TABLE IV
RING PARAMETERS FROM X-RAY STRUCTURAL STUDIES[a]

Complex	M–N	α	β	γ	•	z_1	z_2	z_3	Ref
trans-[Co(tn)₂(NO₃)₂](NO₃)₂	1.99	87.7	117.9	108.8	113.3	+1.06[b]	+0.81[b]	+0.99[b]	f
			120.1	111.0					
trans-[Co(tn)₂Cl₂]Cl·HCl·2H₂O	2.00	95.4	119.1	114.6	111.3	c	c	c	g
[Cu(tn)₂](NO₃)₂	2.06	94.9	119.4	109.6	112.0	+0.61[b]	−0.04[b]	+0.51[b]	h
			119.7	112.1					
trans-[Ni(tn)₂(H₂O)₂](NO₃)₂	2.09	92.9	121.3	110.1	115.1	0.55[b]	0.00[b]	0.55[b]	i
			121.3	110.1					
[Co(tn)₃]Br₃·H₂O[e]	2.00	94.3	117.0	113.7	114.0	d	d	d	
			118.0	111.0					

[a] z_1, z_2, z_3 and M–N in Å, angles in degrees.   [b] Calculated from published atomic parameters.   [c] Atomic parameters not published. [d] Unable to reproduce published ring parameters from published atomic parameters.   [e] Averaged values.   [f] E. Yasaki, I. Oonishi, H. Kawaguchi, and Y. Komiyama, *Bull. Chem. Soc. Jap.*, **43**, 1354 (1970).   [g] K. Matsumoto, S. Ooi, and H. Kuroya, *ibid.*, **43**, 1903 (1970). [h] A. Pajunen, *Suom. Kemistilehti, B*, **42**, 15 (1969).   [i] A. Pajunen, *ibid., B*, **41**, 232 (1968).   [j] T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jap.*, **42**, 1016 (1969).

reduced at the expense of minor increases in ring-strain energy if the NCCCN fragment distorts away from the amine group. As mentioned above, this is the most favored mode of distortion of the chair conformation.

Although the interactions of each skew-boat ring are smaller, the ability of this conformation to reduce the interactions is limited by the nature of the interaction system. The methylene groups of this conformation interact with both apical amine groups. In the D($\delta\delta\delta$) configuration each skew-boat conformation retains its intrinsic twofold symmetry. Consequently, each ring can only relieve its interactions by modes of distortion which preserve this symmetry, resulting in the rings flattening symmetrically. This is a highly unfavorable mode of distortion since it requires large angular and torsional strain.

Clearly, the configurational preferences predicted for M(tn)₃ are heavily dependent on the relative magnitudes of the nonbonded interaction and ring-strain energy terms used in the calculations. If the bond angles and torsional angles are rigid, as is implicit in Woldbye's model, the preference for the tris-chair configuration can only be accounted for by unreasonably weak interaction equations, such that the natural preference of each ring for the chair conformation predominates. By treating the interactions and geometrical distortions in a more realistic manner, the present calculative model is able to account for the observed configuration as well as the rather large angular distortions present in the X-ray structure.

Experimental information concerning the pathway for ring inversion and the energy of activation is not available. However, the nmr spectra of 1,3-diaminopropane complexes are consistent with rapid conformational interconversion at room temperature,[7] which would be expected from the calculated value of about 7 kcal mol⁻¹. Low-temperature nmr studies are presently in progress in this laboratory in an attempt to determine the experimental value of the energy of activation for the chair-to-chair interconversion.

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The Crystal and Molecular Structure of
trans-Bis(triphenyl phosphite)tetracarbonylchromium(0)[1]

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The crystal and molecular structure of trans-bis(triphenyl phosphite)tetracarbonylchromium(0) has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic with a = 7.977 (2) Å, b = 11.779 (3) Å, c = 20.667 (9) Å, β = 108.08 (1)°, V = 1846.02 Å³; density 1.42 g/cm³ (by flotation), 1.417 g/cm³ (calcd for Z = 2). The intensity data were collected with an automated General Electric XRD-6 diffractometer with Nb-filtered Mo Kα radiation. Final refinement of the structure resulted in a residual of 0.056 and a weighted residual of 0.048. The chromium lies on a center of symmetry, and surrounding it, in an approximately octahedral configuration, are four chemically equivalent carbonyl carbons [Cr–C = 1.88 (1) Å] and two phosphorus atoms [Cr–P = 2.252 (1) Å].

Introduction

There have been several recent reports of X-ray structural determinations of phosphorus ligand derivatives of chromium hexacarbonyl.[2–6] The main interest

(1) Supported in part by the National Science Foundation (Grants No. GP-7886 and GP-12539) and the U. S. Army Medical Research and Development Command (Grant No. DADA17-67-C-7160).

