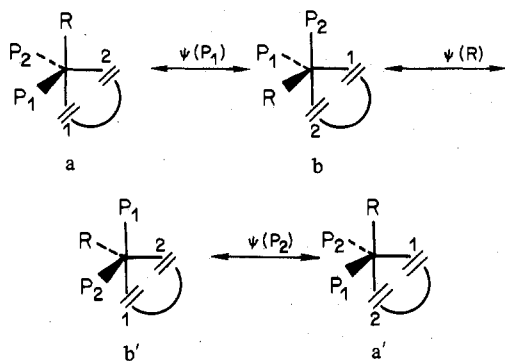


Scheme I



(diphos)Ir(CH₃) and for $(C_8H_{12})[(C_6H_5)(CH_3)_2P]_2Ir(CH_3)$ are entirely consonant with the mechanism suggested by Shapley and Osborn (see Scheme I) in which there are successive "pseudorotations" about P₁, R, and P₂. For equilibration of vinyls 1 and 2 to occur, the reaction must proceed from ground state a, through the high-energy intermediates b and b', back to ground state a'. In the high-energy inter-

mediate, a methyl group occupies an equatorial position and the two phosphine groups occupy an equatorial and an axial position. Since ground state a is of higher energy for the diphos compound, due to extra strain associated with a small equatorial P-Ir-P' angle, the diphos compound is expected (as observed) to undergo the intramolecular interconversion $a \rightarrow a'$ at a greater rate than the analogous bis-(monodentate)phosphine complex in which the P-Ir-P' angle is not strained by chelation and is closer to the ideal equatorial value of 120°.

Further information on these systems is expected to be obtained from current X-ray structural analyses on the species $(C_8H_{12})[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]Ir(CH_3)$ in which *n* has values other than 2. (The case with *n* = 2, of course, is covered by the present article.)

Registry No. $(C_8H_{12})(diphos)Ir(CH_3)$, 36974-34-2.

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Contribution from the Departments of Chemistry, Montgomery College, Takoma Park, Maryland 20012 and University of Maryland, College Park, Maryland 20742

Crystal and Molecular Structures of Pentacarbonyltriphenylphosphinechromium(0) and Pentacarbonyl(triphenyl phosphite)chromium(0)¹

HAROLD J. PLASTAS, JAMES M. STEWART, and SAMUEL O. GRIM*

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The crystal and molecular structures of pentacarbonyltriphenylphosphinechromium(0), $(C_6H_5)_3PCr(CO)_5$, and pentacarbonyl(triphenyl phosphite)chromium(0), $(C_6H_5O)_3PCr(CO)_5$, have been determined by single-crystal X-ray diffraction techniques. Both crystals belong to the triclinic system, space group *P* $\bar{1}$, with cell dimensions $a = 9.709$ (3), $b = 11.942$ (2), $c = 9.559$ (2) Å; $\alpha = 91.73$ (1), $\beta = 95.58$ (2), $\gamma = 74.17$ (1)° for the phosphine complex and $a = 11.212$ (2), $b = 11.497$ (5), $c = 10.695$ (3) Å; $\alpha = 114.33$ (2), $\beta = 105.58$ (2), $\gamma = 66.50$ (3)° for the phosphite complex. The calculated densities, assuming *Z* = 2, are 1.422 and 1.459 g cm⁻³; the observed densities are 1.416 and 1.446 g cm⁻³ for the phosphine and phosphite complexes, respectively. For the phosphine complex the final value of the conventional *R* factor is 4.3% for 3450 independent reflections observed to be greater than three standard deviations above the background. For the phosphite complex the final value of the conventional *R* factor is 4.8% for 3573 independent reflections observed to be greater than three standard deviations above the background. Both structures exhibit slightly distorted octahedral geometry about the chromium with phosphorus and five carbons occupying the coordinate positions. In the phosphine compound, the chromium-phosphorus distance is 2.422 (1) Å; the trans chromium-carbon distance is 1.845 (4) Å, and the four cis chromium-carbon distances are 1.878 (4), 1.894 (4), 1.882 (5), and 1.867 (4) Å, respectively. In the phosphite compound, the corresponding bond lengths are as follows: Cr-P, 2.309 (1) Å; trans Cr-C, 1.861 (4) Å; cis Cr-C, 1.892 (5), 1.895 (4), 1.904 (6), and 1.892 (4) Å, respectively.

Introduction

There have been numerous X-ray structural determinations of coordination compounds in which phosphorus ligands have been present.²⁻⁴ In most cases these were carried out mainly to prove the stereochemistry about the metal atom

or to ascertain the bonding characteristics of other ligands, such as organic moieties or inorganic ligands attached to the metal. In view of the high interest in metal carbonyls and their derivatives and the physical data published on substituted metal carbonyls, such as infrared spectra,⁵ equilibrium constants,⁶ and nmr data⁷ it seemed that X-ray structural data on some fairly simple related compounds would be very

* Address correspondence to this author at the University of Maryland.

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informative, especially in view of all the bonding implications which have been drawn from the earlier physical data. Some recent X-ray structural determinations of phosphorus ligand derivatives of metal carbonyls have been reported.⁸⁻¹⁴ Of particular interest for our purposes are structures of the type, $\text{LM}(\text{CO})_5$, where L is a simple two electron donor such as a nitrogen or phosphorus ligand and M is Cr, Mo, or W. This type compound has been extensively investigated⁵⁻⁷ by other methods but no comparison of the structural parameters of closely related compounds have been examined. The purpose of this investigation is to compare the effects of two different phosphorus ligands, *viz.*, triphenylphosphine and triphenyl phosphite, on the phosphorus-metal bond distance and, if detectable and significant, on the metal-carbon and carbon-oxygen bond distances of the carbonyl groups.

The details of the X-ray structural determination of two compounds, *i.e.*, $(\text{C}_6\text{H}_5)_3\text{PCr}(\text{CO})_5$ and $(\text{C}_6\text{H}_5\text{O})_3\text{PCr}(\text{CO})_5$, are reported here. A preliminary report has been published previously.¹⁵

Experimental Procedure

$(\text{C}_6\text{H}_5)_3\text{PCr}(\text{CO})_5$. The sample of pentacarbonyltriphenylphosphinechromium(0) was prepared by heating a solution of $(\text{C}_6\text{H}_5)_3\text{P}$ and $\text{Cr}(\text{CO})_6$ in diethylene glycol dimethyl ether (diglyme) under a nitrogen atmosphere. Recrystallization from a mixture of dichloromethane and methanol gave clear yellow crystals with a melting point of 127° (lit. mp¹⁶ 127-128°). The crystal used for cell dimension and intensity data measured 0.35 mm × 0.13 mm × 0.10 mm and was mounted on a fine glass fiber with the 0.35-mm edge coinciding with the Weissenberg spindle axis. Based upon Weissenberg and precession photographs and the subsequent solution and refinement of the structure, the space group is $\text{P}\bar{1}$. Accurate unit cell dimensions [$a = 9.709$ (3), $b = 11.942$ (2), $c = 9.559$ (2) Å; $\alpha = 91.73$ (1), $\beta = 95.58$ (2), $\gamma = 74.17$ (1)°] were obtained from 2 θ data collected on a General Electric XRD-6 card-controlled automated diffractometer using niobium-filtered molybdenum $\text{K}\alpha$ X-radiation. The 2 θ method used was that of ω half-heighting.¹⁷ The function R was minimized where $R = \sum n|\theta_{\text{calcd}} - \theta_{\text{obsd}}|^2/\sigma^2$, where n is the number of observed θ 's and σ is the estimated error in observed θ , θ_{obsd} .

The density was measured by flotation in aqueous potassium iodide solution as 1.416 (4) g cm⁻³. The density calculated from the formula weight of 454.343, the unit cell volume of 1061.1 Å³, and $Z = 2$ is 1.422 (3) g cm⁻³. The linear absorption coefficient for the phosphine was calculated to equal 5.844 cm⁻¹ and no absorption correction was applied.

