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Communications

A New Nine-Membered Triphosphorus Macrocycle

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Summary: The first nine-membered triphosphorus macrocycles based on an o-benzobis(ethane-1,2-diyl) core have been prepared in high yield by the coupling of 1,2-diphosphinobenzene with trivinylphosphine on a cationic (η^5-pentamethylcylopentadienyl)iron(II) template. Hydrogenation of the vinyl function followed by alkylation of the secondary phosphines gives the coordinated triethyl macrocycle, which has been structurally characterized.

There are no examples of nine-membered triphosphorus macrocycles in the literature. To date, the smallest 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 by a $Mo(CO)_3$-template-assisted synthesis.[1] This remains the only reported successful template method for the preparation of triphosphorus macrocycles. An 11-membered triphosphorus macrocycle had been prepared previously by Kyba et al.[2] nonstereoselectively via high-dilution methodology. In this paper, we report the first stereoselective synthesis of a nine-membered triphosphorus macrocycle containing an *o*-benzobis(ethane-1,2-diyl) core: (η^5-1,2,3,4,5-pentamethylcyclopentadienyl)-[*meso*-5-vinyl-2,5,8-triphosphabicyclo[7.4.0]trideca-9(1),10,12-triene]iron(II) hexafluorophosphate (**4**).

Our interest in studying nine-membered triphosphorus macrocycles arises from their anticipated ability to form very robust metal−phosphine complexes and their potential advantages in stabilizing otherwise excessively labile complexes of acyclic phosphine ligands. Stereochemical implications arising from these "face-capping" ligands will also be of interest in the properties and reactions of their complexes. In view of the wealth of chemistry surrounding triazacyclononane and its derivatives,[3] it is also surprising that related triphosphines remain unknown and synthetic routes to such macrocycles will be of value. Previous investigations into the formation of smaller ring sizes using vinylphosphines on $Mo(CO)_3$ and $Cr(CO)_3$ templates ended in failure.[4] It was clear that an alternative template methodology was required, and for this reason, we have investigated the $[\eta^5\text{-CpFeL}_3]^+$ class of complexes, the diphosphine monophosphine derivatives of which are well-documented.[5,6] Complexes of this type would provide an ideal environment for the preorganization of appropriate phosphine precursors (such as a bis(primary phosphine) and a tris(alkenyl)phosphine) to be cyclized in a facile process stereospecifically. The cyclopentadienyl-derived template also introduces the opportunity to manipulate both solubility and steric influences over the cyclization reactions, both of these opportunities being absent in templates based on $M(CO)_3$ units. Here we present preliminary results of our investigation of a new template system that enables the synthesis of nine-membered triphosphorus macrocycles for the first time.

The photolytically activated cleavage of carbonyl ligands in $[(CH_3CN)(CO)_2(\eta^5\text{-Me}_5C_5)Fe]PF_6$ (**1**)[6] in the presence of 1,2-diphosphinobenzene[7] in acetonitrile proceeded smoothly to yield $[(CH_3CN)\{(H_2P)_2C_6H_4\}(\eta^5\text{-Me}_5C_5)Fe]PF_6$ (**2**)[8] as a red solid (Scheme 1). In addition to satisfactory analytical and ^1H and ^{13}C NMR data, **2** is characterized by a triplet in its ^{31}P NMR spectrum in a position consistent with coordinated secondary arylphosphines. **2** was dissolved in chlorobenzene and heated to 90 °C with trivinylphosphine[9] for 12 h, yielding the yellow macrocyclic complex **4**.[10] The linear, monocoupled triphosphine intermediate **3** was observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction solution as three equally intense resonances due to an ABC spin