(2) H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).
(3) F. A. Cotton and M. D. La Prade, *ibid.*, **91**, 7000 (1969).
(4) O. S. Mills and A. D. Redhouse, *Chem. Commun.*, 814 (1966).
(5) G. Huttner and S. Schelle, *J. Organometal. Chem.*, **19**, P9 (1969).
(6) L. J. Guggenberger and E. L. Muetterties, private communication.

has centered in the effect of the groups attached to phosphorus on the phosphorus–chromium distance and also the chromium–carbon and carbon–oxygen distances of the remaining carbon monoxide ligands and whether these distances are predictable and/or consistent with the bonding theory and the Cotton–Kraihanzel–Graham interpretation[7,8] of the infrared stretching frequencies in the carbonyl region. For example, a good π-accepting ligand with electronegative groups on phosphorus will result in higher stretching frequencies of the remaining carbonyls, *i.e.*, $\nu_{E \text{ mode}}$ of $(C_6H_5O)_3PCr(CO)_5$ is 1960 cm^{-1} and $\nu_{E \text{ mode}}$ for $(C_6H_5)_3PCr(CO)_5$ is 1940 cm^{-1}. Triphenylphosphine is more basic than triphenyl phosphite but the latter is expected to be a better π acceptor than triphenylphosphine because of the electronagative oxygens attached to phosphorus. It is of interest to note that triphenyl phosphite forms the shorter [2.309 (1) *vs.* 2.422 (1) Å][2] chromium–phosphorus bond of the two ligands in LCr(CO)$_5$. Also, in the analogous tungsten compounds, LW(CO)$_5$, the phosphorus-31–tungsten-183 spin–spin coupling constant, observable directly in the ^{31}P nmr spectrum, of the phosphite compound is larger than that of the phosphine derivative.[9] This also implies a stronger phosphorus–metal interaction in the case of triphenyl phosphite. These data are consistent with predictions based on binding theory allowing some π bonding by phosphorus.

In an extension of these studies, we undertook the X-ray crystallographic determination of *trans*-bis-(triphenyl phosphite)tetracarbonylchromium(0).

Experimental Section

Cr[P(OC$_6$H$_5$)$_3$]$_2$(CO)$_4$ was prepared according to the method of Magee, *et al.*,[10] and was recrystallized from a methanol–dichloromethane mixture. A pale yellow needle-shaped crystal, elongated along the *a* axis, was used for the structure determination.

Approximate unit cell dimensions and the diffraction symmetry were obtained from Weissenberg photographs taken about the *a* (0*kl*–4*kl*) and *b* axes of the crystal. These photographs (taken with λ(Cu Kα) 1.5418 Å) revealed monoclinic symmetry and systematic abscences *h0l* for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, which are consistent only with the space group $P2_1/c$ (C_{2h}^5; no. 14).

More accurate cell parameters were obtained from a least-squares treatment of some 20 diffractometer measurements of 2θ. These values and, subsequently, the intensity data were taken from a crystal of dimensions $0.35 \times 0.09 \times 0.06$ mm on a Datex automated General Electric XRD-6 diffractometer, with Nb-filtered Mo Kα radiation (λ 0.71069 Å).

Crystal data are as follows for C$_{40}$H$_{30}$CrO$_{10}$P$_2$: mol wt 784.6; monoclinic; $a = 7.977$ (2), $b = 11.779$ (3), $c = 20.667$ (9) Å; $\beta = 108.08$ (1)°; $V = 1846.02$ Å^3; $d_m = 1.42$ (by flotation); $Z = 2$; $d_c = 1.417$ g/cm^3; $F(000) = 808$; space group $P2_1/c$ (C_{2h}^5); μ (Mo Kα) = 4.66 cm^{-1}.

Data were collected to a (sin θ)/λ value of 0.6 by the stationary-crystal, stationary-counter method. Each reflection was counted for 10 sec at left and right background and 20 sec at the peak. Standard reflections (100 and 020) were remeasured every 200 reflections. A complete set of the *hkl* and *hk̄l* reflections were collected together with *hk̄l* and *h̄k̄l* where accessible. In order to convert these "peak height" intensities to integrated intensities some 400 of the strongest intensities were recollected, each being measured consecutively by the stationary-crystal, stationary-

counter method and by a θ–2θ scan. The "peak-scan pairs" were measured as "peaks" using counting times of 20 sec (for both the backgrounds and the two measurements at the peak) and as "scans" *via* 20 sec backgrounds and 2°/min scans with the scan range varying from 1.8 to 2.2° as 2θ increased. The peak-to-scan intensity ratio was plotted against (sin θ)/λ and the resulting curve was used for an empirical conversion of the raw peak height data to an approximate integrated intensity. Thus, the intensities I_{hkl} were calculated from

$$I_{hkl} = K(P - B_1 - B_2)$$

where K is the peak-to-scan conversion factor (a function of θ; see Table I), P is the sum of the two measurements at the peak