Intensities were collected using niobium-filtered molybdenum $\text{K}\alpha$ X-radiation out to a θ of 28° by the moving-counter, moving-crystal method.¹⁸ Backgrounds were measured for 20 sec on each side of a peak and peak intensity was scanned at 1° min⁻¹. Peak width, PW, was calculated to conform to the mosaic spread of the crystal for each peak by the formula $\text{PW} = 1.700 + 1.000 \tan \theta$.

Five standard reflections were periodically remeasured showing an overall downward trend of 6.6% in the intensity. This trend was attributed to crystal decay and was compensated for by scaling the data. Of the 6650 measured independent reflections, 3450 were observed to be greater than three standard deviations above the background, 2531 were less than three standard deviations above the background, and 669 were negative.

All calculations were accomplished on the Univac 1108 computer using a set of programs known as X-RAY 67.¹⁹ The chromium and phosphorus positions were located from an origin-removed sharpened Patterson vector map. The conventional R value based on the two atoms from the Patterson was 41.5%. The remaining nonhydrogen atoms were located from successive F_o Fouriers. Scattering factors used for nonhydrogen atoms were taken from ref 20. Hydrogen scattering factors used were those given by Stewart.²¹

Four cycles of full-matrix least-squares refinement using isotropic temperature factors lowered the R to 9.2%. Phenyl hydrogen positions were calculated assuming trigonal-planar geometry around the phenyl carbon atoms and carbon-hydrogen bond lengths of 1 Å. Nine cycles of block-diagonal least-squares refinement on all atom positions and thermal parameters with anisotropic temperature factors for all but the hydrogen atoms and isotropic temperature factor for hydrogen atoms lowered the R value for the phosphine compound to 4.3%. Final cycles of anisotropic full-matrix least squares with isotropic refinement on hydrogen temperature factors gave a final conventional R of 4.3%. During refinement on F_o , a weighting scheme was applied to the $(\Delta F)^2$ values of $0.12/\sigma(F)$ or $0.12/0.01F$ (rel) + 0.12, whichever was found to be larger. $\sigma(F)$ was derived from the counting statistics. The conventional R factor $R = \sum |\Delta F|/\sum |F_o|$ is given above. The weighted R factor is based on F^2 , $R_w = \sum w(\Delta F)^2/\sum (F_o)^2 = 6.0\%$, while the goodness of fit = $[\sum w(\Delta F)^2/(n_o - n_v)]^{1/2} = 0.18$ where n_o is the number of observations and n_v is the number of variables.

Due to limitation of computer core space, carbon atoms 12, 23, and 33 were held constant in the final cycle of refinement. A three-dimensional electron density difference synthesis showed no peak higher than 0.4 e/Å³ and no hole lower than 0.6 e/Å³.

The final thermal and positional parameters are listed in Tables I and II.²²

$(\text{C}_6\text{H}_5\text{O})_3\text{PCr}(\text{CO})_5$. The sample of pentacarbonyl(triphenyl phosphite)chromium(0) was prepared by heating a solution of $(\text{C}_6\text{H}_5\text{O})_3\text{P}$ and $\text{Cr}(\text{CO})_6$ in diglyme under an atmosphere of nitrogen. The clear, colorless crystals produced had a melting point of 59° (lit. mp¹⁶ 59.5-60°). The crystal used for data collection measured 0.38 mm × 0.25 mm × 0.18 mm and was mounted on the end of a fine glass fiber with the 0.38-mm side coinciding with the spindle axis of the Weissenberg camera. The film survey and accurate cell dimension determination [$a = 11.212$ (2), $b = 11.497$ (5), $c = 10.695$ (3) Å; $\alpha = 114.33$ (2), $\beta = 105.58$ (2), $\gamma = 66.50$ (3)°; space group $\text{P}\bar{1}$] were accomplished in the same manner as previously described for the phosphine compound.

The density measured in aqueous potassium iodide is 1.446 (2) g cm⁻³. The density calculated from the formula weight of 502.341, the unit cell volume of 1142.9 Å³, and $Z = 2$ is 1.459 (3) g cm⁻³. The linear absorption coefficient for the phosphite was calculated to equal 6.416 cm⁻¹ and no absorption correction was applied.

Data collection was accomplished as previously described for the phosphine. The five standard reflections showed an overall downward trend in intensity of 7.9% which was attributed to crystal decay and compensated for by scaling the data. Of the 5726 measured independent reflections, 3573 were observed to be greater than three estimated standard deviations above the background, 1683 were less than three estimated standard deviations above the background, and 470 were negative.

Structure solution was accomplished by a direct phasing method using quasinormalized structure factors, E 's,²³ by assuming the space group to be $\text{P}\bar{1}$.

Application of the PHASE program of X-RAY 67 to the direct solution of the phase of the 99 highest E values left five phases undetermined.²³ Defining three of the phases as 0 to set the origin and rejecting the all-0 phase choice left three E maps to be calculated. Initial study of all three maps showed a large peak corresponding to

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Table I. Fractional Coordinates ($\times 10^4$) and Anisotropic^a Thermal ($\times 10^3$) Parameters for (C₆H₅)₃PCr(CO)₅

Atom	X	Y	Z	mB_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2238.6 (6)	496.6 (5)	2309.4 (6)	381 (3)	337 (3)	432 (3)	-146 (2)	61 (2)	-38 (2)
P	1425.6 (9)	2376.0 (8)	3432.4 (9)	309 (4)	345 (4)	362 (4)	-121 (3)	49 (3)	-13 (3)
O1	4957 (3)	894 (3)	1382 (4)	555 (15)	613 (16)	1031 (21)	-219 (13)	343 (15)	-59 (14)
O2	4040 (3)	-810 (3)	4830 (3)	747 (18)	605 (17)	692 (19)	-172 (14)	-70 (15)	158 (14)
O3	-310 (4)	-174 (2)	3268 (4)	763 (19)	790 (19)	1040 (23)	-491 (16)	309 (17)	-58 (16)
O4	586 (3)	1550 (3)	-390 (3)	693 (18)	844 (20)	520 (16)	-154 (15)	-25 (14)	23 (14)
O5	2926 (3)	-1767 (3)	734 (4)	728 (18)	504 (15)	945 (21)	-206 (13)	123 (15)	-294 (15)
C1	3912 (4)	786 (3)	1754 (4)	473 (19)	340 (16)	590 (22)	-127 (15)	114 (17)	-56 (15)
C2	3355 (4)	-278 (3)	3910 (5)	542 (22)	428 (20)	570 (23)	-195 (17)	62 (18)	0 (17)
C3	641 (4)	106 (3)	2914 (4)	566 (21)	482 (20)	577 (22)	-271 (17)	113 (17)	-54 (16)
C4	1201 (4)	1176 (3)	659 (4)	471 (20)	492 (20)	473 (22)	-146 (16)	74 (17)	-88 (17)
C5	2679 (4)	-903 (4)	1355 (4)	480 (20)	456 (19)	621 (23)	-185 (16)	42 (17)	-59 (18)
C11	1522 (4)	3642 (3)	2458 (3)	404 (16)	367 (16)	300 (15)	-123 (15)	45 (12)	-49 (12)
C12	388 (5)	4632 (3)	2267 (4)	471 (18)	427 (17)	459 (19)	-109 (15)	19 (15)	28 (14)
C13	537 (6)	5589 (4)	1582 (5)	663 (24)	427 (21)	537 (22)	-120 (20)	-84 (20)	112 (19)
C14	1797 (6)	5581 (4)	1081 (5)	974 (31)	462 (21)	484 (21)	-333 (21)	59 (20)	66 (16)
C15	2931 (6)	4608 (4)	1258 (5)	721 (26)	545 (23)	739 (26)	-309 (21)	332 (21)	-78 (19)
C16	2793 (5)	3646 (4)	1929 (5)	544 (21)	378 (17)	697 (24)	-145 (16)	243 (18)	-22 (16)
C21	-481 (3)	2730 (3)	3739 (4)	339 (15)	347 (15)	449 (18)	-117 (12)	59 (14)	-33 (13)
C22	-1480 (4)	2661 (4)	2630 (5)	394 (18)	651 (22)	500 (20)	-160 (16)	81 (16)	-105 (17)
C23	-2925 (4)	2873 (4)	2809 (6)	319 (16)	720 (25)	707 (24)	-153 (16)	40 (16)	-101 (17)
C24	-3385 (5)	3170 (4)	4112 (5)	338 (18)	678 (24)	805 (28)	-187 (16)	149 (18)	-75 (20)
C25	-2419 (5)	3236 (4)	5222 (6)	459 (20)	753 (26)	596 (24)	-165 (18)	219 (18)	-123 (20)
C26	-973 (4)	3027 (3)	5034 (4)	403 (18)	567 (20)	485 (20)	-155 (15)	75 (15)	-77 (16)
C31	2304 (3)	2605 (3)	5147 (4)	284 (14)	396 (16)	394 (17)	-79 (12)	80 (12)	-14 (13)
C32	2789 (4)	3574 (4)	5487 (5)	452 (18)	451 (18)	460 (19)	-139 (14)	-21 (14)	-52 (14)
C33	3448 (5)	3699 (5)	6790 (20)	604 (20)	635 (21)	620 (21)	-159 (15)	-76 (16)	-194 (17)
C34	3625 (5)	2877 (6)	7786 (6)	571 (23)	854 (29)	443 (21)	36 (21)	-75 (17)	-158 (20)
C35	3135 (5)	1916 (5)	7498 (5)	611 (24)	625 (24)	460 (22)	74 (19)	110 (18)	47 (19)
C36	2490 (4)	1776 (4)	6180 (4)	479 (19)	552 (20)	428 (20)	-128 (16)	95 (16)	-21 (16)