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[8] All manipulations were carried out under nitrogen with dry, oxygen-free solvents. **1** (1.16 mmol) was dissolved in MeCN (90 mL) in a 100 mL UV reactor, and 1,2-diphosphinobenzene (1.28 mmol) was added. The mixture was irradiated with a Hanovia 125 W UV lamp for 4 h at room temperature, during which time the yellow solution became deep red. All volatile materials were removed in vacuo. The residue was dissolved in dichloromethane (5 mL) and passed through a plug of basic alumina (1 × 2 cm), washing with dichloromethane until the eluant was colorless. The dichloromethane was removed in vacuo to yield **2** (88%). ^1H NMR (δ, ppm; $CDCl_3$, 400 MHz): 1.6 (s, 15H, CpCH_3), 2.05 (s, 3H, CH_3CN), 5.45 (d m, 2H, PH_2), 5.77 (d m, 2H, PH_2), 7.49 (m, 2H, Ph), 7.92 (m, 2H, Ph). ^{13}C NMR (δ, ppm; $CDCl_3$, 100 MHz): 3.8 (CH_3CN), 8.4 (CpCH_3), 87.3 (Cp), 126 ($CH_3$$C$N), 130 (CH), 133 (t, J_{C-P} = 6 Hz, CH), 136 (t, J_{C-P} = 44 Hz, C). ^{31}P NMR (δ, ppm; $CDCl_3$, 36.23 MHz): 13.0 (t, $^1J_{P-H}$ = 341 Hz). Anal. Calcd (found): C, 41.7 (41.9); H, 5.0 (5.3).

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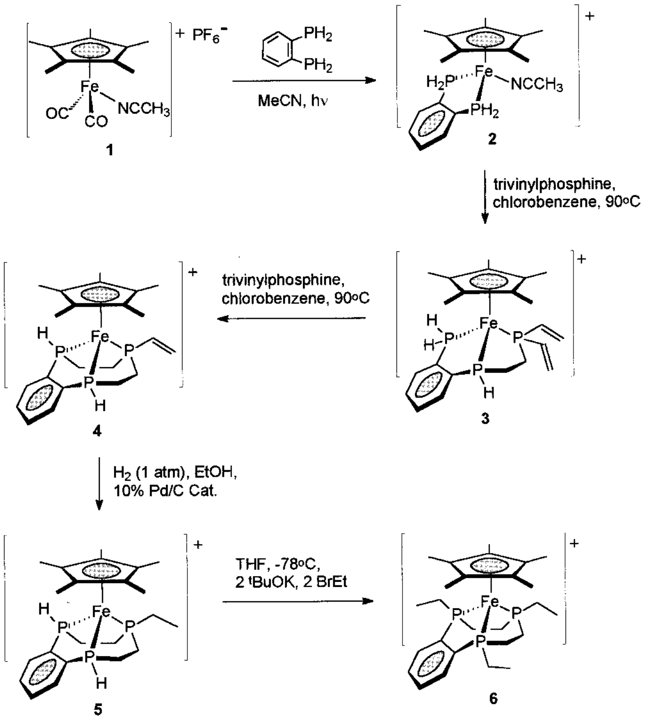
10.1021/om0002879 CCC: $19.00

Scheme 1



system (δ_A 23 ppm, δ_B 84 ppm, and δ_C 98 ppm) grew and decayed simultaneously as the reaction proceeded; the first two are assigned to the primary and secondary phosphines, respectively. The resonance due to P_A appears as a virtual triplet ($J_{AB} = 39.1$ Hz, $J_{AC} = 35.5$ Hz); the other two appear as double doublets ($J_{BC} = 19.5$ Hz). The intermediate was not isolated, as the subsequent coupling reaction to give the product macrocycle complex **4** proceeded in competition with the formation of the intermediate. **4** is readily soluble in most polar solvents such as tetrahydrofuran (THF) and dichloromethane but not in toluene or aliphatic hydrocarbons; it is indefinitely air-stable in the solid state. The ^{31}P{^{1}H} NMR spectrum consisted of an A_2B doublet and triplet (δ 106.4 and 118.35 ppm, respectively); the former being clearly identified as secondary phosphines due to further coupling to the directly bonded P−H proton in the ^{31}P NMR spectrum. The ^{1}H and ^{13}C NMR spectra were consistent with the structure proposed, and a P−H stretch was observed in the IR spectrum (ν_{P-H} 2318 cm^{-1}).

Catalytic hydrogenation of the vinyl function in **4** at atmospheric pressure in the presence of 10% palladium on carbon, afforded the monoethyl macrocycle **5**[11] in 78% yield. **5** is characterized by its ^{31}P{^{1}H} and ^{1}H NMR spectra. The former appears as a doublet and triplet due to the expected A_2B pattern; again the secondary phosphines are identified by further doublet splitting in the ^{31}P NMR spectrum; the latter shows the absence of the set of three vinyl multiplets between 5.7 and 6.4 ppm (observed in **4**) and the appearance of two new multiplets (δ 1.2 and 2.0 ppm) attributed to the ethyl group.

