Experimental and Theoretical Studies of Correlated Rotation in Tris(*ortho*-tolyl) Derivatives of P, As and Si

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Variable temperature NMR studies have established equilibrium constants and/or activation parameters for the *exo*$_2$ ↔ *exo*$_3$ equilibrium in the series M(*o*-tolyl)$_3$ (M = P, As), XM (*o*-tolyl)$_3$ (M = P, X = O, S, Se; M = As, X = O, S) and [MeM(*o*-tolyl)$_3$]$^{n+}$ (n = 0, M = Si; n = 1, M = P, As). The crystal structure of OAs(*o*-tolyl)$_3$H$_2$O is reported. Molecular mechanics studies of P(*o*-tolyl)$_3$ reproduce correctly the ground state *exo*$_3$ conformation and provide an analysis of the lowest energy two-ring flip exchange mechanism.

Molecules of the type Ar$_3$Z and Ar$_3$ZX have been termed molecular propellers since their aryl rings in the ground state structures are twisted in the same sense so as to impart a helical configuration to the molecule. The mechanisms and stereochemical consequences of correlated Ar–Z bond rotation have been investigated in detail primarily by Mislow and co-workers.[1a–d] Experimental studies have been concentrated mainly on bis(*ortho*) substituted molecules where steric demands are sufficient to render the ^{1}H NMR spectra amenable to line-shape analysis.[2a–n] Investigations of the less demanding mono(*ortho*) substituted molecules are less numerous and confined mainly to molecular modelling and dipole moment studies.[3a–c] We report here the results of our experimental and molecular mechanics investigations into conformational isomerism and isomer interconversion in P(*o*-tolyl)$_3$ (**1a**), XP(*o*-tolyl)$_3$ (X = O, S, Se) (**1b–d**) [MeP(*o*-tolyl)$_3$]I (**1e**) and the related compounds MeSi(*o*-tolyl)$_3$ (**2**), As(*o*-tolyl)$_3$ (**3a**), XAs(*o*-tolyl)$_3$ (X = O, S) (**3b,c**) and [MeAs(*o*-tolyl)$_3$]BF$_4$ (**3d**).

Results and Discussion

Synthesis.—Compounds **2** and **3c, d** have not been previously reported. Preparative details for many of the others are also lacking and are included in the Experimental section. With the exception of **3c**, NMR experiments were performed on samples of analytical purity. The propensity of **1b,c** and **3b** to retain solvent was noted.

As(*o*-tolyl)$_3$ reacts with MeI to produce only small amounts of [MeAs(*o*-tolyl)$_3$]I;[5] the arsonium cation is best prepared by reaction of **3a** with Me$_3$OBF$_4$. The lower basicity of arsenic is also evident in the facile extrusion of sulfur from SAs(*o*-tolyl)$_3$ on heating in solution to regenerate As(*o*-tolyl)$_3$ (essentially complete after 2 h at 50 °C in CHCl$_3$).

NMR Studies.—Solid-state structural studies of P(*o*-tolyl)$_3$, XP(*o*-tolyl)$_3$ (X = O, S, Se)[6] and of the related HGe(*o*-tolyl)$_3$[7] reveal either an *exo*$_3$ or *exo*$_2$ conformation of the *o*-tolyl rings.† On the assumption that only these isomers are populated in solution, P–C rotational isomerism *via* ring-flip mechanisms may be represented in Fig. 1 for the lowest energy two-ring flip.

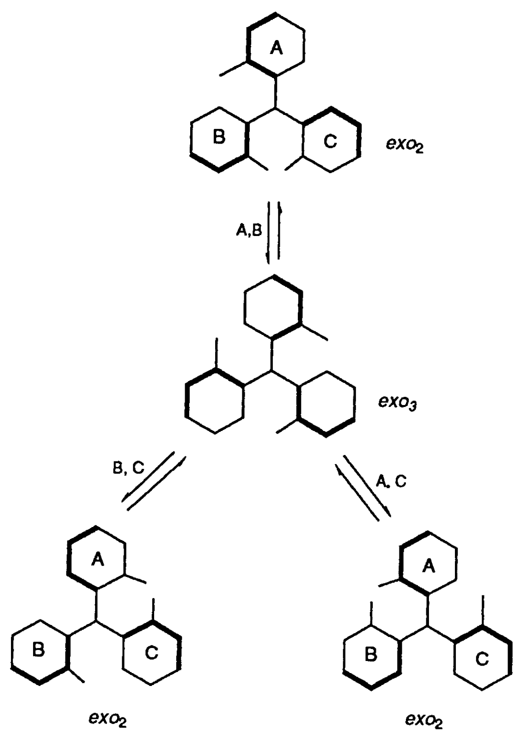

Fig. 1 The two-ring flip mechanism

Only those permutations which interconvert *exo*$_2$ with *exo*$_3$ conformers are shown.

The two-ring flip results in *exo*$_2$/*exo*$_3$ interconversion with consequent ring exchange. A mirror image of Fig. 1 may be drawn differing only in helicity of the phosphine. Interconversion of this residual enantiomerism (not evident in an achiral medium) requires a process of higher energy than the two ring flip (*vide infra*).

For the phosphorus-containing series **1a–d**, all compounds except **1a** yield variable temperature ^{31}P NMR spectra (Fig. 2) which are consistent with an *exo*$_2$/*exo*$_3$ equilibrium, although limiting low-temperature spectra are not seen in all cases.