^a Anisotropic temperature factors were calculated using the expression $t = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Fractional Coordinates ($\times 10^3$) and Isotropic Thermal Parameters for (C₆H₅)₃PCr(CO)₅

Atoms	X	Y	Z	$B, \text{Å}^2$
H(12)	-45 (4)	467 (3)	266 (4)	4.74 (95)
H(13)	-27 (4)	622 (4)	142 (4)	6.40 (103)
H(14)	184 (4)	620 (4)	63 (4)	5.84 (103)
H(15)	378 (4)	455 (3)	95 (4)	4.26 (103)
H(16)	355 (4)	298 (3)	204 (4)	4.50 (95)
H(22)	-116 (4)	249 (3)	176 (4)	4.26 (87)
H(23)	-355 (4)	283 (3)	198 (4)	4.66 (95)
H(24)	-434 (4)	326 (3)	425 (4)	5.76 (103)
H(25)	-268 (4)	337 (3)	612 (4)	5.53 (95)
H(26)	-31 (3)	306 (3)	579 (4)	3.79 (87)
H(32)	267 (4)	413 (3)	482 (4)	4.18 (87)
H(33)	370 (4)	438 (4)	697 (4)	6.87 (111)
H(34)	401 (4)	296 (4)	865 (5)	8.37 (118)
H(35)	316 (4)	133 (4)	803 (4)	5.45 (126)
H(36)	212 (4)	114 (3)	604 (3)	4.58 (87)

the chromium with several smaller peaks that indicated the expected carbonyl-phosphite octahedral symmetry. One *E* map was rejected because the chromium contact distance across the origin was too short to make chemical sense. Fifteen atoms were located from the second *E* map: one Cr, one P, seven O, and six C. Calculation of structure factors gave *R* = 46.5%. Twelve atoms were located from *E* map three: one Cr, one P, six O, and four C. Calculation of structure factors gave *R* = 38.9%. Twenty-one additional atoms were located in the Fourier map based upon the third *E*-map solution.

It is interesting to note that the three solutions found by the direct method correspond to the three simplest interpretations of the Patterson synthesis for this compound. Consider the vectors of Cr and P atoms of the triclinic cell as pictured in Figure 1. The atomic number of P is such that a double-weight Cr-P vector has essentially the same peak value as a single-weight Cr-Cr vector. The three *E* maps obtained corresponded to using the Cr₁-P₁ and Cr₂-P₂ vectors as the Cr₁-Cr₂ vector, the Cr₁-P₂ and Cr₂-P₁ vectors as the Cr₁-Cr₂ vector, and correctly the Cr₁-Cr₂ vector as itself.

Two cycles of full-matrix least-squares refinement with isotropic temperature factors lowered the *R* to 15.0%. Scattering factor sources were the same as those used for the phosphine.^{20,21} Because

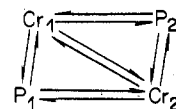


Figure 1. Chromium and phosphorus vectors in the phosphite complex.

of program limitation on the number of parameters, anisotropic refinement was carried out by alternately holding certain parameters constant in such a manner as to have overlap of all parameters during at least one cycle of refinement. When the *R* had dropped to 6.1%, phenyl hydrogen atoms were generated assuming trigonal-planar geometry about the phenyl carbons with a carbon-hydrogen bond length of 1.00 Å. Additional cycles of full-matrix and block-diagonal least-squares refinement, refining on positional and thermal parameters for all atoms, with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms yielded a final conventional *R* for the phosphite compound of 4.8%. The weighting was identical with that previously described for the phosphine. The final weighted *R* factor based on F^2 is 6.3% and the "goodness of fit" is 0.27. A three-dimensional electron density difference synthesis showed no peak higher than or hole lower than $\pm 0.5 \text{ e/Å}^3$. The final thermal and positional parameters for the phosphite complex are listed in Tables III and IV.²²

Results

The compounds (C₆H₅)₃PCr(CO)₅ and (C₆H₅O)₃PCr(CO)₅ have the expected *C*_{4v} symmetry with phosphorus and the five carbonyl carbons occupying the six coordination positions about chromium with one carbonyl trans and four carbonyls cis to the phosphorus.

The bond lengths and angles for (C₆H₅)₃PCr(CO)₅ are given in Table V. Figure 2 presents schematically the important bond lengths in the compound and defines the numbering system in Table V. Figure 3 shows the thermal ellipsoid diagram. The chromium-phosphorus distance is 2.422 (1) Å, which measures the same as the P-Cr bond length (2.42 Å) in *cis*-methylmethoxycarbenetriphenylphosphinetetracar-

Table III. Fractional Coordinates ($\times 10^4$) and Anisotropic^a Thermal ($\times 10^3$) Parameters for $(C_6H_5O)_3PCr(CO)_5$

