

Trans Interaction in a Metal Carbonyl. Structure of ((Triphenylphosphinemethylide)diphenylphosphine oxide)pentacarbonyltungsten(0), $W(CO)_5(O=P(C_6H_5)_2CHP(C_6H_5)_3)$

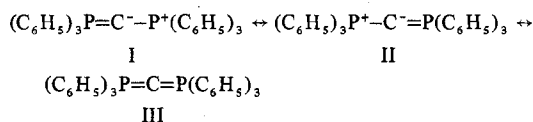
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The compound $W(CO)_5(O=P(C_6H_5)_2CHP(C_6H_5)_3)$ is a hydrolysis product of the complex formed between hexaphenylcarbodi-phosphorane (1) and tungsten pentacarbonyl. The ligand is a phosphine oxide in which one of the alkyl groups is an ylide. The ligand is bound to the tungsten through oxygen to give a W-O bond length of 2.199 (7) Å. There is a pronounced trans interaction; the axial W-C bond length of 1.949 (10) Å is significantly shorter than the average of the four equatorial bond lengths, 2.025 (6) Å. In the ligand, the central P-C-P bond angle is 127.9 (6)°. The two P-C bond lengths are equal and average 1.690 (10) Å; the multiple bond order is approximately equally distributed between the two P-C bonds. The P-O bond length is 1.523 (8) Å and the average of the five equivalent P-C bond lengths of the phenyl rings is 1.803 (8) Å. The structure was determined from single-crystal, three-dimensional X-ray data collected by counter methods. The material crystallizes as yellow-orange plates in the monoclinic space group $P2_1/c$ (C_{2h}^5). The lattice constants are $a = 9.679$ (4), $b = 20.557$ (8), $c = 16.709$ (6) Å, and $\beta = 96.95$ (2)°. There are four molecules in the unit cell. Full-matrix least-squares refinement on F for 1833 independent reflections with $F^2 > 3\sigma(F^2)$ converged to a weighted R factor of 5.05%. Because of the limited resolution of the diffraction data, the C-O carbonyl bond lengths were constrained to be 1.146 Å. The importance of applying such constraints under these conditions is discussed.

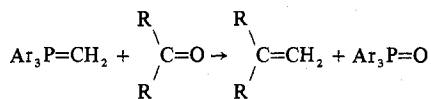
Introduction

Hexaphenylcarbodi-phosphorane (1)^{2,3} is a bis ylide whose unusual synthetic and structural chemistry is to some extent explained by the three resonance forms

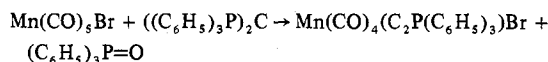


The crystal structure of the bis ylide indicates that the molecule is bent⁴ and suggests that resonance forms I and II make the most important contributions to the structure. The reactions of 1 with a wide range of compounds have been described by Ramirez, *et al.*⁵ Some of these reactions are consistent with the nucleophilic character of resonance forms I and II, while others are consistent with the electrophilic nature implied by III. Recently the structures have been determined for two products formed from the reaction of 1 with diphenylcarbodiimide, $(C_6H_5N)_2C$.^{6,7}

The reactions of 1 with metal complexes are as unusual as those with organic compounds. Kaska, *et al.*, have described two types of reactions with transition metal carbonyls.^{8,9} The first of these is formally a Wittig reaction^{10,11} of the type



where Ar = aryl and R = alkyl. Thus, for example⁸



We have determined the structure of the product manganese complex and found it to contain the unusual phosphonium zwitterion $(C_6H_5)_3P^+-C\equiv C^-$.¹² The direct photolysis of 1 with tungsten hexacarbonyl yields a similar product.⁹ However, the reaction of 1 with the very labile complex $W(CO)_5(THF)$ corresponds to a second type of reaction in which 1 simply displaces THF as a ligand to form $W(CO)_5(C(P(C_6H_5)_3)_2)$ (2).⁹ Although structurally similar to a metal carbene, this complex has one more electron pair than the carbenes and therefore cannot have the strong metal-to-ligand π bonding that stabilizes the latter. This makes the structure of 2 of considerable interest with regard to the bonding in the complex.

Repeated crystallizations of air- and moisture-sensitive solutions of 2 from several solvents gave no samples from which crystals of diffraction quality could be isolated. However one set of recrystallizations from methylene chloride-pentane solutions gave yellow-orange crystals of diffraction quality. In the course of our investigation it became clear that these crystals were of the hydrolysis product $W(CO)_5(O=P(C_6H_5)_2CHP(C_6H_5)_3)$ (3) rather than the starting material. However, our interest in the structure of this unusual derivative led us to complete the analysis which we report here.

