A bent ‘barocene’ based on metallated 2-pyridylphenylmethane: $[Ba\{\eta^5\text{-}PhCH(C_5H_4N\text{-}2)\}_2\{MeO(CH_2)_2O(CH_2)_2OMe\}(thf)]$

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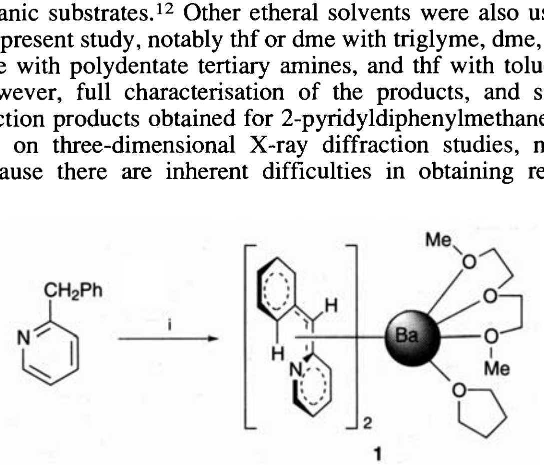
Reaction of barium metal with 2-pyridylphenylmethane in liquid ammonia, thf and diglyme at −50 °C then *ca.* 70 °C yields the metallated bent ‘open metallocene’ with the metal centre bound in an η^5 manner to the *ipso*-C, adjacent C-centres and nearest N, C centres, a tridentate diglyme and a thf molecule [Ba–C, N 2.983(6)–3.303(6) Å, Ba–O 2.766(4)–2.855(4) Å determined at −100 °C].

The chemistry of the heavier Group 2 elements has gained prominence in recent years mainly because of the potential of their compounds in chemical vapour deposition and sol–gel techniques, and the novelty of the resulting structures.[1] In the case of organometallic chemistry the use of substituted cyclopentadienyl ligands has dominated largely as a means to gain control over solubility and kinetic stability, and many of these compounds have been structurally authenticated.[1–7] Well characterised compounds involving other anionic unsaturated systems are limited to butadienediyl complexes of calcium and strontium, $[M(\eta^4\text{-}PhHC{=}CMeCMe{=}CHPh)\text{-}(thf)_4]$ (M = Ca, Sr),[8] and the so-called open metallocene pentadienyl calcium complex, $[Ca\{\eta^5\text{-}H_2CCBu^tCHCBu^tCH_2)(thf)]$.[9,10] No such substantiated complexes based on unsaturated systems have been reported for barium.

Herein we report the synthesis and structure determination of a new class of Group 2 open metallocenes based on metallated 2-pyridylphenylmethane bonding in an η^5 fashion to barium; the same ligand can in principle interact with metal centres in several other ways including as a chelate through the *ipso*-carbon and nitrogen centre. While some related compounds based on metallated triphenylmethane have been described, none have been fully characterised.[11–13]

Reaction of 2-pyridylphenylmethane and barium in liquid ammonia in the presence of thf and diglyme affords compound **1** as air sensitive, massive red crystals (Scheme 1).‡ The reaction is a variation of the method recently studied by Drake and Otway in using ethereal ammonia solutions as a means of activating alkaline-earth metals towards reaction with a range of organic substrates.[12] Other etheral solvents were also used in the present study, notably thf or dme with triglyme, dme, thf or dme with polydentate tertiary amines, and thf with toluene.[14] However, full characterisation of the products, and similar reaction products obtained for 2-pyridyldiphenylmethane, will rest on three-dimensional X-ray diffraction studies, mainly because there are inherent difficulties in obtaining reliable analytical data coupled with apparent variable amounts of ethereal species in the complexes.



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Scheme 1 *Reagents and conditions*: i, Ba/NH$_3$, thf, diglyme, −50° to 70 °C

As to the mechanism for the formation of compound **1**, earlier studies[12] would suggest that reduction of the organic substrate by the solvated electrons rather than metal centres is the primary process, followed by elimination of hydrogen and association of the resulting unsaturated anionic species with solvated Ba^{2+}. This is consistent with bulk ammonia affording solutions of the solvated electrons and dications for the heavier Group 2 metals in general.[12] Reaction of fluorene ($C_{13}H_{10}$) with barium in liquid ammonia gives an ammonia complex $[Ba(\eta^5\text{-}C_{13}H_9)_2(NH_3)_4]$ even when recrystallised from thf,[4] in contrast to the present case where ammonia displacement by thf, and diglyme must prevail.

