metal by the carbonyldiazene is very likely. Second, even if the metal is not oxidized by the ligand, five-membered chelate rings tend to be energetically favorable. Thus, unsymmetrical chelating would again be favored.

It should be possible to prepare a complex with an unsymmetrically bound dibenzoyldiazene by going to metals in higher oxidation states. There would then be less need for electron transfer to the ligand. This form would be of interest structurally because there is a growing list[6,8,9,17-22] (Table XI) of metallocycles with a metal-O-C-N-N ring having varying degrees of saturation and substitution. In spite of this variety, there is still no reported structure of a dibenzoyldiazene complex in which distances found are indicative of an N=N bond. Dibenzoyldiazene and other similar disubstituted diazenes are potentially bridging, bidentate ligands with one metal bound to N(1) and O(2) while the second metal is bound to N(2) and O(1). This is a likely structure for the reported[6] rhodium complex. There would thus be two Rh(I) rather than the two Rh(0) atoms, and the complex would still be symmetric as indicated by spectroscopy. These and other related systems are currently under investigation.

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Registry No. $Pt[P(C_6H_5)_3]_2[C_6H_5CONNCOC_6H_5]\cdot C_2H_5OH$, 41202-93-1.

Supplementary Material Available. Tables V and VI, showing structure factor amplitudes and root-mean-square amplitudes of vibration, 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2290.

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Structure of Tetrahydridotetrakis(methyldiphenylphosphine)molybdenum(IV)

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The molecular and crystal structures of tetrahydridotetrakis(methyldiphenylphosphine)molybdenum(IV), $H_4Mo[CH_3P(C_6H_5)_2]_4$, have been determined from counter data by single-crystal X-ray techniques. The coordination polyhedron around the eight-coordinate molybdenum atom is a somewhat distorted variant of the D_{2d}-$\bar{4}2m$ dodecahedron with hydrogen atoms forming an elongated tetrahedron (A sites) and phosphorus atoms a flattened tetrahedron (B sites). The molecular structure has no imposed symmetry but nearly has idealized $C_2(2)$ point symmetry leading to two Mo–P distances (2.433 (2) and 2.503 (8) Å). All four hydride hydrogen atoms were located and refined giving an average Mo–H distance of 1.70 (3) Å. The ligand selection of the A and B sites as well as the distortion of the coordination polyhedra appear to arise from interligand steric factors. The MoP_4 coordination is midway between a regular tetrahedron and a square-planar configuration. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions of $a = 12.174$ (4), $b = 22.057$ (9), $c = 19.642$ (11) Å, and $\beta = 119.68$ (4)°. The density for four molecules per cell is 1.31 g/cm³. The final R value is 0.071 after least-squares refinement with 3667 reflections.

Introduction

Eight-coordinate complexes are becoming quite commonplace, yet their stereochemistry is not well understood. A half-dozen or so different coordination geometries have been considered for discrete eight-coordinate complexes, and X-ray structures have established the existence of several of these in the solid state. The whole area of eight-coordinate complexes has been reviewed extensively.[1-6]

Many of the systematics with respect to structures in this area are due to Hoard, *et al.*,[7-10] the basic analysis by Hoard and Silverton being most notable.[5] The metal–ligand coordination in eight-coordinate complexes is dominated by the D_{4d}-$\bar{8}2m$ square antiprism and D_{2d}-$\bar{4}2m$ dodecahedron. Both polyhedra appear to be about equally acceptable for an MX_8 complex from the viewpoints of maximization of bonding,[5,11,12] minimization of repulsions,[4,5,13] or crystal-

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field stabilization;[13] hence, it is difficult to predict the ground-state geometry for these complexes. A dodecahedron might be favored for a MX_4Y_4 complex such as studied here, because of its natural symmetry distinction between ligands.[5,14] There are no structural data available for either hydrogens or phosphines in the X or Y positions of a MX_4Y_4 complex. Structural comparisons are made between this H_4MoP_4 structure and the eight-coordinate cyanomolybdenum complexes $K_4Mo(CN)_8 \cdot 2H_2O$[7] and $(CH_3NC)_4Mo(CN)_4$.[15,16]

Apart from the coordination aspects, we have been interested in $H_4Mo(PR_3)_4$ complexes in particular, because of the nature of their nonrigidity in solution and the possibility for analysis in terms of rearrangement mechanisms.[17,18] Complexes of the H_4ML_4 (M = Mo, W; L = phosphine) type are rigid on the nmr time scale at room temperature but undergo line shape changes as the temperature increases; several rearrangement mechanisms have been considered.[17,18] Stereochemical nonrigidity in these complexes was also observed recently by Bell, Chatt, Leigh, and Ito.[19]

The crystal structure of tetrahydridotetrakis(methyldiphenylphosphine)molybdenum(IV), $H_4Mo[CH_3P(C_6H_5)_2]_4$, was determined to establish the metal–ligand coordination polyhedron and assess the stereochemistry in light of current theories about eight-coordination. Also, we expected the solid-state structure to be useful in interpreting the solution nmr behavior. Solid-state structures are frequently helpful in defining routes for intramolecular rearrangements, and hence in the interpretation of temperature-dependent nmr spectra.[20,21]

Experimental Section

The preparation and spectral characterization of $H_4Mo[CH_3P(C_6H_5)_2]_4$ were reported previously.[17] Crystals were enclosed in capillaries for all the film and diffractometer work. Crystals are monoclinic with cell dimensions of $a = 12.174$ (4), $b = 22.057$ (9), $c = 19.642$ (11) Å, and $\beta = 119.68$ (4)°. These parameters resulted from the least-squares measurement of the angular positions of 10 reflections carefully centered on the diffractometer. The systematic extinctions of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$ are uniquely characteristic for the space group $P2_1/c$. The calculated density for four molecules per cell is 1.31 g/cm^3. We were unable to measure the density, but the calculated density is in the range expected for this compound (for example, the densities of $H_2Fe[(C_6H_5)P(OC_2H_5)_2]_4$[22] and $H_2Ru[(C_6H_5)P(OC_2H_5)_2]_4$[23] are 1.27 and 1.30 g/cm^3, respectively). There is no space group imposed molecular symmetry; all atoms are in general space group positions.[24]

Table I. Positional Parameters for $H_4Mo[CH_3P(C_6H_5)_2]_4$[a]

Atom	x	y	z
Mo	0.27286 (6)	0.01506 (3)	0.25220 (4)
P(1)	0.05723 (19)	−0.02330 (11)	0.18380 (13)
P(2)	0.20733 (20)	0.12265 (10)	0.24910 (15)
P(3)	0.46311 (19)	0.02886 (10)	0.23563 (14)
P(4)	0.35372 (21)	−0.07469 (10)	0.33434 (14)
C(1)	0.0254 (8)	−0.0704 (4)	0.0995 (5)
C(2)	0.1013 (9)	0.1332 (4)	0.2899 (6)
C(3)	0.5177 (8)	−0.0419 (4)	0.2119 (5)
C(4)	0.3438 (8)	−0.0717 (4)	0.4244 (5)
C(11)	−0.0779 (7)	0.0291 (4)	0.1330 (5)
C(12)	−0.0887 (8)	0.0624 (4)	0.0698 (5)
C(13)	−0.1924 (9)	0.0987 (5)	0.0249 (6)
C(14)	−0.2842 (9)	0.1044 (5)	0.0449 (7)
C(15)	−0.2755 (10)	0.0737 (5)	0.1081 (7)
C(16)	−0.1750 (8)	0.0355 (4)	0.1503 (6)
C(21)	−0.0061 (8)	−0.0700 (4)	0.2330 (6)
C(22)	0.0076 (9)	0.0508 (5)	0.3049 (7)
C(23)	−0.0526 (11)	−0.0791 (6)	0.3394 (7)
C(24)	−0.1270 (13)	−0.1294 (8)	0.3028 (10)
C(25)	−0.1413 (11)	−0.1515 (6)	0.2331 (10)
C(26)	−0.0790 (9)	−0.1216 (5)	0.1977 (7)
C(31)	0.3285 (8)	0.1781 (4)	0.3102 (6)
C(32)	0.3802 (10)	0.1775 (5)	0.3914 (6)
C(33)	0.4769 (11)	0.2181 (6)	0.4387 (7)
C(34)	0.5221 (11)	0.2583 (6)	0.4068 (9)
C(35)	0.4716 (11)	0.2620 (5)	0.3269 (9)
C(36)	0.3739 (9)	0.2212 (4)	0.2785 (6)
C(41)	0.1259 (8)	0.1664 (4)	0.1579 (6)
C(42)	0.1530 (8)	0.1564 (4)	0.0981 (6)
C(43)	0.0969 (10)	0.1922 (5)	0.0311 (6)
C(44)	0.0073 (10)	0.2363 (5)	0.0204 (7)
C(45)	−0.0164 (11)	0.2455 (6)	0.0801 (8)
C(46)	0.0408 (10)	0.2129 (5)	0.1489 (7)
C(51)	0.6152 (8)	0.0612 (4)	0.3134 (6)
C(52)	0.7280 (8)	0.0479 (5)	0.3140 (6)
C(53)	0.8386 (9)	0.0726 (5)	0.3716 (7)
C(54)	0.8407 (9)	0.1110 (5)	0.4280 (6)
C(55)	0.7289 (9)	0.1244 (4)	0.4263 (5)
C(56)	0.6152 (9)	0.0989 (4)	0.3680 (6)
C(61)	0.4405 (7)	0.0758 (4)	0.1529 (5)
C(62)	0.3731 (9)	0.0506 (5)	0.0761 (6)
C(63)	0.3525 (8)	0.0854 (5)	0.0123 (6)
C(64)	0.3942 (9)	0.1453 (5)	0.0214 (7)
C(65)	0.4615 (9)	0.1700 (5)	0.0964 (7)
C(66)	0.4842 (8)	0.1349 (4)	0.1611 (6)
C(71)	0.2870 (7)	−0.1508 (4)	0.2959 (6)
C(72)	0.2799 (8)	−0.1694 (4)	0.2253 (7)
C(73)	0.2454 (10)	−0.2282 (5)	0.1997 (7)
C(74)	0.2127 (11)	−0.2678 (5)	0.2413 (9)
C(75)	0.2150 (9)	−0.2490 (5)	0.3078 (8)
C(76)	0.2523 (8)	−0.1903 (5)	0.3370 (6)
C(81)	0.5248 (7)	−0.0950 (4)	0.3844 (5)
C(82)	0.5710 (8)	−0.1525 (4)	0.3825 (5)
C(83)	0.6987 (10)	−0.1660 (5)	0.4266 (7)
C(84)	0.7808 (10)	−0.1200 (6)	0.4714 (7)
C(85)	0.7391 (9)	−0.0638 (5)	0.4742 (6)
C(86)	0.6102 (8)	−0.0508 (4)	0.4296 (5)
H(1)	0.2196 (86)	0.0189 (41)	0.3151 (54)
H(2)	0.3711 (85)	0.0453 (41)	0.3481 (54)
H(3)	0.2127 (81)	0.0273 (42)	0.1547 (54)
H(4)	0.2785 (84)	−0.0401 (43)	0.1982 (54)