Atoms	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2530.7 (4)	7,880.5 (5)	587.9 (5)	268 (2)	353 (3)	399 (3)	-71 (2)	48 (2)	167 (2)
P	4335.8 (7)	8,022.3 (8)	2232.6 (8)	313 (4)	366 (4)	350 (4)	-82 (3)	65 (3)	137 (3)
O1	2349 (3)	5,617 (3)	1193 (3)	776 (19)	586 (16)	866 (20)	-300 (14)	14 (15)	411 (15)
O2	586 (3)	9,924 (3)	2594 (3)	512 (16)	754 (19)	834 (20)	73 (13)	345 (15)	250 (16)
O3	2340 (3)	10,085 (3)	-387 (3)	772 (18)	646 (17)	695 (17)	-271 (14)	-25 (14)	433 (15)
O4	4392 (3)	5,817 (3)	-1499 (3)	668 (17)	594 (16)	573 (16)	-150 (13)	262 (14)	28 (13)
O5	308 (3)	7,473 (3)	1656 (4)	627 (18)	1069 (26)	913 (23)	-396 (18)	-296 (18)	442 (20)
O11	4520 (2)	9,426 (2)	3248 (2)	602 (14)	456 (13)	473 (13)	-177 (11)	-10 (11)	177 (11)
O21	4669 (2)	7,345 (2)	3395 (2)	409 (11)	520 (13)	462 (12)	-73 (10)	108 (9)	251 (10)
O31	5650 (2)	7,181 (2)	1548 (2)	298 (10)	537 (13)	399 (11)	-110 (9)	63 (8)	137 (10)
C1	2446 (3)	6,466 (3)	1000 (3)	395 (17)	464 (19)	517 (19)	-150 (14)	19 (14)	219 (16)
C2	1332 (3)	9,163 (4)	1865 (4)	380 (17)	525 (20)	616 (22)	-84 (15)	99 (16)	267 (18)
C3	2462 (3)	9,280 (3)	28 (3)	431 (18)	519 (20)	459 (19)	-156 (15)	11 (14)	224 (16)
C4	3708 (3)	6,592 (3)	-704 (3)	437 (18)	422 (18)	451 (19)	-151 (15)	75 (15)	117 (15)
C5	1139 (3)	7,644 (4)	-795 (4)	410 (19)	589 (22)	676 (25)	-166 (17)	-29 (18)	319 (20)
C11	4126 (3)	10,567 (3)	2854 (3)	490 (19)	414 (18)	478 (19)	-215 (15)	-27 (15)	148 (15)
C12	3025 (4)	11,586 (3)	3310 (4)	612 (24)	466 (21)	738 (26)	-156 (18)	197 (20)	162 (19)
C13	2666 (5)	12,744 (4)	3009 (6)	648 (21)	403 (20)	995 (19)	-77 (15)	56 (15)	180 (15)
C14	3406 (6)	12,863 (5)	2276 (5)	1028 (35)	532 (23)	866 (31)	-402 (24)	-140 (27)	398 (23)
C15	4503 (6)	11,807 (6)	1828 (5)	857 (28)	810 (27)	903 (29)	-396 (18)	153 (17)	402 (17)
C16	4884 (4)	10,667 (4)	2138 (4)	630 (25)	599 (23)	690 (26)	-200 (19)	135 (20)	240 (20)
C21	3785 (3)	7,537 (3)	4224 (3)	365 (15)	562 (20)	332 (15)	-110 (14)	61 (12)	186 (14)
C22	3821 (4)	6,413 (4)	4393 (4)	541 (21)	494 (19)	482 (19)	-72 (16)	96 (16)	230 (16)
C23	3007 (4)	6,530 (5)	5218 (4)	653 (21)	708 (22)	543 (20)	-277 (15)	64 (18)	310 (18)
C24	2167 (4)	7756 (5)	5866 (4)	572 (23)	956 (31)	482 (21)	-270 (22)	142 (18)	277 (21)
C25	2138 (4)	8872 (5)	5696 (4)	617 (20)	651 (21)	564 (22)	-25 (18)	284 (19)	174 (17)
C26	2952 (4)	8794 (4)	4884 (4)	593 (22)	512 (20)	505 (20)	-106 (17)	159 (17)	205 (17)
C31	6960 (3)	7039 (3)	2121 (3)	296 (15)	485 (18)	450 (18)	-76 (13)	54 (13)	114 (15)
C32	7656 (4)	7345 (5)	1503 (5)	355 (19)	898 (31)	1000 (34)	-142 (19)	111 (20)	472 (28)
C33	8973 (5)	7131 (6)	1950 (7)	460 (21)	1123 (23)	1326 (21)	-255 (19)	166 (20)	459 (19)
C34	9549 (5)	6678 (7)	3020 (7)	375 (22)	1493 (52)	929 (37)	-302 (27)	-71 (23)	279 (35)
C35	8886 (5)	6341 (7)	3587 (6)	581 (22)	1597 (50)	814 (31)	-90 (20)	-19 (22)	632 (22)
C36	7520 (4)	6514 (6)	3131 (5)	382 (21)	1495 (48)	807 (32)	-108 (25)	54 (21)	6431 (34)

^a Anisotropic temperature factors were calculated using the expression $t = \exp [-1/4 (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Fractional Coordinates ($\times 10^3$) and Isotropic Thermal Parameters for $(C_6H_5O)_3PCr(CO)_5$

Atoms	X	Y	Z	$B, \text{Å}^2$
H(12)	251 (3)	1156 (4)	383 (4)	6.00 (16)
H(13)	204 (4)	1138 (4)	341 (4)	7.19 (24)
H(14)	332 (4)	1356 (4)	217 (4)	7.19 (24)
H(15)	503 (4)	1194 (4)	134 (4)	7.42 (24)
H(16)	551 (4)	997 (4)	182 (4)	6.16 (16)
H(22)	437 (3)	562 (3)	400 (3)	5.13 (16)
H(23)	310 (3)	573 (3)	538 (4)	6.08 (16)
H(24)	155 (3)	782 (3)	636 (4)	6.32 (16)
H(25)	155 (4)	970 (4)	611 (4)	6.24 (16)
H(26)	298 (3)	954 (3)	478 (3)	5.45 (16)
H(32)	710 (3)	769 (3)	52 (4)	6.87 (24)
H(33)	958 (4)	732 (4)	146 (4)	9.16 (32)
H(34)	1039 (5)	650 (5)	317 (5)	9.08 (32)
H(35)	910 (5)	582 (5)	420 (5)	10.50 (32)
H(36)	693 (4)	608 (4)	319 (4)	7.90 (24)

bonylchromium,²⁴ but is significantly longer than some other known P-Cr(0) distances, e.g., 2.375 (2) and 2.387 (3) Å in $[(C_6H_5)_2PCH_2CH_2N(CH_2CH_3)CH_2CH_2P(C_6H_5)_2]_2Cr(CO)_3$,¹⁰ 2.349 (4) and 2.344 (4) Å in *cis*-(PH_3)₃Cr(CO)₃,¹¹ 2.349 Å in *cis*-(PH_3)₂Cr(CO)₄,²⁵ 2.309 (1) Å in $(C_6H_5O)_3PCr(CO)_5$, and 2.252 (1) Å in *trans*- $[(C_6H_5O)_3P]_2Cr(CO)_4$.²⁶

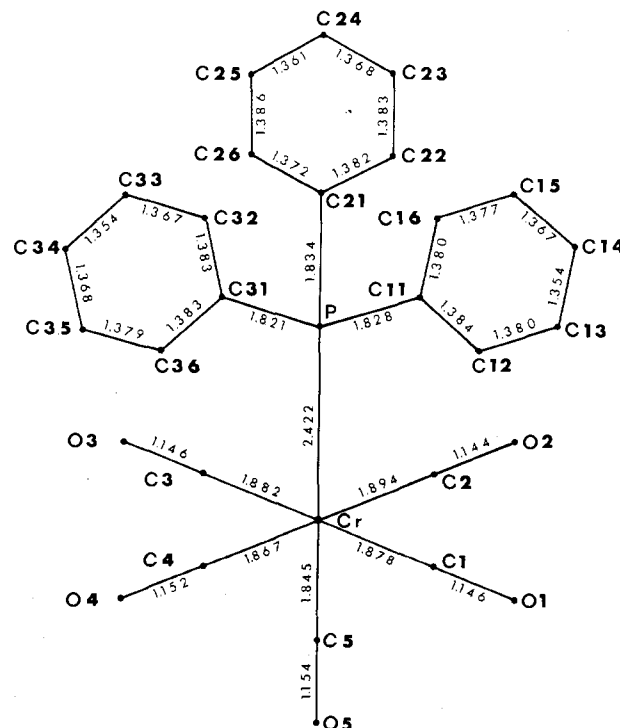
The Cr-C distances in $(C_6H_5O)_3PCr(CO)_5$ *cis* to the phosphorus average 1.880 Å and are significantly longer than Cr-C *trans* to phosphorus which is 1.844 Å. The average Cr-C distance in $Cr(CO)_6$ ²⁷ is 1.909 (3) Å. Concomitantly,

