SCHMID, G. & ETZRODT, G. (1977). *J. Organomet. Chem.* **137**, 367–371.

SCHMID, G., ETZRODT, G. & BATZEL, V. (1976). *J. Organomet. Chem.* **112**, 345–353.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SUMNER, G. G., KLUG, H. P. & ALEXANDER, L. E. (1964). *Acta Cryst.* **17**, 732–742.

Structure of Pentacarbonyl(tribromophosphine)chromium(0)

BY H. JELINEK-FINK, E. N. DUESLER AND R. T. PAINE*

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, USA

Abstract. $[Cr(CO)_5(PBr_3)]$, $M_r = 462 \cdot 75$, triclinic, $P\bar{1}$, $a = 6 \cdot 695$ (1), $b = 6 \cdot 823$ (1), $c = 13 \cdot 641$ (3) Å, $\alpha = 88 \cdot 07$ (1), $\beta = 87 \cdot 16$ (1), $\gamma = 87 \cdot 73$ (1)°, $Z = 2$, $V = 621 \cdot 5$ (2) Å^3, $D_x = 2 \cdot 47$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 112 \cdot 9$ cm^{-1}, $T = 293$ K, $F(000) = 428$, $R = 7 \cdot 12\%$ for 1901 unique observed reflections. The structure displays a slightly distorted octahedral geometry about the Cr atom with five carbonyl C atoms and the P atom of PBr_3 occupying the coordination sites. The Cr–P, Cr–CO (*trans*) and average Cr–CO (*cis*) distances are 2·263 (3), 1·892 (11) and 1·903 (11) Å, respectively.

Introduction. There remains considerable interest in the synergic σ-donor/π-acceptor characteristics of phosphine ligands toward low-valent-metal carbonyl fragments. Previous studies (Plastas, Stewart & Grim, 1973; Cotton, Darensbourg & Isley, 1981) have suggested that there is an approximate correlation between $\nu_{CO}(E$ mode) and M–P bond distances in metal carbonyl phosphine complexes which should make comparative predictions on the nature of new phosphine–metal interactions in $X_3PM(CO)_5$ ($M = $ Cr, Mo and W; $X = $ halide, hydride, alkoxide, alkyl and aryl) possible. Utilizing this correlation and published infra-red spectra (Fischer & Knauss, 1969) it would be expected that the $X_3PCr(CO)_5$ ($X = $ halide) complexes should display some of the shortest metal–phosphine bond distances. The crystal-structure determination of the title compound was undertaken to partially test this prediction.

Experimental. The complex was prepared by literature techniques (Fischer & Knauss, 1969) and air-sensitive orange crystals were obtained by sublimation. Crystal $0 \cdot 1 \times 0 \cdot 3 \times 0 \cdot 4$ mm (glass capillary); Syntex $P3/F$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator; cell parameters from a least-squares fit of 25 reflections with $10 < 2\theta < 32°$, space group $P\bar{1}$; no absorption correction was applied; data collected to $2\theta_{max} = 55°$ with $\pm h$, $\pm k$, $\pm l$ ranges 0 to 8, 8 and 17 respectively; θ–2θ scan mode, $1 \cdot 2°$ range, 4–30° min^{-1} speed; three standard reflections monitored every 141 reflections, 20% intensity variation; rapid crystal deterioration after 48 h of exposure necessitated the merging of data sets for two crystals; 7861 reflections measured, R_{int} 4·4%; 2870 unique data, 1901 data with $F > 5\sigma(F)$ used in solution and refinement (based on F's); structure solved by direct methods; blocked-cascade least-squares refinement using aniso-tropic thermal parameters for all atoms, 136 parameters, $R = 0 \cdot 071$, $wR_F = 0 \cdot 068$, $w = 1/[\sigma^2(F_o) + 0 \cdot 00095 F_o^2]$, $S = 1 \cdot 624$, $(\Delta/\sigma)_{max} = -0 \cdot 091$ for $U(11)$ of C(2); max. and min. heights in final difference Fourier synthesis 1·64 and $-1 \cdot 46$ e Å^{-3}; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs from *SHELXTL* (Sheldrick, 1981). The relatively high R index reflects the instability of the compound during X-ray exposure.

