Synthesis and structure of η^5-bonded pyrrolyl complexes of calcium and strontium

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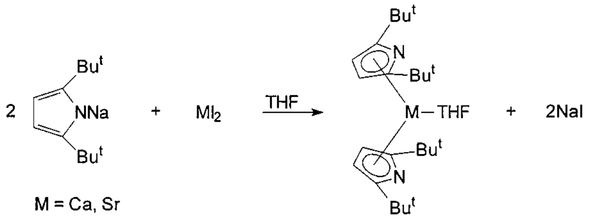
Calcium and strontium diiodide react with 2,5-di-*tert*-butylpyrrolylsodium in THF yielding [M(pyr*)$_2$(THF)] (M = Ca, Sr; pyr* = NC$_4$H$_2$Bu$^t_2$-2,5) for which NMR spectra and the X-ray structures confirm the η^5-bonding character of the ligands.

2,5-Di-*tert*-butylpyrrolyl (pyr*) complexes of some main group elements (Pb, Sn), transition metals (Ti, Fe, Co), and lanthanides (Nd, Sm, Tm, Yb, Lu) are already known.[1,2] In all these complexes, the pyr* ligand coordinates to the metal atom in an η^5-π-bonding fashion. The two bulky *tert*-butyl substituents at the 2,5-carbon atoms of the pyr* ring prevent a σ-donor coordination of the pyrrolyl nitrogen atom to the corresponding metal. Another coordination mode of the pyr* ligand was established for a binuclear zinc complex in which a pyr* ligand is bridging the two metal centers by forming a σ-N donor bond to one zinc atom and coordinating the other zinc atom by the 3,4-carbon atoms of the pyr* ring in an η^2-fashion.[3] Whereas a series of homoleptic alkyl-substituted cyclopentadienyl complexes of alkaline earth metals have been synthesized in recent years,[4] corresponding pyrrolyl (synonymous with azacyclopentadienyl) complexes of these metals have not been described until now. For this reason, we started to examine the coordination behaviour of pyr* towards alkaline earth metals and report here, the results we obtained for calcium and strontium.

The reaction of 2,5-di-*tert*-butylpyrrolylsodium with calcium diiodide or strontium diiodide (2:1 mole ratio, Scheme 1) in THF at room temperature afforded the mono-THF adducts of bis(2,5-di-*tert*-butylpyrrolyl)calcium and bis(2,5-di-*tert*-butylpyrrolyl)strontium [M(pyr*)$_2$(THF)] [M = Ca (**1**), Sr (**2**)], which were isolated in yields of 50% by crystallization from *n*-hexane at −20 °C. The colorless crystals of **1** melt at 113 °C, whereas those of **2** decompose at 200 °C, but sublime at 179 °C/0.5 mbar without decomposition. Both compounds are soluble in polar and non-polar solvents such as THF, diethyl ether, toluene, benzene, or *n*-hexane.



Scheme 1 Synthesis of the pyrrolyl complexes

In the NMR spectra of **1** and **2**, recorded in benzene-d$_6$, the ^{1}H/^{13}C resonances of the 3,4-CH groups of the pyr* ring show shifts of δ 6.34/105.2 for **1** and δ 6.30/104.5 for **2**. Since in the solution spectra of [Li(pyr*)(THF)$_2$][3] (the solid state structure establishes Li–N$_{pyr*}$ σ-bonds) and [Na(pyr*)][2b] (no solid state structure determined) the corresponding signals appear at δ 5.61/96.8 and δ 5.59/100.13, respectively, the low field shifts of the CH resonances of **1** and **2** are indicative of π-bonded pyr* ligands.

