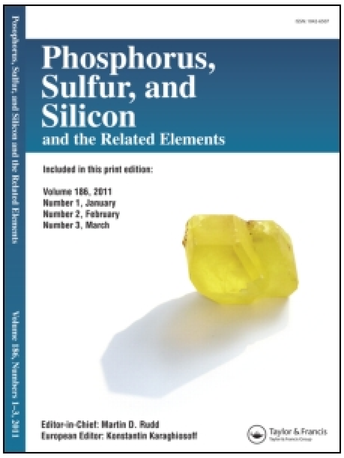

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CONFORMATIONAL ANALYSIS OF TRIMETHYLPHOSPHITE AND ITS METAL COMPLEXES

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CONFORMATIONAL ANALYSIS OF TRIMETHYLPHOSPHITE AND ITS METAL COMPLEXES

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Trimethylphosphite ligands in about 40 different molecular environments in the solid state adopt five distinct conformations, apart from those related by chirality. The ligand symmetry is usually C_1, occasionally C_3 or C_s, but never the maximum attainable C_{3v}. Average experimental P—O and O—C bond lengths in the complexes are 1.583 and 1.440 Å; O—P—O bond angles (average 101.4°) vary considerably from conformer to conformer, whereas the mean P—O—C angle is 124.0°. Conformational analysis, using the MNDO method, indicates that the steric requirements of the metal rule out a C_{3v}, several C_3, C_s and lower symmetry conformations for the ligand which are energetically favorable in case of the isolated molecule. Except for the experimentally observed C_3 symmetry conformer, none of the other ligand geometries (of C_s and C_1 symmetry) is amongst the set of low energy conformations of the free molecule. This stands in relation to the steric requirement of the metal, which induces considerable torsional variations upon coordination together with changes in O—P—O bond angles and C—O bond distances. The metal position is typically displaced by about 0.25 Å away from the cap of the phosphorus pyramid in the P—O—C plane of the *trans* methyl group.

INTRODUCTION

The trimethylphosphite molecule finds frequent application as a ligand in complexes of transition metals because of its potential of stabilizing low valent metal derivatives and in view of the very similar ligand properties of the phosphite group as compared to CN^-.[1] It has been noticed that the conformation of the complexed $P(OCH_3)_3$ molecule is essentially a property of the ligand rather than a configuration induced by the environment in the crystal.[2] Yet, in general, the conformation of a flexible molecule bonded to a metal does not need to be the same as that found in solution (as determined by spectroscopic techniques) or in vacuum (as calculated by molecular mechanics).

It is noticed that although the structure of the trimethylphosphite $P(OCH_3)_3$ molecule has been analyzed previously on the basis of the molecular polarisability,[3] spectroscopic data[4,5] and by means of electron diffraction,[6] no completely unambiguous interpretation of its geometry has been given. The most commonly held view is that both the gaseous and liquid phases contain a mixture of conformers.[6,7] Also the results of numerous structure determinations show striking conformational differences. By comparison of the molecular structure of a representative number of compounds the degree of flexibility of a ligand can be evaluated. It is quite likely that x-ray diffraction results show mainly or exclusively low energy conformations. As molecular models indicate that there can only be restricted rotation about the bonds of the $POCH_3$-groups, in this paper we examine the observed conformations in the solid state and compare these with the stable configurations calculated for the isolated molecule. As various conformations of the isolated molecule have about equal energies, the effects of small structural changes in the solid state (nature of complexing unit, crystal packing forces) finally determine which conformation becomes the preferred one.

Conformational analysis of $P(OCH_3)_3$ in metal complexes

In order to compare the possible conformations of trimethylphosphite, the geometries must be specified by descriptive structural parameters. A picture of the molecule with the atom numbering scheme is given in Figure 1; average distances and angles describing the ligand structure are found in Table I. The coordination about the phosphorus atom is characterized by the P—O bond distances and O—P—O angles. If the ligand exhibits C_3 symmetry two rather than six degrees of freedom need to be specified to describe the geometry of the PO_3 portion (e.g. P—O bond length and the distance of the phosphorus atom to the plane of the three O atoms). Apart from C—O bond length and P—O—C bond angle information, an unambiguous description of the trimethylphosphite framework is completed by specification of the torsion angles E—P—O—C or φ,[8] where the electron lone-pair E is assumed to lie on a line perpendicular to the plane of the three O atoms and passing through the P atom (*cis* C_{3v} conformation: $\varphi_i = 0°$).

Trimethylphosphite metal complexes for which complete geometric data are included in the Cambridge Crystallographic Data File are listed in Tables II and III.

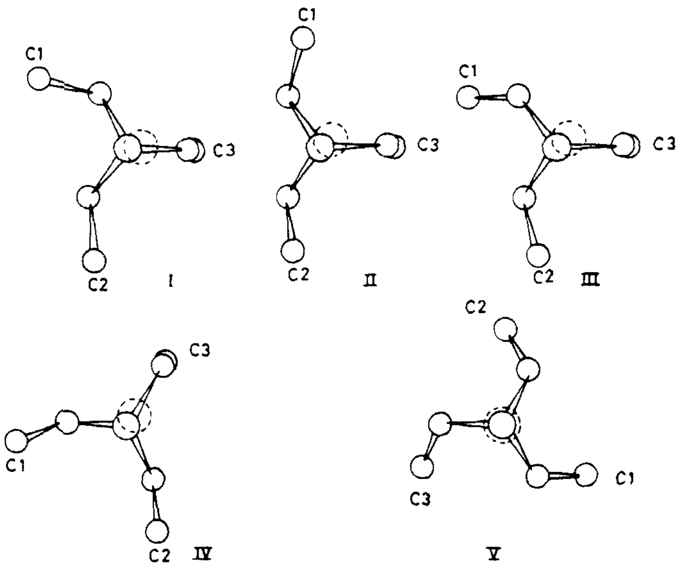

FIGURE 1 Conformations of complexed $P(OCH_3)_3$ projected onto the oxygen plane. Related chiral forms are not shown. ○ Metal position.

