[a]

Compd	Freq, cm^{-1}	
	$\nu_{PH,PD}$[b]	$\delta_{PH,PD}$[b]
$Cr(CO)_5PH_3$	2380 m	1015 s
$Cr(CO)_5PD_3$	1720 m	745 s
cis-$Cr(CO)_4(PH_3)_2$	2350 m	1010 s
		1000 s
cis-$Cr(CO)_4(PD_3)_2$	1705 m	750 s, sh
		740 s
fac-$Cr(CO)_3(PH_3)_3$	2340 m	1030 s
		1010 s
fac-$Cr(CO)_3(PD_3)_3$	1690 m	738 s
		760 w, sh
		750 w, sh

[a] Nujol mull; Perkin-Elmer 137. [b] The frequency shifts due to deuteration are similar to those observed for the corresponding mono and bis molybdenum complexes.[7]

Table II. Line Widths (Hz) at Half-Height of a PH_3 Nmr Resonance Line as a Function of Added Ethylamine

Complex	Microliters of 0.4 *M* ethylamine					
	0	1	2	5	10	25
$Cr(CO)_5PH_3$[a]	0.7	4	Broad			
cis-$Cr(CO)_4(PH_3)_2$[b]	0.8	1.5	3	6		Broad
fac-$Cr(CO)_3(PH_3)_3$[c]	1	2	3	4.5		~8
cis-$Mo(CO)_4(PH_3)_2$[b]	0.7		0.9		1.5	~6
cis-$W(CO)_4(PH_3)_2$[b,d]	0.8		1	~5	Broad	

[a] 0.6 *M*. [b] 0.3 *M*. [c] 0.2 *M*. [d] $[C_2H_5NH_2] = 4$ *M*.

Proton Exchange. Small increments of a 0.4 *M* solution of ethylamine in tetrahydrofuran–methanol (2:1) were added from a microsyringe to serum capped nmr tubes containing 0.6 ml of a solution of the complexes in the tetrahydrofuran–methanol solvent mixture. The original half-width of the phosphine ^1H nmr resonance lines could be restored by the addition of a methanolic solution of hydrogen chloride. The half line widths of the strongest low-field line are tabulated in Table II.

X-Ray Data and Structure Solution for *cis*-$Cr(CO)_4(PH_3)_2$. Crystals of *cis*-diphosphinetetracarbonylchromium are orthorhombic with cell parameters of $a = 12.677$ (9), $b = 11.415$ (9), and $c = 6.759$ (6) Å. These data resulted from averages of precession, Weissenberg, and diffractometer measured values. The calculated density for four molecules per cell is 1.58 g/cm^3; crystals are nearly suspended in CCl_4 ($\rho = 1.59$ g/cm^3). The systematic absences observed on films are $0kl$, $k + l = 2n + 1$, and $h0l$, $h = 2n + 1$. The possible space groups are $Pna2_1$ and $Pnam$ (nonstandard setting for $Pnma$). The correct space group as determined by the refinement is the noncentric group $Pna2_1$. All atoms are in general space group positions;[21] *i.e.*, there is no imposed molecular point symmetry.

An irregularly shaped crystal of approximate dimensions 0.08 × 0.23 × 0.28 mm was used for the data collection. The crystal was mounted on a Picker four-circle automatic diffractometer with the b axis along the diffractometer ϕ axis. About 690 reflections were measured out to 45° 2θ using the θ–2θ scan technique with Zr-filtered Mo radiation (λ 0.7107 Å). The scan range used was 2° (1°/min rate) plus the $K\alpha_1$–$K\alpha_2$ separation. Backgrounds were measured for 20 sec before and after each scan.

The Lorentz and polarization corrections were made in the usual way. The data were corrected for absorption effects using the program ACACA.[22] The linear absorption coefficient for Mo $K\alpha$ radiation is 15.1 cm^{-1}. The crystal was defined by six plane faces for the absorption correction. The minimum and maximum calculated transmission factors were 0.48 and 0.78. The error due to absorption is estimated to be less than 4% in F_o based on the measurement of some equivalent reflections. Structure factors with $F_o < \sigma(F_o)$ were considered "unobserved."[23]

The structure solution was begun in the centric space group

---

(18) The mixture can be separated by chromatography on alumina.[4]

(19) D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, **1**, 433 (1962).