Discussion. Atom coordinates are given in Table 1 and bond distances and angles in Table 2.† A view of the molecular structure and a stereoview of the unit-cell contents are shown in Figs. 1 and 2. The Cr atom displays pseudooctahedral symmetry and it is bonded to the C atom of five terminal CO ligands and the P atom of PBr_3. The Cr–P bond distance is, indeed, short compared to Cr–P distances found in $Cr(CO)_5$-$P(C_6H_5)_3$ 2·422 (1), $Cr(CO)_5P(OC_6H_5)_3$ 2·309 (1) (Plastas *et al.*, 1973), $Cr(CO)_5P(CH_2CH_2CN)_3$ 2·364 (1) (Cotton *et al.*, 1981) and $Cr(CO)_5P(CH_3)_2$-(SH) 2·344 (2) Å (Meier, Strähle & Lindner, 1976). Construction of a plot of d_{Cr-P} *vs* $\nu_{CO}(E)$ utilizing the

---

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43462 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

---

* Address correspondence to this author.

limited amount of data available and the observed $v_{CO}(E)$ for $Br_3PCr(CO)_5$, 1986 cm^{-1}, leads to a prediction of d_{Cr-P} in $Br_3PCr(CO)_5$ of 2·12–2·22 Å. To the degree that the observed distance falls outside this range may indicate the importance of nonbonded steric repulsions between the *cis* carbonyls and the Br atoms.

The metal—C bond distances should also be affected by the phosphine σ-donor/π-acceptor character, with the M—CO$_{ax}$ distance being the most affected. Previous studies have shown that increasing π-acceptor strength by the phosphine results in an increasing set of M—CO distances: $Cr(CO)_5P(OC_6H_5)_3$ Cr—C$_{ax}$ 1·861 (4), Cr—C$_{eq}$ (av.) 1·896 (5); $Cr(CO)_5P(CH_2CH_2CN)_3$ Cr—C$_{ax}$ 1·876 (5), Cr—C$_{eq}$ (av.) 1·891 (5); $Cr(CO)_5P(C_6H_5)_3$ Cr—C$_{ax}$ 1·845 (4), Cr—C$_{eq}$ (av.) 1·880 (4) Å. In the present study the π-acceptor strength is strongest in the series for which data are available and the Cr—C$_{ax}$ and Cr—C$_{eq}$ (av.) distances are also the largest in the series and similar to that found in $Cr(CO)_6$, 1·909 Å.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for* $Br_3PCr(CO)_5$

	x	y	z	$U^*_{eq}(Å^2)$
Br(1)	0·11014 (19)	−0·26252 (25)	0·95078 (9)	0·0768 (5)
Br(2)	0·58435 (16)	−0·36433 (17)	0·87449 (8)	0·0568 (4)
Br(3)	0·40221 (21)	0·10802 (16)	0·87243 (9)	0·0643 (4)
P	0·32223 (35)	−0·18467 (35)	0·82743 (18)	0·0384 (7)
Cr	0·22064 (21)	−0·21935 (21)	0·67341 (11)	0·0368 (5)
C(1)	0·1053 (16)	−0·4591 (16)	0·7175 (8)	0·051 (4)
O(1)	0·0323 (14)	−0·6009 (12)	0·7436 (7)	0·077 (4)
C(2)	0·1223 (16)	−0·2499 (16)	0·5474 (8)	0·049 (3)
O(2)	0·0589 (15)	−0·2652 (14)	0·4724 (7)	0·081 (4)
C(3)	−0·0214 (15)	−0·0803 (14)	0·7061 (8)	0·048 (3)
O(3)	−0·1696 (12)	0·0025 (13)	0·7230 (7)	0·084 (4)
C(4)	0·3400 (16)	0·0179 (15)	0·6274 (7)	0·048 (3)
O(4)	0·4093 (14)	0·1577 (13)	0·5985 (6)	0·075 (3)
C(5)	0·4666 (16)	−0·3541 (15)	0·6340 (8)	0·052 (4)
O(5)	0·6125 (13)	−0·4270 (14)	0·6094 (6)	0·077 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor (Willis & Pryor, 1975).