For compounds rich in the *exo*$_3$ conformer, activation parameters are best obtained by line-shape analysis of ^{31}P NMR spectra. For compounds rich in the *exo*$_2$ conformer, activation parameters are best obtained by line-shape analysis of the three

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† If a regular pyramid is constructed from the 1p, O, S, Se or Me as the apex and the three *para* ring carbons as the base, a proximal (*exo*) substituent will point away from the base, while a distal (*endo*) substituent will point towards the base.

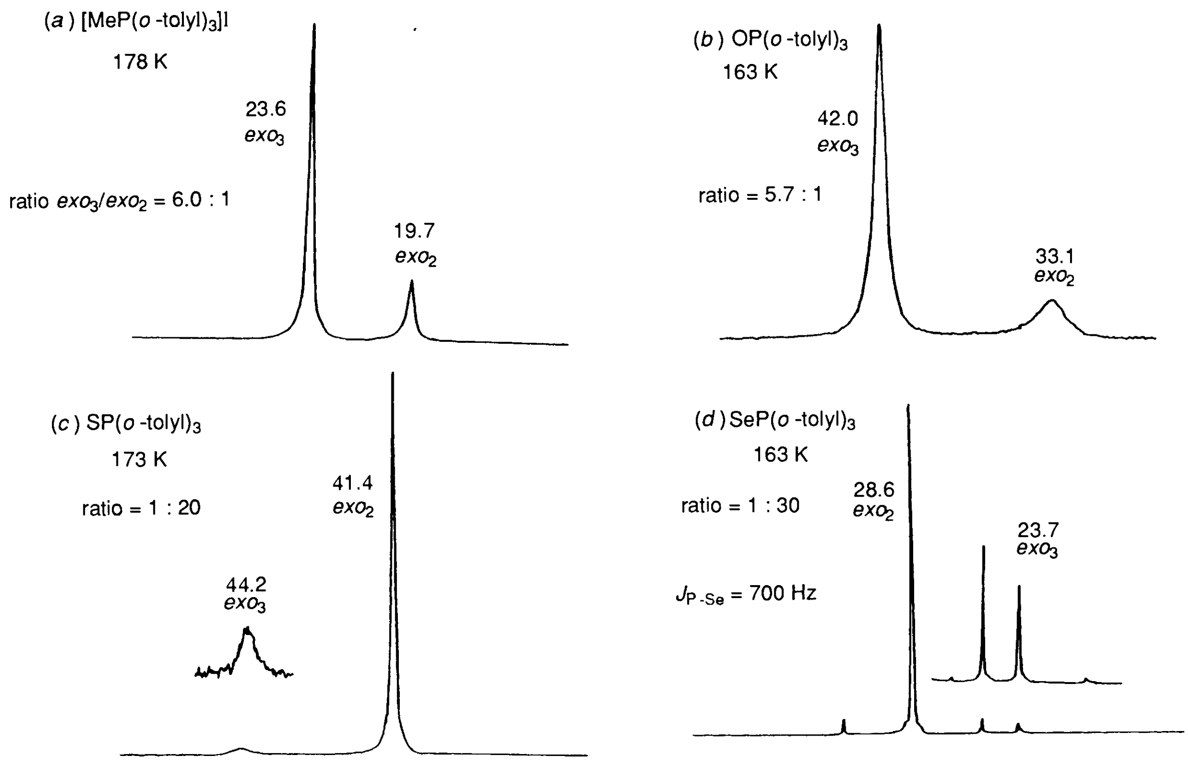


Fig. 2 Low temperature ^{31}P NMR spectra (CD_2Cl_2)

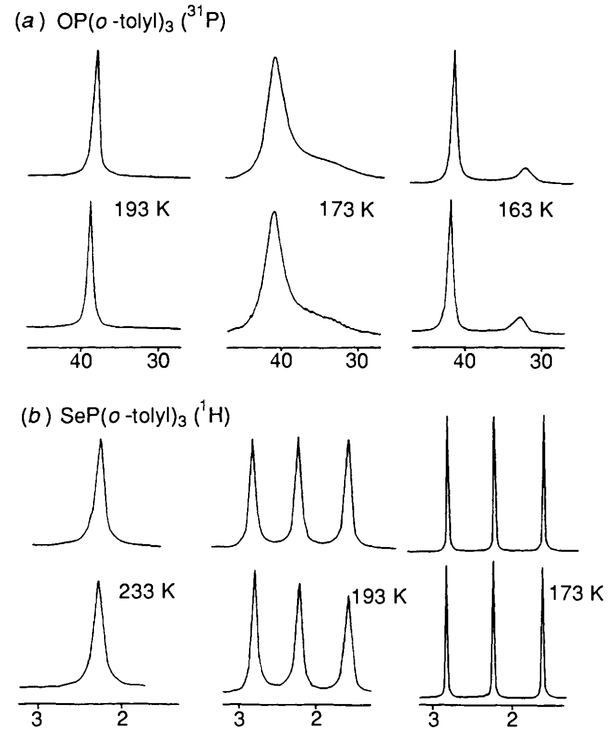


Fig. 3 Calculated and experimental NMR spectra for OP(o-tolyl)$_3$ and SeP(o-tolyl)$_3$

^1H methyl resonances of the C_1 *exo*$_2$ conformer. Even though the small amounts of the C_3 *exo*$_3$ conformer cannot be seen in the ^1H spectra of (**1c**,**d**) at low temperature, the derived rate constants have a higher precision than those obtained from the ^{31}P NMR spectra. Since magnetisation is being transferred from a symmetrical transition state to three methyl resonances, a transmission coefficient of three was used; the fitted rates from the line-shape analysis were multiplied by three to give