Experimental Section

Several crystals were sealed in thin-walled quartz capillaries under an argon atmosphere. Although most crystals were twinned, two suitable crystals were found. Precession photographs showed the crystal had monoclinic symmetry with systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$. These uniquely determine the space group as $P2_1/c$ (C_{2h}^5).¹³

(12) (a) S. Z. Goldberg, E. N. Duesler, and K. N. Raymond, *J. Chem. Soc. D*, 826 (1971); (b) S. Z. Goldberg, E. N. Duesler, and K. N. Raymond, *Inorg. Chem.*, 11, 1397 (1972).

(13) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969.

(1) (a) National Institutes of Health Predoctoral Fellow, 1969-1972. (b) Fellow of the Alfred P. Sloan Foundation, 1971-1973.

(2) F. Ramirez, N. B. Desai, B. Hanson, and N. McKelvie, *J. Amer. Chem. Soc.*, 83, 3539 (1961).

(3) G. H. Birum and C. N. Mathews, *J. Amer. Chem. Soc.*, 88, 4198 (1966).

(4) (a) A. T. Vincent and P. J. Wheatley, *Chem. Commun.*, 582 (1971); (b) *J. Chem. Soc., Dalton Trans.*, 617 (1972).

(5) F. Ramirez, J. F. Pilot, C. P. Smith, B. Hanson, and N. McKelvie, *J. Amer. Chem. Soc.*, 89, 6273 (1967).

(6) F. K. Ross, W. C. Hamilton, and F. Ramirez, *Acta Crystallogr., Sect. B*, 27, 2331 (1971).

(7) F. K. Ross, L. Manojlovic-Muir, W. C. Hamilton, F. Ramirez, and J. F. Pilot, *J. Amer. Chem. Soc.*, 94, 8738 (1972).

(8) D. K. Mitchell, W. D. Korte, and W. C. Kaska, *J. Chem. Soc. D*, 1384 (1970).

(9) W. C. Kaska, D. K. Mitchell, and R. F. Reichelderfer, *J. Organometal. Chem.*, 47, 391 (1973).

(10) G. Wittig and G. Felletschin, *Justus Liebigs Ann. Chem.*, 555, 133 (1944).

(11) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

The crystal orientation and unit cell constants were determined using the data crystal. The final lattice constants were obtained by a least-squares refinement using the setting angles for 12 carefully centered reflections with 2θ angles in the range $25\text{--}35^\circ$.¹⁴ Crystal data are summarized in Table I.

Intensity data were collected on an automated Picker four-circle diffractometer using Mo $K\alpha$ radiation. Data were collected in the $\theta\text{--}2\theta$ scan mode with a scan rate of $1^\circ/\text{min}$ from 0.75° below the $K\alpha_1$ peak to 0.75° above the $K\alpha_2$ peak. Stationary-crystal, stationary-counter background counts of 10 sec each were taken at the start and end of each scan. Attenuators were automatically inserted if the counting rate approached 10^4 counts/sec. The takeoff angle for the X-ray tube was 2° and the Bragg angle for the graphite monochromator was 12.02° . The detector was located 33 cm from the source and had a 7×7 mm receiving aperture. The pulse height analyzer was set to a 95% window centered on the Mo $K\alpha$ peak. The mosaicity of the crystal was measured using the narrow-source, open-counter ω -scan technique.¹⁵ The width of ω scans at half-maximum for typical strong reflections was $0.1\text{--}0.15^\circ$.

Initially data for the octants $\pm h, +k, +l$ were collected to a 2θ angle of 35° . During data collection crystal and instrumental stability was checked by monitoring the 300, 020, and 040 reflections after every 60 reflections. The standards indicated a slow regular decomposition of roughly 5%. During the collection of data in the range of $35^\circ < 2\theta < 50^\circ$ the crystal showed signs of rapid decomposition. No attempt was made to collect further data, and only data with $2\theta \leq 35^\circ$ were used in the structure determination.

Data were processed as previously described.^{16,17} The p factor introduced to prevent overweighting the strong reflections was chosen as 0.04, and the data were corrected for decay as previously described.¹⁸ The data crystal was an irregularly shaped plate with the plate face approximately parallel to the ϕ axis of the diffractometer. For purposes of the absorption correction an origin point was chosen as the intersection of the 111 , $1\bar{1}\bar{1}$, and $3\bar{0}\bar{1}$ planes. The distances from the origin to the $0\bar{1}0$ and $0\bar{2}\bar{1}$ planes were 0.509 and 0.445 mm, respectively. The calculated volume of the crystal was 0.0145 mm^3 . The absorption correction was made using the analytical procedure of De Meulenaer and Tompa.¹⁹ The transmission factors ranged from 0.325 to 0.719 with an average transmission factor of 0.603.²⁰ The final result was a data set of 2110 independent reflections of which 1833 had $F^2 \geq 3\sigma(F^2)$. Only the latter were used in the final refinement.

