Template synthesis of benzannulated triphosphacyclononanes—a new class of phosphacrowns *via* template assisted nucleophilic P–C bond formation

Thomas Albers and Peter G. Edwards*

Received (in Cambridge, UK) 20th September 2006, Accepted 3rd November 2006
First published as an Advance Article on the web 23rd November 2006
DOI: 10.1039/b613672a

A 9-membered triphosphorus macrocycle with *o*-phenylene backbone functions has been stereoselectively prepared on a CpFe$^+$ template by two successive nucleophilic attacks of coordinated phosphide on a coordinated *o*-fluorophenylbiphosphine.

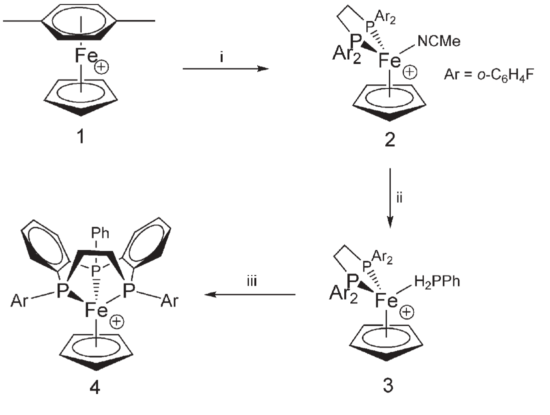
Crown ethers and their nitrogen and sulfur analogues are well known and widely used in coordination chemistry. In contrast, the chemistry of phosphacrowns is much less developed, one of the contributing factors being undoubtedly the high inversion barrier of tertiary phosphorus centres and the existence of *syn,syn* and *syn,anti* isomers, which necessitates either separation of isomers or stereoselective syntheses. A series of 11-membered rings with three donor atoms has been developed by Kyba *et al.*,[1] whereas Stelzer and co-workers synthesized a number of rings containing four phosphorus atoms,[2] and 1,5,9-triphosphacyclododecane was first synthesized by Norman *et al.* using a template assisted, radical catalyzed hydrophosphination, its chemistry being further developed in our laboratory.[3] We are interested in facially-capping triphosphines that may form kinetically robust complexes and it is noteworthy that triphosphorus macrocycles with smaller ring systems have not previously been explored.

Recently, we demonstrated the successful template synthesis of 1,5,9-triphosphacyclododecane[4a] (and tertiary derivatives) on a versatile cationic η^5-CpFe template, with which we have also succeeded in preparing the elusive[5] 1,4,7-triphosphacyclononane and some of its derivatives by metal-templated cyclization.[4b] To date, all these template assisted reactions result in P–C bond formation *via* intramolecular hydrophosphinations of alkenyl (vinyl or allyl) phosphines, in common with the few previously reported template assisted phosphorus macrocycle syntheses. The versatility of the Cp^{R}Fe$^+$ template allows incorporation of a range of different precursor phosphines and, by coupling trivinylphosphines with 1,2-diphosphinobenzenes, a benzannulated triphosphorus macrocycle with an *o*-phenylene bridge was obtained for the first time.[4c] With this system, we demonstrated that the rate of ring closure is greatly accelerated by added base, such as excess trivinylphosphine or a catalytic amount of triethylamine, indicating that the reaction is similar to a Michael addition. This prompted us to investigate nucleophilic P–C bond forming reactions, by attack of a coordinated phosphido anion on a suitable coordinated electrophile. C–F bond activation in the *ortho*-position of arylfluorophenylphosphines within the coordination sphere of transition metals has been observed in several cases already,[6] and arylfluorides show a low propensity to give side reactions, such as metal–halogen exchange, in their reactions with metal phosphides.[7] Thus, the *o*-halophenylphosphine group appeared an attractive potential electrophile for the formation of phospha-macrocycles with backbones consisting of *o*-phenylene–P–*o*-phenylene linkages and would allow us to expand the available P–C bond forming reactions for phosphorus macrocycle syntheses.