(20) E. Moser, E. O. Fischer, W. Bathelt, W. Gretner, L. Knauss, and E. Louis, *J. Organometal. Chem.*, **19**, 377 (1969).

(21) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 119.

(22) Computer programs used, in addition to local programs, were Prewitt's absorption correction program ACACA and least-squares program SFLS5, the Busing–Levy error function program, ORFFE, and the Johnson plotting program, ORTEP.

(23) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

Table III. Positional Parameters for *cis*-$Cr(CO)_4(PH_3)_2$ [a]

Atom	*x*	*y*	*z*
Cr	0.36507 (10)	0.57247 (19)	0.25
P(1)	0.4662 (2)	0.2819 (4)	0.2610 (4)
P(2)	0.2685 (3)	0.4358 (6)	0.0941 (3)
O(1)	0.5213 (9)	0.7432 (24)	0.0805 (9)
O(2)	0.4914 (9)	0.7496 (24)	0.4470 (8)
O(3)	0.2343 (6)	0.9433 (10)	0.2425 (10)
O(4)	0.2134 (9)	0.4023 (15)	0.4315 (8)
C(1)	0.4652 (11)	0.6820 (21)	0.1417 (12)
C(2)	0.4406 (12)	0.6805 (25)	0.3722 (11)
C(3)	0.2837 (8)	0.7998 (14)	0.2465 (12)
C(4)	0.2706 (10)	0.4615 (19)	0.3621 (11)
H(1)	0.5616	0.3194	0.3258
H(2)	0.4933	0.2177	0.1438
H(3)	0.4060	0.1292	0.3181
H(4)	0.4123	0.1248	0.1993
H(5)	0.4807	0.2265	0.3813
H(6)	0.5680	0.3150	0.2070
H(7)	0.2051	0.5868	0.0401
H(8)	0.2008	0.2807	0.1379
H(9)	0.3405	0.3542	0.0090
H(10)	0.2925	0.2277	0.0845
H(11)	0.2968	0.5338	−0.0133
H(12)	0.1571	0.4603	0.1156

[a] Estimated errors for the least significant digits are given in parentheses here and in other tables. The hydrogen atom positions are calculated positions with two sets of three each for both phosphorus atoms (see text).

Pnam. The zero moment statistical test[24] was not definitive with respect to the presence or absence of a center of symmetry. The chromium atom position was found from a Patterson synthesis. The *R* factor ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.40 with the chromium atom only in the model. Attempts were made to add the remaining atoms to the model in several steps, but the best agreement obtained in the space group *Pnam* was an *R* of 0.18.

The structure solution was started again in the space group $Pna2_1$ and proceeded in a straightforward fashion using heavy-atom techniques. The *R* factors for all nonhydrogen atoms in the model with isotropic thermal parameters were 0.065 for *R* and 0.068 for R_w, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The *R* values after several cycles of anisotropic refinement were 0.050 for *R* and 0.049 for R_w.

Electron density difference planes were examined normal to the Cr–P bonds for possible hydrogen atom positions. The indication was that for both phosphorus atoms there were several conformations present. In both cases, the best interpretation seemed to be for two preferred conformations rotated 60° with respect to the Cr–P direction. Accordingly, two sets of hydrogen atoms (three per set) with 0.5 multiplicity were included for each phosphorus atom at calculated positions based on a P–H distance of 1.44 Å.[25] The hydrogen atoms were assigned isotropic thermal parameters of 5.0 $Å^2$ and their positions were not varied. The final *R* values for 621 observed reflections were 0.049 for both *R* and R_w. The *R* values for all the data were 0.060 for *R* and 0.052 for R_w. The standard deviation of an observation of unit weight is 1.35. In a purely statistical sense,[26] the inclusion of the hydrogen atoms in the model is not warranted; we are, however, listing the positions here since there was some indication for them and they allow us to estimate contacts involving the hydrogen atoms. The inclusion, or lack of inclusion, does not influence any of the nonhydrogen atom stereochemical data for this molecule.

Atom form factors[27] for the neutral atoms were used. The chromium and phosphorus atoms were corrected for the real and imaginary parts of the anomalous scattering effect.[28]

The final positional parameters are given in Table III and the final thermal parameters in Table IV. A list of observed and calculated structure factors (×10) is available.[29] Six strong reflections were given zero weight in the final refinements because they appeared to be affected slightly by secondary extinction; each is identified by an *E* in the structure factor table.