TABLE I

Geometry of $P(OCH_3)_3$ complexes and related compounds

Compound	⟨P—O⟩	⟨O—C⟩	⟨O—$\hat{P}$—O⟩	⟨P—$\hat{O}$—C⟩	⟨P—$\hat{O}$—P⟩	Reference
$P(OC_2H_5)_3$[a]	1.600 Å	1.42 Å	96°	120°	—	14
P_4O_6	1.638	—	100	—	126°	14
Substituted phosphates	1.590	1.44	100	116	—	14
$P(OCH_3)_3$ complexes	1.583	1.440	101.4	124.0	—	This work

[a] Gas phase; electron diffraction.

Structures for which no published coordinational parameters are available (cf. footnote *b* to Table III) have not been considered here; similarly, trialkylphosphites ($R \neq CH_3$), trimethylphosphates[9, 10] and phospholes[11] have been ignored.

For the sake of classification of the various conformations (I–V), the structures were projected onto the oxygen plane (Figure 1). The distances of the non-oxygen atoms from this plane are given in Tables II and III (together with a designation of the coordinated metal position). It is noticed that neither the "umbrella" (*trans* C_{3v}) nor the "inverted umbrella" (*cis* C_{3v}) conformations are found experimentally in the solid state. This is easily understood in the former case due to the prohibitively short H--H contacts (1.05 Å) in the free molecule. The absence of a *cis* C_{3v} conformation is statistically significant in view of the relatively large data set considered and is apparently due to the requirements of the metal as no short non-bonded distances are present in the isolated molecule.

Except for conformation V (Figure 1) the complexed $P(OCH_3)_3$ molecules lack three-fold symmetry. An almost ideal propeller-shaped conformation with C_3 symmetry is experimentally found for $(NiL_4Br)BF_4$.[12] This conformation is characterized by C—O—P—O torsional angles of 0°, equal O—P—O bond angles (105.5°) and a metal position exactly on top of the phosphorus pyramid. It is noticeable that C_3 symmetry conformations with C—O—P—O torsional angles of 180° are not found experimentally, in spite of the fact that the H--O non-bonded repulsions are similar or even more favorable than in conformation V. This is again a result of the requirements of the metal coordination site (steric effect). It clearly appears that the methyl-groups avoid location in the area towards the top of phosphorus pyramid.

All other $P(OCH_3)_3$ complexes exhibit various "two up, one down" arrangements of the methyl groups (Figure 1). In such cases two of the methyl groups are in a relatively flat position (at some small angle with respect to the plane of the oxygen atoms), whereas the third is almost perpendicular to this plane (average out-of-plane deviation is close to the O—C distance). Conformers II and IV show C_s symmetry, whereas I and III exhibit C_1 point symmetry.

The data presented show the existence of a restricted number of energetically more or less equally probable conformations of the ligand and also suggest that complexation restricts the available range of molecular conformations.

As may be seen from Table IV, considerable O—P—O bond angle distortions arise as a result of the adoption of a particular conformation. In conformation II the shortest (symmetrical) non-bonded interactions are H--O, 2.63 Å and H--H, 2.79 Å