Deprotonation of the secondary phosphines by base followed by alkylation with bromoethane yielded (η^5-1,2,3,4,5-pentamethylcyclopentadienyl)[*meso*-2,5,8-ethyl-2,5,8-triphosphabicyclo[7.4.0]trideca-9(1),10,12-triene]-iron(II) hexafluorophosphate (**6**) as a yellow powder in 84% yield.[12] In the ^{31}P{^{1}H} NMR spectrum, a doublet and a triplet were observed due to the expected A_2B pattern at chemical shifts consistent with coordinated tertiary phosphines. In the ^{31}P NMR spectrum, no coupling due to directly bonded phosphorus protons was evident; a resonance due to these protons was also absent in the ^{1}H NMR spectrum, and two new signals (δ 0.87 (m) and 2.55 (m) ppm) corresponding to the methylene and methyl groups of the two new ethyl groups had also appeared. A band attributable to ν_{P-H} in the IR spectrum was also absent.

The nature of **6** was confirmed by an X-ray single-crystal structure determination;[13] a view of the molecular structure is shown in Figure 1. The structure clearly shows the conformation of the P_3 macrocycle with fused five-membered chelate rings. Distortions from regular coordination geometry are imposed by the rigid *o*-phenylene biphosphine part of the macrocycle, which holds the iron atom in a position almost coplanar with the P_2-*ipso*-C_2 plane (P1, P2, C11, and C16). The P1−Fe−P2 angle (86.89(9)°) is also greater than the

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(10) Preparation of **4** (typical): all manipulations were carried out under nitrogen with dry and degassed reagents. A 250 mL Schlenk flask fitted with a condenser was charged with **2** (4.29 mmol), chlorobenzene (100 mL), and trivinylphosphine (4.69 mmol). The solution was heated to 90 °C for 24 h. The solution was filtered, and all volatiles were removed in vacuo. The red residue was placed on a basic alumina column (1 × 25 cm) and washed through with dichloromethane until the eluant was colourless. The dichloromethane was removed in vacuo to yield a yellow powder, **4** (72%). ^{1}H NMR (δ, ppm; CD_2Cl_2, 400 MHz): 1.1 (br, 2H, CH_2), 1.67 (s, 15H, $CpCH_3$), 1.85 (br, 4H, CH_2), 2.1 (br, 2H, CH_2), 5.73 (t, 1H, $PCH{=}CH_2$), 6.08 (dd, 1H, $PCH{=}CH_2$), 6.11 (br d, 2H, P*H*, $J_{P-H} = 352$ Hz), 6.40 (m, 1H, $PCH{=}CH_2$), 7.46 (br m, 2H, Ph), 7.72 (br m, 2H, Ph). ^{13}C NMR (δ, ppm; CD_2Cl_2, 100 MHz): 9.6 ($CpCH_3$), 23.7 (t, CH_2, $J_{P-C} = 14$ Hz), 26.2 (d, CH_2, $J_{P-C} = 30$ Hz), 88 (Cp), 127 (d, $PCH{=}CH_2$), 129 (t, $PCH{=}CH_2$), 130 (CH, Ph) 132 (d, CH, Ph), 141 (t, C, Ph). ^{31}P{^{1}H} NMR δ ppm ($CDCl_3$, 36.23 MHz): 106.4 (d, 2P, $J_{P-P} = 5.5$ Hz), 118.4 (t, 1P, $J_{P-P} = 5.5$ Hz). ^{31}P NMR (δ, ppm; $CDCl_3$, 36.23 MHz): 106.4 (s), 118.4 (d, $^1J_{P-H} = 355$ Hz). IR (KBr disk): 2318 cm^{-1} (ν_{P-H}). APCI MS (CH_2Cl_2): *m*/*z* 444 (M^+). Anal. Calcd (found): C, 44.8 (44.9); H, 5.4 (5.3).

