The template synthesis of triaryl functionalised 1,5,9-triphosphacyclododecane on molybdenum using organocopper reagents†

David J. Jones,[a] Peter G. Edwards,*[a] Robert P. Tooze[b] and Thomas Albers[a]

[a] Department of Chemistry, Cardiff University, Cardiff, PO Box 912, UK CF1 3TB.
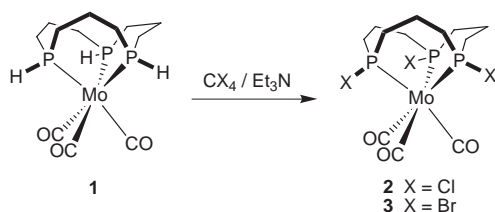E-mail: edwardspg@cardiff.ac.uk
[b] ICI Acrylics PLC, PO Box 90, Wilton, Middlesbrough, Cleveland, UK TS90 8JE

Free triphenyl substituted 1,5,9-triphosphacyclododecane has been prepared *via* the templated reaction of 1,5,9-trichloro-1,5,9-triphosphacyclododecane on molybdenum with phenylcopper or diphenylcuprate.

Previous routes to the symmetrical 12-membered tritertiary triphosphamacrocycles ([12]aneP$_3$R$_3$)[1] do not lead to the successful formation of aryl functionalised macrocycles and the yields for bulky alkyl or perfluoroalkyl substituents are typically poor.[2] In view of the interest in more relatively π-acidic aryl phosphines and their importance in catalysis and other applications, we have investigated alternative synthetic routes to the formation of aryl functionalised P$_3$ macrocycles based upon the [12]aneP$_3$ core and report preliminary observations herein.

One approach to the formation of aryl substituted phosphines is *via* transmetallation of the chlorophosphine. Reactions to form the required P–Cl from secondary phosphines generally require forcing reaction conditions and reagents such as phosgene or phosgene equivalents.[3] In addition these reactions would not be expected to work on coordinated phosphines due to the unavailability of the lone pair and coordination sites in the transition state. The chlorination of free secondary phosphines with CCl_4 in the presence of Et_3N has been reported; a 5-coordinate transition state was proposed.[4] Surprisingly we have found that [([12]aneP$_3$X$_3$)-Mo(CO)$_3$] (where X = Cl **2** or Br **3**) can be readily formed in high yield, >80%, from the reaction of [([12]aneP$_3$H$_3$)Mo(CO)$_3$] **1** with the corresponding CX$_4$ in the presence of Et_3N (Scheme 1). This facile reaction is complete within 2 hours at ambient
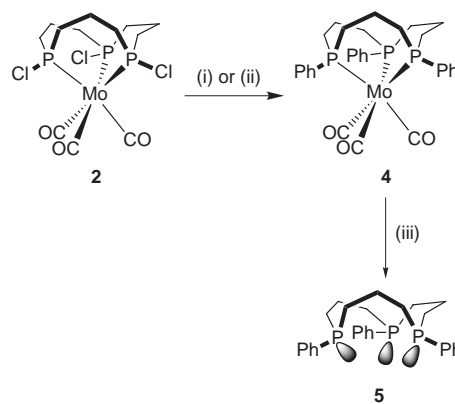

Scheme 1 Halogenation of the templated trisecondarymacrocycle by reaction with an excess of CX$_4$.

temperature and, as the 5-coordinate transition state is not available for the kinetically inert Mo(0) complex, this suggests that a free radical mechanism is involved. These rates are significantly faster than those for the free phosphines reported in the literature where reaction times of days or weeks were required. Bromination is faster than chlorination while reaction

with CI$_4$ is rapid at RT but a stable product could not be isolated.

Reaction of **2** with PhLi or PhMgBr leads, in general, to the formation of an insoluble brown material, presumably polymeric. In one case, however, reacting **2** with PhLi in diethyl ether at 0 °C led to a 20% yield of the required product [([12]aneP$_3$Ph$_3$)Mo(CO)$_3$] **4** while reaction of **2** with PhMgBr in THF at −40 °C led to a small yield of an unstable product which appeared to be fully arylated but had three inequivalent phosphorus atoms as indicated by ^{31}P and ^{1}H NMR. Reaction of **2** with Ph$_2$Zn in refluxing THF gave no reaction after 24 hours, however, reaction of **2** with PhCu or Ph$_2$CuLi in THF overnight at 30 °C or 1 hour in refluxing THF did lead to the required product **4** in high yield, >70%. These reactions are readily monitored by ^{31}P NMR spectroscopy where a new singlet at δ 10.9 due to **4** increases at the expense of the singlet at δ 134 due to **2**.

Oxidation of **4** with I$_2$ and decomplexation in ethanolic NaOH followed by extraction into toluene following our previously reported method[2] results in isolation of the free triphenyl-macrocycle, [12]aneP$_3$Ph$_3$ **5**, according to Scheme 2.

Scheme 2 (i) PhLi or PhMgBr–THF −40 °C to RT; (ii) 6PhCu or Ph$_2$CuLi, THF, RT for 2 hours; (iii) I$_2$, refluxing 1,1,2-trichloroethane, excess NaOH in MeOH, diethyl ether–H$_2$O extraction.