TABLE II

Geometrical parameters of ligand conformation I

Compound	Distance from oxygen plane (Å) C(1)	C(2)	C(3)	P	M	M − P (Å)	Reference[a]
$[CHC(O)]_2OCoL_3$	0.39	0.04	−1.45	0.73	2.87	2.153(2)	*ORG*, 1983, **2**, 627
	0.02	0.26	−1.44	0.73	2.88	2.164(2)	
$Fe(CO)_3L_2$	0.28	0.36	−1.45	0.71	2.85	2.155(1)	*AC*, 1974, **B30**, 2798
$[Co(CNC_6H_4F)_3L_2]BF_4$	0.33	0.40	−1.48	0.69	2.82	2.137(3)	*IC*, 1978, **17**, 1986
$[NiL_4Br]BF_4$	0.44	−0.21	−1.45	0.69	2.85	2.181(2)	*IC*, 1975, **14**, 2665
$\{L(OC)_2Co[(CH_2)_2CCH_2]\}_2CO$	0.55	0.34	−1.43	0.75	2.87	2.129(3)	*IC*, 1978, **17**, 1421
$Ru(CO)_4L$	0.31	0.38	−1.43	0.71	3.02	2.309(2)	*JOC*, 1980, **195**, 77
	0.30	0.43	−1.43	0.72	3.03	2.309(2)	
$[Mo_2Cl_3(CO)_4L_4]^{n+}$	0.16	0.25	−1.50	0.70	3.15	2.428(5)	*JCSD*, 1975, 1984
$[MoOCl_4\{O(POMe)_2\}]^{n-}$	0.06	−0.04	−1.48	0.67	3.07	2.420(7)	
$HFeCo_3(CO)_9L_3$	0.36	0.01	−1.44	0.71	2.88	2.175(2)	*JACS*, 1978, **100**, 3059
	0.03	0.35	−1.44	0.74	2.94	2.173(2)	
$(C_5H_5)Mo[CC(CN)_2]L_2Cl$	0.33	0.28	−1.43	0.70	3.16	2.470(2)	*IC*, 1974, **13**, 1667
$(C_4H_7)_2RuL_2$	0.18	0.28	−1.39	0.78	3.02	2.210(5)	*JCSD*, 1973, 778
	0.33	0.19	−1.49	0.77	3.01	2.233(7)	
$W_2H(CO)_8(NO)L$	0.14	0.30	−1.42	0.69	3.15	2.485(5)	*JACS*, 1976, **98**, 4491
$(CH_3C_5H_4)Mo(CO)_2LI$	0.30	0.35	−1.46	0.72	3.10	2.388(8)	*JCSD*, 1972, 1900
$(C_5H_5)Mo(CO)_2LI$	0.32	0.31	−1.52	0.73	3.12	2.406(9)	*JCSD*, 1972, 1900
$Os_3(CO)_{11}L$	0.08	0.23	−1.49	0.71	3.02	2.285(4)	AC, 1978, **B34**, 666
$[Ir(\mu\text{-}SR)(CO)L]_2$	−0.32	0.39	−1.50	0.73	2.93	2.205(12)	JACS, 1979, **101**, 5940
$Fe(S_2C_2Ph_2)_2L$	0.01	0.08	−1.43	0.70	2.81	2.152(1)	AC, 1977, **B33**, 3942
$(\mu\text{-}H)(\mu\text{-}HC = NPh)Os_3(CO)_9L$	0.25	0.28	−1.49	0.73	3.01	2.281(2)	JACS, 1979, **101**, 2579

[a] For abbreviations cf. ref. 38; $L = P(OCH_3)_3$.

TABLE III

Geometrical parameters of ligand conformations II–V

Compound	Conformation	Distance from oxygen plane (Å)					M − P (Å)	Reference[a]
		C(1)	C(2)	C(3)	P	M		
$[Ir(H)(\mu\text{-}SR)(CO)L]_2$	II	0.31	0.29	−1.46	0.77	2.95	2.241(4)	*JACS*, 1979, **101**, 5940
$[Ir(\mu\text{-}SR)(CO)L]_2$	II	0.15	0.36	−1.49	0.69	2.90	2.211(9)	*JACS*, 1979, **101**, 5940
NiL_3I_3	II	0.20	0.43	−1.46	0.71	2.87	2.169(2)	*IC*, 1975, **14**, 710
$[NiL_4Br]BF_4$	II	−0.03	0.22	−1.47	0.70	2.93	2.239(2)	*IC*, 1975, **14**, 2665
$RhL_2B(C_6H_5)_4$	II	0.14	0.66	−1.52	0.75	2.99	2.18(1)	*AC*, 1974, **B30**, 738
$RhL_2B(C_6H_5)_4$	III	0.48	−0.79	−1.40	0.66	2.74	2.19(1)	*AC*, 1974, **B30**, 738
NiL_3I_2	III	0.41	−0.45	−1.43	0.70	2.87	2.183(2)	*IC*, 1975, **14**, 710
		0.22	−0.83	−1.46	0.68	2.85	2.180(2)	
$[NiL_4Br]BF_4$	III	−1.08	0.12	−1.41	0.67	2.85	2.187(2)	*IC*, 1975, **14**, 2665
$[Mo_2Cl_3(CO)_4L_4]^{n+}\cdot$ $[MoOCl_4(OP(OMe)_2)]^{n-}$	III	−0.97	0.34	−1.44	0.59	2.97	2.402(8)	*JCSD*, 1975, 1984
$[CHC(O)]_2OCoL_3$	III	−0.89	0.27	−1.44	0.72	2.90	2.198(2)	*ORG*, 1983, **2**, 627
$[Ru(NH_2\cdot NCMe_2)L_4][BPh_4]_2$	III	−1.17	−0.13	−1.34	0.60	2.73	2.35(1)	*JCSD*, 1974, 2406
$HFeCo_3(CO)_9L_3$	III	−1.22	0.35	−1.36	0.68	2.88	2.172(2)	*JACS*, 1978, **100**, 3059
$Mo(CO)_4(NHC_5H_{10})L$	IV	0.37	0.30	−1.48	0.73	3.18	2.462(2)	*IC*, 1977, **16**, 2314
$[AgL_2(NO_3)]_2$	IV	0.52	0.53	−1.44	0.70	3.09	2.411(3)	*IC*, 1975, **14**, 632
$[NiL_4Br]BF_4$	V	−1.04	−0.88	−1.20	0.62	2.80	2.180(2)	*IC*, 1975, **14**, 2665

[a] For abbreviations, cf. ref. 38; L = $P(OCH_3)_3$.

[b] No published coordinational parameters are available for the following $P(OCH_3)_3$ derivatives (ref.): *CC*, 1969, 1406; *CC*, 1970, 1297; *JACS*, 1978, **100**, 7407; *AnC*, 1978, **17**, 128; *JCS CC*, 1978, 878; *JACS*, 1979, **101**, 1422; *JOC*, 1976, **114**, C30; *JCSCC*, 1973, 493; *JOC*, 1979, **171**, C14; *JACS*, 1977, **99**, 8091; *Tetrahedron*, 1978, **34**, 799; *IC*, 1979, **18**, 192; *JOC*, 1981, **213**, 63; *JCSCC*, 1982, 640; *PNAS*, 1979, **76**, 2099; *PNAS*, 1978, **75**, 1056; *JCS Dalton*, 1980, 1317.