Table 1 Kinetic data for *exo*$_2$ → *exo*$_3$ exchange[d]

Complex	T/K	K[a]	k/s^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1}
1b[b]	163	3.0 ± 0.6	600 ± 50	30.4 ± 0.3
	173	2.7 ± 0.5	2600 ± 150	30.3 ± 0.3
	183	2.5 ± 0.5	9300 ± 1100	30.3 ± 0.3
	193	2.3 ± 0.5	25 000 ± 3000	30.3 ± 0.3
	213	1.9 ± 0.5	120 000 ± 40 000	30.8 ± 0.8
1c[c]	173		15 ± 3	37.6 ± 0.8
	193		210 ± 21	37.9 ± 0.4
	213		2400 ± 240	37.8 ± 0.4
	233		15 000 ± 1500	37.9 ± 0.2
	253		75 000 ± 15 000	38.0 ± 0.2
	273		300 000 ± 60 000	38.0 ± 0.2
	293		1 500 000 ± 600 000	37.0 ± 0.4
1d[c]	173		5.1 ± 0.9	39.2 ± 0.8
	193		90 ± 9	39.3 ± 0.8
	213		1080 ± 120	39.1 ± 0.4
	233		6900 ± 600	39.4 ± 0.4
	253		33 000 ± 6000	39.7 ± 0.4
	273		120 000 ± 48 000	40.1 ± 0.4
	293		300 000 ± 120 000	41.0 ± 0.8
1e[b]	178	2.6 ± 0.5	80 ± 10	36.3 ± 4
	193	2.4 ± 0.4	450 ± 30	36.7 ± 0.3
	203	2.3 × 0.4	1150 ± 50	37.1 ± 0.3
	213	2.2 ± 0.4	3000 ± 250	37.4 ± 0.3
	223	2.1 ± 0.4	8000 ± 800	37.4 ± 0.4
	233	2.1 ± 0.4	40 000 ± 15 000	35.9 ± 0.8
3d[c]	163		14 ± 3	35.7 ± 0.4
	173		40 ± 4	36.5 ± 0.3
	183		170 ± 17	36.5 ± 0.3
	193		700 ± 60	36.3 ± 0.3
	203		2000 ± 200	36.4 ± 0.4
	218		10 000 ± 1000	36.3 ± 0.4
	233		20 000 ± 3000	37.6 ± 0.8

[a] $K = [exo_3]/[exo_2]$. [b] From ^{31}P NMR spectra. [c] From ^1H NMR spectra. [d] All in CD_2Cl_2 solvent.

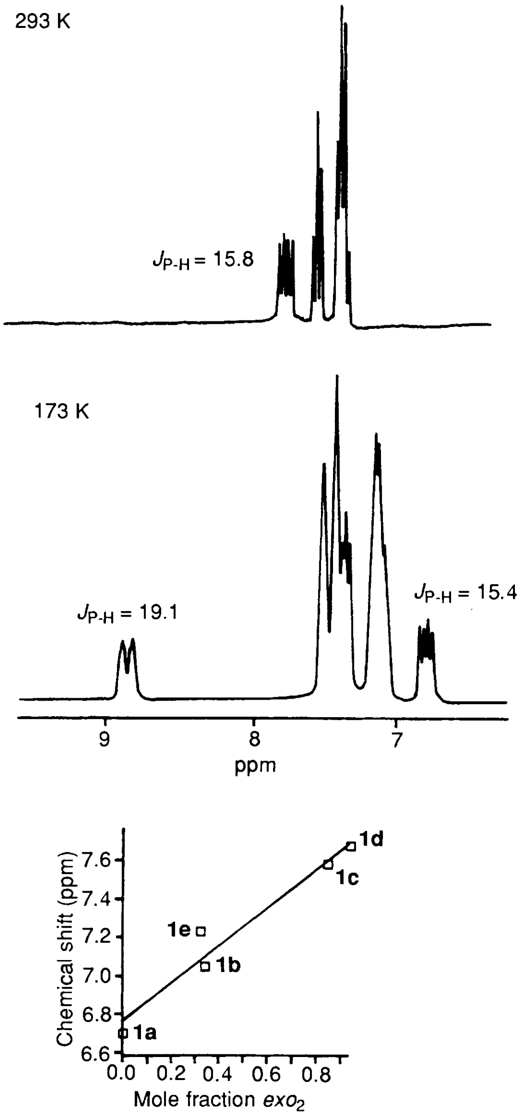
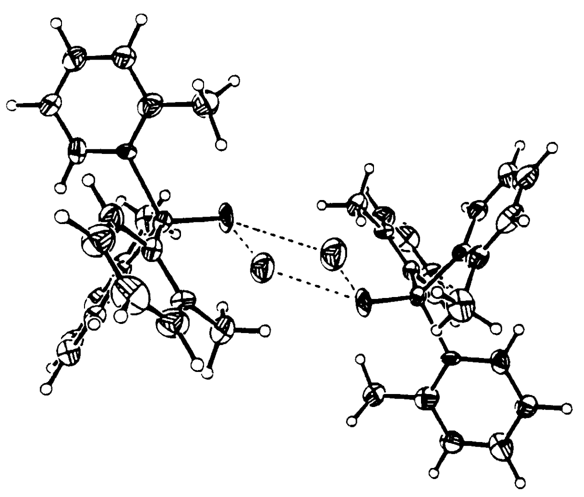