TABLE I
PEAK TO SCAN CONVERSION TABLE

2θ, deg	K	2θ, deg	K	2θ, deg	K
2.5	1.01	20.0	1.03	37.5	1.13
3.7	1.01	22.5	1.04	40.0	1.15
5.0	1.00	25.0	1.06	42.5	1.17
7.5	0.98	27.5	1.08	45.0	1.19
10.0	1.00	30.0	1.10	47.5	1.20
12.5	1.01	32.5	1.11	50.0	1.20
15.0	1.02	35.0	1.12	55.0	1.21
17.5	1.02				

of each reflection, and B_1 and B_2 are the backgrounds. These data were assigned standard deviations according to

$$\sigma(I) = 10^{1/2}(P + B_1 + B_2 + Pd)^{1/2}$$

where Pd ($d = 0.01$) is added to the expression to allow for instrument instability. After performing the conversion and then averaging symmetry-equivalent reflections, the total of 6750 "peak height" measurements yielded 3337 independent reflections. Of these, 2066 were intensities where $I_{hkl} < 3\sigma(I)$. These 2066 reflections were considered to be "less thans" in a subsequent least-squares refinement; that is they were included in any least-squares cycle if, and only if, the corresponding F calculated exceeded the threshold value.

The intensities were corrected for Lorentz and polarization effects but not for extinction or absorption. A calculation based on a variation of path length from 0.03 to 0.08 cm indicated that changes in F observed caused by absorption would be of the order of 3%.

Structure Determination.—The presence of only two molecules in the unit cell restricts the position of the Cr atom to that of a center of symmetry. A Fourier map, phased by the Cr atom at 0, 0, 0, showed the expected "false" symmetry but revealed the P atom. The remaining atoms were located in a subsequent Fourier synthesis.

Four cycles of full-matrix least-squares refinement with individual isotropic temperature factors and unit weights resulted in a residual ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.105. Hydrogen atom positions were calculated (C–H − 1.08 Å) and included with isotropic temperature factors equal to those of the carbon atom to which they were attached. Three cycles of anisotropic refinement of the nonhydrogen atoms (hydrogen parameters were not refined) decreased the residual to 0.068.

At this point unit weights were discarded and the weighting scheme $w = 1.0/\max[\sigma(I), 0.10F_o]$ introduced. A final three cycles of refinement yielded a residual of 0.056 and a weighted residual $R_w = [\Sigma w \Delta^2/w|F_o|^2]^{1/2}$ of 0.048.

A three-dimensional difference Fourier calculated at the end of refinement was relatively featureless except for a negative peak of 2.2 e/Å^3 at the chromium position and positive peaks of 0.5–1.2 e/Å^3 in the neighborhood of the carbonyl groups. The latter are probably attributable to thermal motion incompletely described by the anisotropic temperature factors.

Scattering factors for the heavy atoms were those of Ibers;[11] for hydrogen the values of Stewart, Davidson, and Simpson[12] were used.

Observed and calculated structure amplitudes have been tabu-

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

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

(9) S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Commun.*, 38 (1969).

(10) T. D. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Amer. Chem. Soc.*, **83**, 3200 (1961).

(11) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, C. H. MacGillavry, G. D. Rieck, and K. Longdale, Ed., Kynoch Press, Birmingham, U. K., 1962, p 201.