Solution and Refinement of the Structure

The structure was solved by the application of heavy-atom techniques.²¹ Full-matrix, least-squares refinements were carried out for those reflections with $F^2 \geq 3\sigma(F^2)$. In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, w , is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for W, P, O, and C were taken from the tabulations of Cromer and Mann.²⁰ Hydrogen scattering factor values were those calculated by Stewart.²² Corrections for anomalous dispersion effects for W and P were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.²³

The positions of the W and both P atoms were located from a three-dimensional Patterson map. Subsequent least-squares and dif-

(14) The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by the Picker Corp. for the PDP 8/I.

(15) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(16) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

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

(18) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **11**, 171 (1972).

(19) J. De Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(20) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(21) In addition to local programs for the CDC 7600 computer, modifications of the following programs were used: Ibers' NUCLS, a group least-squares version of the Busing-Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plot program; AGNOST, an absorption correction program by Coppens, Leiserowitz, and Rabinovich as modified by Hamilton, Edmonds, Cahen, and Ibers.

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

(23) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table I. Summary of Crystal Data

| | |
|--------------------------------------|--|
| Molecular formula | $\text{W}(\text{CO})_5(\text{O}=\text{P}(\text{C}_6\text{H}_5)_2\text{CHP}(\text{C}_6\text{H}_5)_3)$ |
| Molecular weight | 800.40 |
| Linear absorption coefficient, μ | 38.46 cm^{-1} |
| Calculated density | 1.61 g/cm^3 |
| Crystal dimensions | $0.11 \times 0.45 \times 0.50 \text{ mm}$ |
| Space group | $P2_1/c$ |
| Formula units per cell | 4 |
| Cell constants ^a | |
| a | 9.679 (4) Å |
| b | 20.557 (8) Å |
| c | 16.709 (6) Å |
| β | $96.95 (2)^\circ$ |
| Cell volume | $3300 (2) \text{ \AA}^3$ |

^a Ambient temperature of 23° . Mo $K\alpha_1$ radiation, λ 0.70926 Å.

ference Fourier calculations located the remaining nonhydrogen atoms. The phenyl rings were refined as rigid groups with a C-C bond length of 1.395 Å.²⁴ At this point the refinement was continued with a model in which each of the nongroup atoms was allowed to vibrate anisotropically and each group atom had an individual isotropic thermal parameter. This model converged to $R_1 = 4.42\%$ and $R_2 = 5.83\%$.²⁵ A difference Fourier indicated the positions of all the hydrogens including the one bonded to C_6 . Rather than use these positions, the hydrogens were positioned on the basis of an ideal D_{6h} geometry for the phenyl groups. The C-H bond distance was chosen as 1.0 Å, and the hydrogen thermal parameter was chosen to be 1 plus the average thermal parameter for the five carbons of each group which has hydrogen atoms. The hydrogen bonded to C_6 was placed 1.0 Å from that atom such that it completed the sp^2 hybridization and was assigned a thermal parameter of 4.0 \AA^2 . This refinement converged to $R_1 = 3.95\%$ and $R_2 = 4.98\%$.

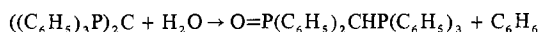
As discussed later, the low resolution of the data set led us to carry out the final refinement with C-O bond lengths constrained^{26,27} to be 1.148 Å, the distance found in $\text{W}(\text{CO})_6$.²⁸ The final values of R_1 and R_2 are 4.02 and 5.05%, respectively. On the final cycle of least squares no parameter shifted by more than one-tenth of its estimated standard deviation. The final error in an observation of unit weight, defined as

$$\left(\frac{\sum w(|F_o| - |F_c|)^2}{N_o - N_v} \right)^{1/2}$$

is 2.13, where N_o and N_v are the number of observation and variables, respectively. The error in an observation of unit weight did not vary systematically as a function either of $(\sin \theta)/\lambda$ or of $|F_o|$ although it was largest for small $(\sin \theta)/\lambda$ and large $|F_o|$. It is possible that the factor of $p = 0.04$ is somewhat too small, but it is more likely that the high value for the error in an observation of unit weight is due to the difficulties encountered in the model used in the absorption correction. Examination of the final difference Fourier revealed no peaks with a density greater than 0.8 e/Å, or roughly 40% of a carbon atom. These peaks were in the region of the tungsten atom. Observed and calculated structure factors, positional and thermal parameters for nongroup atoms, and derived rms amplitudes of thermal motion are in Tables II-IV, respectively.²⁹ Table V gives group parameters, Table VI, positional and thermal parameters for group atoms, and Table VII, hydrogen coordinates and isotropic temperature factors.

