ChemComm

A new template for the synthesis of triphosphorus macrocycles

Andrew J. Price and Peter G. Edwards*

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff, UK CF10 3TB.
Email: edwardspg@cardiff.ac.uk

Received (in Cambridge, UK) 17th March 2000, Accepted 10th April 2000
Published on the Web 9th May 2000

A new template synthesis of triphosphorus macrocycles has been developed based upon the intramolecular hydrophosphination of allylphosphine coordinated to the (η^5-cyclopentadienyl)iron(II) cation; the resulting tri-secondary macrocycle 1,5,9-triphosphacyclododecane is readily alkylated with ethene to give (η^3-1,5,9-[12]aneP_3Et_3)Fe(η^5-Cp)$^+$ which is in turn liberated as the free ligand stereospecifically as the *syn–syn* isomer; related reactions with phenyl(allyl)phosphine lead directly to the triphenyl macrocycle (1,5,9-[12]aneP_3Ph_3) which is also liberated stereospecifically.

The first examples of C_3 symmetrical triphosphamacrocycles were those based upon the 1,5,9-[12]aneP_3 core prepared by a stereoselective metal template assisted synthesis using a $Mo(CO)_3$ template.[1,2] Early results confirm that they support relatively very stable facially capped complexes for a range of transition metals,[3] they may also impose unusual structural distortions on metal centres (*e.g.* for metals that prefer square planar geometries).[4] These observations highlight distinct differences in comparison to the behaviour of analogous nitrogen or sulfur ligands or of related tripodal phosphines. In view of their influences on structure and reactivity and their ability to stabilise low oxidation states, the study of their complexes is of substantial interest.

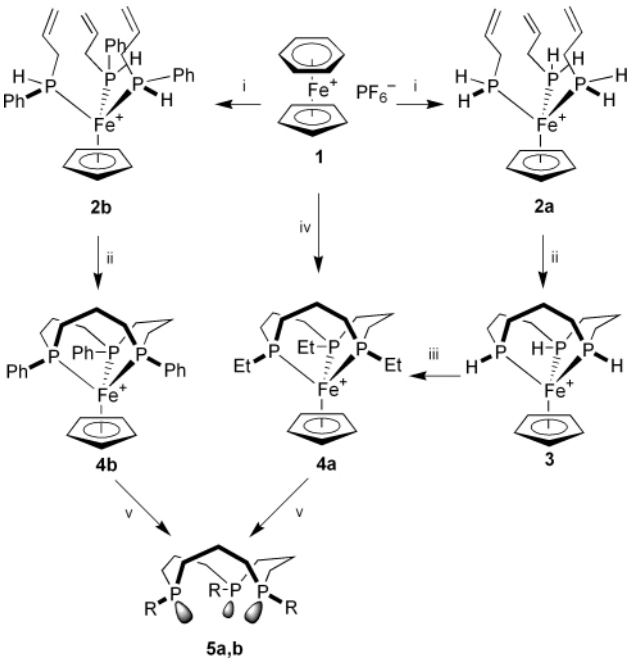
The current and only route to this class of ligands, by radical initiated hydrophosphination, does however have significant preparative limitations. The tris-allylphosphine precursor complexes required for this route are very sensitive to oxygen, moisture and large scale reactions require fastidious care in order to be reproducible. Of greater significance is that this method is currently limited to a minimum ring size of twelve atoms. We have previously commented upon the inability of the $Mo(CO)_3$ template, and its smaller chromium analogue, to support the cyclisation of vinyl phosphines in attempts to achieve smaller ring sizes.[5] These templates lack any possible steric control over the *trans*-coordinated precursor phosphines precluding any freedom to force the ring closure of vinyl phosphines by compression of the non-bonded P–P distances. In order to address these problems and to develop a more reliable synthetic route to tri-phosphines of this nature, we have undertaken a study of alternative methods. For these reasons we have chosen to investigate the [(η^5-Cp)Fe(η^6-arene)]$^+$ class of complexes which readily form tris-phosphine adducts[6] including those of acyclic triphosphines (linear[6b] and tripodal[6c]) and of primary phosphines,[6d] all of which are of course restricted to *facial* coordination by the η^5-Cp group. This approach has led us to an entirely new template method for the stereoselective synthesis of 1,5,9-[12]aneP_3R_3 triphosphorus macrocycles; preliminary results of which are presented herein.