[a] Here, and in other tables, the standard deviations of the least significant digits are given in parentheses.

The crystal used in the data collection was a platelet of approximate dimensions 0.38 × 0.18 × 0.42 mm (a, b, c^* directions). The crystal was mounted on a Picker four-circle automatic diffractometer (Zr-filtered Mo radiation, λ 0.7107) with the c^* axis along the diffractometer ϕ axis. The θ–2θ scan technique was used with a scan rate of 1°/min and a scan range of 2° plus the $K\alpha_1$–$K\alpha_2$ separation. The data were measured out to 45° 2θ for approximately half the data and 40° for the remainder; many unobserved data were found in the 40–45° range. Backgrounds of 10 sec were measured before and after each scan. Attenuation was used for counting rates in excess of 10,000 cps. A total of 4939 reflections were measured.

The data were corrected in the usual way for Lorentz and polarization effects. No absorption correction was applied. The linear absorption coefficient for Mo Kα radiation is 4.6 cm^{-1}. The error due to absorption is estimated to be about 3% in F_o based on equivalent reflections measured. Actually, a serious effort was made to apply an absorption correction, but even after varying the crystal shape parameters extensively, the agreement in equivalent reflections was not significantly better than for the uncorrected data. The cross-sectional shape in the ab plane was a slightly irregular trapezoid. The

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Table II. Thermal Parameters ($\times 10^4$) for $H_4Mo[CH_3P(C_6H_5)_2]_4$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	45.5 (7)	12.4 (2)	26.9 (3)	0.9 (3)	19.3 (4)	0.0 (2)
P(1)	53.6 (22)	15.5 (6)	27.4 (10)	1.8 (9)	22.3 (13)	0.5 (7)
P(2)	54.8 (23)	14.0 (5)	35.2 (11)	1.4 (9)	23.5 (14)	−2.9 (7)
P(3)	53.9 (22)	14.2 (6)	30.9 (11)	−1.0 (9)	22.2 (13)	−2.5 (6)
P(4)	60.4 (24)	15.4 (6)	24.7 (11)	2.2 (9)	19.8 (14)	0.7 (6)
C(1)	80 (10)	27 (3)	37 (5)	0 (4)	24 (6)	−7 (3)
C(2)	100 (11)	26 (3)	62 (6)	4 (5)	63 (7)	−7 (3)
C(3)	101 (11)	19 (2)	52 (5)	3 (4)	54 (6)	−6 (3)
C(4)	104 (11)	32 (3)	32 (4)	10 (4)	42 (6)	5 (3)
C(11)	41 (8)	19 (3)	32 (4)	−3 (3)	17 (5)	0 (3)
C(12)	62 (10)	23 (3)	26 (4)	−9 (4)	12 (6)	1 (3)
C(13)	86 (11)	30 (3)	37 (5)	2 (5)	19 (7)	10 (3)
C(14)	90 (12)	26 (3)	67 (7)	18 (5)	39 (8)	11 (4)
C(15)	134 (14)	37 (4)	81 (7)	34 (6)	82 (9)	26 (4)
C(16)	94 (10)	22 (3)	62 (6)	20 (4)	59 (7)	14 (3)
C(21)	54 (9)	24 (3)	35 (5)	1 (4)	29 (6)	6 (3)
C(22)	78 (11)	30 (3)	55 (6)	9 (5)	47 (7)	16 (4)
C(23)	122 (14)	37 (4)	59 (6)	18 (6)	53 (8)	24 (4)
C(24)	138 (17)	50 (6)	92 (10)	8 (8)	76 (12)	35 (6)
C(25)	133 (15)	28 (4)	89 (9)	−27 (6)	43 (11)	16 (5)
C(26)	110 (12)	24 (3)	67 (6)	−13 (5)	38 (8)	5 (4)
C(31)	62 (10)	15 (2)	36 (5)	4 (4)	25 (6)	−5 (3)
C(32)	121 (13)	24 (3)	27 (5)	15 (5)	22 (7)	−5 (3)
C(33)	110 (15)	43 (4)	48 (7)	15 (6)	14 (8)	−16 (5)
C(34)	139 (16)	30 (4)	78 (9)	−11 (6)	42 (10)	−27 (5)
C(35)	135 (15)	28 (4)	76 (8)	−16 (6)	56 (9)	−9 (5)
C(36)	102 (12)	17 (2)	45 (5)	0 (4)	36 (7)	−3 (3)
C(41)	62 (10)	16 (3)	32 (5)	3 (4)	13 (6)	−3 (3)
C(42)	69 (11)	19 (3)	38 (5)	−4 (4)	21 (6)	−1 (3)
C(43)	110 (13)	23 (3)	37 (6)	−18 (5)	23 (7)	1 (3)
C(44)	131 (11)	17 (3)	46 (7)	18 (4)	9 (8)	11 (4)
C(45)	118 (15)	27 (4)	58 (7)	17 (6)	26 (9)	−3 (4)
C(46)	135 (13)	23 (3)	40 (6)	21 (5)	26 (7)	2 (3)
C(51)	34 (9)	20 (3)	27 (5)	2 (4)	10 (6)	2 (3)
C(52)	55 (10)	38 (3)	41 (5)	−12 (5)	26 (6)	−15 (3)
C(53)	61 (12)	41 (4)	58 (6)	−1 (5)	36 (7)	−10 (4)
C(54)	62 (12)	31 (3)	46 (5)	−9 (5)	18 (7)	−2 (3)
C(55)	79 (11)	25 (3)	34 (5)	1 (4)	26 (6)	−4 (3)
C(56)	74 (11)	19 (2)	39 (5)	−3 (4)	23 (7)	−5 (3)
C(61)	50 (9)	20 (3)	30 (5)	10 (4)	23 (6)	5 (3)
C(62)	105 (11)	27 (3)	35 (5)	−3 (5)	36 (7)	1 (4)
C(63)	82 (11)	33 (3)	42 (5)	−4 (5)	30 (6)	3 (4)
C(64)	71 (10)	37 (4)	53 (6)	12 (5)	42 (7)	20 (4)
C(65)	83 (11)	23 (3)	58 (6)	5 (5)	35 (7)	13 (4)
C(66)	74 (10)	13 (2)	49 (5)	−3 (4)	35 (6)	0 (3)
C(71)	48 (9)	18 (3)	35 (5)	6 (4)	13 (6)	0 (3)
C(72)	82 (11)	12 (3)	53 (6)	5 (4)	17 (7)	1 (3)
C(73)	99 (13)	26 (3)	70 (7)	6 (5)	23 (8)	−10 (4)
C(74)	101 (13)	17 (3)	106 (9)	−7 (5)	33 (9)	−5 (5)
C(75)	93 (11)	24 (4)	95 (8)	−9 (5)	49 (8)	0 (4)
C(76)	91 (11)	20 (3)	67 (6)	−5 (4)	42 (7)	9 (4)
C(81)	45 (9)	22 (3)	19 (4)	4 (4)	11 (5)	4 (3)
C(82)	75 (10)	21 (3)	39 (5)	10 (4)	29 (6)	4 (3)
C(83)	86 (12)	27 (3)	70 (6)	18 (5)	42 (7)	2 (4)
C(84)	59 (13)	46 (4)	63 (6)	9 (7)	32 (8)	2 (4)
C(85)	72 (11)	29 (3)	38 (5)	−5 (5)	5 (6)	1 (3)
C(86)	67 (10)	25 (3)	30 (4)	0 (4)	16 (5)	−2 (3)