Discussion

The complex, shown in Figure 1, is an octahedral tungsten hexacarbonyl derivative in which one carbonyl is replaced by the oxygen-bonded ligand $\text{O}=\text{P}(\text{C}_6\text{H}_5)_2\text{CHP}(\text{C}_6\text{H}_5)_3$ (4). It is known² that 4 is formed by the hydrolysis of 1 *via*



(24) "International Tables for X-Ray Crystallography," Vol. III, Knoch Press, Birmingham, England, 1969.

(25) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

(26) K. N. Raymond, *Acta Crystallogr., Sect. A*, in press.

(27) K. N. Raymond, *Acta Crystallogr., Sect. A*, **28**, 163 (1972).

(28) S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, **20**, 2711 (1966).

(29) See paragraph at end of paper regarding supplementary material.

Table III. Positional and Thermal^a Parameters ($\times 10^4$) for Nongroup Atoms in $W(CO)_5(O=P(C_6H_5)_2CHP(C_6H_5)_3)$

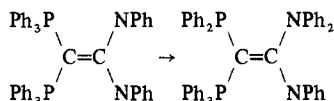
| | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|----------------|--------------------------|--------------|---------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| W | 0.16990 (5) ^b | 0.20051 (2) | 0.30079 (3) | 66.1 (10) | 18.9 (2) | 41.8 (4) | -1.2 (3) | -5.4 (4) | -1.94 (17) |
| P ₁ | 0.4193 (3) | 0.32091 (15) | 0.29235 (19) | 67 (5) | 16.2 (10) | 38.2 (16) | 4.4 (19) | -1 (2) | 0 (10) |
| P ₂ | 0.2660 (3) | 0.44729 (15) | 0.31453 (18) | 65 (5) | 18.1 (10) | 34.6 (15) | 2.0 (18) | -6 (2) | -1.0 (10) |
| C ₁ | 0.1320 (18) | 0.1733 (8) | 0.1843 (11) | 235 (32) | 33 (6) | 67 (9) | 39 (11) | 31 (15) | 0 (6) |
| C ₂ | 0.3128 (15) | 0.1287 (8) | 0.3216 (9) | 90 (22) | 30 (5) | 73 (8) | -7 (9) | 14 (11) | 2 (5) |
| C ₃ | 0.2061 (16) | 0.2299 (7) | 0.4166 (10) | 185 (26) | 26 (5) | 68 (9) | 56 (9) | 60 (14) | 11 (6) |
| C ₄ | 0.0066 (17) | 0.2639 (7) | 0.2828 (8) | 124 (24) | 23 (5) | 69 (9) | -3 (9) | 0 (12) | 9 (5) |
| C ₅ | 0.0477 (14) | 0.1329 (7) | 0.3341 (8) | 106 (22) | 22 (5) | 45 (7) | 12 (8) | 9 (9) | 5 (4) |
| C ₆ | 0.3651 (11) | 0.3834 (5) | 0.3475 (6) | 87 (17) | 23 (4) | 29 (5) | 17 (7) | -10 (7) | 2 (4) |
| O ₁ | 0.0999 (14) | 0.1583 (6) | 0.1185 ^c | 423 (30) | 55 (5) | 59 (6) | -65 (10) | -9 (11) | -15 (5) |
| O ₂ | 0.3820 (11) | 0.0836 (6) | 0.3339 ^c | 152 (19) | 32 (4) | 157 (10) | 35 (7) | 33 (10) | 12 (5) |
| O ₃ | 0.2206 (12) | 0.2467 (5) | 0.4826 ^c | 329 (24) | 49 (4) | 46 (5) | 21 (8) | 22 (9) | -5 (4) |
| O ₄ | -0.0901 (12) | 0.2967 (6) | 0.2741 ^c | 125 (18) | 45 (5) | 141 (10) | 31 (7) | 19 (10) | 31 (5) |
| O ₅ | -0.0230 (9) | 0.0928 (5) | 0.3543 ^c | 108 (14) | 25 (3) | 82 (6) | -4 (6) | 14 (7) | 9 (3) |
| O ₆ | 0.3126 (8) | 0.2713 (4) | 0.2562 (4) | 72 (11) | 18 (2) | 46 (4) | -8 (5) | -13 (5) | -1 (3) |

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Standard deviations of the least significant figures are given here and in subsequent tables in parentheses. ^c Determined by constraining the carbonyl distance.

