A general route for the synthesis of triazacyclononane functionalised with one, two or three pendant phosphine arms: crystal structure of $[Zn_2L_2Cl_3][ClO_4]$, L = *N*-(diphenylphosphinopropyl)-1,4,7-triazacyclononane

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We present a general route for the synthesis of triazacyclononane functionalised with one, two or three pendant phosphine arms and exemplify the method with the synthesis of *N*-(diphenylphosphinopropyl)-1,4,7-triazacyclononane (L) and the crystal structure of its zinc(II) complex $[Zn_2L_2Cl_3][ClO_4]$.

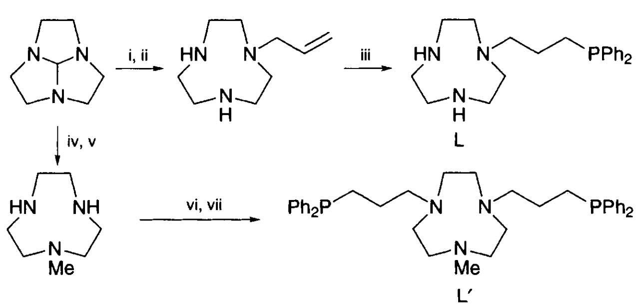
The small, facially coordinating, three nitrogen macrocycle 1,4,7-triazacyclononane [9]aneN_3 has been N-functionalised with a wide variety of pendant arms ending in hard donor groups ($-CO_2H$, –OH, $-NH_2$, pyridyl, polypyridyl, *etc.*).[1,2] There are a few recent examples of functionalisation by soft donor arms, for example $-CH_2CH_2SH$[3] and 4-*tert*-butyl-2-sulfanylbenzyl and 2-sulfanylpropyl,[4] but so far [9]aneN_3 has not been functionalised with pendant arms ending in a phosphine group.†

Indeed there are only two published examples of nitrogen macrocycles with pendant phosphine arms: 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane which is prepared by a 'one-pot' synthesis[5] which can not be generalised, and a series of N_2O_2, N_2S_2 and NO_3 macrocycles with phosphinoethyl arms.[6] Although the synthetic method used to prepare the latter series of ligands should be applicable to all nitrogen macrocycles we have not found it to be suitable in practice for [9]aneN_3. The synthesis of [9]aneN_3 with pendant chloroethyl arms (intermediate in the preparation of the phosphines) does not proceed smoothly, possibly because the high basicity of the nitrogens leads to displacement of chloride and formation of aziridinium ions.

Here, we report a general method for the preparation of phosphine pendant arm macrocycles in which [9]aneN_3 is functionalised with one, two or three arms. The only restriction on the method is that the arms must contain a minimum of three carbon atoms. The method is also applicable to larger nitrogen macrocycles, *e.g.* cyclam or cyclen.

The method is illustrated in Scheme 1 for the preparation of a single pendant arm ligand *N*-(diphenylphosphinopropyl)-1,4,7-triazacyclononane (L) and a doubly armed ligand *N,N'*-bis(diphenylphosphinopropyl)-1,4,7-triazacyclononane (L′) starting in both cases from 1,4,7-triazatricyclo-[5.2.1.0[4.10]]decane[7] 'capped tacn'. The preparation of the corresponding three (*N,N',N''*) armed phosphine starts from [9]aneN_3 itself and proceeds *via* the tris(allyl) derivative in an analogous way. The key step in the synthesis is the free-radical addition of Ph_2PH across the alkene double bond. This is accomplished in essentially quantitative yield by photolysis under strictly anaerobic conditions using a mercury lamp. The method is not restricted to allyl substituents, longer-arm alkenes react in an identical manner (although more slowly) yielding phosphines with longer alkyl (*e.g.* C_5 chains). We originally thought the free amine group might quench the radical addition, but this is not the case, L being synthesised as easily as L′. Both ligands have been fully characterised by NMR spectroscopy.‡

The structure of L is confirmed by the crystal structure of its zinc(II) complex.§ Reaction of L with anhydrous $ZnCl_2$ in ethanol followed by addition of $LiClO_4$ precipitated **1** which was recrystallised from acetonitrile. The molecular structure of the complex is shown in Fig. 1. The cation is an asymmetric dimer in which both Zn atoms are coordinated by both the three amine groups and the phosphine of L. In one half of the dimer, the zinc [Zn(1)] is further coordinated by two chloride ions giving a pseudo-octahedral geometry. The other zinc is formally five-coordinate (N_3PCl) but forms a long bond [2.909(6) Å]



