can be provided at this time. Work devoted to this issue is being carried out using labeled DMDA.

To our knowledge, the pore volume of the current MCM-41AT material (3.31 $cm^3 g^{-1}$) is the highest ever reported. Materials such as aerogels,[8] mesocellular silica foams,[9] and some hexagonal mesoporous silica prepared in the presence of amphiphilic triblock copolymers ("SBA-15")[10] exhibit pore volumes of up to 2.5 $cm^3 g^{-1}$, which is more than 30 % less than that of the current MCM-41AT. Because of its particularly narrow pore size distribution and very high surface area, this material has potential applications in separation or catalysis involving large molecules. Several important applications of such materials ranging from adsorption to catalysis and stabilization of nanoparticles are being developed in our laboratory. In addition, similar pore size expansion procedures using cubic MCM-48 silicas as starting materials are in progress.

Experimental Section

MCM-41 silica was prepared as follows: 3.848 g of tetramethylammonium hydroxide (TMAOH; 25 %) was diluted with water (37.1 g) before adding cetyl trimethyl ammonium bromide (CTAB; 5.466 g) under vigorous stirring. After 15 min, silica (Cab-O-Sil; 2 g) was added. The overall mixture composition was 1.0 SiO_2:0.317 TMAOH:0.45 CTAB:67 H_2O. The gel obtained after stirring for an additional 30 min was transferred into a Teflon-lined autoclave and heated statically under autogenous pressure at 80 °C for 40 h. The obtained materials were filtered, washed extensively, dried, and calcined at 540 °C, first in flowing nitrogen then in air. For post-synthetic pore size expansion, 0.8 g of the as-prepared sample was added to an emulsion of DMDA (1 g) and water (30 g) at RT. After about 1 h of stirring, the mixture was heated at 120 °C for 2 days under autogenous pressure. Further separation and calcination were carried out as described above.

Adsorption measurements were performed using a Coulter Ominorp 100 gas analyzer. Pore size distributions were calculated using the Kruk-Jaroniec-Sayari method.[11] XRD spectra were obtained on a Siemens D5000 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 0.15418$ nm). SEM images were recorded on a JEOL 840A microscope operated at an accelerating voltage of 10–20 kV. TEM images were obtained using a Philips 430 instrument operated at 100 kV. The specimen were embedded in an epoxy resin and ultrathin sections (approximately 60 nm) were cut and examined.

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Template Synthesis of the First 1,4,7-Triphosphacyclononane Derivatives**

Peter G. Edwards,* Paul D. Newman, and K. M. Abdul Malik

The small-ring tridentate macrocyclic ligands 1,4,7-triazacyclononane (tacn) and 1,4,7-trithiacyclononane have occupied a central role in the development of macrocyclic coordination chemistry.[1] Surprisingly, the related homoleptic phosphorus compound, 1,4,7-triphosphacyclononane is unknown in the literature and prior to our present study, the smallest triphosphorus macrocyclic ring system known is 11-membered and was prepared by a nonstereoselective, high-dilution method.[2] To date, the smallest (and indeed only) triphosphorus macrocycle prepared stereoselectively is based upon the 1,5,9-triphosphacyclododecane ([12]-ane-1,5,9-P_3) core by Norman and co-workers who developed a $Mo(CO)_3$ template-assisted synthesis[3] which has led to a number of derivatives and in the free ligand being released subsequently by us.[4] This method has not allowed formation of smaller ring systems;[5] we have consequently chosen to investigate alternative templates that may provide stereospecific routes to smaller facially capping triphosphorus macrocycles.

In this respect, we have studied reactions of cyclopentadienyliron "piano-stool" complexes which appear ideally suited to the formation of *fac*-trisphosphane derivatives. In addition, the sequential selective incorporation of diphosphanes followed by monophosphanes (which is difficult to control in the $M(CO)_3$ templates) is well established;[6] this should give rise to far greater flexibility in the synthetic methodology. Herein we report on the synthesis of the first triphosphacyclononane (9aneP_3) derivatives by an iron(II)-mediated intramolecular cyclization of 1,2-bis(phosphanyl)ethane and trivinylphosphane.