Fig. 4 Variable temperature ^{1}H NMR spectra of SeP(o-tolyl)$_3$

(*a*) Hydrogen bonded dimer



(*b*) OAs(o-tolyl)$_3$

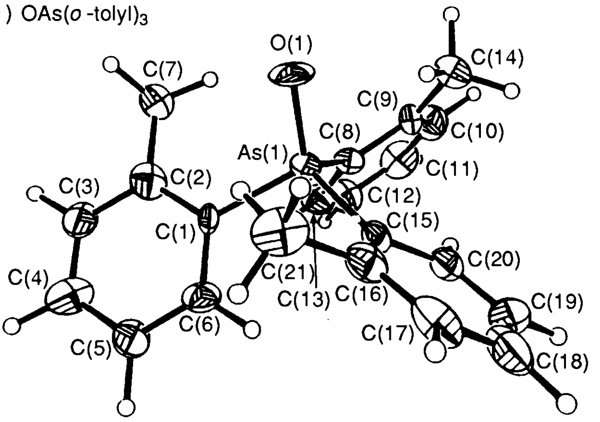


Fig. 5 Molecular structure of OAs(o-tolyl)$_3$ H_2O. Important bond lengths (Å) and angles (°):

As(1)–O(1) 1.67, As(1)–C(1) 1.94, As(1)–C(8) 1.93, As(1)–C(15) 1.92, C(1)–As(1)–C(8) 106.4, C(1)–As(1)–C(15) 107.2, C(8)–As(1)–C(15) 105.7, O(1)–As(1)–C(1)–C(2) 46.2, O(1)–As(1)–C(8)–C(9) 48.1, O(1)–As(1)–C(15)–C(16) 53.3.

the data in Table 1. Representative spectra of **1b** and **1d** are shown in Fig. 3 and full kinetic data are presented in Table 1.

In the XP(o-tolyl)$_3$ series, the ordering of both the exo_2/exo_3 ratio (X = O $\ll$ S < Se) and the barriers to ring exchange (X = O $\ll$ S < Se) follow closely the trend in van der Waals radii [O (1.40) $\ll$ S (1.85) < Se (2.00 Å)]. The approximate similarity of the isomer distribution and barrier to ring exchange of the MeP(o-tolyl)$_3{}^+$ cation to those of OP(o-tolyl)$_3$ seems surprising. While the oxide reveals no intramolecular H–O interactions shorter than the sum of van der Waals radii, modelling of the structure of the MeP(o-tolyl)$_3{}^+$ cation derived from the known structure of [MePPh$_3$]FeCl$_4$[8] indicates H(P–Me)–H(C–Me) interactions which are less than the sum of van der Waals radii. However, it may be noted that in a comparison of the structure of OPPh$_3$[9] with that of MePPh$_3{}^+$, the main structural difference entails an expansion of the average C–P–C angles from 106.6° in the oxide to 109.0° in the phosphonium salt, perhaps indicating a decreased H(P–X)–H(C–Me) interaction in the phosphonium salt. This may arise from the relatively low-energy deformation of H–C–H angles in both P–Me and C–Me groups in both the ground state and the transition state for ring exchange.

For compounds which do not exhibit limiting low-temperature spectra, the averaged chemical shift of the ring *ortho* hydrogen may be used as a semi-quantitative measure of the exo_2/exo_3 ratio. Thus, the temperature invariant *ortho* resonance of P(o-tolyl)$_3$ is consistent with dipole moment studies[3c] which indicate that only exo_3 is present in solution. In contrast, the averaged *ortho* resonance of SeP(o-tolyl)$_3$ is replaced by three resonances at −100 °C, one of which is obscured by other arene hydrogens (Fig. 4). For compounds whose exo_2/exo_3 ratios are known, a plot of averaged chemical shift against mole fraction of exo_2 shows good linearity (correlation coefficient = 0.98), indicating that the chemical shift of the *ortho* hydrogen is essentially independent of the central molecular fragment. Application of this graph to other cases where limiting low-temperature spectra could not be obtained indicate that As(o-tolyl)$_3$ is essentially exo_3, and that the mole fractions of exo_2 for MeAs(o-tolyl)$_3{}^+$, OAs(o-tolyl)$_3$ and MeSi(o-tolyl)$_3$ are 0.45, 0.48 and 0.45, respectively. The close similarity of the first two mirrors the phosphorus analogues, while the value for MeSi(o-tolyl)$_3$ is consistent with a value of 0.48 for HSi(o-tolyl)$_3$ derived from conformational analysis.[3b]

The activation energy for SAs(o-tolyl)$_3$ is about 3 kcal mol^{-1} less than SP(o-tolyl)$_3$. A single-crystal determination of OAs(o-tolyl)$_3$ as the monohydrate provides a structural comparison of the P and As series (Fig. 5). The repeating unit is dimeric,