TABLE IV

Experimental (and idealized) ligand parameters of $P(OCH_3)_3$ in metal complexes

	Distance to oxygen plane (Å)					Bond angles (°)				
Conformation	C(1)	C(2)	C(3)	P	M[a]	O(1)—$\hat{P}$—O(2)	O(1)—$\hat{P}$—O(3)	O(2)—$\hat{P}$—O(3)	Σ angles	Number of coordinations
I	0.30	0.17	− 1.45	0.72	$\vert 0.25 \vert$	98.4	99.2	105.9	303.5	22
	(0.26)	(0.26)	(− 1.44)	(0.70)		(98.4)	(99.2)	(105.9)		
II	0.17	0.29	− 1.48	0.72	$\vert 0.25 \vert$	93.5	105.0	105.0	303.5	5
	(0.26)	(0.26)	(− 1.44)	(0.70)		(93.5)	(105.0)	(105.0)		
III	0.26	−0.90	− 1.42	0.67	$\vert 0.30 \vert$	99.4	106.3	104.5	310.2	8
	(0.26)	(−0.90)	(− 1.44)	(0.70)		(99.4)	(106.3)	(104.5)		
IV	0.45	0.42	− 1.46	0.71	$\vert 0.27 \vert$	100.6	100.0	101.4	302.0	2
	(0.44)	(0.44)	(− 1.44)	(0.70)		(100.6)	(100.6)	(100.6)		
V	− 1.04	−0.88	− 1.20	0.62	$\vert 0.06 \vert$	104.3	106.0	106.1	316.4	1
	(− 1.04)	(− 1.04)	(− 1.04)	(0.62)		(105.5)	(105.5)	(105.5)		

[a] Displacement (in Å) of metal (M) from center of PO_3 pyramid (in projection onto the oxygen plane).

and the opening of the angles O(1)—P—O(3) and O(2)—P—O(3) to 105.0° is reasonably attributable to interaction of the lone pairs of O(1) and O(2) with the third methyl-group and similarly of P and O(3) with hydrogen atoms of C(1) and C(2); absence of non-bonded interactions between C(1) and C(2) leads to the smallest O(1)—P—O(2) angle (93.5°) observed for any ligand conformation. Conformer I (Figure 1) differs from the previous case by the absence of interaction between hydrogen atoms of C(1) and a lone pair of O(3) at the expense of increased electronic interaction with O(2) (H- -O, 2.92 Å); this rationalizes the changes in bond angles as compared to conformation II. In conformation III (Figure 1) the interaction between the hydrogens of C(1) and an O(2) lone pair increases even further (H- -O, 2.64 Å) and non-bonded contacts between the hydrogens of C(1) and C(3) (2.45 Å) determine a greater increase for O(1)—P—O(3) than for O(1)—P—O(2) as compared to conformation I. The effect of the interaction of the methyl-group at C(1) with O(2) is also shown by direct comparison of conformations II and III. The increased interaction between C(1) and C(2) in the other C_s conformation (IV) leads to a higher O(1)—P—O(2) bond angle, up to the point that the three O—P—O angles are almost equal. This is obviously also the case of the C_3 conformation (V), which is the flattest ligand of all. Bond lengths show no systematic variations with conformation.

Conformational analysis of isolated trimethylphosphite

For the purpose of energy calculations a starting set of bonding data for $P(OCH_3)_3$ should be defined. No crystal structure of $P(OCH_3)_3$ has been determined and studies of the molecular structure have not been able to assess with certainty the point symmetry of the molecule. We have therefore proceeded as follows. Although it is known that coordination usually affects the geometry of a complexed molecule (e.g. compare free maleic anhydride with the ligand in its tris(trimethylphosphite) complex with Co(0)[13]), it appears that phosphines, such as triphenylphosphine, undergo only very minor changes (P—C and C—P—C of 1.828 Å and 103.0° for the free molecule; average values of 1.83 Å and 103° for the ligand).[14–17] This probably stands in relation to the bonding mode from the top of the phosphorus pyramid. As to the effect of complexation on the geometry of trimethylphosphite, Table I shows that the average bond lengths and angles in the ligands are close to the related orthophosphate esters and do not deviate considerably from $P(OEt)_3$ in the gas phase and strain-free P_4O_6. Therefore, to a first approximation we are entitled to consider the experimentally observed dimensions for $P(OCH_3)_3$ ligands as close to the geometrical parameters of the free molecule. $P(OCH_3)_3$ was thus taken to have a pyramidal configuration with bond lengths and angles as indicated in Table I.

With regard to the computational procedure a semi-empirical quantum-mechanical method including all valence electrons was chosen. Some conflicting preliminary results were obtained by the Extended Hückel Theory (EHT) and CNDO/2 method. The MINDO/3 parametrization for P[18] is inadequate as it leads to a calculated $P(OCH_3)_3$ geometry which contrasts with all available experimental data. Consequently, we have used the more recent MNDO SCF method,[19] which in the QCPE version (program Nr 353) includes an adequate parametrization for P[20] and the determination of minimum energy geometries by the DFP technique.[21] The same method has recently been used for predicting the ionization energies of trimethylphosphite in the lowest energy conformation.[22]

Following up the indications derived from the experimentally observed conformations we have considered as initial conformers those with OC bonds in staggered or eclipsed positions with respect to the (other) PO bonds or to the previously defined E direction of the molecule. All independent geometrical parameters of the molecular framework were optimized by taking into account the required symmetry constraints. The C_{3v} symmetry was assumed for the methyl groups with one of the hydrogen atoms in staggered position with respect to the PO bond; an optimal C—H bond length and O—C—H bond angle were found in preliminary minimization steps (1.118 Å and 109.5°, respectively).