Table IV. Root-Mean-Square Amplitude of Vibration along Principal Axes ($\text{\AA} \times 10^3$)

| Atom | Axis 1 | Axis 2 | Axis 3 |
|----------------|------------|------------|------------|
| W | 168.8 (14) | 201.0 (12) | 251.1 (10) |
| P ₁ | 166 (7) | 193 (7) | 236 (5) |
| P ₂ | 166 (7) | 196 (6) | 232 (4) |
| C ₁ | 211 (25) | 302 (21) | 368 (25) |
| C ₂ | 197 (24) | 259 (23) | 320 (18) |
| C ₃ | 99 (42) | 256 (21) | 390 (23) |
| C ₄ | 213 (24) | 238 (24) | 324 (19) |
| C ₅ | 188 (25) | 235 (21) | 261 (20) |
| C ₆ | 145 (28) | 217 (19) | 254 (17) |
| O ₁ | 228 (18) | 340 (15) | 487 (16) |
| O ₂ | 185 (20) | 316 (14) | 471 (14) |
| O ₃ | 245 (14) | 316 (15) | 402 (14) |
| O ₄ | 195 (19) | 304 (14) | 468 (15) |
| O ₅ | 211 (16) | 234 (15) | 343 (12) |
| O ₆ | 155 (19) | 208 (13) | 271 (10) |

This type of phenyl migration has also been observed recently in the product first formed from the reaction of **1** with diphenylcarbodiimide, $(C_6H_5N)_2C$.⁷ In that case the phenyl migration is from phosphorus to nitrogen



In the present compound the hydrolysis presumably occurred while the ligand **1** was bound *via* carbon and hydrolysis was then accompanied by isomerism to oxygen coordination.

We have described elsewhere²⁶ the structural artifacts which can occur in carbonyl, cyanide, and isocyanide complexes when diffraction data with a resolution on the order of 1 Å are used in refining an unconstrained model. The short C≡O or C≡N bond lengths in these ligands make the carbon atom position particularly ill determined. This is readily apparent in Table VIII in a comparison of the W-C and W-O bond

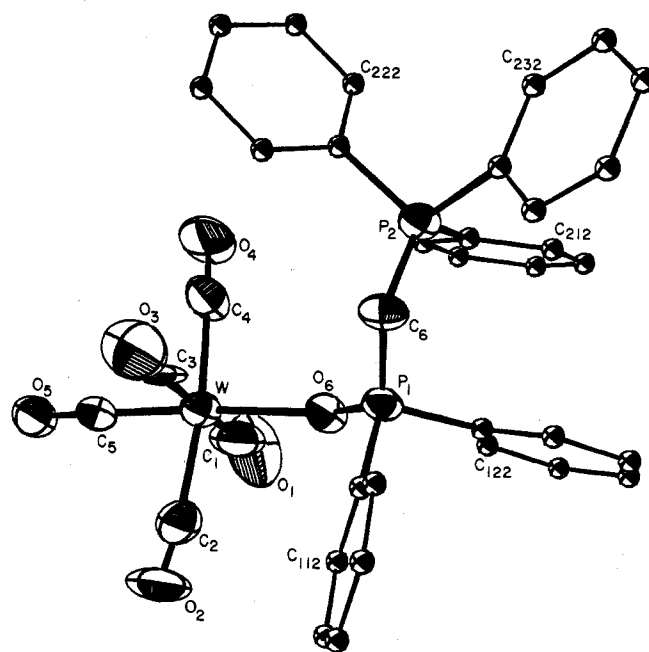


Figure 1. A perspective drawing of $W(CO)_5(O=P(C_6H_5)_2)CHP(C_6H_5)_3$. The thermal ellipsoids enclose 50% of the electron probability distribution. An isotropic temperature factor of 1 \AA^2 was used for the phenyl carbons so as to improve clarity. A single carbon atom in each phenyl group is labeled to identify both the group and the numbering system within each group. Hydrogen atoms are not shown.

lengths for the constrained and unconstrained models. The W-O bond lengths agree well between the two models and the variance of the four equatorial bond lengths is comparable. The poor resolution of the carbon atom position can be seen in the wide range of W-C bond lengths for the unconstrained model; the four equatorial bond lengths, which should be

Table V. Group Parameters^a

| Group | x_c | y_c | z_c | δ | ϵ | η |
|-------------------------------|-------------|------------|------------|-----------------------|------------|------------|
| Ph ₁₁ ^b | -0.3304 (6) | 0.2453 (3) | 0.3953 (3) | -2.141 (5) | -2.742 (5) | 2.400 (5) |
| Ph ₁₂ | -0.4266 (6) | 0.3686 (3) | 0.1442 (3) | -1.049 (8) | 2.173 (4) | 1.722 (9) |
| Ph ₂₁ | 0.2164 (6) | 0.4506 (3) | 0.1234 (3) | 1.53 (4) ^c | 1.710 (5) | 2.28 (4) |
| Ph ₂₂ | -0.0258 (5) | 0.4537 (2) | 0.3865 (3) | 1.487 (5) | -2.609 (4) | 2.190 (6) |
| Ph ₂₃ | -0.4134 (6) | 0.0823 (3) | 0.1293 (3) | 0.500 (5) | 2.916 (4) | -2.867 (5) |

^a x_c , y_c , and z_c are the fractional coordinates of the group center; the angles δ , ϵ , and η (in radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965); *Acta Crystallogr.*, **18**, 511 (1965). ^b The first subscript of the ring indicates to which phosphorus it is bound. ^c The large standard deviations of δ and η for Ph₂₁ are a consequence of the fact that ϵ is near 90° and the two variables are highly correlated. The standard deviations of the derived atomic positions (Table VI) include correlation and have values typical of those in the other groups.