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

structure factor errors were estimated as described previously.[25]

The structure was solved stepwise in fairly straightforward fashion using Patterson, Patterson superposition with the minimum function,[26] and least-squares techniques. The R factor, $\Sigma \| F_o| - |F_c\| / \Sigma |F_o|$, was 0.106 after least-squares refinement with all nonhydrogen atoms in the model with isotropic thermal parameters. The refinement proceeded with anisotropic thermal parameters for the nonhydrogen atoms. The positional and thermal parameters were refined in three sections: (a) Mo, P(1)–P(4), C(1), C(11)–C(16), C(21)–C(26); (b) C(2), C(31)–C(36), C(41)–C(46), C(51)–C(56); (c) C(3), C(4), C(61)–C(66), C(71)–C(76), C(81)–C(86). The R factors, after anisotropic refinement using the 2950 strongest reflections, were 0.069 for R and 0.079 for R_w, $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

At this point an electron density difference map was calculated in order to locate the nonhydride hydrogen atoms. There was evidence for all these hydrogen atom positions; peaks were in the 0.2–0.5 e/Å^3 range. These hydrogen atoms were included in the model in their calculated positions (C–H = 1.00 Å) with isotropic thermal parameters of 5.00 Å^2. A new scale factor was calculated and general plane electron density difference maps were calculated to search for the important hydride hydrogen atoms. The four hydride hydrogen positions were unambiguously located (*vide infra*) and their parameters were added to the first refinement group with fixed isotropic thermal parameters of 5.0 Å^2. The R and R_w for the 2950 strongest reflections after including the hydrogen atoms were 0.061 and 0.066, respectively.

Several final cycles of least squares were done varying the nonhydrogen atoms anisotropically and the positional parameters for the hydride hydrogens, keeping the remaining hydrogen atom positions fixed. In these refinements the data set was expanded to include

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

(26) M. J. Buerger, "Vector Space," Wiley, New York, N. Y., 1959.

3667 observed reflections ($F_o > 2\sigma(F_o)$). The final agreement factors for these observed data were 0.071 for R and 0.066 for R_w. The R and R_w for all the data (4724 reflections) were 0.111 and 0.069, respectively.

The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinement.[27] Neutral atom form factors were used;[28] the molybdenum atom was corrected for the real and imaginary parts of the anomalous scattering effect.[29]

The positional parameters for the refined atoms are given in Table I and the thermal parameters in Table II. The nonhydride hydrogen atom positions are given in Table III. A list of observed and calculated structure factors is available.[30]

Structure Description

The crystal structure is made up of the packing of discrete molecules of $H_4Mo[CH_3P(C_6H_5)_2]_4$ separated by normal van der Waals forces. A view of the molecular structure illustrating the numbering system used is shown in Figure 1. The coordination polyhedron described by the ligands attached to the Mo atom is a D_{2d}-$\bar{4}2m$ dodecahedron. The dodecahedron is characterized by two interpenetrating tetrahedra, an elongated Mo-H tetrahedron and a flattened Mo-P tetrahedron. The two tetrahedra share a common $S_4(\bar{4})$ axis which passes through the Mo atom and the H(1)-H(2) and H(3)-H(4) midpoints. The dihedral twofold axes are normal to the $S_4(\bar{4})$ axis; one is the view direction in Figure 1. The idealized mirror planes are normal to $S_4(\bar{4})$, 45° from the twofold axes. The dodecahedron is also characterized by two orthogonal trapezoids, in this case P(1)H(1)H(2)P(3) and P(2)H(3)H(4)P(4). The coordination dodecahedron is shown in Figure 2 where the symmetry elements and the orthogonal trapezoids are emphasized. A stereoview of the molecule in the $S_4(\bar{4})$ direction is given in Figure 3; the thermal ellipsoids are plotted at the 50% probability level.

The location of the hydride hydrogen atoms was considered important for characterizing the coordination polyhedron. For this reason, special care was taken in handling these atoms and further comments seem warranted. Only after all atoms, including the nonhydride atoms, were in the model was a search made for the hydride hydrogen atoms. General electron density difference maps were calculated through the P(1)MoP(3) and P(2)MoP(4) planes; these define the orthogonal trapezoidal planes of the dodecahedron. These sections are shown in Figure 4. The peaks shown in Figure 4 were the only large peaks in the electron density difference map. Their observed and refined positions as well as the consistency between the sets of hydrogen positions in the two trapezoidal planes define unambiguously the positions of these atoms. The refined positions were all within 0.2 Å from occurring in these planes. The peaks on the top of Figure 4a and the bottom of Figure 4b come from the other hydrogen atom sets (the two sets are orthogonal in the idealized polyhedron).

The point symmetry of a dodecahedron is D_{2d}-$\bar{4}2m$; the actual symmetry observed here is more nearly $C_2(2)$. The twofold axis maintained in the crystal passes through the Mo atom and the P(1)-P(4) and P(2)-P(3) midpoints, the view direction of Figure 1. The interatomic distances and angles are given in Tables IV and V. The distances and angles show that the twofold axis is maintained fairly well, leading to two

Table III. Hydrogen Atom Positions for $H_4Mo[CH_3P(C_6H_5)_2]_4$ [a]

Atom	x	y	z
H(1A)	−0.0647	−0.0844	0.0727
H(1B)	0.0833	−0.1055	0.1160
H(1C)	0.0382	−0.0451	0.0606
H(2A)	0.0771	0.1769	0.2869
H(2B)	0.1434	0.1195	0.3456
H(2C)	0.0215	0.1086	0.2587
H(3A)	0.5942	−0.0342	0.2063
H(3B)	0.4496	−0.0601	0.1622
H(3C)	0.5421	−0.0726	0.2556
H(4A)	0.3790	−0.1096	0.4560
H(4B)	0.2538	−0.0665	0.4118
H(4C)	0.3943	−0.0359	0.4578
H(12)	−0.1058	0.0590	0.0576
H(13)	−0.1978	0.1229	−0.0218
H(14)	−0.3634	0.1286	0.0095
H(15)	−0.3432	0.0810	0.1244
H(16)	−0.1710	0.0119	0.1964
H(22)	0.0664	−0.0157	0.3334
H(23)	−0.0464	−0.0661	0.3913
H(24)	−0.1812	−0.1528	0.3199
H(25)	−0.1940	−0.1916	0.2057
H(26)	−0.0874	−0.1372	0.1462
H(32)	0.3479	0.1476	0.4152
H(33)	0.5134	0.2175	0.4980
H(34)	0.5910	0.2883	0.4415
H(35)	0.5021	0.2941	0.3003
H(36)	0.3359	0.2218	0.2184
H(42)	0.2155	0.1226	0.1050
H(43)	0.1204	0.1857	−0.0125
H(44)	−0.0399	0.2608	−0.0316
H(45)	−0.0800	0.2793	0.0747
H(46)	0.0241	0.2223	0.1943
H(52)	0.7280	0.0205	0.2721
H(53)	0.9223	0.0616	0.3742
H(54)	0.9233	0.1311	0.4701
H(55)	0.7284	0.1525	0.4673
H(56)	0.5321	0.1087	0.3678
H(62)	0.3397	0.0074	0.0670
H(63)	0.3057	0.0676	−0.0435
H(64)	0.3766	0.1720	−0.0257
H(65)	0.4927	0.2133	0.1040
H(66)	0.5336	0.1536	0.2157
H(72)	0.3002	−0.1394	0.1928
H(73)	0.2440	−0.2445	0.1497
H(74)	0.1849	−0.3112	0.2198
H(75)	0.1867	−0.2800	0.3357
H(76)	0.2564	−0.1775	0.3884
H(82)	0.5083	−0.1851	0.3464
H(83)	0.7300	−0.2088	0.4259
H(84)	0.8748	−0.1299	0.5023
H(85)	0.8013	−0.0310	0.5078
H(86)	0.5792	−0.0078	0.4302

[a] The hydride hydrogen positions are listed in Table I.