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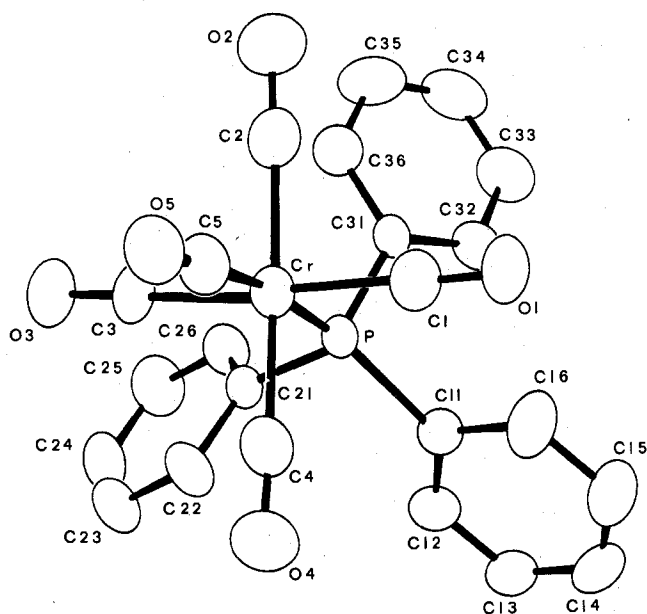
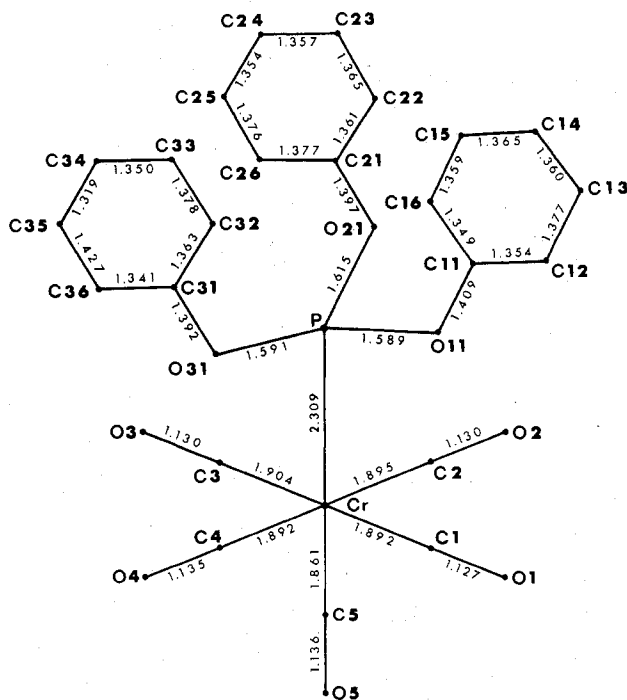
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**Figure 2.** Bond lengths and the numbering system in $(C_6H_5)_3PCr(CO)_5$.

the average *cis* C-O distance (1.147 Å) is shorter than the C-O distance (1.154 Å) but longer than in the unsubstituted hexacarbonyl (1.137 Å).

The average phosphorus-phenyl distance is 1.828 Å which

Figure 3. Thermal ellipsoid diagram of $(C_6H_5)_3PCr(CO)_5$.Figure 4. Bond lengths and the numbering system in $(C_6H_5O)_3PCr(CO)_5$.

compares favorably with other triphenylphosphine compounds. The average CPC angle is 102.6° compared to 103.0° in free Ph_3P^{28} and similar angles in other complexes.⁴

The bond lengths and angles for $(C_6H_5O)_3PCr(CO)_5$ are given in Table VI. Figure 4 presents schematically the important bond lengths and angles and shows the numbering system used in Table VI. Figure 5 gives the thermal ellipsoid diagram. The Cr-P distance is $2.309(1)$ Å. The Cr-O distances cis to the phosphorus average 1.896 Å and are longer than the Cr-C bond trans to phosphorus (1.861 Å). The C-O bond lengths in the phosphite complex average 1.131 Å for the cis ligands compared to 1.136 Å for the trans ligand.

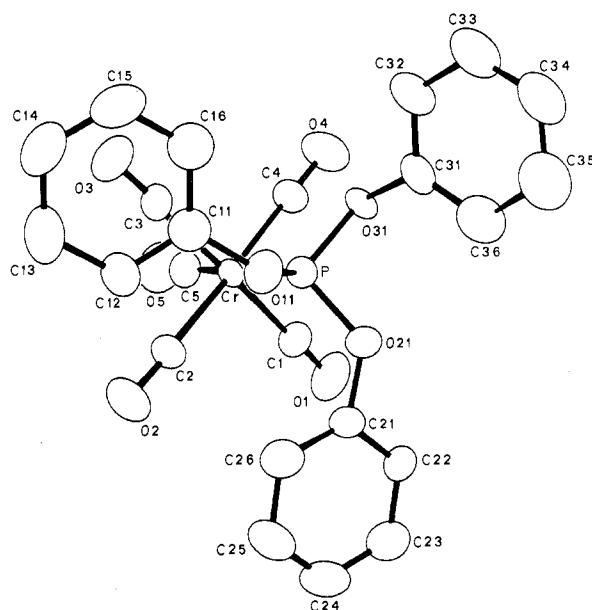
Table V. Bond Lengths (Å) and Angles (deg) in Pentacarbonyltriphenylphosphinechromium(0)

Cr-C1	1.878 (4)	Cr-P-C21	112.2 (1)
Cr-C2	1.894 (4)	Cr-P-C31	118.1 (1)
Cr-C3	1.882 (5)	Cr-C1-O1	175.8 (3)
Cr-C4	1.867 (4)	Cr-C2-O2	175.7 (4)
Cr-C5	1.845 (4)	Cr-C3-O3	177.5 (3)
Cr-P	2.422 (1)	Cr-C4-O4	177.0 (4)
P-C11	1.828 (4)	Cr-C5-O5	178.3 (3)
P-C21	1.834 (4)	C11-P-C21	102.6 (2)
P-C31	1.821 (3)	C11-P-C31	101.8 (2)
O1-C1	1.146 (6)	C21-P-C31	103.4 (2)
O2-C2	1.144 (5)	P-C11-C12	123.0 (3)
O3-C3	1.146 (6)	P-C11-C16	119.5 (2)
O4-C4	1.152 (5)	P-C21-C22	119.0 (3)
O5-C5	1.154 (5)	P-C21-C26	123.3 (3)
C11-C12	1.384 (4)	P-C31-C32	123.6 (3)
C12-C13	1.380 (4)	P-C31-C36	118.8 (3)
C13-C14	1.354 (6)	C11-C12-C13	120.8 (3)
C14-C15	1.367 (6)	C12-C13-C14	121.0 (2)
C15-C16	1.377 (7)	C13-C14-C15	119.1 (4)
C16-C11	1.380 (6)	C14-C15-C16	120.5 (5)
C21-C22	1.382 (5)	C15-C16-C11	121.2 (3)
C22-C23	1.383 (4)	C16-C11-C12	117.4 (3)
C23-C24	1.368 (5)	C21-C22-C23	121.6 (3)
C24-C25	1.361 (6)	C22-C23-C24	119.4 (2)
C25-C26	1.386 (6)	C23-C24-C25	120.0 (4)
C26-C21	1.372 (5)	C24-C25-C26	120.3 (4)
C31-C32	1.383 (5)	C25-C26-C21	121.0 (4)
C32-C33	1.367 (4)	C26-C21-C22	117.7 (3)
C33-C34	1.354 (5)	C31-C32-C33	121.2 (3)
C34-C35	1.368 (8)	C32-C33-C34	120.5 (3)
C35-C36	1.379 (6)	C33-C34-C35	120.1 (4)
C36-C31	1.383 (5)	C34-C35-C36	119.7 (4)
C12-H12	0.917 (4)	C35-C36-C31	120.9 (4)
C13-H13	0.931 (5)	C36-C31-C32	117.6 (3)
C14-H14	0.878 (5)	C11-C12-H12	118.6 (4)
C15-H15	0.880 (5)	C13-C12-H12	120.4 (3)
C16-H16	0.927 (3)	C12-C13-H13	118.5 (2)
C22-H22	0.913 (4)	C13-C14-H14	118.2 (4)
C23-H23	0.959 (6)	C15-C14-H14	122.7 (6)
C24-H24	0.928 (4)	C14-C15-H15	123.6 (5)
C25-H25	0.919 (4)	C16-C15-H15	116.0 (4)
C26-H26	0.926 (4)	C15-C16-H16	121.0 (4)
C32-H32	0.909 (4)	C11-C16-H16	117.7 (4)
C33-H33	0.915 (6)	C21-C22-H22	117.6 (4)
C34-H34	0.885 (4)	C23-C22-H22	120.8 (3)
C35-H35	0.869 (5)	C22-C23-H23	116.3 (2)
C36-H36	0.925 (4)	C24-C23-H23	124.2 (2)
P-Cr-C1	94.3 (1)	C23-C24-H24	119.4 (4)
P-Cr-C2	96.2 (1)	C25-C24-H24	120.4 (4)
P-Cr-C3	88.4 (1)	C24-C25-H25	122.1 (4)
P-Cr-C4	87.5 (1)	C26-C25-H25	117.4 (4)
P-Cr-C5	174.3 (1)	C25-C26-H26	120.7 (4)
C1-Cr-C2	88.3 (2)	C21-C26-H26	118.3 (4)
C1-Cr-C3	176.0 (2)	C31-C32-H32	118.5 (4)
C1-Cr-C4	90.4 (2)	C33-C32-H32	120.3 (4)
C1-Cr-C5	89.2 (2)	C32-C33-H33	117.1 (2)
C2-Cr-C3	88.4 (2)	C34-C33-H33	122.3 (2)
C2-Cr-C4	176.2 (2)	C33-C34-H34	121.9 (6)
C2-Cr-C5	88.4 (2)	C35-C34-H34	117.9 (5)
C3-Cr-C4	92.6 (2)	C34-C35-H35	130.0 (5)
C3-Cr-C5	88.4 (2)	C36-C35-H35	110.3 (5)
C4-Cr-C5	87.9 (2)	C35-C36-H36	117.5 (4)
Cr-P-C11	116.6 (1)	C31-C36-H36	121.3 (4)