(12) R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

TABLE II
THE FINAL HEAVY-ATOM POSITIONAL[a] AND THERMAL[b] PARAMETERS

Atom[c]	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.0	0.5	0.5	3.52 (7)	3.04 (6)	2.70 (6)	0.46 (6)	0.69 (5)	−0.02 (6)
P	0.1773 (2)	0.4085 (1)	0.5913 (1)	3.91 (9)	3.09 (8)	3.03 (7)	−0.14 (17)	1.09 (6)	−0.05 (7)
O(1)	−0.2892 (6)	0.4818 (5)	0.5656 (2)	6.20 (30)	7.32 (29)	5.61 (24)	0.41 (26)	3.34 (21)	−0.91 (23)
O(2)	0.1376 (6)	0.7168 (4)	0.5755 (2)	8.06 (39)	3.91 (22)	7.84 (29)	−0.94 (23)	−0.16 (25)	−2.04 (22)
O(11)	0.2356 (5)	0.2771 (3)	0.5895 (2)	6.12 (24)	2.91 (18)	3.49 (19)	0.86 (17)	2.11 (17)	0.25 (16)
O(21)	0.3592 (5)	0.4751 (3)	0.6232 (2)	4.04 (20)	4.59 (21)	2.75 (17)	−0.24 (17)	0.13 (15)	0.20 (15)
O(31)	0.1094 (5)	0.3980 (3)	0.6559 (2)	6.02 (24)	2.73 (18)	3.23 (18)	0.10 (17)	2.26 (16)	0.45 (16)
C(1)	−0.1824 (9)	0.4931 (6)	0.5392 (3)	5.10 (39)	3.90 (30)	3.40 (29)	0.46 (34)	1.07 (26)	−0.94 (29)
C(2)	0.0832 (7)	0.6361 (5)	0.5465 (3)	3.82 (32)	3.93 (34)	4.08 (30)	−0.42 (26)	0.75 (25)	0.16 (26)
C(11)	0.2858 (9)	0.2258 (5)	0.5366 (3)	4.95 (40)	3.79 (33)	3.07 (31)	1.27 (30)	1.03 (28)	0.10 (26)
C(12)	0.4180 (10)	0.2673 (7)	0.5166 (4)	4.59 (41)	8.57 (52)	5.82 (40)	1.48 (37)	3.10 (33)	0.52 (38)
C(13)	0.4685 (11)	0.2113 (8)	0.4661 (4)	6.85 (50)	8.15 (82)	7.16 (49)	0.99 (45)	3.07 (41)	0.07 (43)
C(14)	0.3760 (14)	0.1111 (9)	0.4405 (4)	11.60 (80)	9.58 (65)	5.97 (48)	4.30 (60)	4.02 (50)	−0.47 (48)
C(15)	0.2433 (13)	0.0706 (7)	0.4635 (4)	10.62 (67)	6.56 (47)	6.59 (47)	−1.27 (44)	4.67 (43)	−3.38 (39)
C(16)	0.1954 (9)	0.1271 (6)	0.5120 (3)	6.01 (42)	5.07 (37)	6.33 (41)	−0.28 (33)	2.62 (33)	−1.00 (32)
C(21)	0.4747 (8)	0.4620 (5)	0.6902 (3)	4.26 (34)	3.48 (31)	3.46 (29)	−0.69 (26)	1.00 (26)	0.18 (25)
C(22)	0.5908 (8)	0.3740 (5)	0.7073 (3)	4.66 (35)	4.39 (34)	4.34 (33)	1.24 (29)	0.17 (28)	−0.43 (27)
C(23)	0.7055 (9)	0.3693 (6)	0.7737 (4)	6.64 (44)	4.82 (39)	6.01 (39)	0.40 (34)	−0.02 (37)	1.04 (32)
C(24)	0.6966 (9)	0.4482 (6)	0.8205 (3)	6.00 (45)	6.08 (41)	4.45 (36)	−0.97 (35)	0.38 (32)	0.15 (33)
C(25)	0.5787 (10)	0.5365 (6)	0.8031 (3)	7.06 (44)	5.49 (39)	4.54 (36)	−0.63 (36)	0.35 (33)	−1.08 (29)
C(26)	0.4667 (8)	0.5441 (5)	0.7360 (3)	4.57 (36)	4.27 (32)	4.93 (35)	0.85 (27)	0.80 (29)	−1.05 (28)
C(31)	0.0815 (8)	0.3010 (5)	0.6892 (3)	5.22 (36)	3.29 (29)	3.18 (30)	0.47 (28)	2.06 (27)	−0.54 (25)
C(32)	0.1853 (9)	0.2827 (5)	0.7540 (3)	6.94 (43)	5.44 (37)	3.30 (32)	−0.28 (32)	1.05 (30)	1.71 (28)
C(33)	0.1530 (11)	0.1920 (8)	0.7894 (4)	8.91 (59)	7.75 (51)	6.30 (45)	2.04 (45)	3.07 (41)	3.62 (42)
C(34)	0.0231 (15)	0.1182 (6)	0.7594 (5)	13.69 (79)	3.54 (39)	10.04 (63)	−1.04 (45)	7.56 (58)	1.44 (43)
C(35)	−0.0835 (11)	0.1361 (7)	0.6939 (5)	8.71 (57)	6.99 (51)	8.60 (54)	−3.67 (44)	4.93 (45)	−3.75 (46)
C(36)	−0.0550 (10)	0.2292 (6)	0.6579 (3)	7.60 (49)	5.72 (40)	4.94 (37)	−2.15 (37)	3.21 (34)	−0.77 (34)