Few macrocycles with adjacent phenyl rings are known. Tribenzo-9-crown-3[8] and trithiaveratrylene[9] are synthesized by variants of the Ullmann coupling, and tribenzodithiaaza-macrocycles and tribenzodithiaoxa-macrocycles have been prepared recently by ring expansion of thianthryl salts.[10] All of these approaches are fairly specialized and do not lend themselves to extension to phosphorus and to the selective synthesis of the all-*syn* isomer.

The reactions and routes to the new compounds described below are summarized in Scheme 1; satisfactory microanalytical and spectroscopic data were obtained for all new compounds.†

The biphosphine complex {η^5-CpFe[(*o*-$C_6H_4F)_2PC_2H_4P$(*o*-$C_6H_4F)_2$](NCMe)}PF_6 (**2**) is prepared by visible-light photolysis of [CpFe(*p*-xylene)]PF_6 (**1**) in acetonitrile in the presence of the biphosphine. Coordination of the biphosphine ligand is evident from a coordination chemical shift of about +115 ppm in the $^{31}P\{^1H\}$-NMR spectrum (the free ligand has a ^{31}P chemical shift of −31.8 ppm), which is in good agreement with other [CpFe(phosphine)]$^+$ complexes;[4,5a,11] the presence of acetonitrile



Scheme 1 *Reagents and conditions*: (i) *hν*, $Ar_2PC_2H_4PAr_2$, MeCN; (ii) H_2PPh, 1,2-dichloroethane, 60 °C; (iii) 2 eq. $KOBu^t$, THF.

School of Chemistry, Cardiff University, Park Place, Cardiff, UK CF10 3AT. E-mail: edwardspg@cardiff.ac.uk; Fax: +44 (0)29 2087 4030; Tel: +44 (0)29 2087 4083

is confirmed by IR and ^{1}H-NMR spectroscopy. The coordinated acetonitrile is then exchanged with phenylphosphine by gentle heating in 1,2-dichloroethane, yielding compound **3**, following a previously reported route to mixed CpFe-biphosphine-monophosphine complexes.[11] Again, upon coordination the signal for the primary phosphine is shifted around 115 ppm downfield (the chemical shift of free phenylphosphine is −123 ppm) in the ^{31}P{^{1}H}-NMR spectrum, which appears as an A_2X pattern of a doublet and triplet assigned to the coordinated tertiary and primary phosphines respectively; the latter is further split into a triplet of doublets in the proton-coupled ^{31}P-NMR spectrum. The IR spectrum shows the disappearance of the band attributable to $\nu_{(CN)}$ and the presence of a band attributable to $\nu_{(PH)}$. Upon addition of two equivalents of base, the ring is then closed, giving rise to the 9-membered macrocyclic triphosphine complex (**4**). This reaction constitutes a rare example of a double coupling between a phosphinidene and a di-electrophile. In the proton-coupled ^{31}P-NMR spectrum, the disappearance of P–H coupling and a further downfield shift of all ^{31}P resonances, consistent with fused, 5-membered chelate rings, is observed.[12] The ^{31}P{^{1}H}-NMR spectrum appears as an A_2B pattern; the resonance assigned to the *o*-C_6H_4F functionalized phosphines (δ_A) is broadened by coupling to ^{19}F. Yields for all these reactions are essentially quantitative, the isolated yield of **4** based upon **1** is 75%.

