A Novel Class of Polyphosphorus Donor Ligands based on a Calix[*n*]arene Skeleton: Structural Characterization of a Dinuclear Iron(0) Complex

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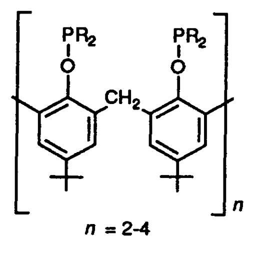
p-tert-Butylcalix[4]arene has been converted into the corresponding tetra(diphenylphosphinite) derivative which has a cone conformation; reaction with $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ led to binding of two $Fe(CO)_3$ units, as confirmed by X-ray analysis, at the surface provided by the four trivalent phosphorus donors.

The introduction of phosphorus binding sites leads to several advantages in the use of calix[*n*]arenes[1] in transition-metal chemistry.[2] These include: (*i*) the introduction of soft donor atoms to enable low-oxidation state metals to be incorporated into the calix[*n*]arene topology; (*ii*) location of the donor atoms on a sort of binding surface; (*iii*) combination of the peculiar properties of calix[*n*]arenes[1] and phosphorus-donor atoms in organometallic chemistry; and (*iv*) the possibility of building up polynuclear compounds in which the polynuclearity and geometrical proximity are not dictated by bridging donor atoms or metal–metal interactions.

The introduction of the phosphinite functionality into a calix[*n*]arene skeleton has been recently described.[3] We report here the synthesis and detailed characterization of a tetrafunctionalised *p-tert*-butylcalix[4]arene (L) I (n = 4, R = Ph) and the synthesis and structural characterization of the iron(0) complex $[\{Fe(CO)_3\}_2L]$.

The introduction of phosphorus-donor atoms on to the *p-tert*-butylcalix[4]arene (L′) skeleton has been achieved according to equation (1). This reaction can be carried out either in two steps, with the isolation of the lithium salt which can be obtained in a crystalline form, or as a one-pot reaction.† Compound L, isolated as a white crystalline solid, was fully characterised by analytical and spectroscopic data. Preliminary X-ray analysis[4] on rather low quality crystals confirms, however, the cone conformation in the solid state for the calix[4]arene skeleton, and an overall shape which is not much different from that in the complexed form (see below). The ^1H NMR spectrum at room temperature shows a unique bridging methylene as a well separated pair of doublets, as expected, without any coupling to phosphorus. A single phosphorus environment was observed in the ^{31}P NMR spectrum at δ 29.72.



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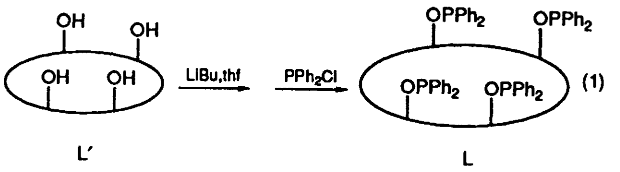
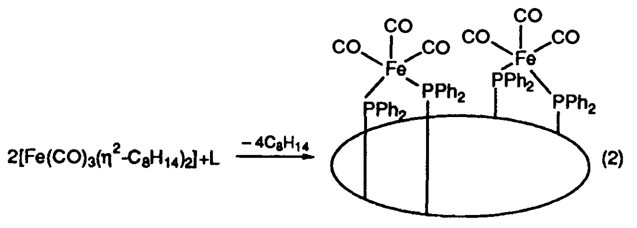


The introduction of complexing metals would be expected to freeze the flexible structure of the calix[4]arene. The reaction of L with the labile iron olefin carbonyl complex $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ in the presence of an excess of cyclooctene at low temperature [equation (2)]‡ led to yellow crystals of



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† Preparation of L. *n*-Butyllithium (125 mmol) was added to a tetrahydrofuran (thf) suspension (300 cm³) of *p-tert*-butylcalix[4]arene (20.0 g, 31.0 mmol) at room temperature. The suspension was then cooled to 0 °C and PPh_2Cl (22.8 cm³, 125.0 mmol) added. The light brown solution was heated at 60 °C for 2 h and then evaporated to dryness and the solid dissolved in toluene (300 cm³). The LiCl was filtered off and the filtrate reduced in volume to 75 cm³ and acetonitrile added until incipient precipitation of L. The solid was recrystallized from toluene–acetonitrile to give 73% of L which was dried for several hours *in vacuo* (Found: C, 79.10; H, 6.70; P, 8.80. $C_{29}H_{92}O_4P_4$ requires C, 79.75; H, 6.65; P, 8.95%). NMR (200 MHz, CD_2Cl_2, room temperature): ^1H, δ 7.33 (m, 40 H, Ph), 6.57 (s, 8 H, calixarene aryl), 4.00 (d, 4 H, CH_2), 2.13 (d, 4 H, CH_2), 1.03 (s, 36 H, Bu^t), *J*(H–H) 14.0 Hz; ^{31}P, δ 29.72.