[a] The standard deviation in the least-significant figure(s) is given in parentheses following each parameter. [b] The anisotropic thermal parameters are of the form $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2C^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$. [c] The numbering system for the chromium, carbonyl groups, phosphorus, and phosphite oxygens corresponds to Figure 1. The first digit in the number of the phosphite oxygens and phenyl carbon atoms refers to the specific phenyl ring.

lated.[13] The final fractional coordinates and anisotropic temperature factors of the heavy atoms are shown in Table II; the hydrogen atom parameters are given in Table III. The

TABLE III
HYDROGEN ATOM PARAMETERS[a]

Atom[b]	x	y	z	B, Å²
H(12)	0.4852	0.3439	0.5394	6.6
H(13)	0.5726	0.2431	0.4478	7.4
H(14)	0.4104	0.0644	0.4104	9.4
H(15)	0.1765	−0.0072	0.4428	8.1
H(16)	0.0910	0.0965	0.5305	5.8
H(22)	0.5938	0.3096	0.6705	4.4
H(23)	0.8025	0.3023	0.7880	5.8
H(24)	0.7835	0.4413	0.8721	5.6
H(25)	0.5726	0.5991	0.8405	5.8
H(26)	0.3750	0.6138	0.7206	4.5
H(32)	0.2391	0.3397	0.7775	5.4
H(33)	0.2319	0.1792	0.8417	7.6
H(34)	0.0027	0.0444	0.7870	10.0
H(35)	−0.1892	0.0776	0.6705	8.2
H(36)	−0.1381	0.2451	0.6065	6.2

[a] Hydrogen atom positions are as calculated (C–H = 1.08 Å) after the last least-squares cycle; no esd's are given as those parameters were not refined. [b] The numbering is consistent with that of the carbon atoms.

hydrogen atom positions given are those calculated after the last cycle of least squares.

Discussion

trans-Bis(triphenyl phosphite)tetracarbonylchromium(0) has the expected distorted octahedral configuration (Figure 1). The chromium atom lies on a crystallographically imposed center of symmetry, and the two phosphorus atoms and four carbonyl carbons

(13) A listing of 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 Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.
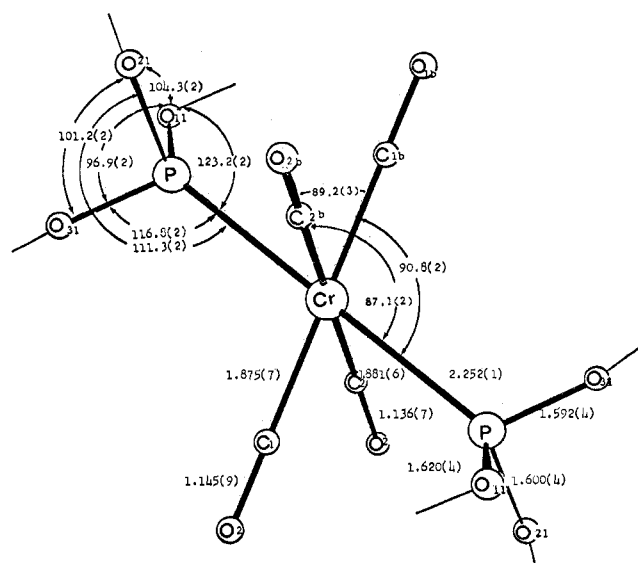
Figure 1.—Bond lengths and angles about chromium and its near neighbors.

lie as opposed pairs about the center. No corrections for thermal motion have been applied to the bond lengths given in Figure 1 and Table IV. A riding motion calculation indicated that the Cr–C distances should be increased: Cr–C(1) from 1.875 to 1.881 Å and Cr–C(2) from 1.881 to 1.888 Å. In any case, the carbonyl groups are, within experimental error, equidistant from the chromium. Bond angles are given in Table V.

The packing of the molecules is illustrated in Figure 2 and the shortest intramolecular contacts are given in Table VI. Only heavy-atom contacts are listed since the hydrogen atom positions were calculated and not

TABLE IV
DISTANCES WITHIN THE $Cr[P(OC_6H_5)_3]_2(CO)_4$ MOLECULE[a]