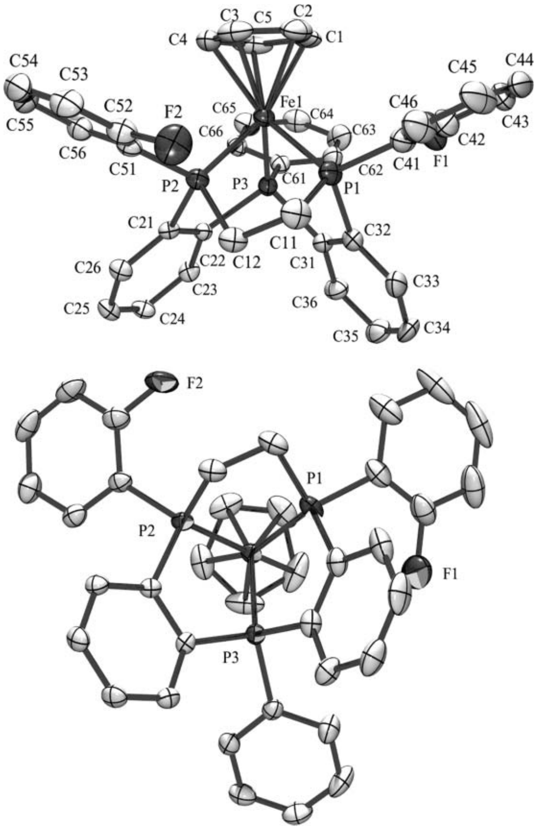


Fig. 1 Caption plots of **4** at 50% probability level (cation only), with hydrogens omitted for clarity. Top: a view across the P_3 coordination plane with the atom labelling scheme. Bottom: a view down the Fe–$Cp_{centroid}$ axis. Selected bond lengths (Å) and angles (°): Fe(1)–P(1): 2.152(1), Fe(1)–P(2): 2.160(1), Fe(1)–P(3): 2.180(1), P(1)–Fe(1)–P(2): 86.14(4), P(1)–Fe(1)–P(3): 87.07(4), P(2)–Fe(1)–P(3): 84.81(4), Fe(1)–P(1)–C(41): 123.0(1), C(11)–P(1)–C(32): 103.7(2).

Structural features of **4** are of interest since this macrocycle would be expected to display increased rigidity and better π-acceptor properties than its counterpart with an aliphatic backbone. The crystal structure supports the conclusions drawn from the spectroscopic and analytical data.‡ The major structural features can be discerned in Fig. 1. The Fe–P bond lengths are 2.156(1) Å (average, to the P-atoms with an *o*-C_6H_4F substituent) and 2.180(1) Å (to the P-atom with the phenyl group), indicating that back-bonding from the $CpFe^+$ fragment is still significant. The average Fe–P bond length in the cation $CpFe(P(OMe)_3)_3^+$ is 2.144 Å.[11] We have reported recently the crystal structure of a Cp*Fe complex of 1,4,7-triethyl-1,4,7-triphosphacyclononane,[4b] which shows fairly similar bond angles around the central atom but the average Fe–P bond length in this complex (with an aliphatic backbone) is significantly longer than in **4** at 2.192 Å. Thus, the present macrocycle appears to be a better donor. The rigid 5-membered chelate rings force all P–Fe–P angles to be around 86°, significantly less than the ideal octahedral angle of 90°. Steric pressure from the Cp ring causes the exocyclic phenyl groups to lie coplanar with the Cp ring and widens the Fe–P–C_{exo} angle to about 120°. The angle around the ring C_{endo}–P–C_{endo} is compressed to 104°.

The scope of this new ring-closure reaction is being explored, as is the chemistry of the macrocyclic ligands. Attempts to liberate the macrocycle from the template, including displacement by chelating agents (EDTA), strong donors (CN^-) and oxidation followed by digestion with base or scavenging agents (EDTA), have not been successful.

