A stereoselective route to medium-ring *cis*-1,*n*-dialkyl-1,*n*-diphosphacycloalkanes

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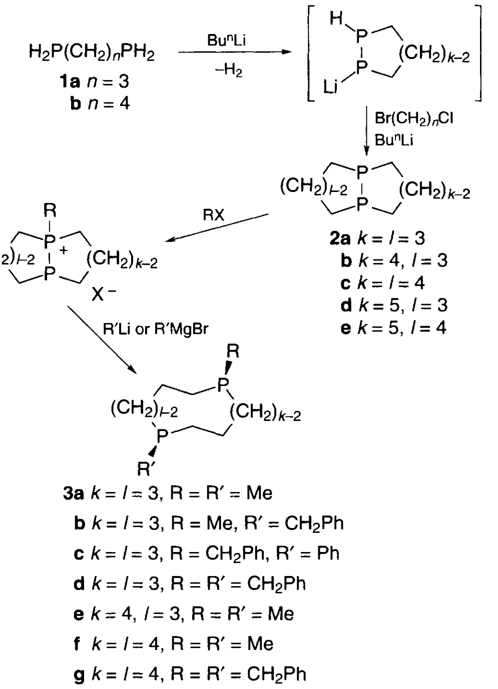
Quaternisation of 1, (k + 2)-diphosphabicyclo[k.l.0]alkanes 2, followed by treatment of the monoquaternary salts with alkyllithium or Grignard reagents produces the *cis*-isomers of 1,*n*-disubstituted-1,*n*-diphosphacycloalkanes 3 exclusively; examples containing eight-, nine- and ten-membered rings are described and the structures of two of these compounds 3a and 3f have been determined.

Compounds in which two phosphines are linked by a single C_1–C_4 chain are extremely important chelating ligands in organometallic chemistry, and a wide variety of structures have been developed. Cyclic diphosphines in which the two phosphine lone pairs are *cis* could be useful ligands, potentially providing tighter control of lone-pair orientation, and thus of chelating properties, but synthetic routes to these compounds are relatively undeveloped and the compounds are obtained as mixtures of stereoisomers, sometimes separable by chromatography. Known compounds include *P,P*-diphenyl- and -dibenzyl derivatives with ring sizes ranging from six to eleven.[1–3] We previously reported a stereoselective route to some medium-ring *trans*-1,*n*-dialkyl-1,*n*-diphosphacycloalkanes.[4] We now report a simple procedure for the preparation of a range of the more useful *cis*-isomers (Scheme 1).

Preparations of 1(k + 2)-diphosphabicyclo[k.l.0]alkanes from the extremely noxious and pyrophoric 1,3-diphosphinopropane **1a** and 1,4-diphosphinobutane **1b** are best carried out without isolation of intermediates, minimising the number of transfers required. A thf solution of the diphosphine (**1a** or **1b**) is treated with 1 equiv. of Bu^{n}Li in hexanes and the resulting yellow solution is left until cyclisation is complete (3 or 24 h respectively).[4,5] The reaction mixture is transferred by small-bore PTFE tubing over 2 h into a solution in diethyl ether of the required α-bromo-ω-chloroalkane, taking care to maintain the temperature throughout at −78 °C. After warming to room temperature, the second cyclisation is initiated by portionwise addition of another equiv. of Bu^{n}Li in hexanes, the heat of the reaction causing gentle refluxing of the solvent. The yellow colour of the monocyclic anion is allowed to disperse before the next portion is added. When the reaction is complete, all volatiles are removed by distillation (760 Torr) and the 1(k + 2)-diphosphabicyclo[k.l.0]alkane **2** is either distilled or sublimed from the solid residue under vacuum (0.1 Torr). The yields and ^{31}P NMR shifts of the pure diphosphines are: **2a**, 39%, δ −27.8; **2b**, 36%, δ −60.0; **2c**, 65%, δ −77.5; **2d**, 11%, δ 49.4; **2e**, 36%, δ −48.3, −70.2. In all cases except **2e**, which is clearly a mixture, the product is obtained as a single isomer, probably *cis*, as has been established for **2a**,[6] **b**[7] and **c**.[4]