The new compounds and synthetic methodologies reported herein are summarized in Scheme 1. The precursor complex $[Fe(CH_3CN)(CO)_2(\eta^5\text{-}Me_5C_5)]BF_4$ (**1**) was prepared by the oxidative cleavage of the dimer $[\{Fe(CO)_2(\eta^5\text{-}Me_5C_5)\}_2]$ by $Cp_2Fe^+ BF_4^-$ as described by Astruc and Catheline.[7] UV photolysis of a 1:1 mixture of **1** and 1,2-bis(phosphanyl)ethane gives the diprimary phosphane acetonitrile cation **2** as the tetrafluoroborate salt. The $^{31}P\{^1H\}$ spectrum of **2** shows the expected singlet at $\delta = 7$, which appears as a triplet ($^1J_{P,H} = 343$ Hz) in the proton-coupled spectrum. Heating **2** with an equimolar quantity of trivinylphosphane in 1,2-dichloroethane or chlorobenzene at 70–80 °C over 2 h gave the diprimary monotertiary phosphane complex **3**. The latter was identified by the presence of a doublet at $\delta = 15.5$ and a triplet at $\delta = 49.5$ ($^2J_{P,P} = 47$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. When **3** was heated at 80 °C in 1,2-dichloroethane or chlorobenzene

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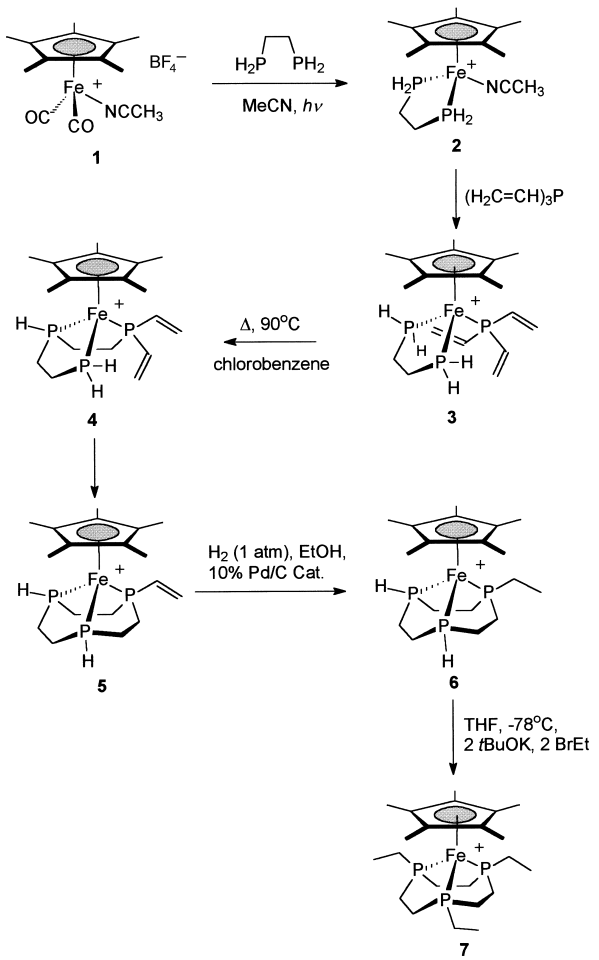

Scheme 1. Synthesis of the fully ethylated complex **7** from the precursor **1**.

for 24 h, the characteristic doublet and triplet in the $^{31}P\{^1H\}$ NMR spectrum were gradually replaced by a new set of peaks consistent with an AMX spin system at $\delta_A = 18.8$ (dd), $\delta_M = 85.0$ (dd), and $\delta_X = 95.2$ (t) (where $J_{A,M} = 36$, $J_{A,X} = J_{M,X} = 22$ Hz) and which correspond to the primary, tertiary, and secondary phosphanes, respectively, of the intermediate complex **4**. The assignments were confirmed by ^{31}P NMR spectroscopy, where the high- and low-field signals appear as a triplet and doublet, respectively ($^1J_{P(A),H} = 344$ Hz, $^1J_{P(M),H} = 348$ Hz). Continued heating led to the gradual disappearance of these resonance signals and the growth of two signals at $\delta = 108.2$ (d, $J_{A,X} = 5$ Hz, secondary phosphanes) and $\delta = 117.0$ (t, $J_{A,X} = 5$ Hz, tertiary phosphane) representing the expected A_2X spectrum of the fully cyclized product **5**. These low-field shifts are characteristic of coordinated phosphanes in fused five-membered chelate rings.[8] When complex **2** is heated with a 50% molar excess of trivinylphosphane in chlorohydrocarbons, complexes **4** and **5** form more rapidly suggesting an intramolecular base-catalyzed Michael-type addition of primary phosphane to the coordinated vinylphosphane adduct. This is further supported by the observation that the addition of triethylamine (≤ 1 molar equivalent) leads to complete conversion to **5** within 12 h.