References

† Selected spectroscopic data: **2**: ^{1}H-NMR ($CDCl_3$): 7.70–7.00 (m, 16H, H_{Ar}), 4.29 (s, 5H, Cp), 2.92 (m, 2H, CH_2), 2.30 (m, 2H, CH_2), 1.40 (s, 3H, NCMe). ^{13}C{^{1}H}-NMR ($CDCl_3$): 165.9 (d, J_{C-F} = 62.0 Hz, CF), 163.4 (d, J_{C-F} = 62.3 Hz, CF), eight overlapping multiplets from 134 to 136 ppm, 127.5, 123.4 (m, CP), 120.0 (m, CP), 118.4 (t, J_{C-P} = 23.4 Hz, N*C*Me), 81.4 (s, Cp), 29.0 (m, CH_2), 5.5 (s, NC*Me*). ^{31}P{^{1}H}-NMR ($CDCl_3$): 85.4 (s). IR (KBr): 3076, 2935, 2262 (CN), 1598, 1568, 1468, 1437, 1260, 1214, 1123, 1076 cm^{-1}.

3: ^{1}H-NMR ($CDCl_3$): 7.70–7.00 (m, 20H, H_{Ar}), 6.57 (m, 1H, H_{Ar}), 4.84 (t, J_{P-H} = 347.4 Hz, J_{F-H} = 5.5 Hz, 2H, PH), 4.72 (s, 5H, Cp), 2.84 (m, 2H, CH_2), 2.51 (m, 2H, CH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$): 163.5 (d, J_{C-F} = 96.5 Hz, CF), 161.0 (d, J_{C-F} = 101.8 Hz, CF), twelve overlapping multiplets between 128 and 133 ppm, 124.7, 124.4, 116.3, 80.7 (s, Cp), 25.2 (CH_2). ^{31}P{^{1}H}-NMR ($CDCl_3$): 80.9 (d, $^2J_{P-P}$ = 51 Hz), −2.7 (t, $^2J_{P-P}$ = 51 Hz, $^1J_{P-H}$ = 347.4 Hz). IR (KBr): 3066, 2955, 2327 (PH), 1597, 1566, 1471, 1438, 1258, 1213, 1123, 1076, 937 cm^{-1}.

4: ^{1}H-NMR ($CDCl_3$): 7.85–7.05 (br m, 21H, H_{Ar}), 3.72 (d, $^3J_{H-P}$ = 0.8 Hz, 5H, Cp), 2.88 (m, 4H, PCH_2CH_2P). ^{19}F{^{1}H}-NMR ($CDCl_3$): −103.0 (br). ^{31}P{^{1}H}-NMR ($CDCl_3$): 127.7 (t, $^2J_{P-P}$ = 31 Hz), 123.8 (br, coupling to P and F unresolved). IR (KBr): 3051, 1600, 1570, 1473, 1434, 1260, 1210, 1109, 1078, 828, 758, 682 cm^{-1}. MS (APCI): 661 (M^+, 100%).

‡ Crystals suitable for X-ray analysis were grown by slow cooling of a solution of the tetraphenylborate salt of **4** in acetonitrile. The compound crystallizes with one molecule of acetonitrile in the asymmetric unit. The structure was solved with direct methods (SHELXS-97)[13] and refined against F^2 using all data (SHELXL-97).[14] Crystal data: $C_{63}H_{53}BF_2FeNP_3$, M = 1021.63 g mol^{-1}, triclinic, a = 11.956(2) Å, b = 12.718(4) Å, c = 18.674(8) Å, α = 69.91(2)°, β = 80.92(2)°, γ = 74.67(2)°, U = 2564.8(14) Å^3, T = 153(2) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo-Kα) = 0.437 mm^{-1}, R_{int} = 0.0345, 9289 independent reflections, 641 parameters, goodness-of-fit (on F^2) = 1.006, w$R2$ (all data) = 0.142, $R1$ ($I > 2\sigma(I)$) = 0.048 for 6312 reflections with $I > 2\sigma(I)$, highest peak/deepest hole 0.66/−0.48 e Å^{-3}. CCDC 140829. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613672a. Figures were drawn using Ortep for Windows and PovRay™.[15]

1 E. P. Kyba, C. W. Hudson, M. J. McPhaul and A. M. John, *J. Am. Chem. Soc.*, 1977, **99**, 8053; E. P. Kyba, A. M. John, S. B. Brown, C. W. Hudson, M. J. McPhaul, A. Harding, K. Larsen, S. Niedzwiecki and R. E. Davis, *J. Am. Chem. Soc.*, 1980, **102**, 139.