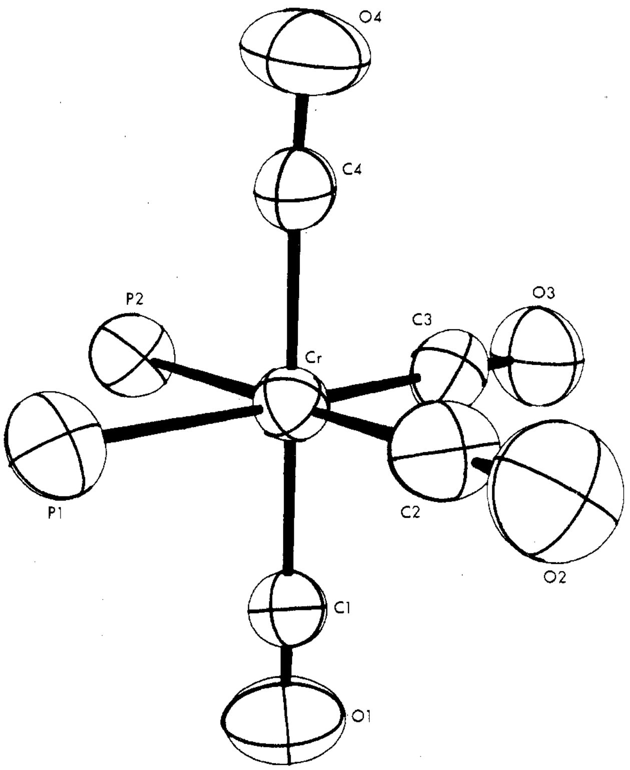

Figure 1. The molecular structure of *cis*-$Cr(CO)_4(PH_3)_2$ (hydrogen atoms omitted).

Discussion

The crystal structure of *cis*-diphosphinetetracarbonylchromium(0) consists of the packing of discrete molecules separated by normal van der Waals contacts. A view of the molecule illustrating the numbering system used here is shown in Figure 1. The thermal ellipsoids are plotted at the 50% probability level. The rms atomic vibrational amplitudes are listed in Table V. The vibrational amplitudes are normal for the types of atoms involved, *i.e.*, the chromium atom is nearly isotropic, and the oxygen atoms are the most anisotropic.

Sets of interatomic distances and angles are given in Tables VI and VII, respectively. These data were not corrected for thermal motion. The average distances in Table VI corrected for thermal motion according to the riding model[30] are 2.360 (2) Å for Cr–P, 1.920 (4) Å for Cr–C(1), 1.859 (4) Å for Cr–C(2), 1.173 (26) Å for C(1)–O(1), and 1.203 (6) Å for C(2)–O(2). The covariances were included in the error estimates in Tables VI and VII. The angles in particular demonstrate that the chromium atom geometry is close to octahedral; all angles subtended at the chromium atom are within 1.5° of the expected 90°. The molecule has no crystallographic symmetry but nearly has the idealized C_{2v} (2*mm*) point symmetry. Accordingly, the data in Tables VI and VII are averaged according to C_{2v} (2*mm*) symmetry (except for Cr–C–O angles, which are all averaged together).

---

(24) "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, p 357.

(25) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, S9s (1965).

(26) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

(27) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(28) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

(29) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1143.

(30) W. R. Busing and L. H. Levy, *Acta Crystallogr.*, 17, 142 (1964).

Table IV. Thermal Parameters ($\times 10^4$) for *cis*-$Cr(CO)_4(PH_3)_2$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	55.9 (10)	207.4 (32)	66.4 (12)	0.7 (16)	0.0 (13)	−6.2 (36)
P(1)	88 (2)	291 (7)	108 (3)	25 (3)	1 (4)	−8 (6)
P(2)	75 (3)	309 (10)	82 (3)	1 (5)	−12 (3)	−9 (5)
O(1)	121 (10)	467 (37)	146 (11)	−48 (16)	42 (10)	50 (18)
O(2)	121 (10)	569 (40)	106 (9)	−12 (19)	−39 (7)	−36 (16)
O(3)	113 (7)	280 (19)	165 (10)	54 (9)	6 (10)	9 (18)
O(4)	219 (9)	498 (34)	111 (10)	−54 (15)	44 (8)	26 (14)
C(1)	63 (10)	227 (35)	78 (10)	−7 (15)	3 (8)	−10 (14)
C(2)	83 (11)	364 (49)	75 (11)	−18 (19)	−13 (10)	9 (18)
C(3)	93 (8)	226 (23)	83 (9)	−13 (12)	−7 (11)	3 (20)
C(4)	85 (10)	230 (29)	79 (10)	−29 (15)	11 (9)	−22 (15)

[a] The thermal parameters are of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The hydrogen atoms were assigned fixed isotropic thermal parameters of 5.0 Å^2.