‡ Preparation of Complex 1. An *n*-hexane suspension (100 cm³) of L (2.0 g, 1.45 mmol) was cooled at −60 °C and cyclooctene (5.0 cm³) added. The addition of $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ (1.10 g, 3.0 mmol) was also carried out at −60 °C, then the temperature was slowly raised to room temperature. The reaction occurs at −30 °C, with the solubilisation of L followed by precipitation of the microcrystalline yellow product $[\{Fe(CO)_3\}_2L]$ 1. The suspension was stirred for 24 h at room temperature, then the yellow microcrystalline solid was collected and dried at 40 °C (Yield 85%). Low temperatures and an excess of cyclooctene were employed to avoid secondary reactions leading to cluster formation from the $Fe(CO)_3$ fragments. Crystallization from toluene or benzene gave crystals suitable for X-ray analysis (Found: C, 74.10; H, 6.15; Fe, 5.70; P, 6.50. $1\cdot4C_6H_6$, $C_{122}H_{116}Fe_2O_{10}P_4$ requires C, 74.00; H, 5.88; Fe, 5.65; P, 6.25%). NMR (200 MHz, CD_2Cl_2, room temperature): ^1H, δ 7.80 (m, 8 H, Ph), 7.31 (m, 8 H, Ph), 7.22 (m, 28 H, Ph and calixarene aryl), 6.05 (d, 4 H, calixarene aryl), 5.11 (d, 2 H, CH_2), 4.00 (t, 1 H, CH_2), 3.93 (t, 1 H, CH_2), 3.43 (d, 2 H, CH_2), 1.88 (d, 2 H, CH_2), 1.00 (s, 36 H, Bu^t), *J*(H–H) 13.5, *J*(P–H) 3.71 Hz; ^{31}P, δ − 24.31. ν(CO)(Nujol): 2006s, 1944s and 1895s cm⁻¹.

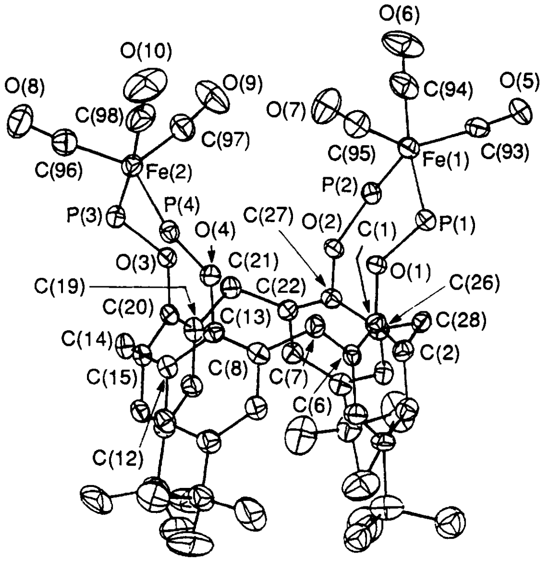

Fig. 1 An ORTEP[7] plot of complex 1 (30% probability ellipsoids). Phenyl rings connected to phosphorus atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe(1)–P(1) 2.214(2), Fe(1)–P(2) 2.218(2), Fe(1)–C(93) 1.742(8), Fe(1)–C(94) 1.761(9), Fe(1)–C(95) 1.779(9), Fe(2)–P(3) 2.229(2), Fe(2)–P(4) 2.222(2), Fe(2)–C(96) 1.739(8), Fe(2)–C(97) 1.766(9), Fe(2)–C(98) 1.745(10), P(1)–C(45) 1.851(5), P(1)–C(51) 1.832(5), P(2)–C(57) 1.840(6), P(2)–C(63) 1.824(5), P(3)–C(69), 1.821(5), P(3)–C(75) 1.841(5), P(4)–C(81) 1.836(4), P(4)–C(87) 1.808(7), P(1)–Fe(1)–P(2) 99.7(1), P(3)–Fe(2)–P(4) 99.3(1)