The single crystal X-ray structure analyses of **1** and **2** show monomers with a bent sandwich structure, thus unequivocally confirming the π-bonding nature of the pyr* ligands. Except for the different ionic radii of calcium and strontium, the two complexes are isostructural. Each structure shows two independent molecules, A and B, and each unit cell contains four molecules A, eight molecules B, and four disordered hexane (solvent) molecules. A and B differ only slightly in bond distances and angles. Molecules A possess a twofold rotation axis. In each of the four molecules **1**A,B (Fig. 1) and **2**A,B, the metal atom is seven-coordinated by two η^5-π-bonded pyr*

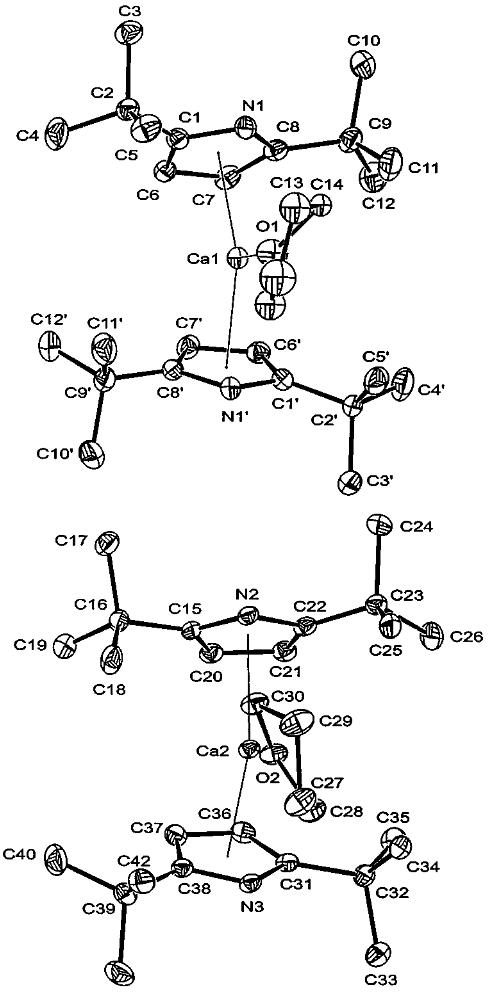


Fig. 1 ORTEP plot of the structure and numbering scheme of **1**, with 30% probability thermal ellipsoids. For clarity, all hydrogens are omitted. Selected bond lengths (Å) and angles (°) with estimated standard deviations of **1** and {**2**}: M–Cg 2.376(16)(A)/2.381(2)(B)/2.381(2)(B) {2.520(1)(A)/2.530(5)(B)/2.530(10)(B)}, M–O 2.373(4)(A)/2.389(3)(B) {2.538(6)(A)/2.533(4)(B)}; Cg–M–Cg 127.4(3)(A)/127.74(7)(B) {122.0(2)(A)/124.0(3)(B)}.

ligands and one THF molecule in a pseudo-trigonal planar arrangement. The pyr* rings are planar within limits of error with the 2,5-*tert*-butyl substituents placed above these planes away from the metal center. The pyr* ring planes form interplanar angles of 47.67 and 45.55° in **1**A and **1**B or 51.11 and 47.77° in **2**A and **2**B, with the ring nitrogen atoms situated at the 'open' side. The Cg–M–Cg angles (Cg defines the centroid of the pyr* ring) of 127° for **1**A,B or 122 and 124° for **2**A and **2**B are smaller than the $Cp_{centroid}$–M–$Cp_{centroid}$ angles in comparable cyclopentadienyl complexes, *e.g.* in $\{M[C_5H_3(SiMe_3)_2\text{-}1,3]_2(THF)\}$[5] [135° (M = Ca), 134° (M = Sr)], whereas the average M–Cg distances of 2.38 Å (**1**A,B) and 2.525 Å (2A,B) are in good agreement with the M–$Cp_{centroid}$ distances estimated for the above mentioned cyclopentadienyl complex [2.397 Å (M = Ca), 2.551 Å (M = Sr)]. The ring slippage towards the nitrogen atom of 0.126 Å (**1**A), 0.172 and 0.178 Å (**1**B), 0.178 Å (**2**A), and 0.214 and 0.207 Å (**2**B) indicates a certain tendency of the pyr* ligand towards an η^3-bonding mode. The third ligand, the O-coordinated THF is disordered in molecules A. The hexane solvent molecules do not have any contacts to the molecules of **1** and **2**.