2 (*a*) R. Bartsch, S. Heitkamp, S. Morton, H. Peters and O. Stelzer, *Inorg. Chem.*, 1983, **22**, 3624; (*b*) D. J. Brauer, F. Gol, S. Heitkamp, H. Peters, H. Sommer, O. Stelzer and W. S. Sheldrick, *Chem. Ber.*, 1986, **119**, 349; (*c*) D. J. Brauer, F. Dörrenbach, T. Lebbe and O. Stelzer, *Chem. Ber.*, 1992, **125**, 1785; (*d*) T. Lebbe, P. Machnitzki, O. Stelzer and W. S. Sheldrick, *Tetrahedron*, 2000, **56**, 157.

3 (*a*) B. N. Diel, R. C. Haltiwanger and A. D. Norman, *J. Am. Chem. Soc.*, 1982, **104**, 4700; (*b*) B. N. Diel, P. F. Brandt, R. C. Haltiwanger, M. L. J. Hackney and A. D. Norman, *Inorg. Chem.*, 1989, **28**, 2811; (*c*) S. J. Coles, P. G. Edwards, J. S. Fleming, M. B. Hursthouse and S. S. Liyanage, *Chem. Commun.*, 1996, 293; (*d*) P. G. Edwards, J. S. Fleming and S. S. Liyanage, *Inorg. Chem.*, 1996, **35**, 4563.

4 (*a*) P. G. Edwards, K. M. A. Malik, L.-l. Ooi and A. J. Price, *Dalton Trans.*, 2006, 433; (*b*) P. G. Edwards, R. Haigh, D. Li and P. D. Newman, *J. Am. Chem. Soc.*, 2006, **128**, 3818; (*c*) P. G. Edwards and M. L. Whatton, *Dalton Trans.*, 2006, 442.

5 For previous unsuccessful attempts see: (*a*) D. C. R. Hockless, Y. B. Kang, M. A. McDonald, M. Pabel, A. C. Willis and S. B. Wild, *Organometallics*, 1996, **15**, 1301; (*b*) P. G. Edwards, J. S. Fleming, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1996, 1801.

6 A. C. Marr, M. Nieuwenhuyzen, C. L. Pollock and G. C. Saunders, *Inorg. Chem. Commun.*, 2006, **9**, 407. For early examples see: M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karaçar, D. R. Russell and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1996, 3215; M. J. Atherton, J. Fawcett, J. H. Holloway, E. G. Hope, D. R. Russell and G. C. Saunders, *J. Organomet. Chem.*, 1999, **582**, 163.

7 K. Issleib, A. Tzschach and H.-U. Block, *Chem. Ber.*, 1968, **101**, 2931.

8 T. Weiss, P. Schulz and G. Klar, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1974, **29**, 156.

9 T. Weiss and G. Klar, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1979, **34**, 448.

10 (*a*) K. Kim, H. J. Rim, H. O. Kim, S. W. Kim and Y. H. Rim, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **96**, 427; (*b*) K. Kim and M. N. Kim, *J. Heterocycl. Chem.*, 1997, **34**, 1; (*c*) K. Kim and M. N. Kim, *J. Heterocycl. Chem.*, 1998, **35**, 235.

11 H. Schumann, L. Eguren and J. W. Ziller, *J. Organomet. Chem.*, 1991, **408**, 361.

12 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

13 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

14 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

15 Ortep-3 for Windows, version 1.08: L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565; *Persistence of Vision™ Raytracer (PovRay™), version 3.6*, Persistence of Vision Pty Ltd., Williamstown, Victoria, Australia, 2004.