Table V. Root-Mean-Square Amplitudes of Vibration (Å) for *cis*-$Cr(CO)_4(PH_3)_2$

Atom	Min	Intermed	Max
Cr	0.207 (3)	0.213 (2)	0.222 (3)
P(1)	0.240 (4)	0.268 (5)	0.284 (4)
P(2)	0.218 (5)	0.258 (5)	0.270 (5)
O(1)	0.228 (16)	0.350 (13)	0.359 (13)
O(2)	0.224 (13)	0.341 (12)	0.367 (13)
O(3)	0.227 (9)	0.318 (13)	0.336 (13)
O(4)	0.216 (14)	0.331 (12)	0.371 (12)
C(1)	0.219 (15)	0.222 (19)	0.240 (16)
C(2)	0.213 (18)	0.259 (18)	0.298 (20)
C(3)	0.226 (12)	0.231 (13)	0.280 (14)
C(4)	0.208 (16)	0.224 (18)	0.284 (17)

Table VI. Selected Interatomic Distances (Å) for *cis*-$Cr(CO)_4(PH_3)_2$[a]

Bonding		Nonbonding	
Cr-P(1)	2.349 (3)	P(1)-P(2)	3.316 (5)
Cr-P(2)	2.349 (4)	P(1)-C(1)	3.028 (16)
Av	2.349 (2)	P(1)-C(2)	2.996 (17)
Cr-C(1)	1.921 (16)	P(1)-C(4)	2.992 (13)
Cr-C(4)	1.906 (13)	P(2)-C(1)	3.047 (15)
Av	1.914 (7)	P(2)-C(3)	3.019 (11)
		P(2)-C(4)	3.063 (13)
Cr-C(2)	1.843 (15)	C(1)-C(2)	2.650 (16)
Cr-C(3)	1.851 (10)	C(1)-C(3)	2.713 (18)
Av	1.847 (4)	C(2)-C(3)	2.582 (17)
C(1)-O(1)	1.080 (14)	C(2)-C(4)	2.617 (20)
C(4)-O(4)	1.146 (14)	C(3)-C(4)	2.646 (16)
Av	1.113 (33)		
C(2)-O(2)	1.168 (15)		
C(3)-O(3)	1.156 (10)		
Av	1.162 (6)		

[a] Here and in Table VII the errors of the mean are estimated according to $[\Sigma(d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the functions and mean function, respectively.

Dihedral angles between planes were calculated, but they merely reflect what is shown by the interatomic angles, namely, that the chromium coordination is nearly octahedral. The atom deviations from the best equatorial plane $(-0.6411X - 0.3948Y + 0.6581Z + 2.609 = 0)$ are −0.008 Å for Cr, 0.028 Å for P(1), −0.029 Å for P(2), 0.008 Å for C(2), −0.028 Å for O(2), 0.020 Å for C(3), and 0.010 Å for O(3). The equation of the plane illustrates its general orientation in the cell accounting for the fact that the space group is $Pna2_1$, rather than *Pnam*.

A stereoview of the crystal packing is shown in Figure 2. All intermolecular contacts were calculated and are normal. Although the hydrogen atoms were placed in calculated positions, the contacts with O(1) are interesting. There are three short intermolecular O(1)-H contacts (2.28, 2.64, and 2.67 Å). The 2.28-Å distance is particularly short and probably means that the assumed hydrogen atom position should be altered somewhat. However, the C(1)-O(1) distance is significantly shorter than C(4)-O(4) and intermolecular contacts may account for some part of this. The derived hydrogen positions (*vide supra*) were approximately symmetrical with respect to a vertical mirror plane through atoms C(1), O(1), Cr, C(4), and O(4), bisecting the phosphorus atoms. Physically, the interpretation would correspond to hydrogen atoms statistically distributed between two conformations rotated 60° with respect to the Cr-P direction and coupled in the sense that the second phosphine chooses the opposite conformation with respect to the vertical mirror plane to minimize intramolecular contacts.