The photolytically activated substitution of the aryl ligand in [(η^5-C_5H_5)Fe(η^6-C_6H_6)]$^+$ (**1**) in the presence of allylphosphine gives the tris-primary phosphine complex [(η^5-C_5H_5)Fe($H_2PC_3H_5$)$_3$]$^+$ **2**, as the hexafluorophosphate salt, in quantitative yield (Scheme 1). In the IR spectrum, a peak due to ν_{P-H} is observed (2318 cm^{-1}). The microcrystalline solid is indefinitely air-stable, although in CH_2Cl_2 solution the complex decomposes over several days to give a green, NMR silent and presumably paramagnetic species of undetermined composition. Complex **2** is readily soluble in most polar solvents, such as THF and CH_2Cl_2, but insoluble in hydrocarbons and other non-polar solvents. The ^{31}P {^{1}H} NMR and ^{31}P NMR spectra consist of a singlet and triplet, respectively (δ −9.0, $^1J_{P-H}$ 328 Hz), consistent with magnetically equivalent coordinated allylphosphine ligands (*cf.* for free allylphosphine, δ−134.4, $^1J_{P-H}$ 195 Hz).

Cyclotrimerisation of **2** has been attempted in tetrahydrofuran (THF), chlorobenzene and anisole, using AIBN [azobis(isobutyronitrile)] as radical initiator (*ca.* 1–2% mol equivalents). In THF, both the cyclisation intermediates and final macrocyclic product slowly precipitate during the reaction which remains incomplete as a result, unless performed in dilute solution. Attempts to separate and characterise these intermediates have not been successful.

In chlorobenzene the cyclisation is more efficient, forming [(η^5-C_5H_5)Fe(η^3-1,5,9-[12]aneP_3H_3)]$^+$[PF_6]$^-$ **3**, in moderate yield. Complex **3** has a band due to the P–H stretch in its IR spectrum (ν_{P-H} 2303 cm^{-1}) and a doublet in the ^{31}P NMR spectrum (δ 12.7, $^1J_{P-H}$ 336 Hz) assigned to phosphorus atoms in the coordinated macrocycle. This increase in chemical shift ($\Delta\delta$ 21.8 ppm) and coupling constant is similar to that observed in the analogous Mo(0) complexes, ($H_2PC_3H_5$)$_3$Mo(CO)$_3$ and (η^3-1,5,9-[12]aneP_3H_3)Mo(CO)$_3$, ($\Delta\delta$ 27.0 ppm, for the latter $^1J_{P-H}$ 318 Hz).

Hydrophosphination of ethene by **3** gives the tris-ethylated macrocyclic complex [(η^5-C_5H_5)Fe(η^3-1,5,9-[12]aneP_3Et_3)]$^+$[PF_6]$^-$ **4** which is characterised by a singlet in the ^{31}P



Scheme 1 *Reagents and conditions*: i > 3 allylphosphine for **2a** or > 3 phenyl(allyl)phosphine for **2b**, CH_2Cl_2, $h\nu$ (> 400 nm); ii, chlorobenzene, AIBN (2 mol%), 90 °C; iii, ethene (2 atm), chlorobenzene, AIBN (2 mol%); iv, [12]aneP_3Et_3, CH_2Cl_2, $h\nu$ (> 400 nm); v, Na/NH_3(l); **5a**, R = Et; **5b**, R = Ph.

DOI: 10.1039/b002174l

{^{1}H} NMR spectrum (δ 38.1) and the absence of a band due to ν_{P-H} in its IR spectrum. The identity of **4** is further supported by its preparation in THF directly from the template precursor complex **1** by addition of free 1,5,9-[12]aneP_3Et_3 obtained by our previously reported route.[2] The products obtained by either method have identical spectroscopic, analytical and physical properties. This independent confirmation of the nature of **4**, in turn confirms the characterisation of **3** as the secondary phosphine macrocycle complex. Both **3** and **4** are air stable for extended periods in both solution and the solid state.