Atoms	Distance, Å	Atoms	Distance, Å
(a) About the Chromium, Carbonyls, and Phosphite			
Cr–P	2.252 (1)	P–O (11)	1.620 (4)
Cr–C(1)	1.875 (7)	P–O(21)	1.600 (4)
Cr–C(2)	1.881 (6)	P–O(31)	1.592 (4)
Cr–O(1)	3.019 (5)	O(11)–C(11)	1.412 (8)
Cr–O(2)	3.017 (4)	O(21)–C(21)	1.413 (6)
C(1)–O(1)	1.145 (9)	O(31)–C(31)	1.387 (7)
C(2)–O(2)	1.136 (7)		
(b) Within the Phenyl Groups			
C(11)–C(12)	1.340 (12)	C(24)–C(25)	1.374 (10)
C(12)–C(13)	1.394 (13)	C(25)–C(26)	1.400 (8)
C(13)–C(14)	1.406 (14)	C(26)–C(21)	1.370 (9)
C(14)–C(15)	1.375 (16)	C(30)–C(32)	1.355 (7)
C(15)–C(16)	1.353 (12)	C(32)–C(33)	1.365 (11)
C(16)–C(11)	1.379 (9)	C(33)–C(34)	1.347 (12)
C(21)–C(22)	1.361 (8)	C(34)–C(35)	1.373 (13)
C(22)–C(23)	1.394 (8)	C(35)–C(36)	1.383 (12)
C(23)–C(24)	1.359 (11)	C(36)–C(31)	1.372 (9)

[a] The standard deviation in the least significant figure(s) is given in parentheses.

TABLE V
BOND ANGLES

Atoms	Angle, deg	Atoms	Angle, deg
(a) About the Chromium, Carbonyls, and Phosphite			
C(1)–Cr–P	89.2 (2)	Cr–P–O(31)	116.8 (2)
C(2)–Cr–P	87.1 (2)	O(11)–P–O(21)	104.3 (2)
C(1)–Cr–C(2)	90.8 (3)	O(11)–P–O(31)	96.9 (2)
Cr–C(1)–O(1)	177.4 (5)	O(21)–P–O(31)	101.2 (2)
Cr–C(2)–O(2)	178.1 (5)	P–O(11)–C(11)	125.4 (4)
Cr–P–O(11)	123.2 (2)	P–O(21)–C(21)	125.6 (4)
Cr–P–O(21)	111.3 (2)	P–O(31)–C(31)	128.9 (4)
(b) About the Phenyl Groups			
O(11)–C(11)–C(12)	121.6 (6)	C(23)–C(24)–C(25)	121.0 (6)
O(11)–C(11)–C(16)	113.9 (6)	C(24)–C(25)–C(26)	118.8 (6)
C(11)–C(12)–C(13)	119.8 (7)	C(25)–C(26)–C(21)	119.2 (5)
C(12)–C(13)–C(14)	116.1 (9)	C(26)–C(21)–C(22)	122.1 (5)
C(13)–C(14)–C(15)	122.1 (9)	O(31)–C(31)–C(32)	118.6 (5)
C(14)–C(15)–C(16)	120.7 (8)	O(31)–C(31)–C(36)	120.0 (5)
C(15)–C(16)–C(11)	116.9 (8)	C(31)–C(32)–C(33)	119.7 (6)
C(16)–C(11)–C(12)	124.4 (7)	C(32)–C(33)–C(34)	120.3 (7)
O(21)–C(21)–C(22)	121.5 (5)	C(33)–C(34)–C(35)	120.5 (9)
O(21)–C(21)–C(26)	116.4 (5)	C(34)–C(35)–C(36)	119.8 (8)
C(21)–C(22)–C(23)	118.2 (6)	C(35)–C(36)–C(31)	118.3 (6)
C(22)–C(23)–C(24)	120.7 (6)	C(36)–C(31)–C(32)	121.3 (6)

TABLE VI
INTRAMOLECULAR CONTACTS[a,b]

Atoms	Distance, Å	Atoms	Distance, Å
O(2)–C(13a)	3.61	O(3)–C(34d)	3.47
O(2)–C(24c)	3.47	O(12)–O(1e)	3.44
O(2)–C(23c)	3.48	C(21)–O(1e)	3.62
C(25)–O(4c)	3.62	C(22)–O(1e)	3.61
C(26)–O(33c)	3.62	O(5)–O(1e)	3.37

[a] The first atom is at x, y, z; the second atom is generated from the parameters of Table II by one of the following operations: (a) $1 - x, 1 - y, 1 - z$; (b) $-x, 1 - y, 1 - z$; (c) $1 - x, 1/2 + y, 11/2 - z$; (d) $-x, 1/2 + y, 11/2 - z$; (e) $x, 1/2 - y, 1/2 + z$; (f) $1 + x, y, z$. [b] Estimated standard deviations are about 0.01 Å.

refined. The shortest hydrogen atom contacts involve the carbonyl oxygen atoms [O(2)–H(13a) = 2.5 Å and H(12)–O(1e) = 2.4 Å].