In the free state there is a wide range of rotational isomers with a probability distribution function reflecting their relative energies. The minimum energy conformations are summarized in Table V. Since the trimethylphosphite molecule may display C_3 symmetry, initial investigation of possible conformations proceeded from this idealized geometry. The potential energy of the molecule was calculated as a function of the (concerted) internal rotation about the P—O axes, C_3 symmetry being maintained ($\varphi_1 = \varphi_2 = \varphi_3 = \varphi$). This calculation was made over 180° starting from *cis*-C_{3v} ($\varphi_i = 0$, $\Delta H_f^0 = -203.4$ kcal · mol^{-1}), since conformations differing in their chiral sense have equal energies. The map of the energy surface shows a range of low energy conformations ($25° < \varphi < 35°$; $\Delta H_f^0 = -203.7$ kcal · mol^{-1}) with a geometry unsuitable for metal complexation (due to shielding of phosphorus by methyl groups at the top of the PO_3 pyramid) and two other relative minima ($\varphi = 81°$ and $\varphi = 112°$; $\Delta H_f^0 \cong -203$ kcal · mol^{-1}) with the molecule in flat conformations, well suited as ligand geometries (cf. experimental conformer V). The non-bonded interactions increase after a rotation exceeding 112° and are extremely unfavorable for the "umbrella" *trans*-C_{3v} geometry (Figure 2; $\varphi = 180°$; $\Delta H_f^0 = -198.7$ kcal · mol^{-1}), where the interactions between the hydrogen atoms of the arms are very severe.

In each of the series of C_s conformations with a geometry consisting of one *cis* ($\varphi_1 = 0°$) or *trans* ($\varphi_1 = 180°$) methoxy-group and the other two arms with opposite chiral sense ($0° < \varphi_2 = -\varphi_3 < 360°$) a minimum energy conformer was found, namely at (0°, 153°, −153°; $\Delta H_f^0 = -204.7$ kcal · mol^{-1}) and (180°, 0°, 0°; $\Delta H_f^0 = -206.0$ kcal · mol^{-1}). The latter (f in Table V) is the absolute minimum; a full agreement was found also with the geometric parameters of ref. 22, received upon request of the authors. None of these geometries is very favorable for metal approach. It should also be noted that the energy of the minimum of the most highly symmetric conformation (*cis* C_{3v}) exceeds that of a C_s conformation.

The next series of calculations involved refinement of all the degrees of freedom of the arms of the molecule by independent rotations about the P—O axes (flexible rotor geometric model), without imposing symmetry restrictions. Examination of the C_1 symmetry conformations was guided on the basis of the indications of the solid state geometries, which invariably indicate one *trans* ($\varphi = 180°$) methoxy-group. Therefore conformations such as (−52°, φ_2, 180°) and (φ_1, −52°, 180°) were examined initially allowing 360° rotation around P(2)—O(2) and P(1)—O(1), respectively (Figures 3 and 4). Minimization of similar starting positions leads either to one of the previous minima or converges by considerable shifts in the rotations to two

TABLE V

Isolated trimethylphosphite minimum energy conformations

Form	Symmetry	i	P—O$_i$	O$_i$—C$_i$	$\mathrm{O}-\hat{\mathrm{P}}-\mathrm{O}$	$\mathrm{P}-\hat{\mathrm{O}}_i-\mathrm{C}_i$	$E-\hat{\mathrm{P}}-\mathrm{O}_i$	φ_i	E (kcal·mol^{-1})	μ (D)
a	C_{3v}		1.609 Å	1.390 Å	98.3°	120.7°	119.1°	0°	−203.4	3.56
b	C_3		1.608	1.389	98.6	121.9	118.9	27.6	−203.7	3.18
c	C_3		1.601	1.387	101.0	131.3	117.0	81.1	−202.8	0.60
d	C_3		1.596	1.386	102.8	135.3	115.5	111.9	−202.9	0.95
e	C_s	1	1.610	1.388	103.7	123.7	117.2	0	−204.7	1.69
		2, 3	1.588	1.387	102.3	137.0	114.8	± 152.9		
f	C_s	1	1.587	1.391	101.7	134.4	113.5	180	−206.0	1.50
		2, 3	1.610	1.389	97.9	122.2	119.4	0		
g	C_1	1	1.589	1.386	103.4	136.9	115.2	165.6	−204.9	1.32
		2	1.592	1.387	101.7	135.5	114.8	123.4		
		3	1.610	1.387	101.5	124.6	118.0	22.2		
h	C_1	1	1.605	1.389	100.5	125.4	117.4	45.8	−203.0	1.26
		2, 3	1.603	1.387	101.0	131.0	117.0	82.3		

E = electron lone-pair on P atom.