The average Cr-P-O angle in the phosphite complex is 117.8° (111.1 , 119.6 , and 122.6°) which is larger than the 115.6° average (112.2 , 116.6 , and 118.1°) of the Cr-P-C angles in the phosphine complex but similar to the 118.2° average in $Rh_2[P(OC_6H_5)_3]_2(C_8H_{12})Cl_2^{29}$ and the 117.1° average in *trans*- $[P(OC_6H_5)_3]_2Cr(CO)_4^{26}$. The O-P-O angles in $(C_6H_5O)_3PCr(CO)_5$ (100.0° average) are correspond-

Table VI. Bond Lengths (Å) and Angles (deg) in Pentacarbonyl(triphenyl phosphite)chromium(0)

Cr-C1	1.892 (5)	Cr-P-O31	111.1 (1)
Cr-C2	1.895 (4)	Cr-C1-O1	176.7 (3)
Cr-C3	1.904 (6)	Cr-C2-O2	177.9 (4)
Cr-C4	1.892 (4)	Cr-C3-O3	174.4 (3)
Cr-C5	1.861 (4)	Cr-C4-O4	178.6 (3)
Cr-P	2.309 (1)	Cr-C5-O5	178.5 (3)
P-O11	1.589 (3)	O11-P-O21	96.9 (2)
P-O21	1.615 (3)	O11-P-O31	104.8 (2)
P-O31	1.591 (2)	O21-P-O31	98.3 (1)
O11-C11	1.409 (6)	P-O11-C11	123.5 (2)
O21-C21	1.397 (6)	P-O21-C21	125.6 (2)
O31-C31	1.392 (4)	P-O31-C31	131.0 (2)
O1-C1	1.127 (7)	O11-C11-C12	117.6 (5)
O2-C2	1.130 (5)	O11-C11-C16	120.4 (3)
O3-C3	1.130 (7)	O21-C21-C22	116.3 (3)
O4-C4	1.135 (5)	O21-C21-C26	122.5 (5)
O5-C5	1.136 (6)	O31-C31-C32	115.8 (4)
C11-C12	1.354 (5)	O31-C31-C36	122.1 (5)
C12-C13	1.377 (8)	C11-C12-C13	118.5 (6)
C13-C14	1.360 (10)	C12-C13-C14	120.7 (4)
C14-C15	1.365 (7)	C13-C14-C15	118.9 (6)
C15-C16	1.359 (9)	C14-C15-C16	121.1 (7)
C16-C11	1.349 (9)	C15-C16-C11	118.8 (4)
C21-C22	1.361 (7)	C16-C11-C12	121.9 (5)
C22-C23	1.365 (8)	C21-C22-C23	119.5 (4)
C23-C24	1.357 (6)	C22-C23-C24	120.4 (6)
C24-C25	1.354 (9)	C23-C24-C25	119.8 (5)
C25-C26	1.376 (8)	C24-C25-C26	121.4 (4)
C26-C21	1.377 (5)	C25-C26-C21	117.8 (5)
C31-C32	1.363 (9)	C26-C21-C22	121.1 (5)
C32-C33	1.378 (7)	C31-C32-C33	118.8 (6)
C33-C34	1.350 (11)	C32-C33-C34	120.4 (8)
C34-C35	1.319 (13)	C33-C34-C35	120.6 (5)
C35-C36	1.427 (8)	C34-C35-C36	120.7 (7)
C36-C31	1.341 (8)	C35-C36-C31	117.5 (7)
C12-H12	0.92 (5)	C36-C31-C32	121.8 (4)
C13-H13	0.84 (4)	C11-C12-H12	124 (2)
C14-H14	0.82 (5)	C13-C12-H12	118 (2)
C15-H15	0.98 (6)	C12-C13-H13	114 (4)
C16-H16	0.84 (3)	C14-C13-H13	125 (4)
C22-H22	0.87 (3)	C13-C14-H14	125 (3)
C23-H23	0.97 (5)	C15-C14-H14	115 (3)
C24-H24	0.94 (5)	C14-C15-H15	117 (2)
C25-H25	0.92 (3)	C16-C15-H15	122 (2)
C26-H26	0.92 (5)	C15-C16-H16	124 (4)
C32-H32	1.20 (4)	C11-C16-H16	117 (4)
C33-H33	1.10 (6)	C21-C22-H22	121 (3)
C34-H34	0.86 (5)	C23-C22-H22	120 (3)
C35-H35	0.99 (7)	C22-C23-H23	118 (2)
C36-H36	1.01 (6)	C24-C23-H23	121 (2)
		C23-C24-H24	120 (2)
		C25-C24-H24	120 (2)
		C24-C25-H25	120 (3)
		C26-C25-H25	119 (3)
		C25-C26-H26	123 (2)
		C21-C26-H26	119 (2)
		C31-C32-H32	118 (2)
		C33-C32-H32	123 (2)
		C32-C33-H33	122 (2)
		C34-C33-H33	118 (2)
		C33-C34-H34	113 (4)
		C35-C34-H34	125 (4)
		C34-C35-H35	136 (3)
		C36-C35-H35	102 (3)
		C35-C36-H36	132 (2)
		C31-C36-H36	107 (2)
P-Cr-C1	90.6 (1)		
P-Cr-C2	93.2 (1)		
P-Cr-C3	95.5 (1)		
P-Cr-C4	87.6 (1)		
P-Cr-C5	176.1 (1)		
C1-Cr-C2	90.2 (2)		
C1-Cr-C3	173.9 (2)		
C1-Cr-C4	89.6 (2)		
C1-Cr-C5	87.3 (2)		
C2-Cr-C3	89.6 (2)		
C2-Cr-C4	179.2 (2)		
C2-Cr-C5	90.1 (2)		
C3-Cr-C4	90.5 (2)		
C3-Cr-C5	86.6 (2)		
C4-Cr-C5	89.1 (2)		
Cr-P-O11	122.6 (1)		
Cr-P-O21	119.6 (1)		

**Figure 5.** Thermal ellipsoid diagram of $(C_6H_5O)_3PCr(CO)_5$.

magnitude based on previous ideas of the bonding characteristics of the ligands inferred mainly from infrared and nmr coupling constant data. Thus it has been shown that the C-O stretching frequencies (E mode) of the compounds $(C_6H_5O)_3PCr(CO)_5$,³⁰ $H_3PCr(CO)_5$,³¹ and $(C_6H_5)_3PCr(CO)_5$ ³⁰ are 1960, 1953, and 1942 cm^{-1} , respectively. Furthermore, the phosphorus ligand with the most electronegative groups attached to it (therefore the most electron deficient and weakest base) generally results in the complex with the highest stretching frequencies. A prevalent explanation³²⁻³⁴ of this phenomenon is that the ligands with the most electron deficient phosphorus can behave as π acceptors and thus compete with the carbonyl groups for the metal $d\pi$ electrons. This results in a lower antibonding character of a CO and a higher stretching frequency.