Compound **1** is only sparingly soluble in hexane, benzene or toluene, and is moderately soluble in thf. The unsaturated anionic groups when attached to barium are chiral and thus with two groups present two diastereoisomers are possible, ignoring the labile ether donor ligands whose orientations can further complicate stereochemical assignment in solution. Attempts to resolve this diastereoisomer issue using variable-temperature ^{1}H NMR spectroscopy down to −80 °C were unsuccessful with the *ipso*-carbon protons remaining as a single resonance. Either a single isomer exists in solution or there is rapid interconversion of isomers on the NMR timescale which could involve contact or solvent separated ion-pair formation of the type that has been described for other unsaturated anionic barium species,[12] or intramolecular rearrangement. Even low-temperature X-ray diffraction studies failed to resolve the issue.

The solid-state structure of **1** at −100 °C, Fig. 1,§ shows the compound crystallises in a chiral space group, $P2_12_12_1$, with one bent, open metallocene molecule in the asymmetric unit; the metal is surrounded by one thf molecule, all three donor groups of the diglyme, and two symmetrically bound η^5-unsaturated anionic groups each through the *ipso*-carbon, the two immediate ring carbons, and their adjacent carbon and nitrogen centres. The two hydrocarbyl groups are in an *anti*-eclipsed conformation, *viz.* one of the *ipso*-carbon centres and associated proton of one group is directed towards the ‘open’ framework of the other; the angle subtended by the centroid of the two ligands is 112.7°. The overall stereochemistry of the metal centre with respect to the donor groups and these centroids is a distorted octahedron with the two centroids and thf oxygen centre *mer* with respect to the tridentate diglyme in a similar fashion to that in the related bent metallocene $[Ba(\eta^5\text{-}C_{13}H_9)_2(NH_3)_4]$.[4]

Unfortunately the phenyl and pyridyl rings are disordered such that the nitrogen centres and intraligand ‘symmetry’ related phenyl ring CH centres are disordered equally over two sites. Thus it is not possible to establish if one of the two diastereoisomers arising from the two metal η^5-ligand interactions is preferred in the solid state, and if so the absolute configuration for the crystal used for the diffraction studies. The disorder model comes from (*i*) electron density considerations, (*ii*) the absence of significant differences in Ba–η^5-C/N distances, (*iii*) each nitrogen centre must be part of an η^5-interaction to the metal centre, Scheme 1 and Fig. 1, otehwise there would be unfavourable inter-ring CH···HC interactions, (*iv*) C–C,N intraligand distances, and (*v*) the expected favourable electronegative nitrogen to barium interactions. While each η^5-ligand is symmetrically bound and shows conjugation through the *ipso*-carbon [C_{ipso}–C distances 1.41(1)–1.43(9) Å], the phenyl and pyridyl rings are tilted away from the metal centre (dihedral angles between the two rings in each ligand, 16.0, 21.8°). The Ba–C distances, 2.983(6)–3.303(6) Å, compare favourably with those in cyclopentadienyl compounds, *e.g.* 3.05–3.57 Å in $[Ba(\eta^5\text{-}C_{13}H_9)_2(NH_3)_4]$,[4] and are consistent with largely ionic character. The same also applies to the Ba–O-donor distances, 2.766(4)–2.855(4) Å, which are unexceptional.[15]

In conclusion we note that this ability for essentially coplanar phenyl and pyridyl rings attached to a sp^2-carbon centre offers scope for the synthesis of other η^5-bound metal complexes. In this context it is noteworthy that lithium can form η^3-azaallyl type complexes with $(C_5H_4N\text{-}2)\ (SiMe_3)_{2-n}H_n^-$ (n = 0,1).[16] Moreover, there are clearly many opportunities for heavier Group 2 element unsaturated anionic ligand chemistry.[10]