Table VII. Selected Interatomic Angles (deg) for *cis*-$Cr(CO)_4(PH_3)_2$

P(1)-Cr-P(2)		89.8 (1)
P(1)-Cr-C(2)		90.4 (5)
P(2)-Cr-C(3)		91.1 (4)
	Av	90.8 (3)
C(2)-Cr-C(3)		88.7 (6)
C(1)-Cr-C(4)		177.5 (6)
P(1)-Cr-C(1)		89.8 (4)
P(1)-Cr-C(4)		88.7 (4)
P(2)-Cr-C(1)		90.5 (4)
P(2)-Cr-C(4)		91.5 (3)
	Av	90.1 (6)
C(2)-Cr-C(1)		89.5 (5)
C(2)-Cr-C(4)		88.5 (6)
C(3)-Cr-C(1)		91.9 (5)
C(3)-Cr-C(4)		89.5 (5)
	Av	89.9 (7)
Cr-C(1)-O(1)		179.8 (12)
Cr-C(2)-O(2)		177.6 (12)
Cr-C(3)-O(3)		178.6 (11)
Cr-C(4)-O(4)		177.2 (12)
	Av	178.3 (6)

The bond data found here are compared with data from similar compounds in Table VIII. The data in Table VIII have been systematized according to the type of distance and the nature of the trans atom(s) since these appear to be structurally important parameters with respect to metal-carbonyl bonding. The rationale for the subtle differences in bond lengths observed here also follows current metal-carbonyl bonding descriptions.[8,13,31,32] The Cr-P bond distances of 2.349 (2) Å are shorter than the "normal single" bond distance of 2.58 Å (assuming radii of 1.48 Å for Cr(0)[33] and 1.10 Å for P[34]) because of d_π-d_π bonding.

---

(31) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

(32) W. A. G. Graham, *Inorg. Chem.*, 7, 315 (1968).

(33) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 5, 1851 (1966).

(34) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

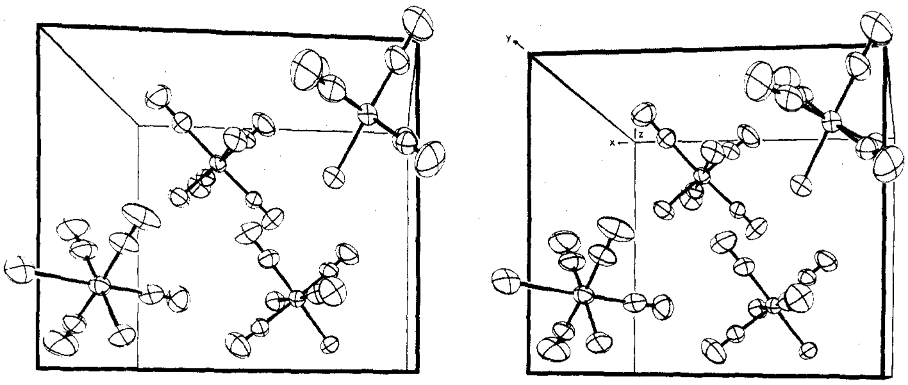

Figure 2. A stereoview of the crystal packing in $Cr(CO)_4(PH_3)_2$.

Table VIII. Comparison of Bond Distances for Octahedral $Cr(CO)_{6-n}(P)_n$ Complexes[a]