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$ with phenyl-(allyl)phosphine in a manner similar to that for the formation of **2a**, leads to the tri-secondary phosphine complex, **2b**, in excellent yield (99%). Complex **2b** is characterised by its ^{31}P{^{1}H} NMR spectrum which has two multiplets from the presence of both diastereomers and enantiomers arising from the three chiral phosphines in **2b** (δ 55.8). The radical induced cyclisation of the coordinated secondary phosphines in **2b** proceeds to the tri-tertiary phosphine macrocycle complex, **4b**. Intermediates which do not readily cyclise are also observed after extended reaction times; these are readily separated from **4b** upon work up. The resistance of these intermediates to cyclisation is presumably dependant upon the relative chirality at adjacent phosphines. Although we have recently reported the synthesis of the triphenyl macrocycle, **5b**,[7] this is the first example of the cyclotrimerisation of a secondary phosphine to a tri-tertiary triphosphorus macrocycle and may offer direct routes to tri-tertiary phosphines which might otherwise be difficult to obtain.

The macrocycle complexes, **4a** and **4b**, are digested by sodium in liquid ammonia resulting in the high yield liberation of the free macrocyclic ligands **5a** and **5b** stereoselectively as the *syn–syn* isomers. The identities and stereochemistries of both the triphosphines **5a** and **5b**, are confirmed by singlets in their ^{31}P {^{1}H} NMR spectra (δ −31.7 and −34.6, respectively); their spectra are identical to those previously reported.[2,7] In all cases analytical, conductivity, ^{1}H and ^{13}C{^{1}H} NMR data are consistent with the formulations.[8]. In addition to the ^{31}P NMR data discussed above, a resonance due to PF_6^- is also observed in each case (δ −144.0, $^1J_{P-F}$ 711 Hz).

This new route to the coordinated secondary phosphine ligands, the facile alkylation of the secondary phosphine macrocycle complex **3** to the corresponding tertiary phosphines and the successful and stereospecific liberation of the free ligands offers an alternative preparation based upon a more readily accessible template than the sole current literature route and *via* relatively air-stable precursor and intermediate complexes. We are currently investigating the influences of variations in substituents on the Cp ring upon the course of the macrocyclisation reactions. We are also investigating the application of this method to the cyclisation of alternative phosphine precursors in order to achieve both different ring sizes as well as different 'backbone' bridging functions; preliminary results are encouraging.

We thank the EPSRC for a studentship (A. J. P.).

Notes and references

1 B. N. Diel, P. F. Brandt, R. C. Haltiwanger and A. D. Norman, *J. Am. Chem. Soc.*, 1982, **104**, 4700; B. N. Diel, P. F. Brandt, R. C. Haltiwanger, M. L. J. Hackney and A. D. Norman, *Inorg. Chem.*, 1989, **28**, 2811.

2 P. G. Edwards, J. S. Fleming and S. S. Liyanage, *Inorg. Chem.*, 1996, **35**, 4563.

3 P. G. Edwards, J. S. Fleming, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1997, 3201.

4 P. G. Edwards, F. Ingold, S. J. Coles and M. B. Hursthouse, *Chem. Commun.*, 1998, 45.

5 P. G. Edwards, J. S. Fleming, S. S. Liyanage, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1996, 1801.

6 (*a*) H. Schumann, L. Eguren and J. W. Ziller, *J. Organomet. Chem.*, 1991, **408**, 361; (*b*) D. Catheline and D. Astruc, *Organometallics*, 1984, **3**, 1094; (*c*) G. T. Crisp, G. Salem and S. B. Wild, *Organometallics*, 1989, **8**, 2360; (*d*) D. C. R. Hockless, Y. B. Kang, M. A. McDonald, M. Pabel, A. C. Willis and S. B. Wild, *Organometallics*, 1996, **15**, 1301; (*e*) **4b**: R. B. King, P. N. Kapoor and R. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1841; (*f*) S. G. Davies, H. Felkin and D. Watts, *J. Chem. Soc., Chem. Commun.*, 1980, 159; (*g*) **4c**: R. B. King, L. W. Houk and K. H. Pannell, *Inorg. Chem.*, 1969, **8**, 1042; (*h*) J. D. Goodrich and J. P. Selegue, *Organometallics*, 1989, **8**, 2360.