Scheme 1 *Reagents and conditions*: i, allyl bromide, thf; ii, NaOH, H_2O; iii, Ph_2PH, *hv*; iv, MeI, thf; v, NaOH, H_2O; vi, allyl bromide, Na/EtOH; vii, Ph_2PH, *hv*

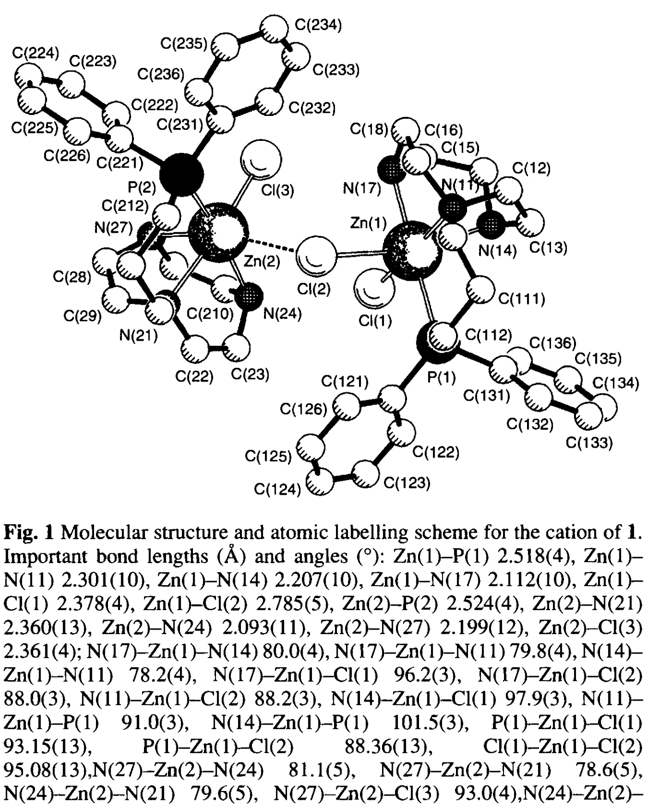


Fig. 1 Molecular structure and atomic labelling scheme for the cation of **1**. Important bond lengths (Å) and angles (°): Zn(1)–P(1) 2.518(4), Zn(1)–N(11) 2.301(10), Zn(1)–N(14) 2.207(10), Zn(1)–N(17) 2.112(10), Zn(1)–Cl(1) 2.378(4), Zn(1)–Cl(2) 2.785(5), Zn(2)–P(2) 2.524(4), Zn(2)–N(21) 2.360(13), Zn(2)–N(24) 2.093(11), Zn(2)–N(27) 2.199(12), Zn(2)–Cl(3) 2.361(4); N(17)–Zn(1)–N(14) 80.0(4), N(17)–Zn(1)–N(11) 79.8(4), N(14)–Zn(1)–N(11) 78.2(4), N(17)–Zn(1)–Cl(1) 96.2(3), N(17)–Zn(1)–Cl(2) 88.0(3), N(11)–Zn(1)–Cl(2) 88.2(3), N(14)–Zn(1)–Cl(1) 97.9(3), N(11)–Zn(1)–P(1) 91.0(3), N(14)–Zn(1)–P(1) 101.5(3), P(1)–Zn(1)–Cl(1) 93.15(13), P(1)–Zn(1)–Cl(2) 88.36(13), Cl(1)–Zn(1)–Cl(2) 95.08(13), N(27)–Zn(2)–N(24) 81.1(5), N(27)–Zn(2)–N(21) 78.6(5), N(24)–Zn(2)–N(21) 79.6(5), N(27)–Zn(2)–Cl(3) 93.0(4), N(24)–Zn(2)–Cl(3) 99.7(3), N(21)–Zn(2)–P(2) 87.2(3), N(27)–Zn(2)–P(2) 104.9(3), P(2)–Zn(2)–Cl(3) 94.61(13).

with Cl(2) to achieve pseudo-octahedral geometry. The Zn–N bond lengths are all unequal. The longest Zn–N bond in both halves of the dimer is to the tertiary nitrogen with the phosphine arm, the shortest Zn–N bonds are to the nitrogens *trans* to the phosphorus.