Complex	Cr-P		Cr-C		C-O		Ref
	P trans	CO trans	P trans	CO trans	P trans	CO trans	
cis-$Cr(CO)_4(PH_3)_2$		2.349 (2)	1.847 (4)	1.914 (7)	1.162 (6)	1.146 (14)[b]	This work
$Cr(CO)_4$(diphos)[c]		2.360 (3)	1.831 (7)	1.884 (7)	1.163 (8)	1.145 (8)	8
fac-$Cr(CO)_3(PH_3)_3$		2.346 (3)	1.84 (1)		1.16 (1)		9
cis-$Cr(CO)_2(PH_3)_4$	2.282 (4)	2.338 (4)	1.817 (7)		1.15 (1)		10
cis-$Cr(CO)_4[P(C_6H_5)_3][(CH_3O)CCH_3]$		2.42 (1)	1.85 (2)	1.88 (1)	1.16 (2)	1.16 (2)	11
trans-$Cr(CO)_4[P(OC_6H_5)_3]_2$	2.252 (1)			1.878 (3)		1.141 (5)	12
$Cr(CO)_5P(C_6H_5)_3$		2.422 (1)	1.845 (4)	1.880 (6)	1.154 (5)	1.147 (2)	13
$Cr(CO)_5P(C_6H_5O)_3$		2.309 (1)	1.861 (4)	1.896 (3)	1.136 (6)	1.130 (2)	13
$Cr(CO)_3$(PNP)[d]		2.381 (6)	1.827 (5)		1.165 (2)		14
$Cr(CO)_6$				1.909 (3)		1.137 (4)	35
Sum of covalent Radii	2.58	2.58					

[a] Where more than one distance is present the mean is taken and the error is estimated as in Table VI. [b] The C(1)-O(1) distance is not included. [c] diphos is the bidentate ligand $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [d] PNP is the tridentate ligand $[(C_6H_5)_2PCH_2CH_2N(CH_2CH_3)CH_2CH_2P(C_6H_5)_2]$.

The Cr-C bonds trans to the phosphines are preferentially shortened because of enhanced π bonding because CO is a better π acceptor than PH_3. Alternatively, the short Cr-P bond may arise because the sterically small PH_3 molecule is a good σ donor. The axial Cr-C distances (Cr-C(1) type) are close to 1.909 (3) Å found in $Cr(CO)_6$.[35]

Several specific structural comparisons between related complexes seem warranted. The overall differences between *cis*-$Cr(CO)_4(PH_3)_2$ and $Cr(CO)_4[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$ are consistent with PH_3 being a better π acceptor than the bidentate ligand. Another noteworthy comparison is between the *trans*-$Cr(CO)_4[P(OC_6H_5)_3]_2$, *cis*-$Cr(CO)_4(PH_3)_2$, and *cis*-$Cr(CO)_4P(C_6H_5)_3[CCH_3(OCH_3)]$ structures where the Cr-P distances are 2.252 (1), 2.349 (2), and 2.42 (1) Å, respectively (Table VIII). The phosphorus atoms in the phosphite complex are trans to each other, but we can estimate the cis value to be about 2.30 Å based on the trans data and the differences observed in the $Cr(CO)_2(PH_3)_4$ structure. Thus, the Cr-P distances for the related $P(OC_6H_5)_3$, PH_3, and $P(C_6H_5)_3$ complexes are ~2.30, 2.349 (2), and 2.42 (1) Å, respectively. This parallels the π-acceptor strength order for these ligands which is $P(OR)_3 > PH_3 > PR_3$.

The protons of the coordinated phosphine rapidly exchange with methanol in the presence of ethylamine. The relative exchange rates may be determined from the broadening of the phosphine ^1H nmr resonance lines; the rate is proportional to the line width at half-height. The line widths as a function of ethylamine concentration are summarized in Table II. The data qualitatively establish the following orders of proton-exchange rate: $Cr(CO)_5PH_3 >$ *cis*-$Cr(CO)_4(PH_3)_2 >$ *fac*-$Cr(CO)_3(PH_3)_3$ and *cis*-$Cr(CO)_4(PH_3)_2 >$ *cis*-$Mo(CO)_4(PH_3)_2 >$ *cis*-$W(CO)_4(PH_3)_2$.

The relative rates can be explained on the basis of the electron-withdrawing abilities of the moiety to which the phosphine is attached. Since the carbonyl ligand is assumed to be a better electron-withdrawing group (*i.e.*, a better π acceptor than phosphine), substitution of a carbonyl ligand by a phosphine ligand should lead to a decrease in the proton-exchange rate as observed for the chromium complexes. The relative rates for the cis complexes suggest that the electron-withdrawing ability of the $M(CO)_4$ moieties decreases in the order M = Cr > Mo > W.

Alternatively, stabilization of a probable intermediate, $M(CO)_{6-x}(PH_3)_{x-1}PH_2^-$,[36] might be important and the observed orders would then be a reflection of the stability of the intermediate.