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Notes and references

† *Syntheses*: the reactions were carried out in an atmosphere of purified argon (Schlenk techniques) using dry, oxygen-free solvents. 2,5-Di-*tert*-butylpyrrole[6] and 2,5-di-*tert*-butylpyrrolylsodium[2b] were prepared according to published procedures.

1: To a suspension of 0.9 g (3.06 mmol) CaI_2 in 50 ml THF 1.23 g (6.12 mmol) of $Na[NC_4H_2Bu^t{}_2\text{-}2,5]$ were added in portions. After stirring the mixture for 12 h at 25 °C, the THF was removed *in vacuo* (10^{-2} mbar) followed by the addition of 80 ml hexane to the remaining solid. The clear solution was decanted from undissolved NaI and concentrated to a volume of 20 ml. Crystallization at −20 °C yielded 0.68 g (47.4%) of colorless **1**. Mp: 113 °C. ^1H NMR (benzene-d_6, 200 MHz): δ 6.34 (s, 4H, H-3,4), 3.83 (m, 4H, THF) 1.36 (s, 36H, Bu^t), 1.18 (m, 4H, THF). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 153.51 (C-2,5), 105.19 (C-3,4), 70.64 (THF), 33.84 (*C*CH$_3$), 31.33 (C*C*H$_3$), 25.12 (THF). MS (EI, 60 °C, ^{40}Ca): *m*/*z* (%) 396 (8) $[M-THF]^+$, 218 (4) $[Ca(pyr^*)]^+$, 179 (21) $[(pyr^*)H]^+$, 164 (100) $[(pyr^*)H-Me]^+$.

2: This complex was synthesized in analogy to **1**, from 0.85 g (2.49 mmol) of SrI_2 and 1.0 g (5.0 mmol) of $Na[NC_4H_2Bu^t{}_2\text{-}2,5]$ in 50 ml THF. Crystallization from hexane (15 ml) at −20 °C yielded 0.65 g (50.6%) of colorless **2**. Subl: 179 °C (0.5 mbar); decomp. 200 °C. ^1H NMR (benzene-d_6, 200 MHz): δ 6.30 (s, 4H, H-3,4), 3.59 (m, 4H, THF) 1.38 (s, 36H, Bu^t), 1.14 (m, 4H, THF). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 153.05 (C-2,5), 104.51 (C-3,4), 69.60 (THF), 33.70 (*C*CH$_3$), 31.31 (C*C*H$_3$), 24.97 (THF). MS (EI, 220 °C, ^{88}Sr): *m*/*z* (%) 444 (1) $[M-THF]^+$, 266 (6) $[Sr(pyr^*)]^+$, 179 (22) $[(pyr^*)H^+]$, 164 (100) $[(pyr^*)H-Me]^+$.

‡ *Crystal data* for $C_{42}H_{72}Ca_{1.5}N_3O_{1.5}(C_6H_{14})_{0.5}$ **1** and $C_{42}H_{72}Sr_{1.5}N_3O_{1.5}(C_6H_{14})_{0.5}$ **2** (corresponding data for **2** in square brackets): M = 746.26 [813.54] monoclinic [monoclinic], a = 36.43(2) [36.693(4)], b = 14.843(3) [14.866(5)], c = 18.053(3) [18.172(10)] Å, β = 108.45(3) [108.61(3)]°, U = 9259(6) [9395(6)] Å, T = 163(2) [163(2)] K, space group $C2/c$ (no. 15) [$C2/c$(no. 15)], Z = 8 [8], μ = 0.225 [1.743] mm^{-1}, 7523 [7541] reflections measured, 7115 [7262] unique reflections (R_{int} = 0.0460 [0.0519]) used in all calculations. Final $wR(F^2)$ 0.1009 [0.1227] (all data) and 0.0730 [0.0594] [$I > 2\sigma(I)$]. An Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα radiation was used (λ = 0.71069 Å). The structures were solved using direct methods. Data were corrected for Lorenz, polarization and absorption effects.

CCDC 182/1411. See http://www.rsc.org/suppdata/cc/1999/2091/ for crystallographic files in .cif format.

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