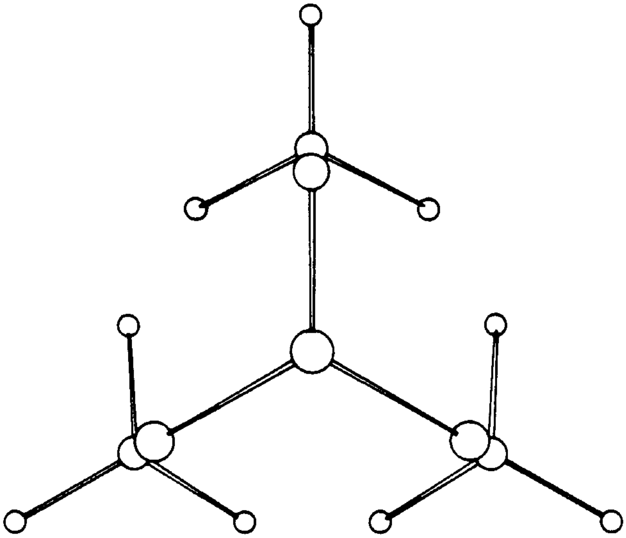

FIGURE 2 *Trans*-C_{3v} conformation of $P(OCH_3)_3$.

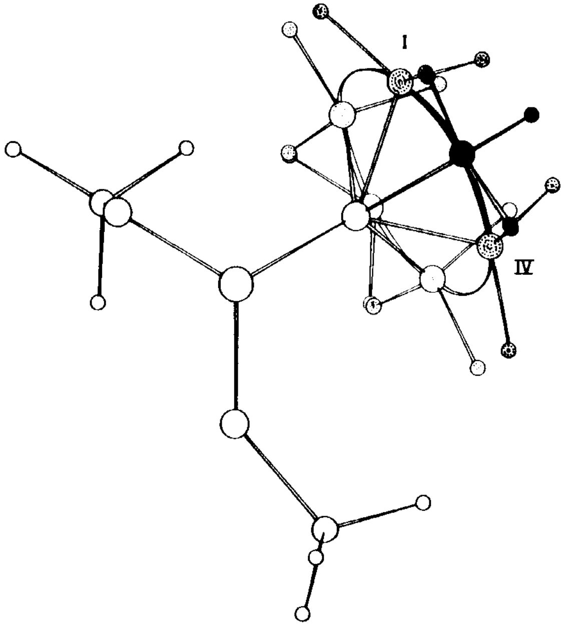

FIGURE 3 Low symmetry conformations of trimethylphosphite with torsional angles ($-52°$, φ_2, $180°$). Experimentally observed ligand conformations are I (C_1 symmetry) and IV (C_s symmetry).

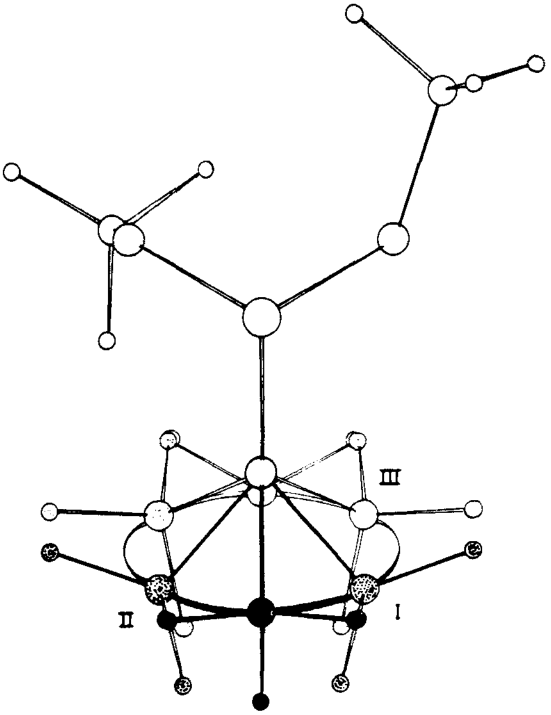

FIGURE 4 Low symmetry conformations of trimethylphosphite with torsional angles (φ_1, −52°, 180°). Experimentally observed ligand conformations are I (C_1 symmetry), II (C_s symmetry) and III (C_1 symmetry).

other minima in the potential energy surface, characterized by (165°, 123°, 22°; $\Delta H_f^0 = -204.9$ kcal · mol^{-1}) and (46°, 82°, 82°; $\Delta H_f^0 = -203.0$ kcal · mol^{-1}). On the whole, on the basis of the steric requirements of the complexing agent (namely access to the cap of the phosphorus pyramid) conformers *c*, *d* and *h* of the free molecule (Table V) are expected to be the most advantageous. The experimentally observed C_3 conformation of the ligand (V) is closer to the calculated geometry (*d*) than to (*c*).

Contrary to the case of triphenylphosphine,[16] it is apparent from the refined geometrical parameters of isolated $P(OCH_3)_3$ (Table V) in comparison to those reported in Tables I and IV for the experimentally observed conformations of the ligand, that coordination affects the molecular bond data of $P(OCH_3)_3$, in particular the O—P—O angles and C—O bond length. Fairly little can be said with regard to variations in P—O—C angles as the methyl-groups often exhibit high thermal parameters or complete disorder (as in case of refs. 2, 23–28). In several cases,[23,28] the experimentally observed electron-density has even been interpreted so as to imply that the oxygen atoms are disordered while the methyl-groups attached to them are ordered. Apparently, in these structures the packing requirements are locally less tight and facilitate the presence of more than one minimum energy conformation in the crystal structure.

