The Syntheses of the Complexes $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot n\text{THF}$ and $(\eta^5\text{-}C_9H_7)Ln(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$ and the Crystal Structure Determination of $(\eta^5\text{-}C_5H_5)Pr(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$ and $(\eta^5\text{-}C_9H_7)Pr(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$

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$LnCL_3$ reacts with NaC_5H_5 and $K_2C_8H_8$ to yield the complexes $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot n\text{THF}$ (Ln = Pr, Nd, $n = 2$; Ln = Gd, $n = 1$) and $LnCl_3$ reacts with KC_9H_7 and $K_2C_8H_8$ to yield the complexes $(\eta^5\text{-}C_9H_7)Ln(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$ (Ln = Pr, Nd; $\eta^5\text{-}C_9H_7$ = indenyl); crystallography reveals $(\eta^5\text{-}C_5H_5)Pr(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$ and $(\eta^5\text{-}C_9H_7)Pr(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$ not to possess the parallel ring sandwich structure.

The cyclopentadienyl and cyclooctatetraenyl lanthanide complexes were synthesized by Jamerson *et al.* in 1974.[1] In subsequent years complexes of this kind were not reported further, nor were the structures determined. Although in 1989, Schumann *et al.* reported the syntheses and X-ray crystal structures of $(\eta^5\text{-}C_5Me_5)Lu(\eta^8\text{-}C_8H_8)$[2] and $\{\eta^5\text{-}C_5(CH_2Ph)_5\}Lu(\eta^8\text{-}C_8H_8)$.[3] In this communication, we report the syntheses of the complexes of $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot n\text{THF}$ and $(\eta^5\text{-}C_9H_7)Ln(\eta^8\text{-}C_8H_8)\cdot 2\text{THF}$ and their Ln = Pr crystal structures.

The complex $(\eta^5\text{-}C_5H_5)Gd(\eta^8\text{-}C_8H_8)\cdot\text{THF}$ was synthesized as follows: solid $GdCl_3$ (0.7 g, 2.66 mmol) and THF (25 ml) were mixed, and the solution left for 24 h. NaC_5H_5 (2.61 mmol) in THF was added at −70 °C, with stirring. After 5 h, $K_2C_8H_8$ (2.66 mmol) was added at room temperature and the reaction continued for 12 h. The solution was centrifuged to

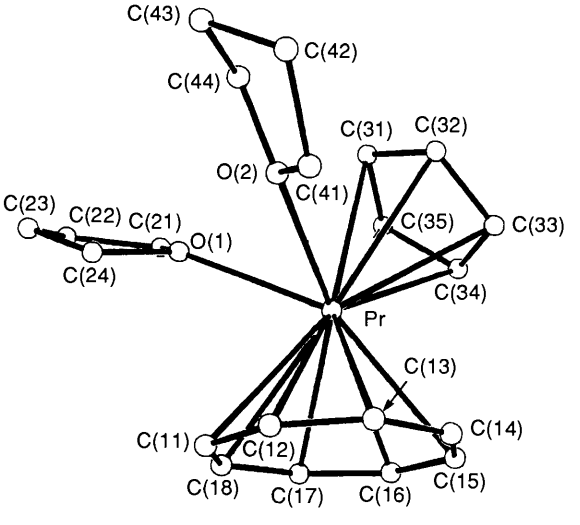

Fig. 1 Molecular structure of $(\eta^5\text{-}C_5H_5)Pr(\eta^8\text{-}C_8H_8)\cdot 2THF$. Important bond distances (Å) and angles (°): Pr–O(1) 2.582(6), Pr–O(2) 2.637(5), Pr–C(COT) COT = ring centroid of C_8H_8; Cp = ring centroid of C_5H_5, av. 2.736(8), Pr–COT 2.027, Pr–Cp 2.530, Pr–C(Cp) av. 2.805(5), COT–Pr–Cp 138.2, COT–Pr–O(1) 115.7, COT–Pr–O(2) 118.7, Cp–Pr–O(1) 96.8, Cp–Pr–O(2) 93.9, O(1)–Pr–O(2) 74.6.

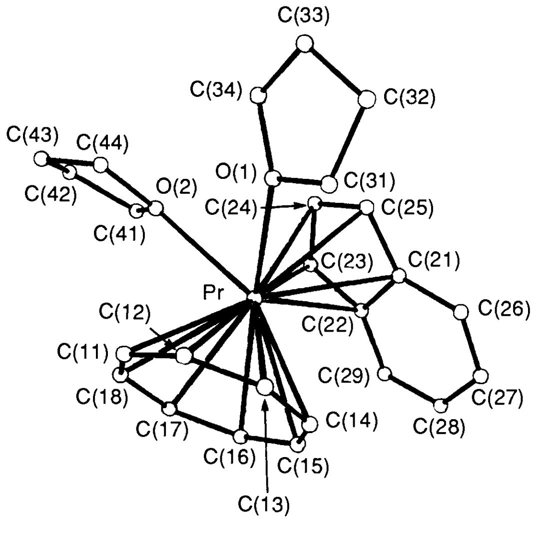

Fig. 2 Molecular structure of $(\eta^5\text{-}C_9H_7)Pr(\eta^8\text{-}C_8H_8)\cdot 2THF$. Important bond distances(Å) and angles(°): Pr–O(1) 2.673(4) Pr–O(2) 2.603(3), Pr–C(COT) COT and In denote centroid of C_8H_8 and C_9H_7 ring, respectively av. 2.72, Pr–COT 2.016, Pr–C(In) av. 2.87, Pr–In 2.607, COT–Pr–In 139.5, COT–Pr–O(1) 116.7, COT–Pr–O(2) 115.1, In–Pr–O(1) 94.3, In–Pr–O(2) 95.1, O(1)–Pr–O(2) 78.9(1).