(11) Preparation of **5**: **4** (0.83 mmol) was dissolved in methanol (100 mL). 10% Pd on carbon was added (0.02 g), and hydrogen was bubbled through the solution for 4 days. The solution was filtered, and all volatiles were removed in vacuo. Dichloromethane (20 mL) was added to the residue; the solution was filtered and the solvent removed in vacuo, depositing yellow **5** (76%). ^{1}H NMR (δ, ppm; $CDCl_3$, 400 MHz): 1.05 (br, 2H, CH_2), 1.2 (m, 3H, PCH_2CH_3), 1.70 (s, 15H, $CpCH_3$), 1.85 (br, 4H, CH_2), 2.0 (m, 2H, PCH_2CH_3), 2.1 (br, 2H, CH_2), 6.12 (br d, 2H, P*H*, $J_{P-H} = 358$ Hz), 7.4 (br m, 2H, Ph), 7.7 (br m, 2H, Ph). ^{13}C NMR (δ, ppm; $CDCl_3$, 100 MHz): 9.3 (d, PCH_2CH_3), 11 ($CpCH_3$), 20 (d, PCH_2CH_3), 24 (m, CH_2), 25 (m, CH_2), 89 (Cp), 131 (t, CH, Ph) 132 (s, CH, Ph), 142 (t, C, Ph). ^{31}P{^{1}H} NMR (δ, ppm; $CDCl_3$, 36.23 MHz): 105.2 (d, 2P, $J_{P-P} = 8.6$ Hz), 123.6 (t, 1P, $J_{P-P} = 8.6$ Hz). ^{31}P NMR (δ, ppm; $CDCl_3$, 36.23 MHz): 105.2 (d, $^1J_{P-H} = 351.6$ Hz), 123.6 (s). IR (KBr disk): 2334 cm^{-1} (ν_{P-H}). APCI MS (CH_2Cl_2): *m*/*z* 446 (M^+). Anal. Calcd (found): C, 44.6 (44.5); H, 5.8 (5.7).

(12) Preparation of **6**: **5** (0.51 mmol) was dissolved in THF (50 mL) and cooled to −78 °C. Potassium *tert*-butoxide (1.01 mmol) was added. The solution was slowly warmed to room temperature with stirring. The yellow color slowly darkened to a deep orange. After 2 h the solution was cooled to −78 °C and bromoethane (2.0 mmol) was added. After it was stirred at room temperature for 24 h, the solution was yellow with a white precipitate visible. The solution was filtered, and all volatiles were removed in vacuo. The orange solid collected was dissolved in dichloromethane (5 mL) and this solution passed through a plug of basic alumina (1 × 4 cm) and washed thoroughly with dichloromethane until the elute was colourless. The dichloromethane was removed in vacuo, and yellow **6** was collected as a solid (0.43 mmol, 85.3%). ^{1}H NMR (δ, ppm; $CDCl_3$, 400 MHz): 0.28 (br m, 2H, CH_2), 0.87 (m, 6H, $PhPCH_2CH_3$), 1.22 (m, 3H, PCH_2CH_3), 1.7−2.0 (br m, 4H, CH_2), 1.83 (s, 15H, $CpCH_3$), 1.95 (m, 2H, PCH_2CH_3), 2.4 (d br m, 2H, CH_2), 2.55 (m, 4H, $PhPCH_2CH_3$), 7.47 (br m, 2H, Ph), 7.53 (br m, 2H, Ph). ^{13}C NMR (δ, ppm; $CDCl_3$, 100 MHz): 9 (s, $PhPCH_2CH_3$), 10 (d, PCH_2CH_3), 12 ($CpCH_3$), 18 (m, $PhPCH_2CH_3$), 22 (m, PCH_2CH_3), 34 (m, CH_2), 89 (Cp), 127 (t, CH, Ph) 131 (s, CH, Ph), 145 (t, C, Ph). ^{31}P{^{1}H} NMR (δ, ppm; $CDCl_3$, 36.23 MHz): 117.44 (d, 2P, $J_{P-P} = 11.7$ Hz), 128.26 (t, 1P, $J_{P-P} = 11.7$ Hz). APCI MS (CH_2Cl_2): *m*/*z* 502 (M^+). Anal. Calcd (found): C, 48.2 (48.4); H, 6.5 (6.4).

