# Lanthanide organometallic chemistry based on the porphyrinogen skeleton: acetylene and ethylene bridging praseodymium and neodymium $\eta^5:\eta^1:\eta^5:\eta^1$-bonded to *meso*-octaethylporphyrinogen

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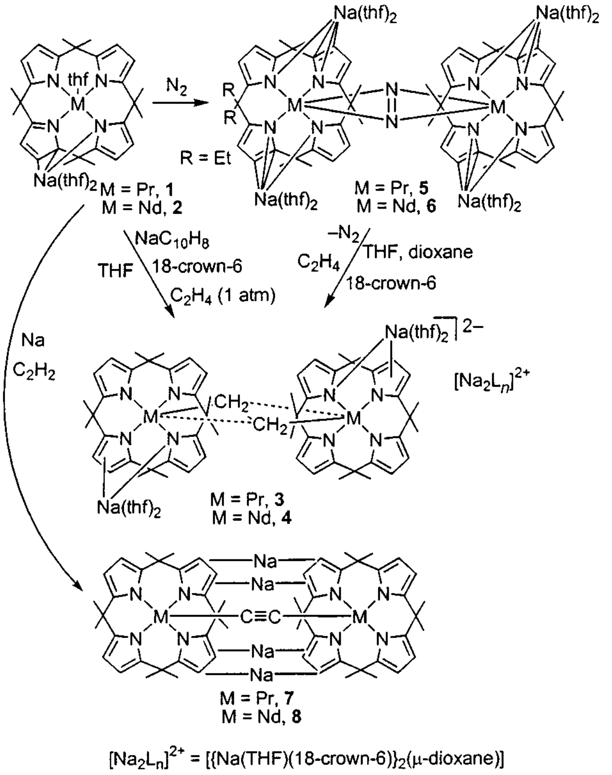
**The reaction of *meso*-octaethylporphyrinogen–lanthanide complexes, [{($\eta^5:\eta^1:\eta^5:\eta^1$-Et$_8$N$_4$)M}Na(thf)$_2$] [M = Pr, Nd], with NaC$_{10}$H$_8$ in an ethylene or acetylene atmosphere leads to the isolation of dimeric species, where the metals are bridged by the [C$_2$H$_4$]$^{2-}$ and [C$_2$]$^{2-}$ anions.**

Porphyrinogen tetraanions provide a unique binding cavity for electron deficient metals, *e.g.* early transition metals.[1] Such metals can exploit the $\eta^5:\eta^3:\eta^1$ bonding mode of each of the pyrrolyl anions according to the metal charge and electronic requirements. In addition, the electron-rich pyrrolyl anions can function as binding countercations in the structure.[1,2] Although the organometallic chemistry of divalent lanthanides[3] is largely confined to Sm(II)[4–6] and, to a lesser extent, Yb(II)[7] and Eu(II),[3] and based on cyclopentadienyl ligands,[4,5] it has been possible, using *meso*-octaethylporphyrinogen as an ancillary ligand, to generate the oxidation state (II) for lanthanides which are usually not available in this oxidation state,[8] and to make them very reactive in the presence of appropriate substrates.

The reduction of complexes **1**[9] and **2**[9] with sodium metal in the presence of 18-crown-6 led to the isolation of the dimetallaethane-like skeleton, where each lanthanide ion is supported by the porphyrinogen tetraanion. It is important that the reaction is carried out in the presence of 18-crown-6 because of its beneficial effect on crystallization and the higher stability of the ethylene complex in case of the ion-separated form. A particularly interesting synthetic route to complexes **3** and **4**† is the replacement of N$_2$ by ethylene from complexes **5**[9] and **6** (Scheme 1).[9] Such a replacement was successful when it was carried out in the presence of 18-crown-6. The solvation of the alkali countercations, though often neglected, can be, in some of the polynuclear compounds like those reported here, a determining factor on the energetics of the reaction. Complexes **3** and **4** have been obtained under such experimental conditions (see synthetic procedures) which rule out any reversible binding of ethylene to the metal in complexes **3** and **4**.