There are very few crystallographically characterised zinc phosphine complexes. The closest structure to **1** is $Zn[(CH_2)_3PPh_2]$ in which the phosphine is part of a five-membered chelate ring.[8] The average Zn–P bond length is 2.589 Å, slightly longer than that in **1** (2.522 Å). The other relevant structures[9,10] contain PPh_3 and have Zn–P distances of 2.425 and 2.392 Å.

The ^{31}P NMR of the crystals of **1** in both MeCN and nitromethane shows that there are more than one species present in solution. The major species (*ca.* 80%) shows a broad singlet at δ −19.30 which must be assigned to either the intact dimer with fluxional ligands or, more likely, to a five-coordinate $[ZnLCl]^+$ species. The change in the ^{31}P chemical shift on coordination to Zn^{II} (−3.2 ppm) is similar to that of $PMePh_2$ (+4 ppm) or PMe_3 (−1 or −12 ppm) coordinated to Zn^{II}.[11]

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Footnotes

† 1,4,7-Tris(diphenylphosphinoylmethyl)-1,4,7-triazacyclononane is incorrectly depicted as the phosphine in ref. 2.

‡ *NMR data* (δ, *J*/Hz) L: ^{13}C, δ 24.25 (d, *J* 16, PCH_2), 25.69 (d, *J* 11.5, CH_2, arm), 58.73 (d, *J* 13, CH_2N, arm), 46.73, 46.82, 53.06 (CH_2, ring) 138.90, 132.67, 128.49, 128.34 (aromatic); ^{31}P, −16.2. L′: ^{13}C, 46.5 (CH_3), 24.38 (d, *J* 16.5, PCH_2), 25.9 (d, *J* 11, CH_2, arm) 60.24 (d, *J* 14, CH_2N, arm) 54.26, 55.09, 55.44 (CH_2N, ring), 128.36, 132.66, 133.94, 138.59 (aromatic); ^{31}P, −16.09.

§ *Crystal data* for **1**: $C_{42}H_{60}Cl_4N_6O_4P_2Zn_2$, M = 1047.44, monoclinic, space group $P2_1/a$, a = 15.806(6), b = 17.069(8), c = 17.955(4) Å, β = 107.11(4)°, U = 4630(3) Å^3, Z = 4, D_c = 1.503 g cm^{-3}, $F(000)$ = 2176. A total of 8147 unique data were measured on a Turbo CAD-4 diffractometer with graphite-monochromated X-radiation (λ = 0.71073 Å) using ω–2θ scans. The structure was solved by direct methods and subsequent electron density difference synthesis and refined by full-matrix least squares using 8141 absorption/extinction (DIFABS) corrected data. The final R_1 ($I > 2\sigma I$, 3521 data) and wR_2 (all data) were 0.109 and 0.368 for 284 parameters. Hydrogen atoms were incorporated at fixed positions with C–H = N–H = 0.96 Å. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/156.

References

1 P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.*, 1987, **35**, 329.
2 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
3 R. P. Hauser, J. A. Halfern, V. G. Young Jr., N. J. Blackburn and W. B. Tolman, *J. Am. Chem. Soc.*, 1995, **117**, 10 745.
4 T. Beissel, K. S. Burger, C. Butzlaff, A. X. Trautwein, G. Voigt and K. Wieghardt, *Inorg. Chem.*, 1993, **32**, 124.
5 H. H. Hope, M. Viggiano, B. Moezzi and P. P. Power, *Inorg. Chem.*, 1984, **23**, 2550.
6 A. Carroy, C. R. Langick, J.-M. Lehn, K. E. Matthes and D. Parker, *Helv. Chim. Acta*, 1986, **69**, 580.
7 T. J. Atkins, *J. Am. Chem. Soc.*, 1980, **102**, 6364.
8 J. Dekker, J. W. Munninghoff, J. Boersma and A. L. Spek, *Organometallics*, 1987, **6**, 1236.
9 R. E. DeSimone and G. D. Stucky, *Inorg. Chem.*, 1971, **10**, 1808.
10 F. A. Cotton, S. A. Duraj, W. J. Roth and C. D. Schmulbach, *Inorg. Chem.*, 1985, **24**, 525.
11 M. Bochmann, G. C. Bwembya, R. Grinter, A. K. Powell, K. J. Webb, M. B. Hursthouse, K. M. Abdul Malik and M. A. Mazid, *Inorg. Chem.*, 1994, **33**, 2290.

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