$[\{Fe(CO)_3\}_2L]$ **1**. The IR spectrum of **1** shows three very strong and sharp CO stretches at 2006, 1944 and 1895 cm^{-1}, consistent with a *cis*-$FeP_2(CO)_3$ fragment.[5] In the ^1H NMR spectrum the bridging CH_2 groups may serve as spectroscopic probes, as in more simplified diphenolic structures.[1,6] There are two different pairs of methylenes. The pair between the P_2Fe units appears as a pair of doublets at δ 3.43 and 5.11, while the pair between the chelating phosphorus atoms appear as a doublet at δ 1.88 and two triplets at δ 3.93 and 4.00, which correspond to the two protons pointing towards the two metallacycles. A single ^{31}P signal was observed at δ −24.31, significantly shifted from the free ligand value.

A simplified view of the structure of **1*** having approximate C_2 symmetry, is shown in Fig. 1. The O_4 and P_4 planes are almost parallel with a dihedral angle of only 0.4(1)°, similar to that observed in the free ligand.[4] The structure shows that the shape adopted by L is determined by functionalization of PPh_2 and by the steric hindrance at the phosphorus atoms which act as bidentate chelating ligands. The four P atoms would not be expected to bind to one metal centre and binding to two metal sites in a stepwise process is more probable. The di- or poly-nuclearity of complexes derived from L does not depend on the existence and strength of any metal–metal bonds or bridging ligands. The four oxygen and phosphorus atoms can be said almost to define a binding surface. The average distance of each oxygen from the O_4 plane is 0.010(5) Å, and that of phosphorus from the P_4 plane ranges from −0.057(2) to 0.074(2) Å. Complex **1** crystallizes with four molecules of C_6H_6, none of which are complexed by the calix[4]arene cavity. Each iron atom has a very similar pseudo-trigonal bipyramidal co-ordination geometry with the equatorial plane defined by two carbonyls and P(2) around Fe(1) and two carbonyls and P(4) around Fe(2). The displacement of atoms Fe(1) and Fe(2) from the equatorial planes [C(93),C(95),P(2)] and [C(97),C(96),P(4)] are 0.061(1) and 0.086(1) Å respectively. The structural parameters of the *cis*-$FeP_2(CO)_3$ fragments are very close to those found previously.[8] The steric hindrance due to the phenyl groups at phosphorus prevents close interaction of the iron atoms [Fe(1)••• Fe(2) 7.060(2) Å].

Functionalization and metal binding are primary factors in determining the calix[4]arene skeleton conformation. The use of a ligand such as L is conceivable for building up polynuclear structures and the generation of reactive metallic surface-type structures. These may be derived from the binding of metal carbonyls and subsequent treatment of the resulting complexes.

Acknowledgements

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* Crystal data for $1\cdot4C_6H_6$. $C_{98}H_{92}Fe_2O_{10}P_4\cdot4C_6H_6$, M = 1977.8, monoclinic, space group $P2_1/c$, a = 21.413(3), b = 19.256(3), c = 25.817(4) Å, β = 94.03(2)°, U = 106 18.8(28) Å^3, Z = 4, D_c = 1.237 g cm^{-3}, F(000) = 4160. Pale yellow prisms. Crystal dimensions 0.25 × 0.28 × 0.35 mm, λ = 0.710 69 Å, μ(Mo-Kα) = 3.88 cm^{-1}. The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropic, then anisotropic for all non-hydrogen atoms except for the methyl carbon atoms, which were found to be disordered over two positions with site-occupancy factor of 0.5 for the unprimed and the primed ones. All the aromatic rings were refined as regular hexagons having D_{6h} symmetry. One of the four independent benzenes of crystallization was found to be affected by disorder. The best fit was found by considering the molecule to be distributed over two positions with site-occupancy factors of 0.7 and 0.3 for the unprimed and the primed carbon atoms respectively. The hydrogen atom positions were all calculated and added as fixed contributions prior to the last cycle of refinement. For 7517 unique observed structure amplitudes [$I > 2\sigma(I)$ corrected for absorption] collected at room temperature on a Siemens AED diffractometer in the range 6 < 2θ < 46°, the R value is 0.062 (R' = 0.065). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, 1993, pp. xxiii–xxviii.