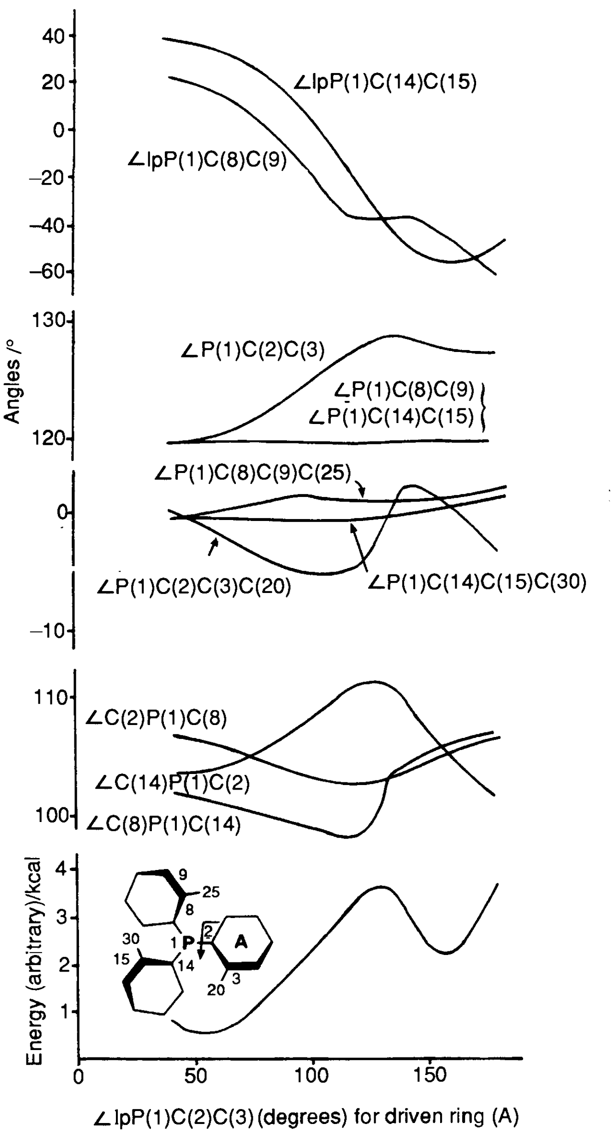


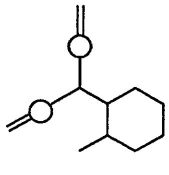
Fig. 6 Energy and geometric changes during two-ring flip

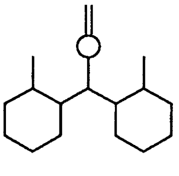
containing two water molecules of crystallisation hydrogen bonded to As=O with O–O contacts of 2.87 and 2.98 Å.[10] The structures of OAs(*o*-tolyl)$_3$ and OP(*o*-tolyl)$_3$ differ primarily in an elongation of the P/As–C bonds by *ca.* 5% and an elongation of the P/As=O bond by *ca.* 13%. The decreased barrier to ring exchange may thus be attributed primarily to lengthening of the P/As=O bond.

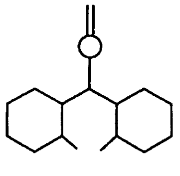
NMR spectra of SP(*m*-tolyl)$_3$ are temperature independent. In the solid state, P(*m*-tolyl)$_3$ and XP(*m*-tolyl)$_3$ (X = Se, S) have *exo*$_2$ and *exo*$_1$ conformations respectively, though the conformation seems to be influenced largely by crystal-packing effects.[11]

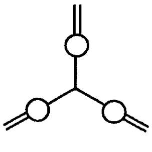
Molecular Mechanics Studies.—We have used MM2[12] to investigate both ground-state conformation and barriers to ring exchange for P(*o*-tolyl)$_3$; calculations on other compounds described herein are not currently possible owing to lack of parameterization. As a starting point, we have used a molecule generated from the literature coordinates[6] to which has been added a lone pair at 0.6 Å from the phosphorus atom. Unconstrained minimisation of this structure yields a molecule whose main geometric features [P–C = 1.82 Å, ∠C–P–C = 104.4°, ∠1p–P–C_{ipso}–C(Me) = 37.1°] reproduce well those of the literature structure [P–C = 1.84 Å, ∠C–P–C = 102.6 ± 0.7°, ∠1p–P–C_{ipso}–C(Me) = 42 ± 4°] at the 3σ level. Constraining to C_3 symmetry results in minimal changes in both energy and molecular dimensions.

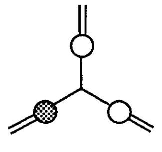
The idealized transition states for one- and two-ring flip mechanisms which result in *exo*$_2$/*exo*$_3$ exchange are shown below. Only the two-ring flip A is energetically competitive; energies for the one-ring flip transition states B and C are higher by factors of three and ten, respectively. Consideration of idealized transition states D and E for the three-ring flip, which results only in helix inversion, shows that only D is energetically competitive, and differs little in energy from A.


A


B


C


D


E

○ = methyl(*exo*)

● = methyl(*endo*)

The dihedral driver facility of MM2 may be used both to generate an energy surface for the two-ring flip mechanism, and to establish the lowest energy conformation of the *exo*$_2$ isomer for P(*o*-tolyl)$_3$. The energy profile (Fig. 6) confirms the greater stability of the *exo*$_3$ conformation by *ca.* 2 kcal and indicates an activation energy for *exo*$_3$ → *exo*$_2$ conversion of *ca.* 3 kcal. The geometry of the lowest energy *exo*$_2$ conformation [P–C = 1.82 Å, ∠C–P–C = 105.7 ± 0.4, ∠1p–P–C_{ipso}–C(Me) = 160, −46, −55°] is comparable to the dimensions of *exo*$_2$ SP(*o*-tolyl)$_3$[6] [P–C = 1.83 Å, ∠C–P–C = 106 ± 3°, ∠1p–P–C_{ipso}–C(Me) = 168, −52, −57°].