Figure 3 shows the thermal ellipsoid diagram of the structure. In view of the high standard deviations of the thermal parameters of the phenyl carbons, only the ring carbons attached to the oxygen atoms are included in the diagram.
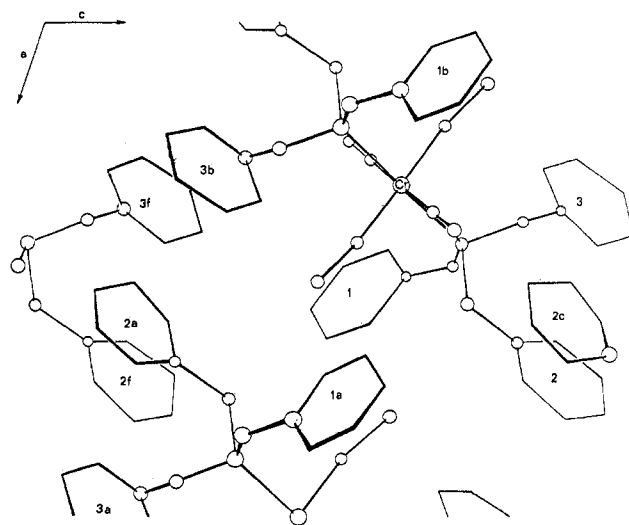

Figure 2.—Packing of molecules as projected onto the *ac* plane. The benzene rings are numbered according to the first digits of the subscripts of the carbon atoms in Table II. The letters refer to the symmetry operations described in footnote *a* of Table VI. The labeled chromium atom is at 0, $1/2$, $1/2$.
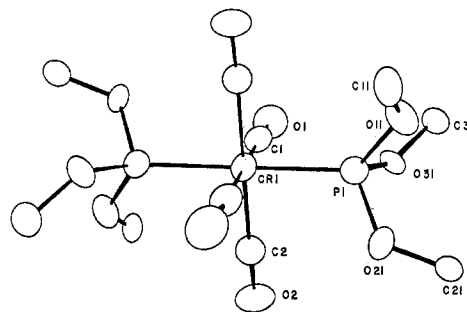

Figure 3.—Thermal ellipsoid plot. Except for the ring carbons attached to the oxygen atoms, the other phenyl carbons have been omitted from the diagram.

As indicated in the Introduction the most interesting aspects of this compound are the phosphorus–chromium, chromium–carbon, and possibly the carbon–oxygen bond lengths compared to $(C_6H_5O)_3PCr(CO)_5$. In the trans bis compound, the predictions according to the π theory would be that the phosphorus–chromium bond should be shorter than the phosphorus–chromium bond in the monophosphite or in the cis bis compound. The reason for expected shorter bond in the trans compound is that the phosphorus is competing mainly with the phosphorus trans to itself for the π-electron density of the metal $d\pi$ electron, compared to competition with carbon monoxide, a better π acceptor, in the case of the mono- and cis-disubstituted compounds

cis   trans
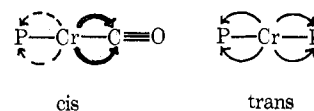
The P–Cr distance in the trans compound [2.252 (1) Å] is significantly shorter than in the monosubstituted compound [2.309 (1) Å].[2] The cis-$L_2Cr(CO)_4$ compound has not been investigated. Also consistent with these observations is the fact that the phosphorus-31–tungsten-183 coupling constant in $trans$-[$(C_6H_5O)_3$-

P]$_2$W(CO)$_4$ is larger than in (C$_6$H$_5$O)$_3$PW(CO)$_5$ (480 *vs.* 411 Hz).[14]

Replacement of carbon monoxide ligands by phosphorus ligands in the series LCr(CO)$_{6-n}$ will result in a higher electronic density on chromium which will be partially distributed to the remaining carbonyl groups by back-bonding from the filled dπ metal orbitals to the empty π^* orbitals of CO; *i.e.*, the chromium–carbon bond order theoretically should increase while the carbon–oxygen bond order (and stretching force constant) should decrease as the negative charge on Cr increases. This phenomenon has been investigated very extensively by infrared analysis[7,8,15] but this present work is the first case in which simple bond length comparisons can be made. The average Cr–C bond length [1.878 (6) Å] in *trans*-L$_2$Cr(CO)$_4$ is significantly shorter than the average of the four cis Cr–C bond lengths[2] [1.896 (4) Å] in LCr(CO)$_5$, which in turn is shorter than the mean Cr–C bond length [1.909 (3) Å] in the unsubstituted chromium hexa-

(14) P. R. McAllister, Ph.D. Thesis, University of Maryland, 1967.