The structure of the anion in complex **4**‡ is shown in Fig. 1 along with selected structural parameters. The porphyrinogen moieties display a saddle-shaped conformation with the metals being $\eta^5:\eta^1:\eta^5:\eta^1$ bonded to them. The solvation of the two sodium cations linked to the dimetallic tetraanion is provided by two adjacent pyrrole moieties, which act, at the same time, as $\eta^5$ ligands for the lanthanide and $\eta^1$ for the sodium and *vice versa*; solvation is completed by two THF molecules.[2] The other sodium cations are bonded together by a dioxane, and they both complete their coordination spheres with an 18-crown-6 and a THF molecule. The C–C bond distance [C37–C37′, 1.49(2) Å] tells us that the original ethylene has been converted into a 1,2-dimetalla-ethane moiety. The M–C bond distances [M–C37, 2.497(7); M–C25, 2.790 Å][10] however, when compared with those of olefin complexes from the literature,[5,10] leave the possibility of assuming a $\mu$-$\eta^2:\eta^2$-bonding mode for the bridging [C$_2$H$_4$] fragment. The metals in complexes **3** and **4** are in the oxidation state (III) according to the magnetic moments, which are very close to those of the starting complexes **1** and **2**.

When the same synthetic method was applied to the reaction of **1** and **2** in the presence of acetylene, deprotonation of the substrate occurred instead of reduction of the metal, leading to **7**† and **8** (Scheme 1). The resulting acetylido complex **7**‡ is shown in Fig. 2 with selected structural parameters. The dimer



**Scheme 1**

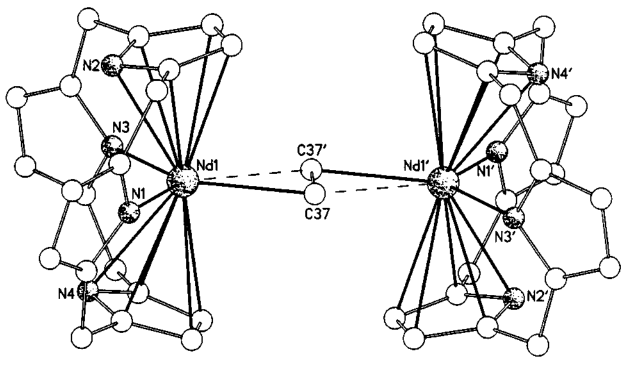


**Fig. 1** A view of complex **4**. Selected bond distances (Å): Nd(1)–$\eta^5$(Pyr)$_{av}$ 2.584(4), Nd(1)–$\eta^1$(Pyr)$_{av}$ 2.564(7), Nd(1)–C(37) 2.497(7), Nd(1)–C(37′) 2.790(7), C(37)–C(37′) 1.49(2). $\eta^5$(Pyr)$_{av}$ indicates the centroid. Prime indicates a transformation of $-x$, $-y$, $-z$. (*meso*-Ethyl groups omitted for clarity).

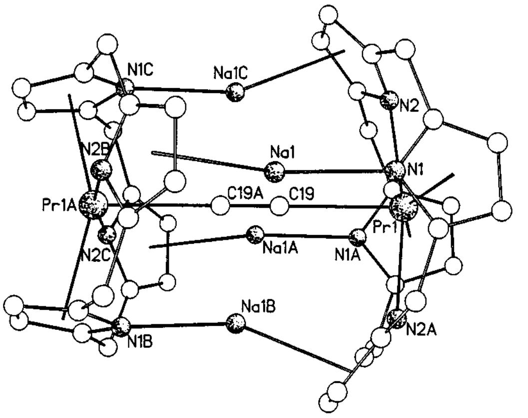


**Fig. 2** A view of complex **7**. Selected bond distances (Å): Pr(1)–$\eta^5$(Pyr) 2.492(1), Pr(1)–$\eta^1$(Pyr) 2.408(2), Na(1)–$\eta^4$(Pyr) 2.612(2), Na(1)–$\eta^1$(Pyr) 2.376(2), Pr(1)–C(19) 2.670(4), C(19)–C(19A) 1.250(8). $\eta^5$(Pyr) indicates the centroid. Letters A, B and C indicate symmetry operations of $-x + 1/2$, $-y + 1/2$, $z$; $y$, $-x + 1/2$, $-z + 1/2$; $-y + 1/2$, $x$, $-z + 1/2$, respectively. (*meso*-Ethyl groups omitted for clarity).

has $C_4$ symmetry and the porphyrinogen, in the saddle-shaped conformation, displays an $\eta^5:\eta^1:\eta^5:\eta^1$ bonding mode. The two metal–porphyrinogen moieties are bridged by the $C_2{}^{2-}$ $\mu$-$\eta^2:\eta^2$-bonded anion [C–C, 1.250(8) Å]. The rather long M–C bond distances [2.670(4) Å][11] account for the high coordination number of the metals when bonded to the *meso*-octaalkylporphyrinogen tetraanion.[1,2] The $C_2{}^{2-}$ anion is an appropriate spacer determining the cavity inside which are bound four Na cations, which are sandwiched by the two metalla-porphyrinogen moieties.[2d] Each Na is alternately bonded $\eta^1$ and $\eta^4$ to the two metalla-porphyrinogens, which assure complete solvation of all four alkali metal cations without the help of any additional solvent.[2]

The methodology reported in this paper represents a new entry into the organometallic chemistry of lanthanides for a number of issues: (i) the use of non-conventional ancillary ligands; (ii) the possibility to exploit the high reactivity of transient Ln(II) derivatives, *i.e.* for those metals which are not stable in this oxidation state; and (iii) the possibility to form M–C σ bonds readily directly from olefins and alkynes.