There appears to be no correlation between the infrared PH stretching frequency and the exchange rate. Data in Table I show that the chromium complexes decrease with an increase in the phosphine substitution but the frequency of the cis complexes is constant at 2325 cm^{-1}.[38]

---

(35) A. Whitaker and J. W. Jeffery, *Acta Crystallogr.*, **23**, 977 (1967).

(36) The following mechanism appears to be reasonable

$$Cr(CO)_5PH_3 + B \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} Cr(CO)_5PH_2^- + BH^+$$

$$Cr(CO)_5PH_2^- + CH_3OH \overset{\text{fast}}{\rightleftharpoons} Cr(CO)_5PH_3 + CH_3O^-$$

$$CH_3O^- + BH^+ \overset{\text{fast}}{\rightleftharpoons} CH_3OH + B$$

An analogous molybdenum anion, $Mo(CO)_5PH_2^-$, has been isolated.[37]

(37) G. Becker and E. A. V. Ebsworth, *Angew. Chem., Int. Ed. Engl.*, **10**, 186 (1971).

(38) E. O. Fischer, E. Louis, W. Bathelt, E. Moses, and J. Muller, *J. Organometal. Chem.*, **14**, P9 (1968).

The PD_3 analog can be best prepared by chromatography on alumina deactivated with 8% D_2O; this method is preferential to several solution exchanges.

Registry No. $Cr(CO)_5PH_3$, 18116-53-5; $[(C_2H_5)_4N][CrCl(CO)_5]$, 14780-95-1; *cis*-$Cr(CO)_4(PH_3)_2$, 21676-58-4; $Cr(CO)_4DTO$, 21948-40-3; *cis*-$Mo(CO)_4(PH_3)_2$, 21676-59-5; *cis*-$W(CO)_4(PH_3)_2$, 21479-60-7; *fac*-$Cr(CO)_3(PH_3)_3$, 26068-81-5; $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; *fac*-$Mo(CO)_3(PH_3)_3$, 23623-68-9; *fac*-$W(CO)_3(PH_3)_3$, 38496-37-6; $Cr(CO)_5PD_3$, 38496-38-7; *cis*-$Cr(CO)_4(PD_3)_2$, 38496-39-8; *fac*-$Cr(CO)_3(PD_3)_3$, 38496-40-1.

Acknowledgment. We thank Mr. W. G. Peet for providing the crystals of *cis*-$Cr(CO)_4(PH_3)_2$, Professor S. O. Grim of the University of Maryland for communicating results prior to publication, and Drs. E. L. Muetterties and G. W. Parshall for helpful discussions.

Contribution from the Department of Chemistry,
Simon Fraser University, Burnaby 2, British Columbia, Canada

Crystal Structure of (1,3-Dimethylarsino-2,2,4,4-tetramethylcyclobutane-*As,As*)tetracarbonylchromium at −150°

F. W. B. EINSTEIN* and R. D. G. JONES

Received November 3, 1972

The crystal structure of $\{Me_2As)\overline{CH(CH_3)_2C(Me_2As)CH(CH_3)_2C}\}Cr(CO)_4$ has been determined at −150° from the three-dimensional X-ray diffraction data collected by counter methods ($2\theta \leqslant 60°$) using Mo Kα radiation. The compound crystallizes in the tetragonal space group $I4_1cd$; the unit cell contains 8 molecules and has dimensions a = 12.115 (2), c = 27.514 (5) Å; d_m = 1.51 g/cm^3; d_c = 1.41 g/cm^3 for 8 molecules. The structure was determined from the Patterson function and refined by full-matrix least-squares techniques to R = 0.025 and R_w = 0.028 for 1437 observed reflections. A crystallographic twofold axis passes through the chromium atom and the midpoints of the two vectors joining nonbonded carbon atoms in the cyclobutane ring. The asymmetric unit is thus half of the molecule. The chromium atom has approximately octahedral coordination, Cr–As being 2.486 (1) Å. The carbonyl group trans to an arsenic atom has Cr–C = 1.841 (4) Å while those cis have Cr–C = 1.885 (4) Å. These Cr–C bond lengths are significantly different and reflect the superior π-acceptor properties of the carbonyl group. In the cyclobutane ring, the two independent carbon–carbon bond lengths are 1.570 (5) and 1.565 (5) Å. The cyclobutane group is nonplanar, the dihedral angle being 31.9 (5)°.