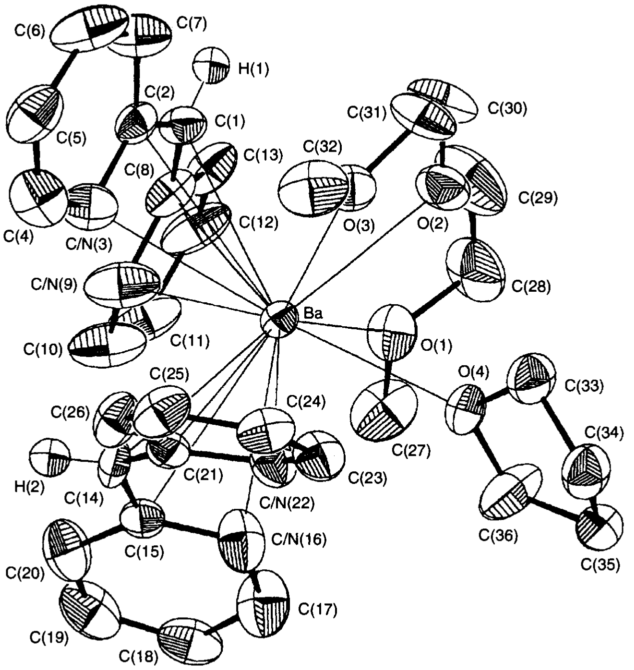

Fig. 1 Crystal structure of $[Ba\{\eta^5\text{-}PhCH(C_5H_3N\text{-}2)\}_2\{MeO(CH_2)_2OMe\}(thf)]$; the phenyl and 2-pyridyl ligands are disordered (50% occupancy). Selected distances (Å) and angles (°): Ba–C(1) 3.146(7), Ba–C(2) 3.245(6), Ba–C(3)/N(3) 2.983(6), Ba–C(8) 3.223(7), Ba–C(9)/N(9) 3.060(8), Ba–C(14) 3.138(7), Ba–C(15) 3.215(6), Ba–C(16)/N(16) 3.009(6), Ba–C(21) 3.303(6), Ba–C(22)/N(22) 3.156(6); Ba–2.761, Ba–Cnt(2), 2.798; Ba–O(1), 2.800(4), Ba–O(2) 2.855(4), Ba–O(3) 2.766(4), Ba–O(4) 2.819(4); Cnt(1)–Ba–O(1) 94.7, Cent(1)–Ba–O(2) 112.7, Cnt(1)–Ba–O(3) 94.2, Cnt(1)–Ba–O(4) 159.6, Cnt(2)–Ba–O(1) 122.0, Cnt(2)–Ba–O(2) 153.8, Cnt(2)–Ba–O(3) 111.7, Cnt(2)–Ba–O(4) 87.5, Cnt(1)–Ba–Cnt(2) 112.7; O(1)–Ba–O(2) 58.9(1), O(1)–Ba–O(3) 116.2(1) O(1)–Ba–O(4) 70.8(1), O(2)–Ba–O(3) 57.7(1), O(2)–Ba–O(4) 67.7(1), O(3)–Ba–O(4) 80.3(1). Cnt(1) and Cnt(2) represent the centroids of rings C(1)C(2)C/N(3)C(8)C/N(9) and C(14)C(15)C/N(16)C(21)C/N(22) respectively.

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Footnotes

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‡ Ammonia (*ca.* 30 ml) was condensed into a rapidly stirred mixture of barium (1.0 g, 7.0 mmol), 2-pyridylphenylmethane (1.7 g, 10 mmol), diglyme (0.94 g, 7.0 mmol) and thf (30 ml) at −78 °C. After 15 min the mixture was warmed to −50 °C, stirred for 2 h then refluxed for 2 h. On cooling to room temp., thf (50 ml) was added, and the resulting mixture filtered. After the addition of hexane (5 ml) massive red prisms deposited (1.5 g); further hexane gave a second crop (0.9 g). Overall yield 71%. Mp > 260 °C (decomp.); ^{1}H NMR (200 MHz, [$^2H_8$]toluene) δ 1.52 (4 H, m, CH_2 of thf), 2.98 (14 H, m, $OCH_{2,3}$ of diglyme), 3.63 (OCH_2 of thf), 4.86 (2 H, s, CHPh), 6.00–8.44 (18 H, m, aromatic CH). Found C 58.01, H 6.48, N 4.40. Calc. for $C_{34}H_{42}BaN_2O_4$: C 59.87, H 6.23, N 4.11%.

§ *Crystal structure determination* (T = 173 K; Rigaku AFC7R diffractometer, crystal mounted in oil). $[Ba\{\eta^5\text{-}PhCH(C_5H_4N\text{-}2)\}_2\{MeO(CH_2)_2O(CH_2)_2OMe\}(thf)]$: $C_{34}H_{44}BaN_2O_4$, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 16.463(6), b = 17.713(7), c = 10.894(6) Å, U = 3176(1) Å^3, D_c = 1.426, μ(Mo-Kα) = 12.88 cm^{-1} (no correction), Z = 4, Mo-Kα radiation, 3173 unique reflections [2740 observed, $I > 3.0\sigma(I)$], refinement on F^2, 383 parameters, R = 0.029, wR = 0.032 (sigma weights). Solution by direct methods with a refined Flack parameter of 0.009(7) for the refined absolute configuration. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/140.

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