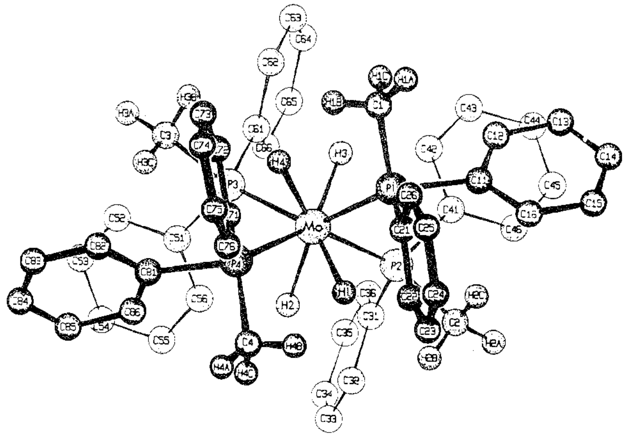

Figure 1. The molecular configuration of $H_4Mo[CH_3P(C_6H_5)_2]_4$. The ring hydrogen atoms were omitted for clarity.

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(27) Programs used in addition to various local programs were Prewitt's least-squares program SFLS5, the Busing-Levy error function program ORFFE, the Johnson plotting program ORTEP, and the Fourier Program FOUR, a modified version of program written by Dr. C. J. Fritchie, Jr.

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

(29) See ref 24, Vol. III, 1962, p 216.

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

Table IV. Interatomic Distances for $H_4Mo[CH_3P(C_6H_5)_2]_4$ (Å)[a]

Bonding

Mo-P(1)		2.433 (2)	P(1)-C(1)		1.826 (11)
Mo-P(4)		2.433 (3)	P(2)-C(2)		1.841 (14)
	Av	2.433 (2)*	P(3)-C(3)		1.845 (10)
Mo-P(2)		2.495 (3)	P(4)-C(4)		1.832 (12)
Mo-P(3)		2.512 (2)		Av	1.836 (4)
	Av	2.503 (8)*	P(1)-C(11)		1.847 (8)
			P(1)-C(21)		1.823 (12)
Mo-P (all)	Av	2.468 (21)	P(2)-C(31)		1.833 (8)
Mo-H(1)		1.66 (13)	P(2)-C(41)		1.835 (10)
Mo-H(4)		1.64 (11)	P(3)-C(51)		1.862 (8)
	Av	1.65 (10)*	P(3)-C(61)		1.829 (11)
Mo-H(2)		1.79 (9)	P(4)-C(71)		1.855 (9)
Mo-H(3)		1.70 (10)	P(4)-C(81)		1.865 (8)
		1.75 (5)*		Av	1.844 (6)
Mo-H (all)		1.70 (3)			

Nonbonding Polyhedral

a Type			b Type		
H(1)-H(2)		1.73 (14)	P(1)-P(2)		3.609 (3)
H(3)-H(4)		1.70 (13)	P(3)-P(4)		3.648 (4)
	Av	1.72 (2)		Av	3.628 (20)*
g Type			P(1)-P(4)		3.534 (3)
H(1)-P(2)		2.60 (10)	P(2)-P(3)		3.855 (4)
H(1)-P(4)		2.54 (10)	P-P (all)	Av	3.66 (7)
H(2)-P(2)		2.61 (8)	m Type		
H(2)-P(4)		2.66 (9)	H(1)-P(1)		2.53 (8)
H(3)-P(1)		2.50 (12)	H(4)-P(4)		2.48 (10)
H(3)-P(3)		2.65 (8)		Av	2.51 (3)*
H(4)-P(1)		2.59 (11)	H(2)-P(3)		2.95 (13)
H(4)-P(3)		2.50 (10)	H(3)-P(2)		2.83 (10)
	Av	2.58 (2)		Av	2.89 (6)*
			H-P (all)	Av	2.70 (11)

Benzene

C(11)-C(12)		1.392 (11)	C(51)-C(52)		1.398 (16)
C(12)-C(13)		1.382 (12)	C(52)-C(53)		1.371 (12)
C(13)-C(14)		1.361 (13)	C(53)-C(54)		1.385 (18)
C(14)-C(15)		1.371 (13)	C(54)-C(55)		1.377 (17)
C(15)-C(16)		1.375 (12)	C(55)-C(56)		1.406 (11)
C(16)-C(11)		1.390 (11)	C(56)-C(51)		1.359 (16)
	Av	1.378 (5)		Av	1.383 (7)
C(21)-C(22)		1.404 (13)	C(61)-C(62)		1.426 (12)
C(22)-C(23)		1.369 (13)	C(62)-C(63)		1.382 (13)
C(23)-C(24)		1.388 (17)	C(63)-C(64)		1.394 (13)
C(24)-C(25)		1.380 (18)	C(64)-C(65)		1.393 (13)
C(25)-C(26)		1.420 (16)	C(65)-C(66)		1.394 (12)
C(26)-C(21)		1.398 (12)	C(66)-C(61)		1.387 (11)
	Av	1.393 (7)		Av	1.396 (6)
C(31)-C(32)		1.395 (16)	C(71)-C(72)		1.408 (13)
C(32)-C(33)		1.404 (15)	C(72)-C(73)		1.380 (14)
C(33)-C(34)		1.351 (23)	C(73)-C(74)		1.381 (16)
C(34)-C(35)		1.376 (23)	C(74)-C(75)		1.357 (16)
C(35)-C(36)		1.418 (14)	C(75)-C(76)		1.398 (14)
C(36)-C(31)		1.392 (16)	C(76)-C(71)		1.386 (12)
	Av	1.389 (9)		Av	1.385 (7)
C(41)-C(42)		1.386 (18)	C(81)-C(82)		1.395 (11)
C(42)-C(43)		1.391 (14)	C(82)-C(83)		1.386 (12)
C(43)-C(44)		1.399 (16)	C(83)-C(84)		1.389 (14)
C(44)-C(45)		1.355 (24)	C(84)-C(85)		1.351 (14)
C(45)-C(46)		1.376 (17)	C(85)-C(86)		1.397 (12)
C(46)-C(41)		1.405 (15)	C(86)-C(81)		1.381 (11)
	Av	1.385 (7)		Av	1.383 (7)
C-C (all C_6H_5)	Av	1.387 (2)			

Nonbonding General

H(22)-H(4B)	2.31	H(2)-H(56)	2.28
H(26)-H(1A)	1.98	H(2)-H(86)	2.52
H(32)-H(2B)	2.25	H(2)-H(4C)	2.71
H(46)-H(2A)	1.89	H(2)-H(32)	2.70
H(52)-H(3A)	1.92	H(3)-H(42)	2.33
H(62)-H(3B)	2.24	H(3)-H(1C)	2.57
H(76)-H(4A)	2.07	H(3)-H(12)	2.57
H(1)-H(22)	2.20	H(4)-H(72)	2.21
H(1)-H(4B)	2.56	H(4)-H(3B)	2.55
H(1)-H(2B)	2.59	H(4)-H(1B)	2.56
H(1)-H(4C)	2.82		

[a] Mean values are given where meaningful and the error of the mean estimated by $[\Sigma(d_i - \bar{d})/(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the distances and mean distance, respectively. Asterisks after values define subaverages for values equivalent by the $C_2(2)$ axis.

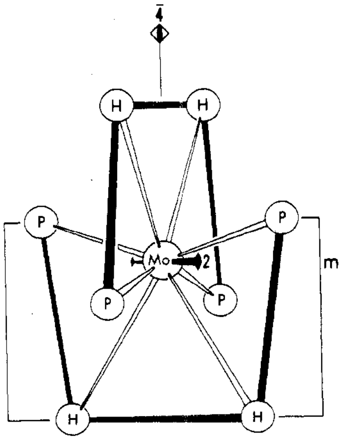

Figure 2. A dodecahedron indicating the location of the symmetry elements. The solid lines identify orthogonal trapezoids.

types of Mo-P and Mo-H distances. It is clear from Figure 1 that this symmetry is maintained in the rotations of the phosphorus tetrahedra (but not in the rotations of the benzene rings). Even the distortions from an isoceles trapezoid in Figure 4 are in keeping with the idealized $C_2(2)$ symmetry.