Complex **5** is isolated as its air- and moisture-stable tetrafluoroborate salt in 50% yield. Catalytic hydrogenation of the vinyl group in **5** occurs readily at room temperature and 1 atm pressure with a Pd/C catalyst to give **6** in high yield (85%). Treatment of **6** with 2 molar equivalents of potassium *tert*-butoxide and excess bromoethane gives the fully ethylated complex $[Fe(\eta^5\text{-}Me_5C_5)(9aneP_3\text{-}Et_3)]^+$ (**7**), which was isolated as a mixed bromide/tetrafluoroborate salt in quantitative yield (Scheme 1), the bromide counterion originating from the bromoethane.

The structure of the $[Fe(\eta^5\text{-}Me_5C_5)(9aneP_3\text{-}Et_3)]^+$ ion is shown in Figure 1.[9] The structure clearly shows the nine-membered triphosphamacrocycle coordinating in a facial

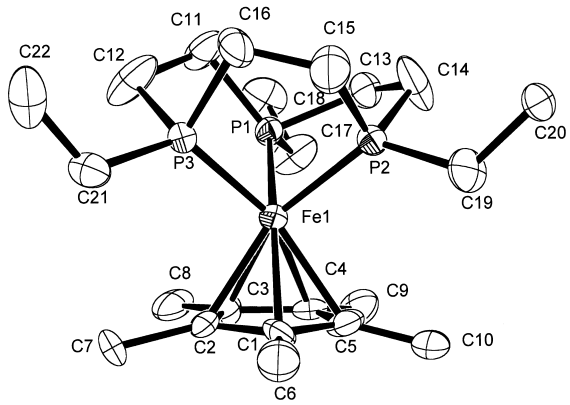

Figure 1. Structure of the cation **7** (Ortep representation[15]). Selected bond lengths [Å] and angles [°]: Fe-P1 2.1912(12), Fe-P2 2.195(2), Fe-P3 2.195(2); P1-Fe-P2 85.02(8), P1-Fe-P3 84.15(7), P2-Fe-P3 86.41(5), Fe-P1-C11 110.6(2), Fe-P1-C13 109.3(2), Fe-P1-C17 122.9(7), Fe-P2-C14 109.9(3), Fe-P2-C15 110.2(4), Fe-P2-C19 127.7(3), Fe-P3-C12 109.5(3), Fe-P3-C16 110.8(3), Fe-P3-C21 125.8(3).

fashion to the Fe^{II} center. The Fe–P bond lengths (av 2.194(2) Å) are very similar to those in related cyclopentadienyl complexes of acyclic phosphanes (e.g. in $[(1,2\text{-}C_6H_4\{PMePh\}_2)(PHMePh)(\eta^5\text{-}Cp)Fe]^+$, Fe–P av 2.179(2) Å[7a]) and the P-Fe-P angles (av 85.2(1)°) are somewhat compressed in comparison to those observed in related Mo^0 complexes of the 12-membered triphosphane analogue.[4b] The cyclopentadienyl methyl groups are displaced out of the C_5 ring plane away from the macrocycle indicating steric repulsion between the two rings; this is also manifested in the Fe-P-C(ethyl) bond angles (av 125.5(7)°).

In conclusion, the metal-templated cyclization of 1,2-bis(phosphanyl)ethane with trivinylphosphane at an Fe^{II} center has produced coordinated 1-vinyl-1,4,7-triphosphacyclononane. The vinyl substituent is readily hydrogenated to an ethyl group and this resulting disecondary phosphane macrocycle is then cleanly converted to the C_3-symmetrical triphosphorus macrocycle. This is the first reported synthesis of triphosphacyclononanes; the further chemistry of this and related compounds is being investigated. Preliminary studies indicate that this template system is indeed very versatile; details of variations in macrocyclic structure and substituents, and of the chemistry of derived complexes will appear in the near future.

Experimental Section

2: A solution of **1** (1.0 g, 2.42 mmol) and 1,2-bis(phosphanyl)ethane (2.30 mL of a 10% wt/v solution in toluene, 2.42 mmol) was irradiated for

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12 h with a Hanovia 125 W UV lamp. The solvent was subsequently removed and the resultant residue crystallized from hot tetrahydrofuran to give complex **2** as large red crystals. Yield = 0.9 g (82 %). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.23 MHz): $\delta = 7.0$; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.72$ (d br., 4H, $^1J_{PH} = 334$ Hz; PH_2), 2.46 (s, 3H; CH_3CN), 2.0 – 1.7 (m, 4H; CH_2), 1.56 (s, 15H; $CpCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 130.2$ (s; CH_3CN), 85.8 (s, C; Cp), 15.3 (m; CH_2), 8.6 (s; $CpCH_3$), 3.7 (s; CH_3CN); elemental analysis calcd for $C_{14}H_{26}NP_2BF_4Fe$ (%): C 40.71, H 6.36, N 3.39; found: C 40.5, H 6.4, N 3.2; IR (KBr): $\tilde{\nu} = 2315$ m (ν_{PH}), 2241 m (ν_{CN}).

