The liberation, characterisation and X-ray crystal structure of 1,5,9-triphospha-1,5,9-tris(2-propyl)cyclododecane

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1,5,9-Triphospha-1,5,9-tris(2-propyl)cyclododecane is liberated from the molybdenum template upon which it is formed by action of aqueous base and after oxidation of the metal with halogens.

Complexes of triphosphorus macrocycles are rare. A series of macrocyclic ligands generated from 1,2-diphosphinobenzene and derivative complexes has been reported by Kyba *et al.*[1] Since these ligands are prepared by high-dilution methods, the syntheses are not stereospecific. Some while ago Norman and coworkers[2] reported the first 1,5,9-triphosphacyclododecane complex; they also prepared the 1,6,11-triphosphacyclopentadecane analogue. We have extended this chemistry to tungsten and have recently reported the syntheses and characterisations of the first complexes of tritertiary derivatives of 1,5,9-triphosphacyclododecane.[3] These complexes are the only examples of symmetrical triphosphorus macrocycles (*i.e.* where all three backbone links are identical) and the free, uncoordinated macrocycles until now were unknown, despite attempts at their liberation from the metal template upon which they were prepared. We have also recently reported oxidations of molybdenum and tungsten complexes of 1,5,9-triphosphacyclodo- decane and its tertiary derivatives with halogens[4] and chromium analogues.[5] In this communication we report the high yield and stereoselective liberation of the tritertiary macrocycle 1,5,9-triphospha-1,5,9-tris(2-propyl)cyclododecane, L, from its molybdenum(II) dihalogeno complex $[MoL(CO)_2Br_2]$ and the spectroscopic and crystallographic characterisation of the free macrocycle.

Reaction of $[MoL(CO)_2Br_2]$ with strong base (NaOH) in ethanol followed by digestion of inorganic by-products in water, causes a loss of colour of the mixture and the separation of a colourless oil. Extraction of this oil with light petroleum enables the isolation of colourless needles of the free macrocycle in good yield {80% based on $[MoL(CO)_2Br_2]$}.† These crystals are readily characterised spectroscopically. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ −19.8 consistent with an uncoordinated tertiary trialkylphosphine and shifted upfield from the parent molybdenum(II) complex by 29.5 ppm. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra‡ consist of 4 resonances assignable to the four different proton and carbon environments respectively and are similar to the spectra observed for the molybdenum-(0) and -(II) precursors. Since there are two possible geometric isomers of L, the spectra indicate that the liberation is stereospecific for isomer **a** (Fig. 1) since isomer **b** would require an A_2B spin pattern in the $^{31}P\{^1H\}$ NMR spectrum as well as correspondingly more complex ^1H and ^{13}C NMR spectra. The IR spectrum of L shows absorptions assignable to ν(C–H), ν(P–C) and the absence of bands that would arise from any metal–ligand vibrations. In the mass spectrum, the molecular ion is observed (*m/z* 349, 9%) along with a fragmentation pattern due to loss of CH_3 and Pr^i groups. No heavier ions are evident.

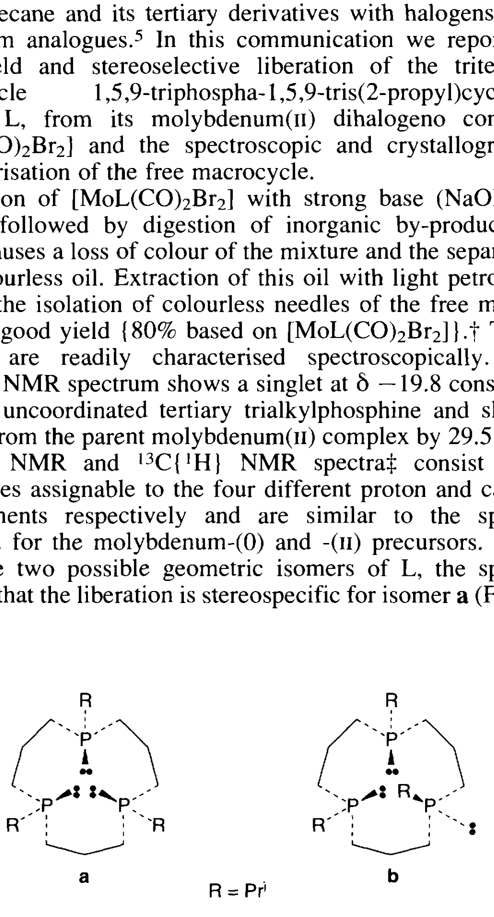

Fig. 1 Possible conformations for L

The X-ray crystal structure (Fig. 2)§ confirms the characterisation of L and that only one stereoisomer is present in the solid state with all lone pairs on the same side of the molecule, consistent with the solution NMR data. The P–C distances and angles are within expected ranges. Of interest are the non-bonded P···P distances [average 5.199(4) Å]. This compares with 3.660(8) Å in the molybdenum(II) complex cation $[MoL(CO)_3Br]^+$ and 3.487(5) Å in the molybdenum(0) parent complex, $[MoL(CO)_3]$.[3,4] Clearly, the macrocycle opens out upon decomplexation as might be expected for such a flexible ring system. This flexibility indicates that this macrocycle may well be an effective tridentate ligand for a range of metals of different radii.