Table VIII. Bond Distances in $W(CO)_5(O=P(C_6H_5)_2CHP(C_6H_5)_3)$

| Atoms | Dist, Å | |
|----------------------------------|-------------------------|-------------------|
| | Unconstrained model | Constrained model |
| W-C ₁ | 1.951 (19) ^a | 2.015 (12) |
| W-C ₂ | 2.039 (17) | 2.024 (12) |
| W-C ₃ | 1.956 (18) | 2.017 (12) |
| W-C ₄ | 2.070 (18) | 2.043 (12) |
| W-C ₅ (ax) | 1.923 (15) | 1.949 (10) |
| W-C (av) ^{b,c} | 2.004 (30) | 2.025 (6) |
| W-O ₆ | 2.200 (7) | 2.199 (7) |
| P ₁ -C ₆ | 1.701 (11) | 1.701 (11) |
| P ₂ -C ₆ | 1.681 (11) | 1.679 (11) |
| P ₁ -O ₆ | 1.521 (8) | 1.523 (8) |
| W-O ₁ | 3.162 (13) | 3.160 (14) |
| W-O ₂ | 3.162 (11) | 3.166 (11) |
| W-O ₃ | 3.166 (12) | 3.164 (13) |
| W-O ₄ | 3.182 (12) | 3.189 (12) |
| W-O ₅ | 3.099 (10) | 3.097 (8) |
| P ₁ -C ₁₁₁ | 1.808 (7) | 1.809 (7) |
| P ₁ -C ₁₂₁ | 1.801 (8) | 1.801 (8) |
| P ₂ -C ₂₁₁ | 1.775 (6) | 1.778 (6) |
| P ₂ -C ₂₂₁ | 1.811 (7) | 1.811 (7) |
| P ₂ -C ₂₃₁ | 1.816 (8) | 1.816 (8) |
| P-C (phenyl) (av) | 1.802 (8) | 1.803 (8) |
| C ₁ -O ₁ | 1.216 (17) | |
| C ₂ -O ₂ | 1.129 (15) | |
| C ₃ -O ₃ | 1.211 (16) | |
| C ₄ -O ₄ | 1.114 (15) | |
| C ₅ -O ₅ | 1.176 (13) | |

^a Standard deviations of derived quantities were calculated using the full variance-covariance matrix, except for quantities involving group atoms, in which case only the variances were used. ^b The average in this and other quantities reported is calculated by $\bar{x} = (\sum x_i)/n$ and the standard deviation of the average is calculated from $\sigma(\bar{x}) = [\sum(x_i - \bar{x})^2/(n-1)n]^{1/2}$, where n is the number of independent values. ^c Average is for the four equatorial carbonyls.

chemically equivalent, range from 1.951 to 2.070 Å. Since the W-O bond lengths remain relatively constant, short equatorial W-C bond lengths correspond to long C-O bond lengths; the range in the unconstrained model is from 1.114 to 1.216 Å. The C≡O distance in terminal carbonyls is relatively insensitive to changes in the M-C bond order (and concomitant change in distance). Our explanation of the range in C-O distances as an artifact of the resolution of the diffraction data is confirmed by the chemical reasonableness of the results from the constrained refinement. Note in particular the dramatic improvement of the four chemically equivalent equatorial W-C bond lengths.

This structure is not an isolated instance. Many structure analyses of carbonyl-, cyanide-, or isocyanide-containing compounds are determined from diffraction data with a resolution on the order of 1 Å (a 2θ of about 40° for Mo K α radiation). Use of resultant metal-carbon bond lengths in discussions of the chemical bonding for such structures should be made with great caution unless constraints are applied to the C-O or C-N bond lengths.^{26,27}

The coordination symmetry of the complex is C_{4v} . The average equatorial W-C bond length of 2.025 (6) Å is significantly longer than the axial W-C bond length of 1.949 (10) Å. This difference is readily explained by the relative trans interaction of the phosphine oxide and carbonyl ligands. The oxygen atom in phosphine oxide is a strong σ donor but is not a π acceptor and so does not compete with the trans carbonyl for the metal π orbitals. This makes the bond order for the axial carbonyl greater than for the equatorial carbonyls, since in the latter case there are two trans carbonyls competing for the metal π orbitals. We have described the trans interaction in carbonyls (where π bonding dominates the