5: A solution of [Fe(η^5-Me_5C_5)(CH_3CN)(1,2-bis(phosphanyl)ethane)]BF_4 (1.0 g, 2.42 mmol) and trivinylphosphane (0.28 mL, 2.50 mmol) in 1,2-dichloroethane (50 mL) was heated at 80 °C for 2 h. After cooling, the mixture was filtered and the volatiles removed in vacuo to give **3** as a yellow-orange solid. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.23 MHz): $\delta = 49.5$ (t, $J =$ 47 Hz), 15.5 (d, $J = 47$ Hz). The solid was dissolved in chlorobenzene (50 mL) containing triethylamine (0.1 mL, 0.72 mmol) and the solution heated at 80 °C for 12 h. After the mixture had been filtered, the solvent was removed in vacuo and the orange-yellow residue extracted into ethanol (150 mL). Removal of solvent gave **5** as a yellow solid which was crystallized from dichloromethane/diethyl ether at 4 °C to give bright yellow plates. Yield = 600 mg (50 %). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.23 MHz): $\delta = 115.2$ (t, $J = 5$ Hz), 106.2 (d, $J = 5$ Hz); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 6.38$ (m, 1H; PC*H*:CH_2), 6.04 (dd, 1H, $J = 12$ and 33 Hz; PCH:C*H*$_2$), 5.70 (t, $J = 18$ Hz, 1H; PCH:C*H*$_2$), 5.55 (d br., 2H, $J = 343$ Hz; PH), 2.1 – 1.5 (m, 12H; CH_2), 1.66 (s, 15H; $CpCH_3$); ^{13}C NMR ($CDCl_3$, DEPT, 100 MHz): $\delta = 134.0$ (d, 30 Hz; P*C*H:CH_2), 128.2 (d, $J = 5$ Hz; PCH:*C*H$_2$), 89.0 (s; Cp), 28.9 (dd, $J = 30$ and 5 Hz; CH_2), 23.3 (m; CH_2), 22.0 (dd, $J = 29$ and 5 Hz; CH_2), 10.9 (s; $CpCH_3$); IR (KBr): $\tilde{\nu} = 2335$ m (ν_{PH}); MS (APCI): m/z: 397 (100) [(η^5-Me_5C_5)FeL]$^+$; elemental analysis calcd for $C_{18}H_{32}BF_4P_3Fe$ (%): C 44.66, H 6.68; found: C 44.7, H 6.6.

6: Hydrogen was bubbled slowly through a solution of **5** (0.30 g, 6.2×10^{-4} mol) in 1 % aqueous ethanol containing 10 % palladium on carbon for five days. The catalyst was filtered off with the aid of celite and the solvent removed in vacuo to give a yellow solid. Yield = 0.30 g (quant.); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.23 MHz): $\delta = 124.6$ (t, $J = 7$ Hz), 108.7 (d, $J = 7$ Hz); ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 5.54$ (d br., 2H, $J = 343$ Hz; PH), 1.95 (m, 2H; C*H*$_2$CH$_3$), 1.9 – 1.0 (m, 12H; CH_2), 1.70 (s, 15H; $CpCH_3$), 1.20 (dt, $J =$ 14 and 7 Hz, 3H; CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT, 100 MHz): $\delta = 89.3$ (s; Cp), 27.4 (m; CH_2), 23.8 (m; CH_2), 22.7 (ddd, $J = 31$, 14, and 3 Hz; CH_2), 21.1 (d, $J = 18$ Hz; CH_2), 11.4 (s; $CpCH_3$), 9.6 (d, $J = 7$ Hz; CH_3); IR (KBr): $\tilde{\nu} = 2350$ m (ν_{PH}); MS (APCI): m/z: 399 (100) [(η^5-Me_5C_5)FeL]$^+$; elemental analysis calcd for $C_{18}H_{34}BF_4P_3Fe$ (%): C 44.47, H 7.06; found: C 44.4, H 7.0.