Scheme 1

The *cis*-1(k + 2)-diphosphabicyclo[k.l.0]alkanes **2** undergo monoquaternisation in nearly quantitative yield with iodomethane[5] and benzyl bromide; formation of diquaternary salts only occurs with extremely reactive alkylating reagents, such as alkyl triflates.[4] The monoquaternary salts react with methyllithium, phenyllithium and benzylmagnesium chloride in ether solvents by addition of the alkyl group to the non-quaternised phosphorus atom and P–P bond cleavage,[8,9] giving single isomers of 1,*n*-dialkyl-1,*n*-diphosphacycloalkanes **3**, as shown by ^{31}P NMR spectroscopy. Yields of **3** (based on **2**) and ^{31}P NMR chemical shifts are: **3a**, 77%, δ −39.6; **3b**, 77%, δ −21.6, −40.2, J_{PP} 40 Hz; **3c**, 65%, δ −22.6, −23.7, J_{PP} 55 Hz; **3d**, 72%, δ −22.4; **3e**, 85%, δ −39.8; **3f**, 70%, δ −37.5; **3g**, 84%, δ −19.0. The observation of a substantial J_{PP} coupling for **3b** and **c** is interesting, and probably reflects the small P···P distance in these compounds (see below). Methyl groups in **3a** are virtual coupled triplets for the same reason, but those for **3f** are doublets, suggesting a much smaller J_{PP} in the latter case reflecting the greater P···P distance. The configurations are established as *cis* in the cases of **3a** and **f** by X-ray crystal-structure determination (see Figs. 1 and 2), and are probably *cis* in all other examples. The stereoselectivity of this reaction

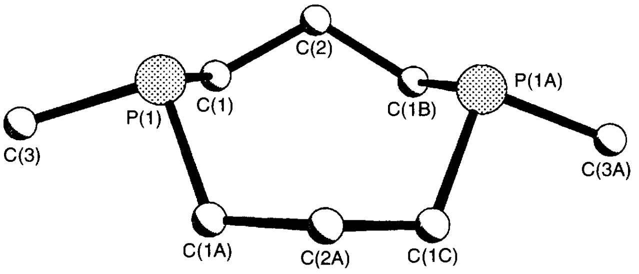
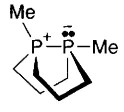


Fig. 1 Molecular structure of **3a** with hydrogen atoms omitted for clarity. Important molecular dimensions include: bond lengths (Å): P–Me 1.831(5), P–CH_2 1.850(3), C–C 1.536(4); bond angles (°): Me–P–CH_2 96.9(2), CH_2–P–CH_2 105.3(2).



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could be due to attack of the organometallic reagent along the P–P axis, perhaps with the initial formation of a neutral P–P bonded intermediate, *e.g.* **4** in the case of **3a**.

The structure analyses confirm *cis* stereochemistry for both **3a** and **3f**. The molecular structure of **3a** in the solid has exact C_{2v} symmetry with a P···P distance of 3.860 Å,† while that of **3f** has approximate C_2 symmetry with a P···P distance of 4.969 Å‡ (see Figs. 1 and 2). The conformation of **3a** is a classic crown, while that of **3f** is [55][10] rather than the usual [3232] or BCB structure. Molecular mechanics calculations, using MM2, give a BC structure for **3a** as the global minimum, with the crown conformation only 0.07 kJ mol^{-1} higher in energy. In the crystal the molecules of **3a** are stacked directly on top of one another, with all the phosphorus lone pairs oriented in the same direction. The [55] conformation for **3c** is also calculated by MM2 to be the second lowest, with the [3232] structure (3.4 kJ mol^{-1}) the most stable. It is notable that while the conformation of **3a** is pre-organised to chelate an electrophile such as a transition metal (albeit the P···P distance is large compared with those in analogous bound ligands) or to bridge two metals at an M···M distance of *ca.* 3 Å, considerable rearrangement would be required for **3f** to act as a chelating ligand.

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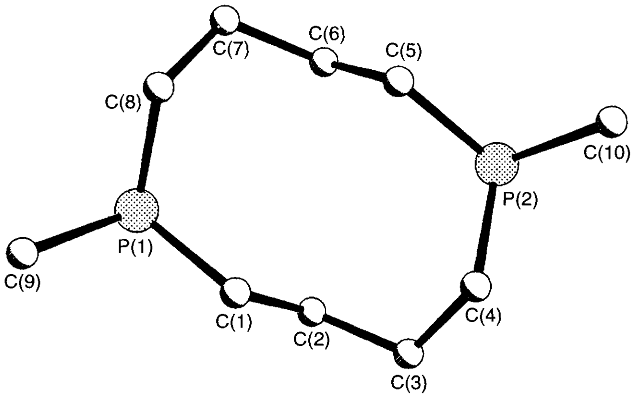

Fig. 2 Molecular structure of **3f** with hydrogen atoms omitted for clarity. Important molecular dimensions include: mean bond lengths (Å) (typical individual e.s.d.s 0.005): P–Me 1.838, P–CH$_2$ 1.854(5), C–C 1.525(6); mean bond angles (°) (typical individual e.s.d.s 0.02) Me–P–CH$_2$ 98.5, CH$_2$–P–CH$_2$ 103.5.