The Mo-P distances here of 2.433 (2) and 2.503 (8) Å may be compared with other Mo(IV)-P distances of 2.522 (4)-2.580 (5) Å in $[P(C_2H_5)_2(C_6H_5)]_3MoOCl_2$,[31] 2.500 (3)-2.558 (3) Å in $[P(CH_3)_2(C_6H_5)]_3MoOCl_2$,[32] 2.57 Å in the $\{[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]_2MoOCl\}^+$ cation,[33] and the W(IV)-P value of 2.550 (3) Å in $[P(CH_3)_2(C_6H_5)]_2WCl_4$.[34] Observed Mo(II)-P distances are 2.50 (1) Å in $[P(C_4H_9)_3]Mo(\pi\text{-}C_5H_5)(CO)_2I$,[35] 2.435 (3) and 2.498 (2) Å in $[(C_6H_5)_2PCH_2]_2Mo(\pi\text{-}C_5H_5)(CO)Cl$,[36] 2.473 (3) Å in $[(C_6H_5)_3P]Mo(\pi\text{-}C_5H_5)(CO)_2COCH_3$,[37] 2.477 (5) Å for the terminal distance in $\{(C_2H_5)_3PMo[P(CH_3)_2](CO)_3\}_2$,[38] and 2.421 (5) Å for the bridging distance in $(C_5H_5)_2Mo_2H[P(CH_3)_2](CO)_4$.[39] Observed Mo(0)-P distances are 2.518 Å in $[(C_6H_5)_2P]_2CH_2Mo(CO)_4$,[40] 2.425 (4)-2.527 (4) Å in $[(C_6H_5)_2PN(C_2H_5)P$-

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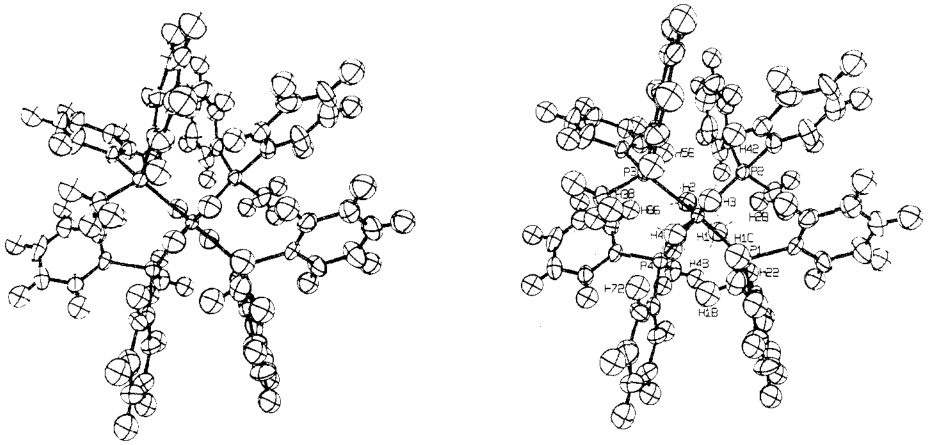

Figure 3. A stereoview of the $H_4Mo[CH_3P(C_6H_5)_2]_4$ molecule in the $S_4(\bar{4})$ direction. The hydrogen atoms labeled are those involved in short interligand contacts (see text).

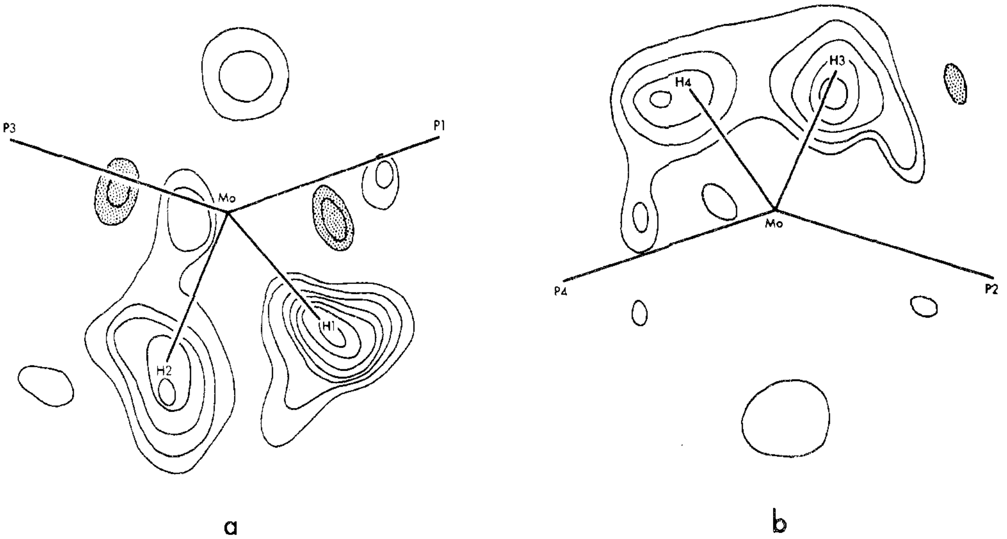

Figure 4. Electron density difference maps in the trapezoid planes of the coordination dodecahedron. Contours start at 0.2 e/Å^3 and increase in intervals of 0.1 e/Å^3. The shaded areas represent areas of negative electron density. The solid lines terminate at the refined positions for these atoms.

$(C_6H_5)N(C_2H_5)P(C_6H_5)_2]Mo(CO)_3$,[41] 2.517 (3) Å in $[(C_6H_5)_2P(C_6H_4CH{=}CHCH_3)]Mo(CO)_4$,[42] 2.52 Å in $[(C_2H_5)P]_5Mo(CO)_4$,[43] and 2.505 (5) Å in $[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]Mo(CO)_4$.[44] What emerges from this comparison is that the Mo-P distances in $H_4Mo[CH_3P(C_6H_5)_2]_4$ are in the range of previously observed values, but significantly shorter than any observed Mo(IV)-P values with trans P atoms. We note that most observed structures are six-coordinated with additional oxygen, chlorine, or CO ligands, obscuring the significance of changes in Mo-P bond lengths.

The average observed Mo-H distance of 1.70 (3) Å is in good agreement with the M-H distances frequently found in transition metal hydrides.[45] A value of 1.8 Å was estimated for bridging Mo-H distances in $(C_5H_5)_2Mo_2H[P(CH_3)_2](CO)_4$.[39]

Discussion

The primary interest in this structure was the nature of the molybdenum coordination. The differentiation between coordination polyhedra in eight-coordinate complexes is frequently difficult. The dodecahedral description here is made easier by the natural geometrical disposition of ligands between two sets of four each. A comparison of an idealized D_{2d} dodecahedron with the observed polyhedron is given in Figure 5.

Another criterion used to differentiate between a dodecahedron and a square antiprism is the dihedral angles between the trapezoidal planes,[46] *i.e.*, P(1)H(1)H(2)P(3) and P(2)H(3)H(4)P(4). For an idealized dodecahedron this angle is 90° while it is 79.4° for an idealized square antiprism (with equal ligands). The observed angle here of 88.7° (Table VII) also establishes the dodecahedral geometry. A coordination model based on T_d-$\bar{4}3m$ point symmetry would also have orthogonal trapezoids; however, the local symmetry is definitely not T_d since this would require a regular Mo-P tetrahedron.[47] The distortions from a regular tetrahedron are significant (142.8 (13)° for P(1)-Mo-P(3) type angles).

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(45) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, p 42.

(46) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7, 1686 (1968); 11, 1446 (1972).

(47) The T_d-$\bar{4}3m$ model would be considered unlikely in the solid state since hydride hydrogens are usually stereochemically active in coordination complexes, but this is not always the case. In five-coordinate $[(C_6H_5)_3P]_4RhH$ type complexes, the Rh-P coordination polyhedron is a regular tetrahedron within experimental error: R. W. Baker, B. Ilmaier, P. J. Pauling, and R. S. Nyholm, *Chem. Commun.*, 1077 (1970); R. W. Baker and P. J. Pauling, *ibid.*, 1495 (1969).

Table V. Interatomic Angles for $H_4Mo[CH_3P(C_6H_5)_2]_4$ (deg)[a]