7: To a solution of **6** (100 mg, 2.1×10^{-4} mol) in THF (25 mL) at −78 °C was added potassium *tert*-butoxide (60 mg, 5.4×10^{-4} mol) and the mixture stirred for five minutes at this temperature before warming to 0 °C. The mixture was cooled to −78 °C and ethyl bromide (0.2 mL, 2.68 mmol) added thereto. The mixture was stirred at −78 °C for 30 min then at room temperature overnight. After the mixture had been filtered, the solvent was removed in vacuo to give a yellow solid. Yield = 110 mg (97 %); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 36.23 MHz): $\delta = 124.9$ (s); ^1H NMR ($CDCl_3$, 400 MHz): $\delta =$ 2.04 (br., 6H; C*H*$_2$CH$_3$), 1.85 – 1.45 (m, 12H; CH_2), 1.72 (s, 15H; $CpCH_3$), 1.22 (br., 9H; CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT, 100 MHz): $\delta = 87.2$ (s; Cp), 25.7 (m; *C*H$_2$), 20.2 (m; CH_2), 11.3 (s; $CpCH_3$), 8.4 (s; CH_3); MS (APCI): m/z: 455 (100) [(η^5-Me_5C_5)FeL]$^+$; elemental analysis calcd for $C_{22}H_{42}B_{0.5}Br_{0.5}F_2P_3Fe$ (%): C 49.04, H 7.87; found: C 49.0, H 7.8.

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[9] Crystal data for complex **7**, $C_{22}H_{42}P_3Fe(BF_4)_{0.4}Br_{0.6}$, $M_r = 537.99$, $T =$ 150(2) K, monoclinic, space group $P2_1$, $a = 8.479(2)$, $b = 11.493(2)$, $c = 13.015(3)$ Å, $\beta = 96.32(3)^\circ$, $V = 1260.6(5)$ Å^3, $Z = 2$, $\rho_{calcd} =$ 1.417 g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.971$ cm^{-1}, $F(000) = 565$, crystal size $0.2 \times 0.15 \times 0.12$ mm. All crystallographic measurements were made on an Enraf Nonius Kappa CCD area detector diffractometer. Data collection and processing were carried out using the programs COLLECT,[10] DENZO,[11] and maXus.[12] The unit-cell parameters obtained from all the reflections in a ϕ range of 15°. The structure was solved by direct methods (SHELXS-86)[13] and refined by full-matrix least-squares on F^2 using all unique data (SHELXL-93).[14] The non-hydrogen atoms were refined anisotropically. The structure was solved and refined in space group $P2_1$ (51/49 racemic twin) without imposing any crystallographic symmetry on the molecule, and only one CH_2 group (C17) being disordered. The structure can also be solved and refined in the space group $P2_1/m$ ($Z = 2$) to $R = 0.088$; in this case the molecule possesses a crystallographic mirror plane and the PCH_2CH_2P groups show conformational disorder. The refinement was therefore completed based on the space group $P2_1$ (final $R =$ 0.0581). The hydrogen atoms were included in calculated positions (riding model) with U_{iso} tied with the U_{eq} of the parent atoms. The ethyl carbon atom C17 was disordered but satisfactorily refined in two positions with 50 % occupancies; hydrogen atoms on C17 were ignored. The disorder model clearly indicates rotational freedom of the ethyl group; both positions giving realistic molecular conformations and only one is displayed in Figure 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142396. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). We thank Dr. M. Thornton-Pett of Leeds University (UK) for the data collection.

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Note added in proof: During publication of this manuscript we also reported on a similar iron template mediated macrocyclization of 1,2-arylene biphosphane precursors ("A New Nine-Membered Triphosphorus Macrocycle", *Organometallics* **2000**, *19*, 2652); this paper dealt with the formation of a rigid ring system related to the larger eleven-membered macrocycles previously described by Kyba and co-workers (see, for example: E. P. Kyba, R. E. Davies, S.-T. Liu, K. A. Hasset, S. B. Larsen, *Inorg. Chem.* **1985**, *24*, 4629). In view of the rigidity of the chelating 1,2-arylene biphosphane functionality in these macrocycles, they may be expected to offer substantially different coordination properties than the parent aliphatic ring system reported for the first time herein; they would also be expected to be electronically distinct. Indeed, the versatility of the new template methodology described is emphasized by the opportunity to introduce stereochemical control, which in turn enables synthetic routes to alternative macrocyclic structures and supports unprecedented ring-closure reactions. These observations are exemplified in our recent discussion of the formation of chiral, intermediate ring sizes (*Angew. Chem.* **2000**, *112*, 2834; *Angew. Chem. Int. Ed.* **2000**, *39*, 2722). Our oversight in not cross-referencing the three articles is partly corrected through this note, added in proof upon the request of the editor.

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