TABLE VI

Conformations of trimethylphosphite ligands

		Experimental conformation[a]				Minimized conformation[b]			
Form	Symmetry	φ_1	φ_2	φ_3	E (kcal · mol^{-1})	φ_1	φ_2	φ_3	E (kcal · mol^{-1})
I	C_1	−52.6	−52.6	180	−196.52	13.4	48.5	175.4	−197.93
II	C_s	52.6	−52.6	180	−195.01	0	0	177.5	−199.89
III	C_1	−125.4	−54.6	180	−195.03	−103.2	−25.2	−174.5	−196.59
IV	C_s	−54.6	54.6	180	−187.36	−5.3	5.2	180	−197.60
V	C_3	−124.2	−124.2	−124.2	−192.66	−29.3	−168.3	−45.2	−197.05

[a] Cf. Figure 1.

[b] Based on idealized geometrical parameters of Table IV.

Use of the idealized ligand geometries (Table IV; P—O 1.583 Å; C—O 1.440 Å) in the energy calculations, specific of each of the five reported conformations (instead of the previously minimized overall parameters), leads invariably to higher total energies than found for the free molecule (Table VI). By mere removal of the constraints on the torsional angles φ_i some geometries refine to minimum energy conformations similar to those of Table V, calculated for the free molecule. In particular, C_s conformations II and IV both lead to the same form *f* of C_s symmetry, whereas conformer III converges to form *g* (both of C_1 symmetry). However, in the same way geometries I (C_1 symmetry) and V (C_3 symmetry) converge to a common energy minimum which has no counterpart in the free molecule.

DISCUSSION

The results reported above strongly suggest the effect of complexation on the bond data of trimethylphosphite. Apart from affecting the geometry of the ligand, as is evident from the data displayed in Table IV, metal bonding also restricts the available range of low total energy molecular conformations, mainly on the basis of the steric requirement which prevents protruding groups of the ligand from being in the vicinity of the cap of the phosphorus pyramid. This is apparent by comparison of calculated free molecular and observed ligand geometries (Tables V and VI). Consequently, $P(OCH_3)_3$ ligand arms are spread away from the metal and the ligand mostly adopts a low symmetry conformation which differs from that of the free molecule and has a higher energy content. The most common ligand conformations are those with the smallest O—P—O angle sum. Apparently, flattening of the phosphorus coordination is less appreciated.

It should be noticed that the minimum energy conformation *f* of the free molecule, which is unsuitable for ligation for the reasons mentioned above, is rendered accessible to the metal by rotation of the arms by about 50–60° each in the same or opposite directions, leading to conformations I ($\varphi_1 = \varphi_2 = 53°$), II ($\varphi_1 = -\varphi_2 = 53°$) and IV ($\varphi_1 = -\varphi_2 = -55°$), respectively. In all three cases, further rotation ($|\varphi_1| = |\varphi_2| > 55°$) from the (0°, 0°, 180°) position leads to severe interactions. We should therefore consider these conformations as limiting geometries imposed by the complexing agent. Which of these conformations is found in a particular crystal structure is probably conditioned by the nature of the species to which trimethylphosphite is complexed. The selection will depend both on which conformations are compatible with the rest of the complex (intramolecular non-bonding features) and what the packing requirements of the lattice may be. Typical examples of crystal structures in which the ligand is present in various conformations are $(NiL_4Br)BF_4$,[12] $\{Mo_2Cl_3(CO)_4L_4\}[MoOCl_4\{OP(OMe)_2\}]$[27] and $[CHC(O)]_2OCoL_3$.[29]

As to the next energetically favorable conformation of the free molecule (g, C_1 symmetry), ligand conformation III (C_1 symmetry) is reached readily by rotation of one CH_3O-arm by about 30°. Also in this case the rotation is away from the side of approach of the metal. No further adjustments are necessary in case of the flat conformation d (Table V), which occurs as ligand conformation V (Figure 5). On the whole, the important point is, however, that the conformation found in the solid state is close to one of the conformations in the free state. Similar conclusions hold for triphenylphosphine.[16]

Our results are qualitatively in good agreement with Nyquist's interpretation of vibrational spectra (IR and Raman) of $P(OCH_3)_3$ in the liquid phase, which indicates that the symmetry of $P(OCH_3)_3$ is less than C_{3v} (in accordance with ref. 30) or C_3, and eventually C_s.[4] In a recent paper[7] the liquid state is described in terms of a three-conformer equilibrium mixture composed of A (C_{3v} or C_3: $0° < \varphi_i < 60°$), B (C_1: 180°, $0° < \varphi_2 = \varphi_3 < 60°$) and C ($C_s$: 180°, $300° < \varphi_2 < 360°$, $0° < \varphi_3 < 60°$). We notice the correspondence with our results, namely A = a or b, B = I and C = II. In the solid state (pure trimethylphosphite) two such conformations are stabilized in different polymorphic forms.[7]

Electron diffraction results indicate a structure with P—O 1.620(1) Å, C—O 1.420(4) Å, OPO 100.5(3)° and POC 118.9(5)° (in agreement with Table I) and a