It was also found in the corresponding tungsten compounds, $LW(CO)_5$, that the less basic phosphorus ligands (better π acceptor) had the larger tungsten-183-phosphorus-31 coupling constants⁷ and specifically that J_{W-P} for $(C_6H_5O)_3PW(CO)_5$ is much larger than for $(C_6H_5)_3PW(CO)_5$, 411 Hz³⁵ vs. 280 Hz, respectively. This indicates a greater interaction between the metal and triphenyl phosphite than between the metal and triphenylphosphine. Indeed, there is also a correlation between the phosphorus-tungsten coupling constants and the carbonyl stretching frequencies in the $LW(CO)_5$ compounds.⁷

The chromium-phosphorus bond lengths found in this investigation are predictable in terms of the above theory; *i.e.*, the chromium-triphenylphosphine bond is significantly longer (2.422 Å) than the chromium-triphenyl phosphite bond (2.309 Å). It is essentially the same as that in *cis*- $CH_3(CH_3O)CCr(CO)_4P(C_6H_5)_3$, 2.42 Å.²⁴ This is expected since triphenylphosphine is *trans* to carbon monoxide in each of the compounds. The Cr-P bond lengths in $[(C_6H_5)_2-$

ingly smaller than the C-P-C angles (102.6° average) in $(C_6H_5)_3PCr(CO)_5$.

Discussion

The main purpose of this study was to ascertain if phosphorus-chromium bond distances are significantly different in various phosphorus ligand derivatives of chromium carbonyl and especially if these distances are of a predictable

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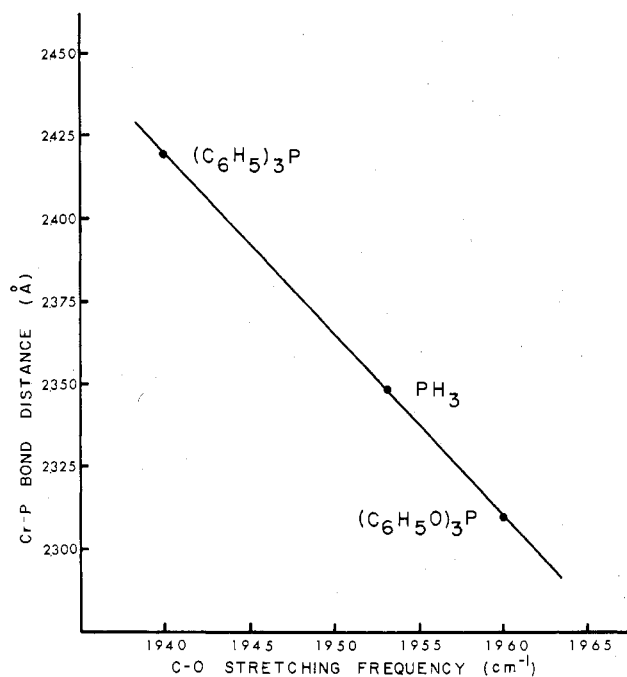


Figure 6. Correlation of the Cr-P bond length and the CO stretching frequency (E mode) in $LCr(CO)_5$.

$PCH_2CH_2N(C_2H_5)CH_2CH_2P(C_6H_5)_2]Cr(CO)_3$ are 2.375 and 2.387 Å, respectively, and are apparently somewhat distorted by the steric requirement of the two chelate rings.¹⁰ The Cr-P bond distances in *cis*-(PH_3)₂Cr(CO)₄²⁵ of 2.349 and 2.344 Å and in *cis*-(PH_3)₃Cr(CO)₃¹¹ of 2.344 Å are intermediate between the bond lengths of the triphenylphosphine and triphenyl phosphite complexes, which is predictable from the infrared data. In fact, a plot of the P-Cr bond lengths against the CO-stretching frequency gives a straight line (Figure 6).³⁶ The Cr-P bond length (2.309 Å) in *trans*-[(C_6H_5O)₃P]₂Cr(CO)₄ is the shortest presently known in a chromium(0) complex.²⁶ Again this has been rationalized by the enhanced π bonding of mutually trans phosphorus ligands, which compete mainly with each other rather than mainly with CO for the $d\pi$ electrons of the metal. Another case where this is illustrated is *cis*-(PH_3)₄Cr(CO)₂,³⁷ in which the two types of phosphorus ligands have different Cr-P bond lengths. The phosphines trans to CO have Cr-P lengths of 2.338 (4) Å whereas the mutually trans phosphines have Cr-P lengths of 2.282 (4) Å. Other cases in which the metal-phosphorus bond length depends on the ligand trans to it are *cis-mer*-[(CH_3)₂(C_6H_5)P]₃MoOCl₂³⁸ and *cis*-(π - C_5H_5)-[(C_6H_5)₂PCH₂CH₂P(C_6H_5)₂]Mo(CO)Cl.³⁹ In the former, the mutually trans phosphorus atoms have longer Mo-P bond lengths, 2.541 (3) and 2.558 (3) Å, than the phosphorus atom which is trans to chlorine, for which the Mo-P distance is 2.500 (3) Å. This is to be expected if phosphorus is a better π acceptor than chlorine. In the latter case, which is a

(36) The E-mode carbonyl stretching frequency of (PH_3)₃Cr(CO)₃ is known but the X-ray crystallographic structure has not been determined. Nonetheless, it is assumed that the P-Cr distance in (PH_3)₃Cr(CO)₃ would not be substantially different from that in *cis*-(PH_3)₂Cr(CO)₄ and *fac*-(PH_3)₃Cr(CO)₃, because in each case the PH_3 is trans to a carbonyl group and this seems to be the important factor in determining the bond properties. This is also confirmed by the discussion of W-P coupling constants (see text).

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(38) L. Manojlovic-Muir, *J. Chem. Soc. A*, 2796 (1971).

(39) M. A. Bush, A. D. U. Hardy, L. Manojlovic-Muir, and G. A. Sim, *J. Chem. Soc. A*, 1003 (1971).

"square pyramid" with the cyclopentadienyl group at the apex and the other groups in the square base, the phosphorus which is trans to CO has a Mo-P distance of 2.496 (4) Å whereas the phosphorus trans to chlorine has a Mo-P distance of 2.439 (5) Å. Again this is expected if CO is a better π acceptor than chlorine.

Additional evidence of the increased metal-phosphorus interaction when the ligands are mutually trans is given by the larger magnitude of J_{W-P} in *trans*- $L_2W(CO)_4$ (453,³⁵ 446⁴⁰ Hz) compared to J_{W-P} in $LW(CO)_5$ (411,³⁵ 415.5⁴⁰ Hz), *cis*- $L_2W(CO)_4$ (415.0⁴⁰ Hz), and *fac*- $L_3W(CO)_3$ (412,³⁵ 410.5⁴⁰ Hz) when L is triphenyl phosphite.

All these data do not prove π bonding between phosphorus and chromium, molybdenum, or tungsten, but they are consistent with it and are very useful predictively. For example, it will be interesting to ascertain if the Cr-P bond is shorter than 2.309 Å in $PF_3Cr(CO)_5$ and longer than 2.422 Å in $(C_4H_9)_3PCr(CO)_5$ as would be predicted from Figure 6 and the known CO stretching frequencies.