We are currently studying the application of this synthetic route to the liberation of 1,5,9-triphosphacyclododecane itself as well as other derivatives; preliminary results indicate that this approach is successful for a range of homologues. We are also studying the coordination chemistry of 1,5,9-triphosphacyclododecane macrocycles with other metals. Again, preliminary results indicate that a range of new complexes are readily formed.

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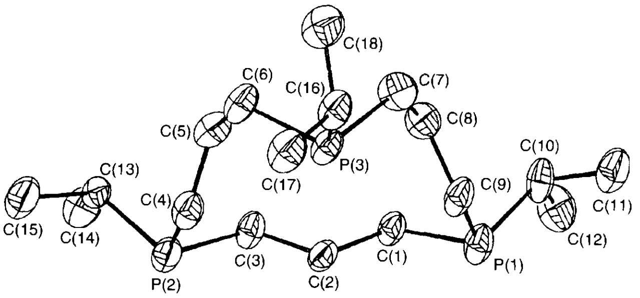

Fig. 2 X-Ray structure and atom labelling scheme for 1,5,9-triphospha-1,5,9-tris(2-propyl)cyclododecane L. Selected bond lengths (Å): P(1)–C(1) 1.842(5), P(1)–C(9) 1.831(5), P(1)–C(10) 1.855(5), P(2)–C(3) 1.862(5), P(2)–C(4) 1.852(5), P(2)–C(13) 1.844(5), P(3)–C(6) 1.835(5), P(3)–C(7) 1.859(5), P(3)–C(16) 1.861(5). Selected bond angles (°): C(1)–P(1)–C(9) 100.9(2), C(1)–P(1)–C(10) 99.9(2), C(9)–P(1)–C(10) 103.2(2), C(3)–P(2)–C(4) 101.1(2), C(3)–P(2)–C(13) 100.9(2), C(4)–P(2)–C(13) 101.6(2), C(6)–P(3)–C(7) 102.5(2), C(6)–P(3)–C(16) 101.6(2), C(7)–P(3)–C(16) 99.3(2).

Footnotes

† In a typical experiment, a suspension of $[MoL(CO)_2Br_2]$ (1.99 g, 0.30 mmol) in ethanol (30 cm^3) was stirred at room temp. for 16 h. The mixture was cooled to 0 °C and a large excess of NaOH pellets ($>$ 1.0 g) added. The mixture was allowed to warm to room temp. and stirred for a further 4 h. The solvent was removed *in vacuo* to give an oily grey residue. The mixture was cooled to 0 °C and water (30 cm^3) was added and the mixture allowed to warm to room temp. and stirred for 1 h. The product was extracted with light petroleum (bp 40–60 °C, 3 × 50 cm^3). The combined organic phases were dried over $MgSO_4$ (8 h), filtered, and the solvent removed *in vacuo* to give L as a white solid (0.84 g, 0.24 mmol, 80%) which is readily recrystallised from aliphatic hydrocarbons (mp 114.8–115.3 °C). The macrocycle can be liberated in similar yields from the analogous chloro and iodo molybdenum complexes.

‡ ^1H NMR (360 MHz, $CDCl_3$, 27 °C), δ 1.74 (br, m, 4 H, PCH_2CH_2), 1.56 [spt, ^3J(H–H) 7 Hz, 1 H, PCH], 1.42 (br, m, 2 H, PCH_2CH_2), 0.99 [dd, ^3J(H–H) 7 Hz, ^3J(P–H) 15 Hz, 6 H, PCH_3]; $^{13}C\{^1H\}$ (90 MHz, $CDCl_3$, 27 °C), δ 25.7 [dd, ^1J(P–C) 17 Hz, ^3J(P–C) 8 Hz, PCH_2], 24.3 [d, ^1J(P–C) 8 Hz, PCH], 19.6 (s, PCH_3), 19.4 (br, s, PCH_2CH_2).

§ *Crystal data* for L: $C_{18}H_{39}P_3$. $M_r = 348.4$, triclinic, space group $P\bar{1}$ (no. 2). $a = 5.5248(8)$, $b = 12.2124(10)$, $c = 16.857(2)$ Å, $\alpha = 107.81(4)$, $\beta = 94.08(4)$, $\gamma = 95.70(2)°$ (by least-squares analysis of 50 reflections), $U = 1071.3(2)$ Å^3, $Z = 2$, $D_c = 1.08$ g cm^{-3}, $F(000) = 384$, $\mu = 0.273$ mm^{-1}, $T = 150$ K, crystal size 0.21 × 0.14 × 0.035 mm^3 (approx.). Data were collected on a Delft Instruments FAST TV area detector at the window of a rotating anode generator (50 kV, 45 mA), with a molybdenum target [λ(Mo-Kα) = 0.71069 Å]. 4388 reflections collected ($1.77 < \theta < 24.93°$), index ranges $-4 < h < 6$; $-14 < k < 14$; $-19 < l < 18$, producing 2890 unique data ($R_{int} = 0.0885$ after absorption correction, DIFABS[6]). The structure was solved by direct methods (SHELX-S[7]) and subjected to full-matrix least-squares refinement based on F_o^2 (SHELXL-93[8]). The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. Final wR_2 ($wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$) and R_1 [$R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$] values are 0.1385 and 0.1258 respectively, for all 2890 data and 196 parameters (ρ_{max}, ρ_{min} 0.265, -0.179 e Å^{-3}). The corresponding wR_2 and R_1 values for 892 data with $F_o > 4\sigma(F_o)$ are 0.0778 and 0.0431 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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