Table 2. *Bond lengths* (Å) *and angles* (°) *for* $Br_3PCr(CO)_5$

Br(1)—P	2·212 (3)	Br(2)—P	2·210 (3)
Br(3)—P	2·203 (3)	P—Cr	2·263 (3)
Cr—C(1)	1·903 (11)	Cr—C(2)	1·892 (11)
Cr—C(3)	1·887 (10)	Cr—C(4)	1·907 (11)
Cr—C(5)	1·916 (11)	C(1)—O(1)	1·140 (14)
C(2)—O(2)	1·136 (14)	C(3)—O(3)	1·139 (13)
C(4)—O(4)	1·128 (14)	C(5)—O(5)	1·120 (14)

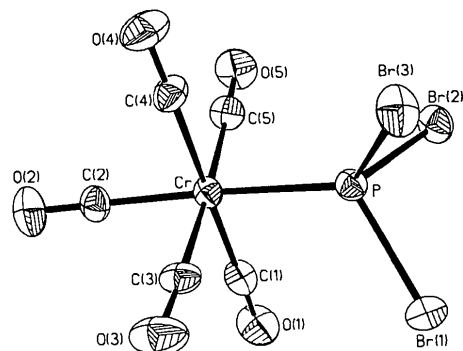| Br(1)—P—Br(2)	98·3 (1)	Br(1)—P—Br(3)	99·5 (1)
Br(2)—P—Br(3)	100·8 (1)	Br(1)—P—Cr	117·4 (1)
Br(2)—P—Cr	118·1 (1)	Br(3)—P—Cr	118·9 (1)
P—Cr—C(1)	88·3 (3)	P—Cr—C(2)	177·1 (3)
C(1)—Cr—C(2)	90·0 (5)	P—Cr—C(3)	90·2 (3)
C(1)—Cr—C(3)	90·4 (4)	C(2)—Cr—C(3)	87·5 (5)
P—Cr—C(4)	92·3 (3)	C(1)—Cr—C(4)	178·8 (4)
C(2)—Cr—C(4)	89·5 (5)	C(3)—Cr—C(4)	90·7 (4)
P—Cr—C(5)	92·0 (3)	C(1)—Cr—C(5)	91·4 (5)
C(2)—Cr—C(5)	90·4 (5)	C(3)—Cr—C(5)	177·2 (4)
C(4)—Cr—C(5)	87·5 (5)	Cr—C(1)—O(1)	178·6 (10)
Cr—C(2)—O(2)	178·2 (10)	Cr—C(3)—O(3)	177·8 (10)
Cr—C(4)—O(4)	178·7 (9)	Cr—C(5)—O(5)	177·6 (9)

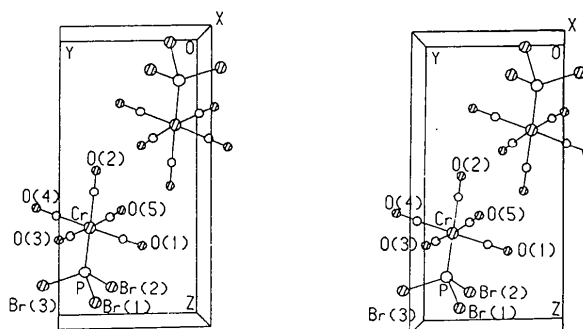Fig. 1. Molecular structure and atom-labeling scheme for $Br_3PCr(CO)_5$ (30% thermal ellipsoids).

Fig. 2. Stereoview of the contents of the unit cell of $Br_3PCr(CO)_5$.

Lastly, it is noticed that the average P—Br bond distance in $Br_3PCr(CO)_5$, 2·208 Å, is slightly shorter than in uncoordinated PBr$_3$, 2·220 (3) Å (Kuchitsu, Shibata & Yokozeki, 1971).

References

COTTON, F. A., DARENSBOURG, D. J. & ISLEY, W. H. (1981). *Inorg. Chem.* **20**, 578–583.

FISCHER, E. O. & KNAUSS, L. (1969). *Chem. Ber.* **102**, 223–229.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KUCHITSU, K., SHIBATA, T. & YOKOZEKI, A. (1971). *Inorg. Chem.* **10**, 2584–2587.

MEIER, W.-P., STRÄHLE, J. & LINDNER, E. (1976). *Z. Anorg. Allg. Chem.* **424**, 154–160.

PLASTAS, H. J., STEWART, J. M. & GRIM, S. O. (1973). *Inorg. Chem.* **12**, 265–272.

SHELDRICK, G. M. (1981). *Nicolet SHELXTL Operations Manual*, revision 3. Nicolet XRD Corporation, Cupertino, California.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.