The metal-carbon and carbon-oxygen bond lengths are directly affected by the other ligands attached to the metal. In compounds of the type $LCr(CO)_5$, the carbonyl trans to the phosphorus has a shorter chromium-carbon bond than the carbonyls cis to the phosphorus ligand in the same molecule. In orbital terms this means that the carbon monoxide trans to phosphorus more effectively competes with phosphorus for metal $d\pi$ electrons to form a partial multiple Cr-C bond which is of higher bond order than the carbon monoxide ligands cis to phosphorus and trans to each other. In valence-bond terms, the trans CO has a greater contribution of resonance form II than the cis CO's.



In the triphenyl phosphite compound the Cr-C distances are as follows: *trans*, 1.861 (4) Å; *cis*, 1.892 (5), 1.895 (4), 1.904 (6), and 1.892 (4) Å. In the triphenylphosphine compound the Cr-C distances are as follows: *trans*, 1.845 (4) Å; *cis*, 1.878 (4), 1.894 (4), 1.882 (5), and 1.867 (4) Å. The difference between the *trans* Cr-C bond length and the average of the four *cis* Cr-C bond lengths is 0.035 Å for the phosphite compound and 0.036 Å for the phosphine compound.

In a comparison of the two structures, the *trans* Cr-C (1.861 Å) bond in the phosphite compound is longer than the *trans* Cr-C (1.845 Å) bond in the phosphine compound, and the average of *cis* Cr-C bond lengths (1.896 Å) in the phosphite compound is longer than the average of the *cis* Cr-C bond lengths (1.880 Å) in the phosphine compound. This is expected because the better π acceptor, triphenyl phosphite, removes more charge from the chromium, so that resonance form II becomes less important for triphenyl phosphite than for triphenylphosphine. Thus the better the π acceptor is, the longer the remaining metal-carbon bonds to the carbonyls should be, especially in the case of the carbonyl trans to the ligand. The long chromium-carbon bond length (1.909 Å) in the unsubstituted chromium hexacarbonyl is consistent with this expectation. Thus, the importance of resonance form II (*i.e.*, back-bonding) decreases in the order: CO trans to P > CO cis to P > CO in $Cr(CO)_6$.

It should also be pointed out that there is an apparent exception to those arguments. This occurs in the structure¹³ of *cis*-Mn(CO)₄(Ph_3P)Cl in which the Mn-C distances trans to phosphorus and trans to chlorine are the same, *viz.*, 1.752

(40) G. G. Mather and A. Pidcock, *J. Chem. Soc. A*, 1226 (1970).

(14) and 1.752 (15) Å, respectively. If phosphorus is a better π acceptor than chlorine, the Mn-C bond trans to phosphorus would be expected to be longer. However the standard deviations of the bonds in the manganese compound are rather large compared to the ones reported here.

The C-O bond lengths in $(\text{PhO})_3\text{PCr}(\text{CO})_5$ are less (cis average, 1.131 Å; trans, 1.136 Å) than in $\text{Ph}_3\text{PCr}(\text{CO})_5$ (cis average, 1.14 Å; trans, 1.154 Å), which is the consistent expectation for less antibonding character of the CO multiple bond in the phosphite compound (resonance form II being less important).

The bond angles in the triphenylphosphine complex are normal with the C-P-C angles averaging 102.6° and the C-P-Cr angles averaging 115.6°.

Only a few crystal structures have been reported^{26,29,41-45} for coordination compounds containing a triorganophosphite, and several of the reports are notes which do not describe the phosphite geometry. Its geometry is of interest because

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from models it has been suggested⁴⁶ that triphenyl phosphite would be less bulky than triphenylphosphine since the P-O-C bond angle allows more flexibility in relieving neighboring ring interactions. The O-P-O bond angles in $(\text{PhO})_3\text{PCr}(\text{CO})_5$ average 100.0° and the O-P-Cr angles average 117.8°. This does indeed indicate that the groups on phosphorus are collapsed together more in the case of the phosphite than in the case of the phosphine.

It follows that the Cr-P bond contains a larger amount of s character from the phosphorus hybrid in the case of the phosphite.⁴⁷

The greater steric influence, if any, of triphenylphosphine is not evident from the distortion of the cis CO ligands from the plane of the chromium and cis carbons. The P-Cr-C (cis) bond angles are 87.5, 88.4, 94.3, and 96.2° (91.6° average) in the phosphine compared to 87.6, 90.6, 93.2, and 95.5° (91.7° average) in the phosphite.

The P-O-C angles of 123.5, 125.6, and 131.0° (126.7° average) in the phosphite are about the same as in the other triphenyl phosphite coordination compounds.^{26,29,44,45}

Registry No. $(\text{C}_6\text{H}_5)_3\text{PCr}(\text{CO})_5$, 14917-12-5;
 $(\text{C}_6\text{H}_5\text{O})_3\text{PCr}(\text{CO})_5$, 18461-39-7.

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Contribution from the Department of Chemistry and the Radiation Laboratory,¹ University of Notre Dame, Notre Dame, Indiana 46556

Crystal and Molecular Structure of Dimethyldiisothiocyanato(terpyridyl)tin(IV)

DATTA V. NAIK² and W. ROBERT SCHEIDT*

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A three-dimensional X-ray crystal structure analysis of the compound of composition $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2(\text{C}_{15}\text{H}_{11}\text{N}_3)$ has established that it is a seven-coordinate compound with a pentagonal-bipyramidal configuration. The crystals are triclinic, space group $P\bar{1}$ with $a = 9.440$ (4), $b = 15.446$ (5), $c = 7.595$ (4) Å; $\alpha = 95.50$ (2), $\beta = 93.04$ (1), $\gamma = 71.30$ (2)°. There are two formula units per unit cell, observed and calculated densities are 1.59 and 1.588 g/cm³. The intensities of all independent reflections having $(\sin \theta)/\lambda \leq 0.648 \text{ \AA}^{-1}$ were measured with graphite-monochromated Mo K α radiation by θ - 2θ scanning on a computer-controlled four-circle diffractometer; the 4395 data retained as statistically observable were employed for structure determination and refined by Patterson, Fourier, and anisotropic least-squares techniques to a conventional R of 0.029. Tin is bonded to three terpyridyl nitrogens and two isothiocyanato nitrogens so as to form a pentagonal plane. The methyl groups are trans at axial positions with a C-Sn-C angle of 173.7 (2)°. The average bond distances are Sn-C = 2.105 Å, Sn-N(NCS) = 2.283 Å, Sn-N(terpyridyl) = 2.515 Å. The terpyridyl group is distorted from planarity, although the individual pyridine rings are planar. Of the two isothiocyanate groups, one is essentially linear, while the other is bent with a SnNC angle of 155.1 (4)°. This bending is attributed to crystal packing.

Recently May and Curran³ of our laboratory have reported the preparation and Mossbauer data of terpyridyl adducts with $\text{R}_2\text{Sn}(\text{NCS})_2$ where R is an alkyl or aryl group. On the basis of infrared spectra and Mossbauer data they proposed that these complexes were seven-coordinate with axial carbon atoms and five nitrogen atoms in the equatorial plane of a pentagonal-bipyramidal coordination polyhedron. Seven-co-

ordinate tin complexes are not uncommon; crystal structures of tris(tropolonato)monochlorotin(IV) and tris(tropolonato)monohydroxytin(IV),⁴ methyltris(nitrato)tin(IV),⁵ and methyltris(diethylthiocarbamate)tin(IV)⁶ have established seven-coordination for tin in these complexes. However, seven-coordination has not been established for complexes having two carbon atoms bonded to tin. The possibility that these adducts were ionic six-coordinate complexes could not be ruled out since they show partial ionization in dimethylformamide and also react readily with sodium tetra-

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(2) (a) Peter C. Reilly Fellow, 1971-1972. (b) Taken in part from the dissertation submitted by D. V. N. to the Graduate School of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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