P(1)-Mo-P(2)		94.17 (7)
P(3)-Mo-P(4)		95.06 (6)
	Av	94.62 (44)*
P(1)-Mo-P(4)		93.15 (7)
P(2)-Mo-P(3)		100.71 (5)
P-Mo-P (all)	Av	95.8 (17)
H(1)-Mo-P(1)		73.5 (24)
H(1)-Mo-P(3)		144.7 (28)
H(1)-Mo-P(2)		74.4 (30)
H(1)-Mo-P(4)		74.1 (31)
H(2)-Mo-P(3)		85.0 (17)
H(2)-Mo-P(1)		133.5 (24)
H(2)-Mo-P(2)		73.1 (29)
H(2)-Mo-P(4)		76.4 (30)
Mo-P(1)-C(1)		112.65 (23)
Mo-P(2)-C(2)		113.21 (29)
Mo-P(3)-C(3)		113.59 (19)
Mo-P(4)-C(4)		114.38 (30)
	Av	113.5 (4)
Mo-P(1)-C(11)		120.60 (22)
Mo-P(1)-C(21)		121.83 (25)
Mo-P(2)-C(31)		118.35 (27)
Mo-P(2)-C(41)		122.41 (31)
Mo-P(3)-C(51)		123.12 (21)
Mo-P(3)-C(61)		116.18 (19)
Mo-P(4)-C(71)		121.00 (31)
Mo-P(4)-C(81)		121.66 (25)
	Av	120.6 (8)
P(1)-C(11)-C(12)		118.5 (5)
P(1)-C(11)-C(16)		124.7 (5)
P(1)-C(21)-C(22)		119.5 (7)
P(1)-C(21)-C(26)		121.9 (7)
P(2)-C(31)-C(32)		120.1 (7)
P(2)-C(31)-C(36)		122.2 (7)
P(2)-C(41)-C(42)		120.2 (6)
P(2)-C(41)-C(46)		121.0 (7)
P(3)-C(51)-C(52)		120.1 (6)
P(3)-C(51)-C(56)		119.6 (6)
P(3)-C(61)-C(62)		118.3 (7)
P(3)-C(61)-C(66)		123.2 (7)
P(4)-C(71)-C(72)		117.7 (6)
P(4)-C(71)-C(76)		122.0 (7)
P(4)-C(81)-C(82)		124.3 (6)
P(4)-C(81)-C(86)		117.2 (6)
	Av	120.7 (6)
C(11)-C(12)-C(13)		121.8 (8)
C(12)-C(13)-C(14)		119.4 (9)
C(13)-C(14)-C(15)		120.6 (9)
C(14)-C(15)-C(16)		119.7 (9)
C(15)-C(16)-C(11)		121.6 (9)
C(16)-C(11)-C(12)		116.7 (8)
C(21)-C(22)-C(23)		122.3 (10)
C(22)-C(23)-C(24)		118.8 (12)
C(23)-C(24)-C(25)		121.6 (12)
C(24)-C(25)-C(26)		119.2 (12)
C(25)-C(26)-C(21)		119.8 (11)
C(26)-C(21)-C(22)		118.3 (9)
C(31)-C(32)-C(33)		120.4 (9)
C(32)-C(33)-C(34)		120.9 (11)
C(33)-C(34)-C(35)		121.0 (13)
C-C-C (all C_6H_5)	Av	120.0 (2)
P(1)-Mo-P(3)		141.50 (7)
P(2)-Mo-P(4)		144.07 (8)
	Av	142.8 (13)
H(1)-Mo-H(2)		60.0 (36)
H(3)-Mo-H(4)		61.4 (44)
	Av	60.7 (7)
H(4)-Mo-P(4)		72.1 (33)
H(4)-Mo-P(2)		143.7 (32)
H(4)-Mo-P(1)		76.3 (24)
H(4)-Mo-P(3)		70.7 (20)
H(3)-Mo-P(2)		82.4 (30)
H(3)-Mo-P(4)		133.1 (31)
H(3)-Mo-P(1)		71.8 (23)
H(3)-Mo-P(3)		75.2 (18)
C(11)-P(1)-C(21)		98.21 (31)
C(21)-P(2)-C(41)		99.13 (41)
C(51)-P(3)-C(61)		99.40 (37)
C(71)-P(4)-C(81)		98.43 (34)
	Av	98.8 (3)
C(1)-P(1)-C(11)		97.73 (37)
C(1)-P(1)-C(21)		101.71 (38)
C(2)-P(2)-C(31)		98.14 (35)
C(2)-P(2)-C(41)		101.69 (37)
C(3)-P(3)-C(51)		101.23 (35)
C(3)-P(3)-C(61)		99.75 (38)
C(4)-P(4)-C(71)		101.52 (40)
C(4)-P(4)-C(81)		95.14 (32)
	Av	99.6 (9)
C(34)-C(35)-C(36)		118.7 (10)
C(35)-C(36)-C(31)		121.4 (9)
C(36)-C(31)-C(32)		117.7 (8)
C(41)-C(42)-C(43)		120.0 (8)
C(42)-C(43)-C(44)		121.3 (8)
C(43)-C(44)-C(45)		117.3 (10)
C(44)-C(45)-C(46)		123.4 (10)
C(45)-C(46)-C(41)		119.2 (9)
C(46)-C(41)-C(42)		118.7 (8)
C(51)-C(52)-C(53)		118.9 (8)
C(52)-C(53)-C(54)		121.7 (8)
C(53)-C(54)-C(55)		119.0 (8)
C(54)-C(55)-C(56)		119.8 (7)
C(55)-C(56)-C(51)		120.2 (6)
C(56)-C(51)-C(52)		120.4 (8)
C(61)-C(62)-C(63)		119.5 (9)
C(62)-C(63)-C(64)		121.3 (10)
C(63)-C(64)-C(65)		119.5 (10)
C(64)-C(65)-C(66)		119.6 (9)
C(65)-C(66)-C(61)		121.6 (9)
C(66)-C(61)-C(62)		118.4 (9)
C(71)-C(72)-C(73)		119.4 (11)
C(72)-C(73)-C(74)		120.2 (12)
C(73)-C(74)-C(75)		120.1 (12)
C(74)-C(75)-C(76)		121.7 (12)
C(75)-C(76)-C(71)		118.2 (11)
C(76)-C(71)-C(72)		120.2 (9)
C(81)-C(82)-C(83)		121.3 (9)
C(82)-C(83)-C(84)		118.2 (10)
C(83)-C(84)-C(85)		121.9 (10)
C(84)-C(85)-C(86)		119.4 (10)
C(85)-C(86)-C(81)		120.8 (9)
C(86)-C(81)-C(82)		118.3 (8)

[a] Footnote to Table IV applies here also.

The parameters frequently used to characterize the shape of a dodecahedron[5] are the bond lengths M-A and M-B and the angles the bonds make from the $S_4(\bar{4})$ axis, θ_A and θ_B (Figure 6). The polyhedron in Figure 6 is the observed polyhedron (Mo coordination sphere of Figure 1). A comparison of the $H_4Mo[CH_3P(C_6H_5)_2]_4$ parameters with the classic eight-coordinate $Mo(CN)_8^{4-}$ structure,[7] the $(CH_3NC)_4Mo(CN)_4$ structure,[15,16] and the data derived from a hard-sphere model[4,5] is given in Table VI. This comparison is representative; other observed dodecahedral parameters can be found in review articles.[1,2] There are no bond distance comparisons available with observed eight-coordinate structures for hydrogen or phosphine ligands. However, our angle parameters agree quite well with those found for other dodecahedral structures (lists in ref 1 and 2). Our θ_A is the smallest observed angle for a discrete dodecahedron. The explanation for this seems obvious, the hydrogen ligand is the least steric demanding of all possible ligands; hence the *a* edge here of 1.72 (2) Å should be the shortest possible for ligands not directly bonded (bidentate type). The distortion of polyhedral edges in Table VI seems reasonable for the sizes of the ligands involved.

The bonding in eight-coordinate complexes has been studied from the point of view of hybridization schemes[11,12,48] and ligand-field theory[49] and discussed generally by Hoard, *et al.*[5,7-10] We will limit the discussion here to the aspects of the $H_4Mo[CH_3P(C_6H_5)_2]_4$ structure which bear on the nature of the metal-ligand bonding. The structural features which are possibly pertinent to the bonding question are (a) the dodecahedral geometry with hydrogen atoms in the A sites and phosphorus atoms in the B sites, (b) the Mo-P and Mo-H bond lengths, and (c) the distortions from the idealized D_{2d} symmetry. These will be discussed in turn.

The positioning of H in the A sites and P in the B sites in this MX_4Y_4 molecule is undoubtedly due to the steric requirements of the ligands. Hoard and Silverton have shown that A-A interactions make a proportionately large contribution to the closed-shell repulsive energy.[5] On the basis of mutual repulsions of ligands alone, the smaller ligand should prefer the A sites.[50] There is also a bonding argument for directing the phosphines to the B sites. In the valence-bond language after d^4sp^3 hybrid orbitals are used for the dodecahedron, there remains one d orbital pointing along the dihedral twofold axis (d_{xy} or $d_{x^2-y^2}$ depending on the coordinate system, we will use d_{xy}).[5,14] This d orbital is pointed out of the plane of the paper in Figure 6 between the B sites and in position to π bond to atoms in the B sites. Certainly P is a better π bonder than H and would prefer the B site if the π-bonding mechanism is operating.