Introduction

Recently, Cullen[1] has shown that when arsenic atoms are substituted in the 1,3 positions of cyclobutane, a chelate complex can be formed with chromium carbonyl compounds. Using the geometry of cyclobutane as a model, arsenic atoms in the 1,3 positions and cis (axial-axial) positions (see ref 2 for nomenclature) would have a separation of ~3.6 Å. Since one might expect some nonbonded repulsion between arsenic atoms, the separation is probably greater in the hypothetical uncoordinated ligand. This ligand bite has to be shortened to form a chelate compound and this study was undertaken to ascertain if any distortions occur, especially of the cyclobutane ring on chelation. A second feature of interest was whether differences in the Cr–C bond lengths could be determined. It was expected that the use of low temperature would assist this aim.

Experimental Section

The pale yellow crystals of the compound were octahedral. A zero-level Weissenberg photograph with (110) as the rotation axis and precession photographs with (110) as the dial axis, taken with Cu Kα radiation, indicated that the crystals were tetragonal. The following spectra were observed: for hkl, $h + k + l = 2n$; for $0kl$, $l(k) = 2n$; for hhl, $2h + l = 4n$. The space group $I4_1cd$ is unequivocally indicated by these spectra and the Laue symmetry ($4/mmm$).

Crystal Data. $C_{16}H_{26}As_2CrO_4$, mol wt 436.04, crystallizes in the tetragonal space group $I4_1cd$, with a = 12.115 (2) Å, c = 27.514 (5) Å, U = 4038.2 Å^3 (cell at −150°), d_m = 1.5 (1) g/cm^3 (flotation in $ZnBr_2$ solution), d_c = 1.41 g/cm^3, Z = 8, $F(000)$ = 1760, λ(Cu Kα) 1.5418 Å, λ(Mo Kα_1) 0.70926 Å, and μ(Mo Kα) = 40.3 cm^{-1}.

A small octahedral crystal (for absorption corrections, the crystal was assumed a sphere of 0.3-mm diameter) was used to measure cell dimensions and the intensity data. It was mounted on a single-crystal Cryo-Tip refrigerator (manufactured by Air Products and Chemicals, Inc.) with a general orientation in order to minimize intrinsic multiple reflection. Cell dimensions were obtained at 22 and −150° by least-squares analysis of the 2θ values $\{2\theta > 34°$; the function minimized was $\Sigma(\Delta\theta)^2\}$ of 11 reflections which had been accurately centered on a computer-controlled Picker diffractometer. Mo Kα_1 radiation was used and the takeoff angle was 1°. The errors in the cell dimensions are those determined in the least-squares process.

Intensity data were collected at −150°. The variation in temperature throughout the data collection was from −145 to −150°. The unique set of intensities was measured using the θ–2θ scan technique with Mo Kα radiation (niobium filtered) and a scintillation counter equipped with pulse height analysis. The takeoff angle was 2°. Each reflection was scanned symmetrically for 1.3° (extended for spectral dispersion) at a scan rate of 2° min^{-1}. At each end of the scan range, the background scattering was counted 20 sec. Every 75 reflections, two standard reflections were measured and the maximum deviation of any individual standard from the mean was 3%. In this manner, intensities for 1506 reflections with $2\theta \leqslant 60°$ were measured.

Intensities were corrected for background (normalized to the scan time) and for the Lorentz–polarization factor. An absorption correction was applied by assuming the crystal to be a sphere, μR = 0.6. For each reflection, the esd in the intensity, σ_I, was determined from $\sigma_I = \{(TC) + (t_s/t_b)^2(B_1 + B_2) + (kI)^2\}^{1/2}$ where TC is the total count, B_1 and B_2 are the background counts at each end of the scan range, t_s is the scan time, t_b is the background count time, and k is a constant set to 0.03.[3] If $I \leqslant 2.3\sigma_I$ (I is the net intensity), the reflection was considered unobserved. The number of observed reflections was 1437.

Structure Determination. In an ordered structure comprising 8 molecules per unit cell the chromium atom would be expected to lie on a crystallographic twofold axis with half of the molecule as the asymmetric unit. The chromium atom was placed at (0, 0, 0) and

---

(1) W. R. Cullen, personal communication.

(2) P. Anderson, O. Bastiansen, and S. Furberg, Ed., "Selected Topics in Structure Chemistry," Universitetsforlaget, Oslo, 1967, p 91.

(3) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).