7 D. J. Jones, P. G. Edwards and R. P. Tooze, *J. Chem. Soc., Dalton Trans.*, 1999, 1045.

8 *Selected data*: for **2a**: yield: 99%. Anal. Found (calc.): C, 34.5 (34.4); H, 5.3 (5.4)%. MS(ES), *m/z* 343 (100%, $[M-PF_6]^+$). IR (KBr disc): ν(P–H), 2319.4 cm^{-1}. Λ_M = 25 Ω cm^2 mol^{-1}. ^{31}P NMR: δ −9.1 (t, $^1J_{P-H}$ = 328 Hz, cation), −145.0 (septet, $^1J_{P-F}$ 711 Hz, anion). ^{1}H NMR, δ 2.54 (m, $H_2PCH_2CHCH_2$), 4.12, 5.00 (d m, $^1J_{P-H}$ 328 Hz, $H_2PCH_2CHCH_2$), 4.55 (q, $^3J_{P-H}$ 2 Hz, Cp-H); 5.20 (m, $H_2PCH_2CHCH_2$), 5.82 (m, $H_2PCH_2CHCH_2$). ^{13}C{^{1}H} NMR: δ 28.2 (d, $^1J_{P-C}$ = 40 Hz, $H_2PCH_2CHCH_2$), 80.1 (s, Cp), 119.7 (s, $H_2PCH_2CHCH_2$), 133.9 (s, $H_2PCH_2CHCH_2$). For **2b**: yield: 95%. Anal. Found (calc.): C, 53.6 (53.7); H, 5.3 (5.4)%; Λ_M = 39 Ω cm^2 mol^{-1}. IR (KBr disc): δ(P–H), 2303 cm^{-1}. MS(ES), *m/z* 571(100%) $[(\eta^5\text{-}C_5H_5)Fe(PhPHC_3H_5)_3]^+$. ^{31}P{^{1}H} NMR ($CDCl_3$, 36.23 MHz), δ 56.5 (m); 60.2 (m). ^{1}H NMR: δ 4.30 (q), 4.55 (s), 4.69 (s), 4.78 (br m), 4.93 (s), 5.08 (br m), 5.24 (br m), 5.35 (br m), 5.52 (br m), 5.76 (br m), (15H, allyl groups). For **3**: yield: 40%. Anal. Found (calc.): C, 33.5 (34.4); H, 4.8 (5.4)%. MS(ES), *m/z* 343 (100%, $[M-PF_6]^+$). IR (KBr disc): δ(P–H), 2302.6 cm^{-1}. Λ_M = 32 Ω cm^2 mol^{-1}. ^{31}P NMR: δ 12.7 (d, $^1J_{P-H}$ 336 Hz, cation), −145 (septet, $^1J_{P-F}$ = 711 Hz, anion). For **4a**. Yield: 95%. Anal. Found (calc): C, 47.0 (46.7); H, 7.6 (7.4)%. MS(ES), *m/z* 427 (100 %, $[M-PF_6]^+$). Λ_M = 40 Ω cm^2 mol^{-1}. ^{31}P NMR: δ 38.1 (s, cation), −145 (septet, $^1J_{P-F}$ = 711 Hz, anion). ^{1}H NMR: δ 1.28 (br m, PCH_2CH_3), 1.61 (br m, PCH_2CH_3 and $PCH_2CH_3CH_2P$); 1.87 (br m, $PCH_2CH_2CH_2P$), 4.26 (q, $^3J_{P-H}$ 2 Hz, Cp-H). For **4b**: yield: 30%. Anal. found (calc.): C, 53.6 (53.6); H, 5.4 (5.3)%. MS (ES), *m/z* 571 (100%, $[M-PF_6]^+$).^{31}P{^{1}H} NMR: δ 35.0 (s). ^{1}H NMR: δ 1.97, 2.10, 2.20, 2.33, 2.46, 2.60 (all br m, PCH_2 CH_2 CH_2P), 3.99 (q, $^3J_{P-H}$ 2 Hz, Cp-H), 7.19 (s, phenyl-H), 7.46 (m, phenyl-H), 7.56 (br m, phenyl-H), 7.66 (br m, phenyl-H).