Bond length comparisons with literature values were given in the Structure Description section. The Mo-H bonds are considered normal in view of the accuracy with which H atoms can be determined by X-ray techniques. The difference between the two sets of Mo-H distances (1.65 *vs.* 1.75 Å) may be at least partly real since they follow the established $C_2(2)$ point symmetry, but they are equivalent in view of the estimated errors involved. The Mo-P distances are clearly not equivalent and form two sets according to the $C_2(2)$ molecular point symmetry (2.433 (2) and 2.503 (8) Å, Table IV). It is difficult to estimate the Mo-P bond order since we cannot reliably estimate the radius of Mo(IV). Molybdenum radii of 1.45,[51] 1.60,[52] and 1.61 Å[39] have been estimated in the past and used by others for Mo in various oxidation states and with different coordination numbers. Using 1.10 Å for the P radius, this puts the Mo-P single-bond value somewhere between 2.55 and 2.71 Å. We can also estimate an eight-coordinate Mo(IV) value of 1.39 Å from the data on $Mo(CN)_8^{4-}$ (2.16[7a] − 0.77 Å[7b]), putting the calculated Mo-P distance at 2.49 Å, but then the Mo-CN bond could have some multiple-bond character. Looking at the problem from a different point of view, we observe that the P atoms are favorably situated for d_π-d_π bonding.[53] Also, since the A ligands are H in this d^2 complex, there could well be a tend-

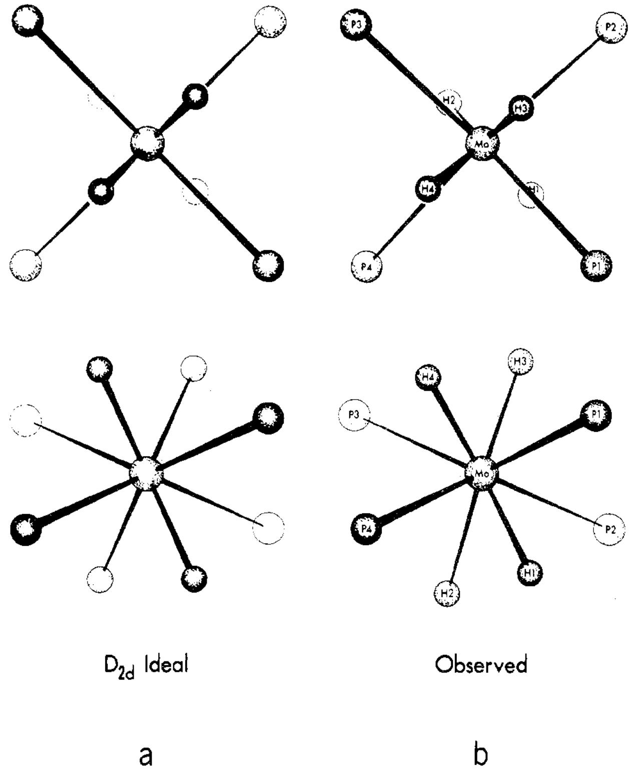

Figure 5. Comparison of the observed coordination polyhedron with that of an ideal D_{2d} dodecahedron (side and top views shown).

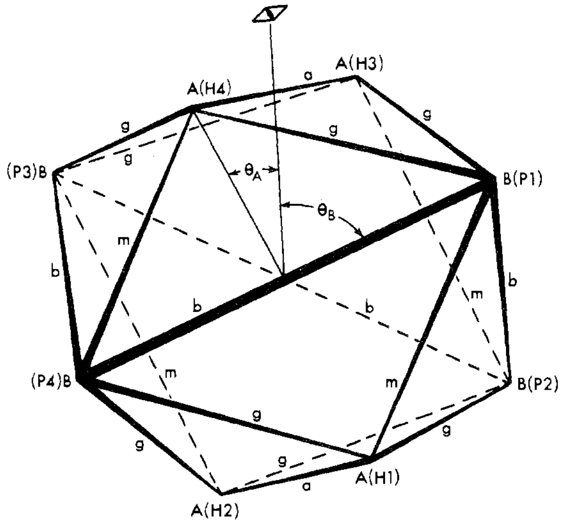

Figure 6. Conventional dodecahedral structural description.[5] The polyhedron is the observed polyhedron (as in Figure 1).

Table VI. Dodecahedral Coordination Parameters[a]

	Mean $H_4Mo[CH_3P(C_6H_5)_2]_4$	$Mo(CN)_8^{4-}$ [b]	$(CH_3NC)_4Mo(CN)_4$ [c]	Hard sphere
M-A(H), Å	1.70 (3)	2.165	2.177	r^d
M-B(PR_3), Å	2.503 (8)	2.162	2.148	r^d
θ_A, deg	30.3 (7)	36.0	35.7	36.9
θ_B, deg	71.4 (13)	72.9	75.7	69.5
(M-A)/(M-B)		1.00	1.01	1.00
a(2), Å	1.72 (2)	2.545	2.54	$1.199r^d$
m(4), Å	2.48-2.95	2.448-2.596	2.455	$1.199r^d$
g(8), Å	2.58 (2)	2.673	2.73	$1.199r^d$
b(4), Å	3.66 (7)	3.187	2.99, 3.26	$1.499r^d$

[a] The errors of the mean values were estimated from the observed sample as in Table IV. The hard-sphere values were taken from ref 5. [b] From ref 7. [c] From ref 15. [d] *r* is the metal-ligand distance.

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(48) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(49) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, **85**, 249 (1963).

(50) A possible exception to this (discussed in ref 5) is the $TiCl_4$·diars (diars is *o*-phenylenebis(dimethylarsine)) molecule where the bidentate diarsine ligands span the A sites. The authors in ref 5 show how the site selection is determined primarily by the ligand bite.

(51) D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, **87**, 921 (1965).

(52) M. J. Bennett and R. Mason, *Nature (London)*, **205**, 760 (1965).

(53) The P d_{xz} and d_{yz} orbitals (taking the *z* axis along the bond) are probably better able to overlap with the Mo d_{xy} than second-row atom atomic orbitals; however, the energies may not be as favorable.

ency to promote Mo→P d_π-d_π bonding to remove density on the metal.[54] This molecule appears to be set up to optimize whatever π bonding with d_{xy} that is possible. This coupled with the short M-P distance is certainly consistent with some π bonding in the B bonds but is not proof that it exists.

In $Mo(CN)_8{}^{4-}$ both the M-A and M-B bond lengths are essentially identical. Based on this, Hoard, *et al.*,[7,55] concluded that the π back-bonding in the d^2 $Mo(CN)_8{}^{4-}$ was less than the forward π bonding in the d^0 oxozirconate(IV) complexes.[55] However, $H_4Mo[CH_3P(C_6H_5)_2]_4$ is probably better set up for π bonding than $Mo(CN)_8{}^{4-}$ from the point of view of the nature of the ligands and the coulombic repulsions due to the overall charge on the latter.[56] A bond length difference was observed in $(CH_3NC)_4Mo(CN)_4$ [15] (Table VI), and it was attributed to increased π bonding to the B ligands.

The difference in Mo-P bond lengths is surely statistically significant but it is difficult to assess the chemical significance, especially since steric effects are known to be important in systems of this type.[5] In particular, it is difficult to determine whether the shorter distance results from increased π bonding or increased, or at least altered, σ bonding due to relief of steric strain. The P(1) and P(4) atoms do not appear to be significantly better positioned than P(2) and P(3) for enhanced bonding to the Mo atom. Also, removal of the degeneracy of the E orbital under the local $C_2(2)$ symmetry would not seem to be the driving force for distortions from D_{2d} symmetry, although it could be important after the molecule distorted, say, from steric effects.

All the intramolecular distances were examined closely for signs of steric effects. There were a good number of short contacts involving hydrogen atoms; the shortest of these are listed in Table IV. All the hydride hydrogens in particular had short contacts, primarily with benzene rings (Table IV). Figure 3 was designed to illustrate these contacts. The hydrogens involved in contacts less than 2.55 Å from the hydride hydrogens are labeled in Figure 3 and the contact directions from the hydride hydrogens are indicated by short dotted lines. The net effect seems to be that packing forces (primarily intramolecular, interligand) distort the molecule with concomitant rehybridization of atomic orbitals to optimize the bonding.

There is nothing usual about the structural data for the phosphine ligands (Tables IV and V). The $P-C(CH_3)$ and $P-C(C_6H_5)$ distances of 1.836 (4) and 1.844 (6) Å, respectively, are similar to frequently observed values in organophosphines and orthophosphate esters.[57] Also, as is common for this type of structural feature, the Mo-P-C angles are significantly greater than 109° while the C-P-C angles are significantly less than 109°.

The least-squares planes for the dodecahedral trapezoidal planes (planes 1 and 2) and the benzene planes were examined and the results are summarized in Table VII. The deviations from the trapezoidal planes are somewhat large (maximum deviation 0.05 Å); this could be legitimate distortion or reflect some inaccuracy in the hydride hydrogen atom positions. All the benzene rings are quite planar. The dihedral angles show that the benzene rings on the same phosphorus atom are nearly orthogonal (87-97°). Although the benzene rings related by the idealized $C_2(2)$ axis are generally positioned according to $C_2(2)$ symmetry, the rotations about the C(n1)-C(n4) bonds do not follow the $C_2(2)$ symmetry (19-82°).