Table IX

| Bond Angles in $W(CO)_5(O=P(C_6H_5)_2CHP(C_6H_5)_3)$ | | | |
|--|------------|--|------------|
| Atoms | Angle, deg | Atoms | Angle, deg |
| O ₆ -W-C ₁ | 84.5 (5) | W-O ₆ -P ₁ | 137.1 (4) |
| O ₆ -W-C ₂ | 95.6 (4) | O ₆ -P ₁ -C ₆ | 118.8 (5) |
| O ₆ -W-C ₃ | 94.8 (5) | O ₆ -P ₁ -C ₁₁₁ | 104.7 (4) |
| O ₆ -W-C ₄ | 92.0 (4) | O ₆ -P ₁ -C ₁₂₁ | 109.1 (4) |
| O ₆ -W-C ₅ | 175.5 (4) | C ₆ -P ₁ -C ₁₁₁ | 107.5 (4) |
| C ₁ -W-C ₂ | 90.2 (6) | C ₆ -P ₁ -C ₁₂₁ | 111.9 (5) |
| C ₁ -W-C ₃ | 178.6 (5) | C ₁₁₁ -P ₁ -C ₁₂₁ | 103.9 (4) |
| C ₁ -W-C ₄ | 89.3 (6) | C ₆ -P ₂ -C ₂₁₁ | 111.8 (5) |
| C ₁ -W-C ₅ | 91.8 (6) | C ₆ -P ₂ -C ₂₂₁ | 113.3 (5) |
| C ₂ -W-C ₃ | 91.0 (6) | C ₆ -P ₂ -C ₂₃₁ | 112.2 (5) |
| C ₂ -W-C ₄ | 172.4 (5) | C ₂₁₁ -P ₂ -C ₂₂₁ | 108.3 (4) |
| C ₂ -W-C ₅ | 81.8 (5) | C ₂₁₁ -P ₂ -C ₂₃₁ | 106.6 (4) |
| C ₃ -W-C ₄ | 89.5 (5) | C ₂₂₁ -P ₂ -C ₂₃₁ | 104.2 (4) |
| C ₃ -W-C ₅ | 88.9 (6) | W-C ₁ -O ₁ | 174.8 (15) |
| C ₄ -W-C ₅ | 90.6 (5) | W-C ₂ -O ₂ | 172.7 (12) |
| | | W-C ₃ -O ₃ | 177.1 (13) |
| | | W-C ₄ -O ₄ | 176.0 (13) |
| | | W-C ₅ -O ₅ | 179.2 (11) |

Torsional Angles C₆-P-C-C

| Atom | Group | Angle, deg | Atom | Group | Angle, deg |
|----------------|------------------|------------|----------------|------------------|------------|
| P ₁ | Ph ₁₁ | 52.9 (7) | P ₂ | Ph ₂₂ | 17.3 (6) |
| P ₁ | Ph ₁₂ | 15.5 (6) | P ₂ | Ph ₂₃ | 5.5 (7) |
| P ₂ | Ph ₂₁ | 87.0 (8) | | | |

Table X. Weighted Least-Squares Planes^a through the Tungsten Coordination Sphere

| Atom | Plane 1 | Plane 2 | Plane 3 |
|----------------|--------------------------|-------------|-------------|
| W | -0.0001 (5) ^b | 0.0021 (5) | 0.0021 (5) |
| C ₁ | -0.027 (15) | | 0.016 (17) |
| O ₁ | -0.126 (15) | | -0.044 (12) |
| C ₂ | | -0.004 (15) | -0.117 (13) |
| O ₂ | | -0.035 (14) | -0.328 (11) |
| C ₃ | -0.015 (12) | | -0.010 (15) |
| O ₃ | -0.069 (11) | | -0.026 (12) |
| C ₄ | | -0.020 (14) | -0.149 (13) |
| O ₄ | | -0.032 (14) | -0.314 (11) |
| C ₅ | 0.023 (12) | -0.009 (13) | |
| O ₅ | 0.051 (8) | -0.008 (9) | |
| O ₆ | 0.074 (7) | -0.124 (7) | |

| Parameter of plane eq | Plane 1 | Plane 2 | Plane 3 |
|-----------------------|---------|---------|---------|
| A | 7.314 | 0.8581 | 6.831 |
| B | -13.12 | 6.279 | 13.65 |
| C | 0.9149 | 15.55 | -5.530 |
| D | -1.112 | 6.079 | 2.232 |

| Planes | Dihedral angle, deg | Planes | Dihedral angle, deg | Planes | Dihedral angle, deg |
|--------|---------------------|--------|---------------------|--------|---------------------|
| 1-2 | 89.4 | 1-3 | 86.0 | 2-3 | 87.1 |

^a The equation of the plane in monoclinic coordinates is $Ax + By + Cz - D = 0$. See W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961).