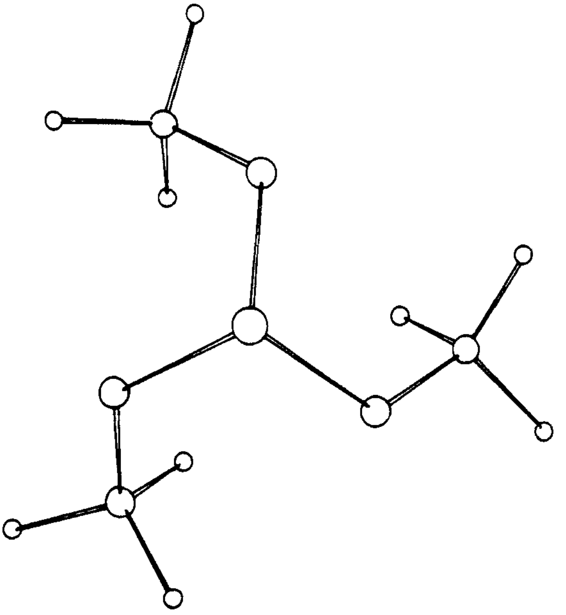

FIGURE 5 Ligand conformation of $P(OCH_3)_3$ with C_3 symmetry (torsional angles: 124°, 124°, 124°).

preference for C_s symmetry.[6] However, a mixture of conformers in the gas phase has not been excluded.[5,6] This is in line with the small energy differences between a manifold of conformations of Table V. While Cowley *et al.*[31] employ a C_3 model for assignment of UPS bands of $P(OCH_3)_3$, according to the recent MNDO SCF MO computations of Worley *et al.*[22] the lowest-energy conformation of the molecule possesses near C_s symmetry and is 2.8 kcal · mol^{-1} more stable than a C_3 conformation, not unlike the results of Table V. Comparison of the results of the energy calculations and ligand conformations (Tables V and VI) with those based on electron diffraction rdf curves[6] shows that the rdf derived most favorable C_3 conformation (76.7°, 76.7°, 76.7°) corresponds to the conformer *c* (Table V) of the free molecule. The favored C_s conformation (80.7°, 180°, −80.7°) is close to either II or IV (one of these conformers was not considered by ref. 6). Out of the three C_1 geometries best fitting the rdf curves (57.0°, 180°, 57.0°; 180°, 0°, −64.1°; 180°, 0°, 79.8°) the former is equivalent to our conformation I (Table VI) and the latter close to conformation *g* (Table V).

The view that $P(OCH_3)_3$ does not occur in the *cis* C_{3v} geometry in the gas phase[6] is not corroborated by our results, which indicate that this conformation is quite stable. Although apparently C_{3v} geometry does not satisfactorily account for the experimental data,[3-6] there is no good reason why this species should not be a minor component of the mixture in the gaseous phase. Clearly, the "average" $P(OCH_3)_3$ molecule has a much lower symmetry, as may be understood from Table V. Comparison of the calculated dipole moments (Table V) with the experimental value (1.81 D)[3] justifies a small contribution of forms *a* and/or *b* to the gas phase composition besides other major components (*e–h*).

The metal–phosphite M—P bond is significantly (about 0.1 Å) shorter than the analogous metal–phosphine bond (Table VII and ref. 31). This can be rationalized by the π-bonding capability of the phosphite ligand being greater than that of the phosphine ligand,[32,33] or by the minor steric requirements of the phosphite ligands as compared to phosphines[23,34,35] rather than basicity. The M—P distances (Table

TABLE VII

Single-order metal-phosphorus distances in $MP(OCH_3)_3$ and $MPPh_3$ complexes[a]

Metal (M)	M − P bond distance (Å)[b] $MP(OCH_3)_3$	$MPPh_3$
Co	2.165/11	2.268/5
Fe	2.149/7	2.240/2
Ni	2.188/7	2.215/11
Ru	2.282/5	2.326/2
Mo	2.430/17	2.477/2
W	2.485/1	—
Os	2.262/7	2.374/4
Ir	2.219/3	2.367/17
Rh	2.200/20	2.362/6
Ag	2.411/1	—

[a] $MP(OCH_3)_3$ complexes are those cited in Tables II and III and refs. 34 and 39; $MPPh_3$ complexes were taken from a compilation in ref. 15.

[b] Figure after slash stands for number of data sets considered.

VII) suggest considerable back-donation from the metal atom to the trimethylphosphite ligand. As the C—P—C angles in triphenylphosphine complexes are larger (103.0°) than the O—P—O angles in phosphites (101.4° on average), apparently the *s* component of the phosphorus orbital directed towards an atom is reduced as the electronegativity of the atom is increased. It may also be concluded that the P—O bond lengths in the phosphite ligands (1.583 Å) must have some double-bond character for they are shorter than the P—C bonds (1.828 Å) in triphenylphosphine[17] by an amount which cannot be accounted for by the difference between the covalent radii of oxygen (0.66 Å) and carbon (0.77 Å) atoms. In fact, the P—O lengths fall short of the theoretical single bond value of 1.71 Å.[36] Also, the linear relationship between π-bond order and P(V)—O bond lengths, with π-bond order of $\frac{1}{2}$ in PO_4^{3-} and 1 for the 1.71 Å single bond,[37] is applicable to P(III) compounds with a slight correction (about 0.05 Å) and thus confirms the view.

Finally, it should be mentioned that the M—P—O and O—P—O angles are related, namely the smaller the former the larger the latter and vice versa. As the phosphorus coordination is pseudotetrahedral, the M—P—O angles are about 116°. The metal is generally slightly displaced from the position on top of the cap of the PO_3 pyramid by about 0.25 Å (Table IV) in the P—O—C plane of the *trans* methyl group (Figure 1) except in the case of the ligand with C_3 symmetry where the metal is located exactly on top of the phosphorus pyramid.

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