The maximum in energy lies at a ∠1p–P–C_{ipso}–C(Me) value of 125° for the driven ring, considerably past the 90° value of the idealized transition state. Though some elongation of P–C bonds is observed, energy minimisation along the isomerisation pathway is accomplished mainly through variation of ∠C–P–C for all three rings, ∠1p–P–C_{ipso}–C(Me) for the non-driven rings B and C and ∠P–C_{ipso}–C(Me) and ∠P–C_{ipso}–C(Me)–Me for the driven ring (Fig. 6). Thus, as ring A is driven as shown, there is a bending of C2O out of the arene plane by about 6° and an enlargement of the P–C(2)–C(3) angle to about 130° at the energy maximum. Changes in C–P–C angles are primarily confined to the non-driven rings and correspond to a shearing motion in which rings B and C move away from, and closer to, the lone pair, respectively. The dihedral angles ∠1p–P–C_{ipso}–C(Me) of the non-driven rings show the inversion of helicity required for the two-ring flip mechanism.

Finally, it may be noted that the observed ∠1p–P–C_{ipso}–C(Me) value of 42 ± 4° also minimizes intermolecular interactions in the solid state. Using CHEM-X,[13] the intermolecular interactions within a unit cell may be calculated as a function of ∠1p–P–C_{ipso}–C(Me) (Fig. 7). The minimum in this curve occurs at a value of approximately 37°.

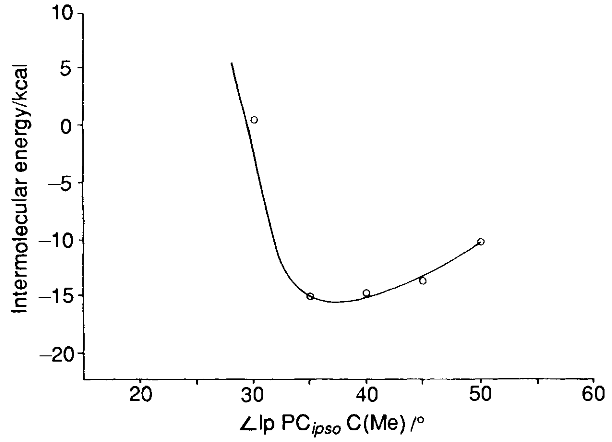


Fig. 7 Variation of intermolecular energy with torsion angle

Experimental

NMR spectra were recorded using a JEOL GSX270 spectrometer. Temperatures were measured using the in-built copper-constantin thermocouple. P(*o*-tolyl)$_3$ was prepared by a literature procedure.[14] NMR data are listed in Table 2. Line-shape analyses were performed using the EXCHANGE program (R. E. D. McClung, University of Alberta).

Preparations.—(*a*) SP(o-*tolyl*)$_3$. Following Michaelis,[15] P(*o*-tolyl)$_3$ (2.0 g, 5.5 mmol) and sulfur (0.42 g, 13 mmol) were refluxed in carbon disulfide (20 cm^3) under nitrogen for 3 h. After filtration and removal of the solvent, the residue was purified by preparative TLC [1:9 ethyl acetate–light petroleum (b.p. 60–80 °C) eluent] to give unchanged P(*o*-tolyl)$_3$ (0.8 g) and SP(*o*-tolyl)$_3$ (0.9 g, 41%) in order of elution. The product was crystallised from hexane as a white solid and dried *in vacuo* at 100 °C (Found: C, 74.9; H, 6.15. Calc. for $C_{21}H_{21}PS$: C, 75.0, H, 6.29%); m.p. 160–161 °C. SP(*m*-tolyl)$_3$ was prepared in the same way. (Found: C, 74.8; H, 6.24. Calc. for $C_{21}H_{21}PS$: C, 75.0; H, 6.29%); m.p. 153–154 °C.

(*b*) OP(o-*tolyl*)$_3$. Following Granoth *et al.*,[16] P(*o*-tolyl)$_3$ (1.0 g, 3.3 mmol) was dissolved in glacial acetic acid (20 cm^3) and heated to 80 °C; 30% H_2O_2 (0.5 cm^3) was added and the mixture was refluxed for 1.5 h. After addition of water (80 cm^3) and cooling, the product (0.7 g, 67%) was filtered, crystallised from ethanol as a white solid and dried *in vacuo* at 78 °C (Found: C, 78.6; H, 6.75. Calc. for $C_{21}H_{21}PO$: C, 78.8; H, 6.56%); m.p. 149–151 °C.

(*c*) SeP(o-*tolyl*)$_3$. Following Allen *et al.*,[17] P(*o*-tolyl)$_3$ (1.0 g, 3.3 mmol) and selenium (0.8 g, 10 mmol) were refluxed under nitrogen in $CHCl_3$ (10 cm^3) for 5 h. After filtration through Celite and removal of solvent, the solid was purified by preparative TLC [1:9 ethyl acetate–light petroleum (b.p. 40–60 °C)] to give the product (0.29 g, 23%) which was crystallised from ethanol as a white solid and dried *in vacuo* at room temperature (Found: C, 65.6; H, 5.5. Calc. for $C_{21}H_{21}PSe$: C, 65.8; H, 5.48%); m.p. 162–163 °C.

(*d*) [MeP(o-*tolyl*)$_3$]I. Following Deacon *et al.*,[18] P(*o*-tolyl)$_3$ (1.5 g, 4.9 mmol) and MeI (22.8 g, 160 mmol) were dissolved in dry diethyl ether (25 cm^3) and refluxed under nitrogen for 4 h. After cooling and filtration, the product (1.26 g, 57%) was obtained as a white solid which was dried *in vacuo* at room temperature (Found: C, 58.9; H, 5.2. Calc. for $C_{22}H_{24}PI$: C, 59.2; H, 5.42%); m.p. 199–200 °C.