^b Displacement of atom from plane (A).

interaction) and in cyanide ligands (where σ bonding dominates) in greater detail elsewhere.³⁰

The average equatorial W-C bond length of 2.025 (6) Å is slightly less than the distance of 2.059 (8) Å reported for the electron diffraction analysis of $W(CO)_6$.²⁸ Since any correction for thermal motion would increase our reported bond length, this difference is not chemically significant (in contrast to our comparison of axial and equatorial W-C bond lengths in which any correction for thermal motion would give about the same change in each bond distance and so not change the difference between them).

The P-O bond length in the ligand of 1.523 (8) Å is length-

Table XI. Geometrical Distortions Involving Phosphorus Atoms and Phenyl Groups

| Atom | Group | Dist, ^a Å | Total angular distortion, ^b deg | Out-of-plane bend, ^c deg | In-plane bend, ^d deg |
|----------------|------------------|----------------------|--|-------------------------------------|---------------------------------|
| P ₁ | Ph ₁₁ | 0.153 (17) | 6.3 (4) | 4.9 (5) | 4.6 (5) |
| P ₁ | Ph ₁₂ | 0.119 (16) | 3.9 (4) | 3.8 (5) | 1.7 (5) |
| P ₂ | Ph ₂₁ | 0.058 (16) | 1.9 (5) | 1.9 (5) | 0 (5) |
| P ₂ | Ph ₂₂ | 0.140 (15) | 4.5 (4) | 4.5 (5) | 0.5 (5) |
| P ₃ | Ph ₂₃ | 0.069 (17) | 3.1 (5) | 2.2 (5) | 2.2 (5) |

^a Distance from phosphorus atom to plane of phenyl ring. ^b Angle made by P_i-C_{ij1} and C_{ij1}-C_{ij4} vectors. ^c Projection of the angular distortion onto the plane perpendicular to the phenyl ring. ^d Projection of the angular distortion onto the plane of the phenyl ring.

ened from that found in triphenylphosphine oxide, 1.46 (1) Å,³¹ as a result of coordination. The equivalence of the two phosphorus bonds to C₆, which average 1.690 (10) Å, shows that the molecule is not composed of two parts, one an alkylphosphine oxide and the other an ylide. This length falls at the long end of the reported range for ylides,^{4,6,7,32-39} which is consistent with the multiple P-C bond order being distributed between two phosphorus atoms. The five phenyl carbon to phosphorus distances are also equivalent and average 1.803 (8) Å. The P₁-C₆-P₂ angle of 127.9 (6)^o is consistent with trigonal sp² bonding in which the substituent group repulsions have forced open the angle. The geometries about the phosphorus atoms are nearly tetrahedral. The bending of the phenyl rings from the central phosphorus atoms, the least-squares planes through the W coordination sphere, and the deviations from idealized geometry can be found in Tables IX-XI. The phosphorus atoms are displaced from the planes of the rings by distances of 0.06-0.15 Å. These displacements correspond to values of 1.8-4.9^o for the angle between the P_i-C_{ij1} vector and the phenyl plane. Another distortion may be described by the angle made by the P_i-C_{ij1} vector and the C_{ij1}-C_{ij4} vector when the vector is projected onto the plane of the phenyl group. These angles are in the range 0.8-4.6^o. The other bond angles for the ylide portion of the ligand fall within the range established by other ylide structures.^{4,6,7,32-39}

The packing of the structure, shown in Figure 2, is domi-

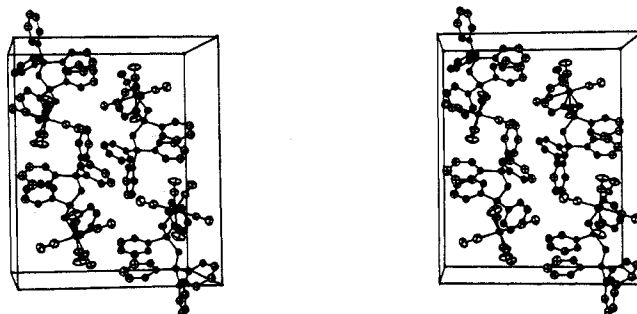


Figure 2. A stereoscopic view of the unit cell for W(CO)₅(O=P(C₆H₅)₂CHP(C₆H₅)₃). The origin is at the front lower left. The vertical axis is *b* and the horizontal axis is *c*. Thermal ellipsoids enclose 30% of the electron probability. Hydrogen atoms are not shown.

nated by the packing of the phenyl rings. The ligand 4 adopts an orientation with respect to the metal carbonyl group so as to minimize nonbonded interactions.

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Registry No. W(CO)₅[OP(C₆H₅)₂C(H)=P(C₆H₅)₃], 41697-48-7.

Supplementary Material Available. Table II, a listing of structure factor amplitudes, Table VI, a listing of positional and thermal parameters for group atoms, and Table VII, a listing of hydrogen coordinates and isotropic temperature factors, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2923.

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