(15) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.* **8**, 1 (1966).

carbonyl.[16] The C–O bond lengths are also in the expected direction for the substituted compounds; *viz.*, in *trans*-L$_2$Cr(CO)$_4$ the average C–O length [1.140 (8) Å] is larger than that of the average cis CO's [1.131 (6) Å] in LCr(CO)$_5$; however, the differences are too small to be statistically significant. In addition the C–O bond length for Cr(CO)$_6$ is intermediate [1.137 (4) Å] between these two values. Again the standard deviation is large compared to the differences in lengths. It has been pointed out earlier that the C–O bond length is relatively insensitive to bond order,[17] and therefore perhaps it is not surprising that these relatively insignificant differences in C–O bond lengths were obtained.

The geometry of the triphenyl phosphite found in this work is very similar to that found in (C$_6$H$_5$O)$_3$-PCr(CO)$_5$.[2] Slight differences in the bond angles about phosphorus in these two cases have been discussed elsewhere.[18]

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

(17) F. A. Cotton and R. M. Wing *Inorg. Chem.*, **4**, 314 (1965).

(18) S. O. Grim, H. J. Plastas, C. L. Huheey, and J. E. Huheey, *Phosphorus*, **1**, 61 (1971).

The Crystal and Molecular Structure of Bis(cyclopentadienyl)-2,2'-bi-π-allyl-bis(nickel) (C$_5$H$_5$·Ni·C$_3$H$_4$–C$_3$H$_4$·Ni·C$_5$H$_5$)

By A. E. SMITH*

The structure of bis(cyclopentadienyl)-2,2'-bi-π-allyl-bis(nickel) (C$_5$H$_5$·Ni·C$_3$H$_4$–C$_3$H$_4$·Ni·C$_5$H$_5$) has been determined from three dimensional X-ray data collected by counter methods using graphite and LiF monochromatized Mo Kα radiation. The unit cell is monoclinic, space group $P2_1/n$, a = 9.934 (4) Å, b = 7.775 (4) Å, c = 9.573 (4) Å, β = 110.55 (10)°, two molecules per unit cell. The calculated and observed densities are 1.570 and 1.59 ± 0.04 g/cm^3. The structure was refined by full-matrix least-squares to a conventional R factor on F of 3.47% and a weighted R factor of 2.80% for 1387 reflections. The C–C bonds in the cyclopentadienyl ring differ significantly at the 5σ level and consist of an "allyl" group with C–C bond distances of 1.398 and 1.394 Å and a "short" bond of 1.401 Å separated by two "long" bonds of 1.438 and 1.423 Å, respectively. The estimated standard deviation of the C–C bonds is 0.006 Å. The partial localization of the bonds in the cyclopentadiene ring can be explained, as suggested by Dahl and Wei[1] and Bennett, *et al.*,[2] in terms of the removal of the cylindrical symmetry around the Ni atom resulting in the removal of the metal orbital degeneracy, which in turn serves to remove the degeneracy of the bonding orbitals of the cyclopentadienyl ring. Results of extended Hückel molecular-orbital calculations on this complex are in agreement with the observed partial localization of the bonds in the cyclopentadienyl ring.

Introduction

Several crystalline bimetallic π-allyl complexes of nickel and palladium and cyclopentadienyl have been prepared and reported by Keim.[3] Since no structural information was available for these complexes an X-ray investigation was undertaken of a complex whose chemical analysis indicated it to be of composition C$_5$H$_5$·Ni·C$_3$H$_4$–C$_3$H$_4$·Pd·C$_5$H$_5$. It became apparent from the space group and calculated and measured density that the molecule possessed a center of symmetry and was actually C$_5$H$_5$·Ni·C$_3$H$_4$–C$_3$H$_4$·Ni·C$_5$H$_5$. Later,

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(1) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963).

(2) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature (London)*, **201**, 1318 (1964).

(3) W. Keim, *Angew. Chem.*, **80**, 968 (1968).

nmr evidence[3] suggested that a disproportionation had occurred in solution 2NiPdLn = Ni$_2$Ln + Pd$_2$Ln (Ln = C$_{16}$H$_{18}$). Chemical analysis of crystals grown with the X-ray specimen confirmed the composition as C$_5$H$_5$·Ni·C$_3$H$_4$–C$_3$H$_4$·Ni·C$_5$H$_5$.

It was decided however to proceed with the structure determination to establish the molecular configuration of this type of complex. In addition, at the time the structure became of interest, the monochromator for the automatic diffractometer arrived. The crystals of the complex were well suited for checking the Lorentz-polarization corrections for the LiF and graphite monochromator crystals. This required the collection of accurate data sets for the spherical crystal using LiF and graphite monochromatized and Zr-filled Mo Kα radiation. Subsequent comparison of the data sets