(*e*) As(o-*tolyl*)$_3$. Following Burrows *et al.*,[19] $AsCl_3$ (9.2 g, 51 mmol) dissolved in dry THF (30 cm^3) was added dropwise at room temperature under nitrogen to the Grignard prepared by addition of *o*-bromotoluene (26 g, 152 mmol) in THF (30 cm^3) to Mg (3.7 g, 152 mmol) suspended in THF (30 cm^3). Following addition of water (50 cm^3), the aqueous layer was extracted with diethyl ether (3 × 50 cm^3). After drying with $MgSO_4$ and removal of solvent, the residue was crystallised from ethanol to give As(*o*-tolyl)$_3$ (13 g, 74%) as a white solid, m.p. 106–107 °C.

(*f*) OAs(o-*tolyl*)$_3$. Following Lobana,[20] As(*o*-tolyl)$_3$ (2.0 g, 5.7 mmol) was dissolved under nitrogen in acetone (30 cm^3) and $KMnO_4$ (0.9 g, 5.7 mmol) dissolved in acetone (50 cm^3) was added dropwise over 30 min. After filtration and extraction of the solid MnO_2 with boiling $CHCl_3$ (3 × 20 cm^3), the combined solvents were removed to give an orange-brown oil which solidified when heated at 60 °C *in vacuo*. Crystallisation from toluene–light petroleum (b.p. 60–80 °C) gave the product as a white solid (1.8 g, 86%). Samples of anhydrous composition were obtained by grinding and heating *in vacuo* at 56 °C for 6 h. (Found: C, 69.2; H, 5.8. Calc. for $C_{21}H_{21}AsO$: C, 69.4; H, 5.77%); m.p. 152–154 °C.

(*g*) [MeAs(o-*tolyl*)$_3$]BF_4. In a glove box, As(*o*-tolyl)$_3$ (2.8 g, 8.0 mmol) was added to a solution of Me_3OBF_4 (1.2 g, 7.9 mmol) in dry CH_2Cl_2 (100 cm^3). After an hour of heating at 30 °C, the CH_2Cl_2 was removed and diethyl ether (20 cm^3) added. The product (3.5 g, 96%) was collected as a white solid, recrystallised from CH_2Cl_2–diethyl ether and dried *in vacuo* at room temperature (Found: C, 69.2; H, 5.8. Calc. for $C_{21}H_{21}AsO$: C, 69.4; H, 5.77%); m.p. 167–168 °C.

(*h*) SAs(o-*tolyl*)$_3$. Following Reichle,[21] OAs(*o*-tolyl)$_3$ (250 mg, 0.68 mmol) was stirred under nitrogen at room temperature in CS_2 (10 cm^3) for 2.5 h. The solvent was removed under reduced pressure to give 200 mg (77%) of a white powder (Found: C, 66.4; H, 5.7; S, 8.45. Calc. for $C_{21}H_{21}AsS$: C, 66.3; H, 5.52; S, 8.42%); m.p. 195 °C (decomp.). NMR analysis showed a ratio SAs(*o*-tolyl)$_3$: As(*o*-tolyl)$_3$ of 20:1.

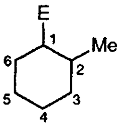
(*i*) MeSi(o-*tolyl*)$_3$. Following Benkeser *et al.*,[22] $MeSiCl_3$ (3.79 g, 25 mmol) dissolved in dry THF (20 cm^3) was added dropwise at room temperature under nitrogen to the Grignard prepared from *o*-bromotoluene (13 g, 76 mmol) and Mg (1.85 g, 76 mmol) suspended in THF (10 cm^3). Following addition of water (50 cm^3), the aqueous layer was extracted with diethyl ether (2 × 50 cm^3). After drying with $MgSO_4$ and removal of solvent, the residue was purified by preparative TLC [1:9 ethyl acetate–light petroleum (b.p. 40–60 °C)]. Collection of the faster moving of the two bands gave the product (0.5 g, 10%) which was crystallised from methanol as a white solid and dried *in vacuo* at room temperature. (Found: C, 83.2; H, 7.93. Calc. for $C_{22}H_{24}Si$: C, 83.5; H, 7.64%); m.p. 87–88 °C.

Crystal Structure Determination of OAs(o-*tolyl*)$_3$ H_2O.—Suitable crystals were grown from toluene–light petroleum. Data were collected on an Enraf–Nonius CAD4F diffractometer using Mo-Kα radiation (λ = 0.7093 Å) (see Table 3).

The structure was solved by direct methods (SHELX86)[23] and refined by full-matrix least squares (SHELX76).[24] Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The non-hydrogen atoms were refined anisotropically. Atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[25–27] All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings. Atomic coordinates are listed in Table 4. The asymmetric unit of the crystal consists of one OAs(*o*-tolyl)$_3$ molecule and one water molecule. The crystal lattice consists of hydrogen-bonded dimers with halves of the dimers related by centres of inversion.

Molecular Mechanics Calculations.—All calculations were performed with the MM2(87) program running on the Sequent

Table 2 NMR spectral data[f]