Fig. 1 shows the crystal structure of **4** with molybdenum in a distorted octahedral environment.‡ Complex **4** crystallises with two independent molecules in the asymmetric unit differing only in the orientation of one phenyl ring; the phenyl ring is approximately parallel to the C_{3v} mirror plane through the phosphorus to which it is attached in one form and orthogonal in the other (Fig. 1 **4b**).[5] There is no obvious structural reason for this orientation and it may simply be due to crystal packing forces. Five of the six β-methylene groups of the macrocycles are disordered over the two possible positions to give the pseudo-chair and -boat configurations for the adjacent P–P chelate rings with the molybdenum, *e.g.* P$_1$C$_4$C$_5$C$_6$P$_2$Mo, all
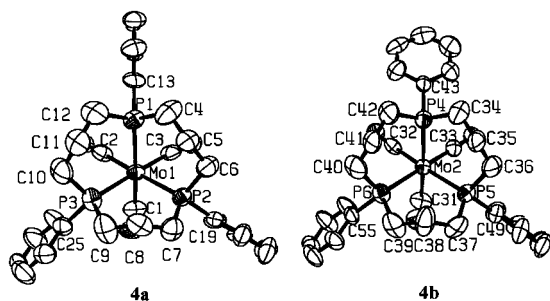
Fig. 1 ZORTEP plot of **4** (50% probability ellipsoids), showing the two crystallographically independent molecules **4a** and **4b**. Selected average bond distances (Å) and angles (°): P–C (ring) 1.817(13), Mo–P 2.493(4), Mo–C 1.933(13), C–O 1.174(13), non-bonded P–P 3.536(6); P–Mo–P 90.37(14), C–Mo–C 90.27(5), C–Mo–P 177.38(4), R–P–Mo 116.3(4).

have been drawn in the chair configuration with greatest occupancy. The exception is the methylene (C38) lying in the C_{3v} plane opposite P4 which is found only in the chair configuration. The metrical parameters are otherwise comparable to the 2-propyl analogue, $[([12]aneP_3Pr^i_3)Mo(CO)_3]$.[1d]

The methylene protons on both the α- and β-ring carbons are diastereotopic and could be expected to have distinct environments while structural evidence indicates they could exist in either the boat or chair conformation. In solution, a rapid equilibrium between these conformations would be expected to broaden their NMR resonances, the disorder of the β-ring carbons in the solid state structure for **4** presumably reflects a low energy difference between the two conformations. This expected behaviour is seen for the new complexes and for the free ligand where small differences in δ (NMR) are observed for the diastereotopic α-methylene protons in **4**§ and the α- and β-methylene protons appear as broad multiplets. These resonances are shifted significantly upfield in the free macrocycle **5** as compared to **4** especially the β-methylene peaks δ_H 2.05 to 1.73 and 1.57.

It is interesting to note that long range phosphorus coupling is seen for the *meta*-carbon on the phenyl ring for **4** where a doublet of doublets is seen, this is absent for the free ligand **5** where only a doublet is observed.

In conclusion we have developed a new, facile route to P–Cl bond formation for coordinated secondary phosphines. This simple transformation allows for alternative routes to functionalised macrocycles. One of these routes, notably aryl/alkylation using organocopper reagents, offers the possibility of introducing a broad range of substituents due to the extensive range of organocopper reagents available and including options for which alternative methods have failed. The chemistry of these new ligands is currently being examined and this new class of triaryl-substituted 1,5,9-triphosphacyclododecanes should also allow a more extensive examination of structure/reactivity relationships in their metal complexes. This study is currently under investigation.

Notes and references

‡ Crystal data for complex **4**, $C_{30}H_{33}MoO_3P_3$, $M = 630.41$, $T = 20$ °C, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.399(4)$, $b = 17.59(3)$, $c = 34.22(2)$ Å, $\beta = 90.15(3)$°, $V = 5656(10)$ Å³, $Z = 8$, $D = 1.481$ g cm⁻³, μ(Mo-Kα) = 0.664 mm⁻¹, independent reflections = 14926 (R_{int} = 0.0968), 2θ range for data collection $3.6 < 2\theta < 39.6$°, $R1$ ($I > 2\sigma$) = 0.0484, $wR2$ (all data) = 0.0924. Equivalent 1,2- and 1,3-distances involving the disordered atoms were restrained to be equal. Rigid-bond and similarity restraints were used as well. Pseudo-orthorhombic twinning was encountered ($a' = -a$, $b' = b$, $c' = c$), contribution of minor component 0.1954(15). CCDC reference number 186/1351. See http://www.rsc.org/suppdata/dt/1999/1045/ for crystallographic files in .cif format.

§ See supplementary data for experimental details: Selected data for complex **2**: δ_P 134.0; δ_H PCH_2 2.33 and 2.14, PCH$_2$CH_2 2.22 and 1.57; v(CO) cm⁻¹ 1970 and 1879. Complex **3**: δ_P 119.0; δ_H PCH_2 2.55 and 2.27, PCH$_2$CH_2 2.21 and 1.74; v(CO) cm⁻¹ 1961 and 1876. Complex **4**: δ_P 10.9; δ_H PCH_2 2.06 and 1.90, PCH$_2$CH_2 2.05; δ_C 128.26 (dd, *m*-Ph, $^3J_{PC} = 6$, $^5J_{PC} = 3$ Hz); v(CO) cm⁻¹ 1917 and 1809. Compound **5**, δ_P −34.6; δ_H PCH_2 2.16 and 1.93, PCH$_2$CH_2 1.73 and 1.57. Analytical data: **2**, found: C, 28.74; H, 3.41. Calc. for $C_{12}H_{18}O_3P_3Cl_3Mo$: C, 28.51; H, 3.59. **3**, found: C, 23.10; H, 2.78. Calc. for $C_{12}H_{18}O_3P_3Br_3Mo$: C, 22.56; H, 2.84. **4**, found: C, 56.98; H, 5.32. Calc. for $C_{30}H_{33}O_3P_3Mo$: C, 57.15; H, 5.25. **5**, found: C, 71.99; H, 7.38. Calc. for $C_{27}H_{33}P_3$: C, 71.99; H, 7.33%. Satisfactory mass spectroscopic data were obtained.

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