Footnotes

† *Crystal data* for **3a**: $C_8H_{18}P_2$, M = 176.2, orthorhombic, space group $Imm2$ (no. 44), a = 9.229(2), b = 11.162(2), c = 5.0290(10) Å, V = 518.1(2) Å^3, Z = 4, D_c = 1.129 g cm^{-3}, $\bar{\lambda}$ = 0.71073 Å, graphite-monochromated Mo-Kα X-radiation, μ = 0.36 mm^{-1}, $F(000)$ = 192, T = 293 K. Data were collected on a Siemens R3m diffractometer for a hemisphere of reciprocal space for $3 < 2\theta < 50°$. The structure was solved by direct methods and refined by full-matrix least-squares methods (42 parameters) against all 283 unique intensity data with $I > 3\sigma(I)$ to final $R1$ = 0.022 for the 274 reflections with $I > 2\sigma(I)$.

‡ *Crystal data* for **3f**: $C_{10}H_{22}P_2$, M = 204.2, monoclinic, space group $P2_1/c$ (no. 14), a = 5.1363(10), b = 25.837(5), c = 9.284(2) Å, β = 106.09(3)°, V = 1183.9(4) Å^3, Z = 4, D_c = 1.146 g cm^{-3}, $\bar{\lambda}$ = 0.71073 Å, graphite-monochromated Mo-Kα X-radiation, μ = 0.32 mm^{-1}, $F(000)$ = 448, T = 200 K. Data were collected on a Siemens R3m diffractometer for a quadrant of reciprocal space for $3 < 2\theta < 55°$. The lattice is pseudo B-centred orthorhombic (a = 5.136, b = 25.837, c = 17.841 Å, α = β = γ = 90°) but the Laue symmetry is clearly inconsistent with this pseudo-symmetry (R_{int} = 0.045 for monoclinic merging, R_{int} = 0.520 for orthorhombic). The intensity data suffer from twinning (by two-fold rotation about the a axis of the pseudo B-centred orthorhombic cell) with twin components refined to 0.730(2) and 0.270(2). The structure was solved by direct methods and refined by full-matrix least-squares methods (112 parameters) against all 2707 unique intensity data with $I > 3\sigma(I)$ to final $R1$ = 0.056 for the 1788 reflections with $I > 2\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters for **3a** and **f** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 L. Horner, P. Walch and H. Kunz, *Phosphorus Sulfur*, 1978, **5**, 171.
2 P. J. Brooks, M. J. Gallagher, A. Sarroff and M. Bowyer, *Phosphorus Sulfur Silicon*, 1989, **44**, 235.
3 S. D. Toto, B. W. Arbuckle, P. K. Bharadwaj, J. T. Doi and W. K. Musker, *Phosphorus Sulfur Silicon*, 1991, **56**, 27; B. W. Arbuckle and W. K. Musker, *Polyhedron*, 1991, **10**, 415; for a review of ligands of this type see: W. K. Musker, *Coord. Chem. Rev.*, 1992, **117**, 133.
4 R. W. Alder, C. Ganter, C. J. Harris and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1992, 1170.
5 K. Issleib and P. Thorausch, *Phosphorus Sulfur*, 1978, **4**, 137.
6 The X-ray crystal structure of the derived disulfide has been determined: H. Hartung, S. Hickel, J. Kaiser and R. Richter, *Z. Anorg. Allg. Chem.*, 1979, **458**, 130.
7 An X-ray crystal structure determination of the disulfide of **2b** shows this to be *cis*: C. Ganter, M. R. Gil and A. G. Orpen, unpublished results.
8 1,2-Diphenyl-1,2-diphospholane and -1,2-diphosphane react with alkyllithium reagents with P–P cleavage: T. Kaufmann, E. Antfang and J. Olbrich, *Chem. Ber.*, 1985, **118**, 1022.
9 Cleavage of P–P bonds in reactions of some diphosphine derivatives with alkyl halides has been reported: V. L. Foss, Y. A. Veits and I. F. Lutsenko, *Zh. Obshch. Khim.*, 1978, **48**, 1705.
10 J. Dale, in *Topics in Stereochemistry*, ed. N. L. Allinger and E. L. Eliel, Wiley, New York, 1976, vol. 9, p. 199.

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