Compound[a]	^{13}C[b]								^1H[c]							^{31}P[d]
	1	6	5	4	3	2	Me	E–Me	6	5	4	3	2	Me	E–Me	
P(*o*-tolyl)$_3$	134.9	130.4	126.5	129.0	133.3	143.1	21.2	—	6.70	7.06	7.24	7.24	—	2.37	—	−29.1
	(11)	(5)				(27)	(21)		(4.4)					(1.2)		
OP(*o*-tolyl)$_3$	131.0	132.0	125.6	131.8	132.9	143.6	21.6	—	7.05	7.16	7.45	7.34	—	2.44	—	37.5
	(102)	(11)	(13)		(13)	(7)			(14.1)			(4.4)				
SP(*o*-tolyl)$_3$	129.9	132.9	126.2	132.0	133.6	143.0	22.9	—	7.58	7.25	7.45	7.25	—	2.32	—	42.4
	(82)	(10)	(13)	(3)	(13)	(9)	(4)		(15.5)							
SeP(*o*-tolyl)$_3$	128.1	133.1	126.3	132.1	134.1	143.0	23.0	—	7.67	7.27	7.45	7.27	—	2.31	—	28.4
	(73)	(10)	(13)	(3)	(13)	(9)	(4)		(16.6)							
[MeP(*o*-tolyl)$_3$]I	117.6	134.2	128.1	135.8	134.7	143.6	23.2	15.5	7.23	7.43	7.77	7.60	—	2.38	3.02	22.2
	(85)	(11)	(13)	(3)	(13)	(9)	(4)	(56)	(15.2)			(6.2)			(12.7)	
SP(*m*-tolyl)$_3$	133.6	129.6	128.5	132.7	138.9	132.9	21.6	—	7.30	—	7.45	—	7.59	2.35	—	43.6
	(87)	(10)	(13)	(3)	(13)	(11)							(13.8)			
As(*o*-tolyl)$_3$	137.8	130.3	126.6	129.0	133.5	143.0	22.0	—	6.76	7.05	7.25	7.25	—	2.40	—	—
OAS(*o*-tolyl)$_3$	*e*	*e*	126.6	*e*	*e*	142.9	21.6	—	7.25	7.25	7.47	7.36	—	2.48	—	—
[MeAs(*o*-tolyl)$_3$]BF_4	121.3	133.0	128.6	135.0	133.9	142.4	22.6	14.4	7.21	7.45	7.73	7.58	—	2.38	2.86	—
SAs(*o*-tolyl)$_3$	132.0	131.2	126.6	132.4	131.8	142.0	21.9	—	7.59	7.20	7.49	7.20	—	2.12	—	—
MeSi(*o*-tolyl)$_3$	135.6	129.9	125.4	136.7	130.4	144.9	23.7	0.74	7.20	7.09	7.32	7.20	—	2.24	0.96	—

[a] All spectra in CD_2Cl_2. [b] ppm from Me_4Si; J_{P-C} in parentheses. [c] ppm from Me_4Si; J_{P-H} values in parentheses; *ortho* and *meta* J_{H-H} values are in the range 7.2–7.8 and 1.0–1.5 Hz respectively. [d] ppm from 85% H_3PO_4. [e] Overlapping resonances at 132.2–132.3. [f] C(1) and C(2) were assigned on the basis of intensity; other assignments are based on reported chemical shifts and coupling constants for the triphenyl series.[28]

Table 3 Crystal data for OAs(*o*-tolyl)$_3$ H_2O

Crystal habit	Monoclinic
Space group	$P2_1/c$
a	9.386(1) Å
b	16.336(2) Å
c	12.287(3) Å
β	101.5(2)°
U	1846 Å^3
Z	4
*F*000	791.97
μ	17.71 cm^{-1}
Range	$2 < 2\theta < 48°$
Reflections $I > 3\sigma(I)$	1892
Variable parameters	218
Maximum shift/esd	<0.001
Maximum excursion	0.64 e A^{-3}
Maximum excursion	−0.60 e Å^{-3}
R	7.80%
R_w	8.26%

Table 4 Fractional atomic coordinates (Å) for OAs(*o*-tolyl)$_3$ H_2O

Atom	*x*	*y*	*z*
As(1)	0.176 58(9)	0.007 38(5)	0.255 75(7)
O(1)	0.272 2(7)	0.003 6(4)	0.385 6(5)
C(1)	−0.026 5(9)	−0.019 1(5)	0.250 2(7)
C(2)	−0.102 1(10)	0.014 2(6)	0.322 2(8)
C(3)	−0.245 4(11)	−0.011 0(6)	0.318 4(8)
C(4)	−0.306 0(11)	−0.072 5(7)	0.242 5(8)
C(5)	−0.230 3(10)	−0.012 7(6)	0.168 0(8)
C(6)	−0.087 8(10)	−0.079 2(5)	0.173 9(7)
C(7)	−0.041 0(12)	0.083 8(6)	0.403 3(9)
C(8)	0.178 9(9)	0.112 6(5)	0.184 8(6)
C(9)	0.312 5(9)	0.154 1(6)	0.189 1(7)
C(10)	0.305 2(12)	0.228 8(6)	0.133 9(8)
C(11)	0.176 9(14)	0.260 8(6)	0.076 1(9)
C(12)	0.045 4(12)	0.218 3(6)	0.072 8(8)
C(13)	0.046 8(10)	0.144 5(6)	0.126 4(7)
C(14)	0.454 7(10)	0.121 8(7)	0.248 0(8)
C(15)	0.248 6(8)	−0.069 0(5)	0.161 5(7)
C(16)	0.267 2(9)	−0.152 6(6)	0.186 9(8)
C(17)	0.330 5(11)	−0.202 1(6)	0.118 4(9)
C(18)	0.373 5(11)	−0.171 7(7)	0.025 7(9)
C(19)	0.356 4(11)	−0.088 5(7)	−0.001 4(8)
C(20)	0.295 5(9)	−0.038 8(6)	0.066 7(7)
C(21)	0.220 0(12)	−0.189 3(6)	0.287 9(8)
O(2)	0.491 3(8)	0.394 7(5)	0.034 6(6)

Symmetry S81 computer at the University of Keele. Parameters used were those contained in the program, with additional values being estimated from these.

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