remove solids, and hexane was added to the clear solution. Colourless crystals (31%) formed once the solution was cooled. The reaction is represented by eqn. (1).

$$GdCl_3 + NaC_5H_5 \xrightarrow{THF} C_5H_5GdCl_2\cdot nTHF \xrightarrow{K_2C_8H_8} (\eta^5\text{-}C_5H_5)Gd(\eta^8\text{-}C_8H_8)\cdot THF + NaCl + 2\ KCl \quad (1)$$

The complexes $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF$ (Ln = Pr, Nd) were synthesized by concomitant addition of NaC_5H_5 and $K_2C_8H_8$ to $LnCl_3$ (Ln = Pr, Nd) THF. Yellow crystals of the Pr complex (35% yield) were formed. Purple crystals of the Nd complex were formed in 30% yield, eqn. (2).

$$LnCl_3 + NaC_5H_5 + K_2C_8H_8 \xrightarrow{THF} (\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF + NaCl + 2\ KCl \quad (Ln = Pr, Nd) \quad (2)$$

The complexes $(\eta^5\text{-}C_9H_7)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF$(Ln = Pr, Nd) were synthesized by the same method as for $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF$, eqn. (3).†

$$LnCl_3 + KC_9H_7 + K_2C_8H_8 \xrightarrow{THF} (\eta^5\text{-}C_9H_7)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF + 3\ KCl \ (Ln = Pr, Nd) \quad (3)$$

The reaction of $LnCl_3$ (Ln = La, Ce, Pr, Nd) with NaC_5H_5 at a molar ratio of 1 : 1 in THF does not give $C_5H_5LnCl_2\cdot 3THF$ owing to the large ratio and coordination unsaturation of the lighter lanthanides.[4] Adopting the method shown in eqn. (2) avoids the disproportionation reaction to give $(\eta^5\text{-}C_5H_5)Ln(\eta^8\text{-}C_8H_8)\cdot 2THF$ (Ln = Pr, Nd).

The molecular structures are shown in Figs. 1 and 2.‡ The cyclooctatetraene behaves as a $C_8H_8^{2+}$ anion and has eight-fold symmetry with normal aromatic C–C bond distances and aromatic character. The $C_5H_5^-$ and $C_9H_7^-$ moieties also show aromatic character.

The average Pr–C (C_5H_5 ring) and Pr–C (indienyl) distances are 2.81 and 2.87 Å, respectively. The Pr–C (C_8H_8 ring) distances in structure **1** and **2** are 2.74 and 2.72 Å, respectively. The Pr–C (C_8H_8 ring) distance is 0.07 Å shorter than the corresponding distance in Pr–C (C_5H_5 ring). This is mainly due to the presence of eight Pr–C bonds between Pr^{3+} and $C_8H_8^{2-}$ and only five Pr–C bonds between Pr^{3+} and $C_5H_5^-$. However, the Pr–C (indenyl) distance is 0.06 Å longer than the Pr–C(C_5H_5 ring) distance owing to the steric hindrance of $\eta^5\text{-}C_9H_7$.

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† Elemental analyses values were satisfactory.

‡ *Crystal data* for: $(\eta^5\text{-}C_5H_5)Pr(\eta^8\text{-}C_8H_8)\cdot 2THF$, monoclinic, space group $P2_1$. a = 8.427(2), b = 9.835(2), c = 11.799(2) Å, β = 102.82(2)°. V = 953.58 Å^3, Z = 2, F(000) = 498e, μ = 28.36 cm^{-1}. Data were collected on a Nicolet XRD Corporation R3m/E four circle diffractometer at −70 °C using a graphite monochromator, Mo-Kα radiation. Scan type θ-2θ, 2θ_{max} = 62 °. 3375 Independent reflections were measured and 2917 reflections satsifying $I \geq 3\sigma(I)$ were accepted as being unique observations. Corrections were made for Lorentz and polarisation effects. The structure was solved by the heavy atom method and parameters were refined by block-matrix least-squares analysis with refinement on F. R = 0.038, R_w = 0.042. All calculations were carried out on a Eclipse S/140 computer.

Crystal data for: $(\eta^5\text{-}C_9H_7)Pr(\eta^8\text{-}C_8H_8)\cdot 2THF$, monoclinic, space group $P2_1$, a = 8.446(0), b = 10.083(2), c = 13.407(3) Å, β = 105.48(1)°, V = 1100.43 Å^3, Z = 2, D_c = 1.52 g cm^{-3}, F(000) = 490e, μ = 28.36 cm^{-1} (Mo-Kα). Data were collected on a Nicolet XRD Coorporation R3m/E four circle diffractometer at room temperature using a graphite monochromator, Mo-Kα radiation. Scan type θ-2θ, 2θ_{max} = 65°. 4418 Independent reflections were measured and 3340 reflections satisfying $I \geq 3\sigma$ (I) were accepted as being unique observations. The structure was determined by using the same method as $(\eta^5\text{-}C_5H_5)Pr(\eta^8\text{-}C_8H_8)\cdot 2THF$. The final R value is 0.033 and R_w is 0.030.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.