## Notes and references

† *Synthesis of* **4**. The addition of 18-crown-6 (2.61 g, 9.87 mmol) to a sky-blue suspension of **2** in THF (130 cm$^3$) caused the formation of a sky-blue solution. The addition of sodium metal (0.124 g, 5.38 mmol) under a $C_2H_4$ atmosphere did not cause any change until a small amount of naphthalene was added (0.172 g, 1.34 mmol). After 2 h a green suspension was obtained and was kept at room temperature until the complete disappearance of sodium metal. The solvent was evaporated to 10 cm$^3$, then pentane (40 cm$^3$) was added (5.3 g, 44%). Crystals appropriate for X-ray analysis were obtained from refluxing THF in the presence of a small amount of dioxane. (Found: C, 60.15; H, 8.25; N, 4.28. **4**·(18-crown-6)$_2$(THF)$_8$(dioxane), $C_{134}H_{220}N_8Na_4Nd_2O_{22}$ requires C, 60.15; H, 8.29; N, 4.19%). $\mu_{\text{eff}}$ = 3.18 $\mu_B$ at 298 K. The magnetic susceptibility was measured with an MPMS5 SQUID susceptometer. Complex **4** was obtained equally well from the reaction of **6** with ethylene in the presence of 18-crown-6. *Synthesis of* **7**. Sodium metal (0.089 g, 3.85 mmol) was added to a yellow suspension of **1** (2.94 g, 3.48 mmol) in THF (130 cm$^3$) under an acetylene atmosphere. The sodium reacted within 24 h at room temperature. Some white solid was filtered out and the solvent evaporated to dryness. The solid residue was collected using pentane (2.20 g, 72%). (Found: C, 61.40; H, 7.54; N, 6.23. **7**·4THF, $C_{90}H_{128}N_8Na_4Pr_2O_4$ requires C, 61.43; H, 7.33; N, 6.37%). $\mu_{\text{eff}}$ = 2.61 $\mu_B$ at 298 K. Crystals for X-ray analysis were obtained from refluxing benzene, as **7**·4$C_6H_6$.

‡ *Crystal data for* **4**: $C_{90}H_{132}N_8Na_2Nd_2O_4{\cdot}C_{36}H_{72}Na_2O_{16}{\cdot}2C_4H_8O$, $M$ = 2675.62, triclinic, space group $P\bar{1}$, $a$ = 15.530(3), $b$ = 15.847(4), $c$ = 16.647(5) Å, $\alpha$ = 113.08(3), $\beta$ = 111.51(2), $\gamma$ = 95.86(2)°, $V$ = 3358.8(15) Å$^3$, $Z$ = 1, $D_{\text{calc}}$ = 1.323 g cm$^{-3}$, $F(000)$ = 1420, $\lambda$(Mo-K$\alpha$) = 0.71070 Å, $\mu$ = 0.846 mm$^{-1}$; crystal dimensions 0.31 × 0.22 × 0.17 mm. Diffraction data were collected on a mar345 Image Plate Detector at 143 K. For 6344 observed reflections [$I > 2\sigma(I)$] and 767 parameters the final $R1$ index is 0.0842 ($wR2$ = 0.2489 for 8475 independent reflections). For **7**: $C_{74}H_{96}N_8Na_4Pr_2{\cdot}4C_6H_6$, $M$ = 1783.80, tetragonal, space group $P4_2/n$, $a$ = 15.2320(10), $c$ = 18.729(2) Å, $V$ = 4345.4(6) Å$^3$, $Z$ = 2, $D_{\text{calc}}$ = 1.363 g cm$^{-3}$, $F(000)$ = 1852, $\lambda$ (Mo-K$\alpha$) = 0.71070 Å, $\mu$ = 1.179 mm$^{-1}$; crystal size 0.38 × 0.31 × 0.24 mm. Diffraction data were collected on a mar345 Image Plate Detector at 143 K. For 3239 observed reflections [$I > 2\sigma(I)$] and 255 parameters the final $R1$ index is 0.0303 ($wR2$ = 0.0971 for 3801 independent reflections). CCDC 182/1333. See http://www.rsc.org/suppdata/cc/1999/1617/ for crystallographic files in .cif format.

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