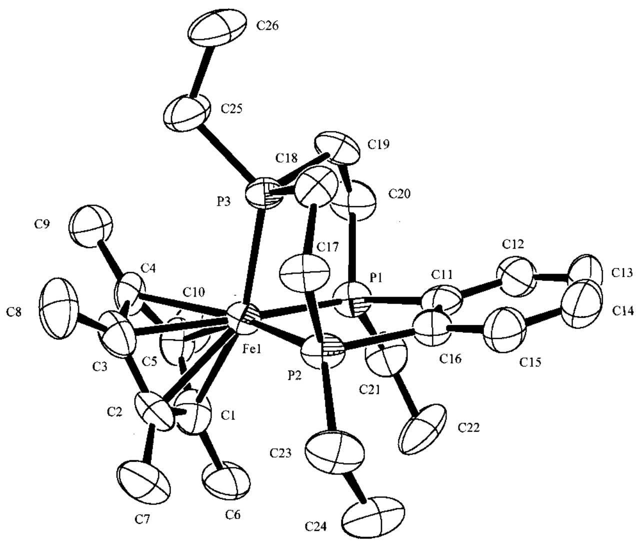

Figure 1. Molecular diagram of one cation of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−P1 = 2.162(2), Fe1−P2 = 2.193(3), Fe1−P3 = 2.224(2), Fe−Cp centroid = 1.738(8); Fe1−P1−C11 = 109.9(3), Fe1−P1−C20 = 108.1(3), Fe1−P1−C21 = 127.6(4), Fe1−P2−C16 = 109.1(3), Fe1−P2−C17 = 107.2(3), Fe1−P2−C23 = 130.9(4), Fe1−P3−C18 = 110.3(3), Fe1−P3−C19 = 109.4(3), Fe1−P3−C25 = 127.5(4).

other two P−Fe−P angles (average 83.75(9)°). The Fe−P distances to the *o*-phenylene phosphorus atoms are also significantly shorter (average 2.177(3) Å) than that to the unique phosphorus atom (Fe−P3 = 2.224(2) Å). These features suggest that the *o*-phenylene part of the macrocycle is more firmly attached to iron. The nonbonded P−P distances (P1−P2 = 2.994(3) Å, P1−P3 = 2.918(3) Å, and P2−P3 = 2.954(3) Å) show small variations with the *o*-phenylene P atoms farther apart; all these distances, however, are markedly shorter than related distances in 6-coordinate complexes of the 12-membered macrocycle [12]-ane-1,5,9-P_3 (in ([12]-ane-1,5,9-P_3Ph_3)Mo(CO)$_3$, the average nonbonded P−P distance is 3.536(6) Å).[14] The angles around the phosphorus atoms indicate substantial intramolecular repulsion between the pentamethylcyclopentadienyl group and the ethyl groups on phosphorus. Whereas the Fe−P−(ring C) angles are close to tetrahedral (average 109.0(5)°), all the ethyl groups are bent away from the iron atom to a similar extent (average Fe−P−(ethyl C) = 128.7(4)°). The methyl groups of the η^5-C_5Me_5 ring are also bent away from the macrocycle.

Thus, this new template method for the formation of triphosphorus macrocycles allows, in addition to the formation of smaller ring sizes not previously achieved, the sequential incorporation of different precursor phosphines which automatically result in selectively functionalized macrocycles in high yield. The secondary phosphine functions are also readily alkylated. We are currently studying further variations of this method in the synthesis of related triphosphorus macrocycles, the reactivity of these compounds, and routes to the stereospecific liberation of the free ligands.

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Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, H atom coordinates, bond distances, bond angles, anisotropic displacement coefficients, and torsion angles for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for **6**: $C_{26}H_{42}P_4F_6Fe$, M_r = 648.33, monoclinic, space group *Pn* (No. 7), a = 13.584(3) Å, b = 13.527(3) Å, c = 17.136(3) Å, α = 90.00°, β = 109.18(3)°, γ = 90.00°, V = 2974.0(11) Å^3, Z = 4, D_c = 1.448 Mg/m^3, μ(Mo Kα) = 7.75 cm^{-1}, F(000) = 1352, T = 150(2) K; orange-yellow prisms, 0.30 × 0.20 × 0.15 mm, 5590 reflections collected, 5590 unique reflections, R1(all data) = 0.0652, R1($I > 2\sigma(I)$) = 0.0598, wR2(all data) = 0.1737, wR2($I > 2\sigma(I)$) = 0.1623. A crystal of **6** suitable for X-ray structure determination was mounted in silicone oil. All crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least squares (SHELX97)[15] using all unique data. All non-hydrogen atoms are anisotropic, with H atoms included in calculated positions (riding model). Empirical absorption corrections were carried out by the DIFABS method.[16] Compound **6** crystallized with two crystallographically independent molecules in the asymmetric unit. There are no significant geometric differences between the two molecules, and the molecular structure of only one of them is shown in Figure 1.

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