Table VII

Least-Squares Planes for $H_4Mo[CH_3P(C_6H_5)_2]_4$ [a]

1. $-0.1744X + 0.9198Y - 0.3517Z + 1.401 = 0$
   Mo (0.042),[b] P(1) (0.016), P(3) (−0.011), H(1) (−0.038), H(2) (0.034)
2. $0.9300X + 0.2878Y + 0.2287Z - 1.830 = 0$
   Mo (0.058),[b] P(2) (0.015), P(4) (−0.019), H(3) (−0.044), H(4) (0.049)
3. $0.2212X + 0.7664Y + 0.6031Z - 1.367 = 0$
   C(11) (−0.001), C(12) (0.016), C(13) (−0.014), C(14) (−0.003), C(15) (0.017), C(16) (−0.015)
4. $0.6331X - 0.5899Y + 0.5012Z - 1.438 = 0$
   C(21) (−0.016), C(22) (0.013), C(23) (−0.001), C(24) (−0.007), C(25) (0.003), C(26) (0.009)
5. $0.7485X - 0.6598Y + 0.0664Z + 1.518 = 0$
   C(31) (0.013), C(32) (−0.006), C(33) (−0.007), C(34) (0.015), C(35) (−0.008), C(36) (−0.006)
6. $0.6227X + 0.6652Y + 0.4119Z - 3.560 = 0$
   C(41) (−0.011), C(42) (−0.011), C(43) (0.025), C(44) (−0.018), C(45) (−0.004), C(46) (0.018)
7. $0.1821X + 0.7859Y - 0.5909Z + 1.285 = 0$
   C(51) (−0.006), C(52) (0.008), C(53) (−0.004), C(54) (−0.002), C(55) (0.004), C(56) (0.001)
8. $0.9426X - 0.3241Y + 0.0800Z - 3.328 = 0$
   C(61) (−0.007), C(62) (−0.001), C(63) (0.010), C(64) (−0.010), C(65) (0.002), C(66) (0.007)
9. $0.7939X - 0.3018Y + 0.5279Z - 4.141 = 0$
   C(71) (0.017), C(72) (−0.019), C(73) (0.007), C(74) (0.008), C(75) (−0.009), C(76) (−0.003)
10. $-0.5757X - 0.2709Y + 0.7715Z - 4.094 = 0$
    C(81) (0.009), C(82) (−0.008), C(83) (0.006), C(84) (−0.004), C(85) (0.005), C(86) (−0.007)

Dihedral Angles, Deg

MoP(1)P(3) MoP(2)P(4)	89.41	C(11)-C(16) C(21)-C(26)	90.56
P(1)P(3)H(1)H(2) P(2)P(4)H(3)H(4)	88.73	C(11)-C(16) C(81)-C(86)	82.51
MoH(1)H(2) MoH(3)H(4)	88.42	C(21)-C(26) C(71)-C(76)	19.05
MoP(1)P(3) P(1)P(3)H(1)H(2)	2.77	C(71)-C(76) C(81)-C(86)	88.17
MoH(1)H(2) P(1)P(3)H(1)H(2)	3.05	C(31)-C(36) C(41)-C(46)	86.87
MoP(2)P(4) P(2)P(4)H(3)H(4)	4.55	C(31)-C(36) C(61)-C(66)	22.38
MoH(3)H(4) P(2)P(4)H(3)H(4)	3.77	C(41)-C(46) C(51)-C(56)	66.87
		C(51)-C(56) C(61)-C(66)	97.49

[a] The planes are relative to the cartesian coordinate system based on a, b, and c^*. The atoms defining the planes and the deviations from the planes follow the equations. [b] The Mo atoms in the first and second equations were not included in the refinement.

All the intermolecular contacts were examined. The shortest intermolecular C-H and H-H distances were 2.802 and 2.17 Å (between benzene hydrogen atoms), respectively. There was nothing unusual in the thermal ellipsoids. The Mo and P atoms were fairly isotropic while the minimum and maximum rms vibrations for the carbons were 0.137 and 0.445 Å, respectively, the most anisotropic atom being C(25) (0.163-0.419 Å).

The solution behavior of $H_4Mo[CH_3P(C_6H_5)_2]_4$ and similar eight-coordinate hydrides was discussed previously.[17] A few comments seem in order here on the implications of the

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(54) The simple argument used here is that H would tend to put more density on the metal than CO, CN, or Cl, for example, because of the lack of a π-acceptor route for back-bonding and the much higher Coulomb energy (less negative) for the valence atomic orbital.

(55) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 90, 3374 (1968).

(56) Interestingly, the Mo-C distance in the eight-coordinate d^2 $Mo(CN)_8{}^{4-}$ (2.163 Å) is shorter than in the six-coordinate d^2 $MoO_2(CN)_4{}^{4-}$ (2.205 Å). This is attributed to increased coulombic repulsions in the latter.

(57) D. E. C. Corbridge, *Top. Phosphorus Chem.*, 3, 212 (1966).

solid-state structure with respect to possible exchange routes in solution. The two transition-state structures considered most likely for rearrangement in these H_4ML_4 complexes are (a) a T_d-$\bar{4}3m$ symmetry model of interpenetrating tetrahedra and (b) an $S_4(\bar{4})$ symmetry model where the four phosphorus and molybdenum atoms are coplanar, with the hydrogen tetrahedron staggered with respect to the P atoms. The observed structure is nearly midway between a planar MoP_4 and a regular tetrahedral MoP_4 configuration; it is slightly closer to the S_4 planar model based on rms deviations from the idealized transition states. Hence, based on the solid-state evidence both transition states are about equally accessible. In fact, it was not possible even with all the available data to establish unequivocally the rearrangement mechanism operating in these complexes (discussed in ref 17), although the T_d model is certainly preferred on steric grounds.

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Supplementary Material Available. A listing of structure factor amplitudes 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2295.

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Reactions of Ammonia and Ammonia–Chloramine Mixtures with Monochloroarsines and Diarsines and X-Ray Crystallographic Study of 2,2,4,4,6,6-Hexaphenylcyclotriarsazene, $[(C_6H_5)_2AsN]_3$

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It has been shown that ammonia and deuterated ammonia react with dimethylchloroarsine to give the respective arsenoammonium chloride. The dialkylchloroarsines and diarsines react with ammonia–chloramine mixtures to form $R_4As_2N_2$·HCl (R = CH_3 or C_2H_5) and $[(C_6H_5)_2AsN]_3$·HCl. Physical properties and mass spectral data suggest that $(CH_3)_4As_2N_2$·HCl is a hydrochloride intermediate to an arsenonitrile, while $(C_2H_5)_4As_2N_2$HCl is a multiple arsenic–nitrogen bonded polymer containing arsenic–chlorine bonds. The results of the diarsine reactions suggest that arsenic–arsenic bonds are cleaved and give the same products as those obtained by the analogous reaction with dimethyl- or diphenylchloroarsines. The formation of tris(diethylarsino)amine is difficult to explain by an acceptable reaction path. The crystal structure of 2,2,4,4,6,6-hexaphenylcyclotriarsazene, $[(C_6H_5)_2AsN]_3$, has been determined from three-dimensional X-ray data collected with an automated diffractometer by use of nickel-filtered copper radiation. The compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a = 9.713$ (1) Å, $b = 11.825$ (2) Å, $c = 15.645$ (2) Å, $\alpha = 67.72$ (1)°, $\beta = 93.49$ (1)°, $\gamma = 105.79$ (1)°, and $Z = 2$. The observed and calculated densities are 1.51 and 1.515 g/cm³, respectively. The structure was refined by least-squares calculations to a conventional R index of 0.061 for 3818 independent intensities. The As_3N_3 ring of the molecule is slightly puckered. The six As–N bond distances appear to be equivalent with an average value of 1.758 (4) Å. The structure is discussed relative to that of $[(C_6H_5)_2AsN]_4$. The mass spectral data for $[(C_6H_5)_2AsN]_4$ show As_4N_4 ring opening with formation of $[(C_6H_5)_2AsN]_3$. The possible fragmentation mechanisms suggested by the metastable peaks are discussed.

Introduction

Reichle[1] prepared the arsenonitrilic tetramer $[(C_6H_5)_2AsN]_4$, mp 316–317°, by pyrolyzing the reaction product of diphenylchloroarsine with lithium azide. The tetramer was also synthesized by Haque and Din[2] by mixing $(C_6H_5)_2AsCl_3$, NH_4Cl, and liquid NH_3 at −35° for 2 hr. Glick[3] has shown that this tetramer has S_4-$\bar{4}$ symmetry with a tub-like configuration and two nonequivalent types of arsenic–nitrogen bonds, 1.67 ± 0.03 and 1.79 ± 0.03 Å. The arsenonitrilic trimer $[(C_6H_5)_2AsN]_3$, mp 155–157°, was prepared by the ammonolysis of $(C_6H_5)_2AsCl_3$.[4] The reaction of ammonia-chloramine mixtures with diphenylchloroarsine gives a product which upon heating and recrystallizing from dimethylformamide (DMF) yields the DMF adduct of the trimer, $[(C_6H_5)_2AsN]_3$·DMF.[4] Whereas analytical and infrared data for the trimer and adduct were given, no molecular weight data were cited to substantiate the postulated molecular formula. We have reinvestigated these latter two reactions in an attempt to isolate and characterize completely the pure trimer. In addition, we have determined the crystal structure of this compound to obtain details of the stereochemistry of the molecule and to give useful bond distance information for comparison with other known arsenic–nitrogen bond distances.[3,5,6]

The preparation of the trimer *via* the chloramination reaction is analogous to the ammonolysis and chloramination of chlorophosphines[7,8] to give diaminophosphonium chlorides which undergo self-condensation to yield phosphonitriles.

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