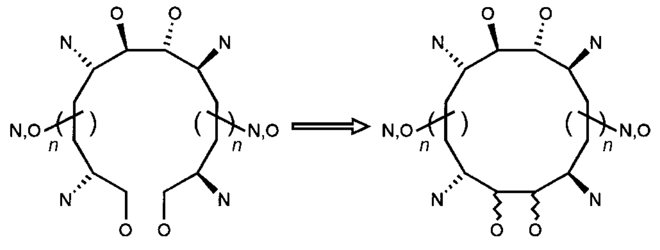

E **F**

poly(per)functionalized macrocycles (e.g. **F**), are intensively pursued projects.

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The π-Pyrrole Complexation of Alkali Metal Ions by Zirconium *meso*-Octaalkylporphyrinogens: Encapsulation of Li_4H_4 and Li_2O in Sandwich Structures[**]

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Much attention has been focused on methodologies that allow ionic compounds to be carried into a nonpolar organic phase, either as an ion pair or in an ion-separated form.[1] For alkali metal salts and polar organometallic compounds, two

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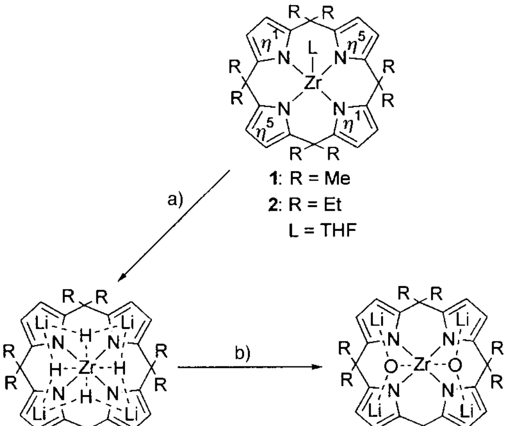
approaches have been devised for achieving their solubility in nonpolar organic solvents. The first one requires the use of a polyoxo crown-type macrocycle for complexing the alkali metal ion,[1] the second one uses bifunctional complexes.[2] In the latter case, the carrier binds the alkali metal ion at the basic center and at the same time the corresponding counterion at the acidic site. This event can occur either with the separation of the two ions, or keeping them in the tight ion-pair form.[2]

meso-Octaalkylporphyrinogen–zirconium assists a number of organic–organometallic transformations, in which it functions as a carrier of polar organometallic compounds.[2–4] The carrier properties depend on the electron richness of the pyrrolyl anion in metal-porphyrinogen complexes; it acts as a π-binding (η^5, η^3) site solvating alkali metal ions.[5, 6] The considerable difference between the π-binding strength of pyrrole units in porphyrinogen and those in the less basic porphyrins should be emphasized, since alkali metal ion π-complexation has never been revealed for the latter.[7, 8] We report here the best exemplification of the bifunctionality and the π-binding ability of **1** and **2**, which can complex lithium hydride and lithium oxide. One would expect that the reaction of **1** or **2**[3a] with LiH would lead to different results depending on the solvent conditions and the *meso* substituent R. In the case of **2** (R = Et), when the reaction was carried out in toluene with small amounts of THF, we observed the β-metalation of one of the *meso* ethyl groups.[4] In the absence of THF (except for that derived from the coordination to Zr in **1** and **2**), we isolated **3** and **4** as green crystalline solids[9] (see Scheme 1). The synthesis of **4** always presents more problems since the ethyl group undergoes metalation in the presence of even small amounts of THF. The methyl substituent prevents such a side reaction, and **3** was obtained much more cleanly. The rather low solubility of **3** and **4** in hydrocarbons and their reactivity with the polar solvents normally used prevented their characterization in solution. Both compounds have the same structure in the solid state, as seen from the X-ray structure determinations, and we report here the structure of **4**[10] (Figure 1).



Scheme 1. Complexation of lithium hydride and lithium oxide by zirconium-*meso*-octaalkylporphyrinogens. a) Toluene, excess LiH; b) H_2O, toluene, $-H_2$. Projection of the dimers **3**–**6** along the Zr–Zr axis (see Figures 1 and 2).

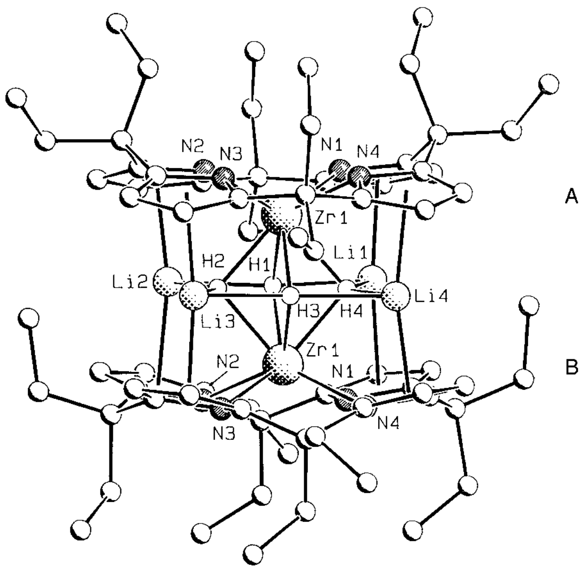


Figure 1. SCHAKAL drawing of complex **4**. Selected bond lengths [Å] and angles [°] (values in square brackets refer to moiety B): Zr1–N1 2.239(3) [2.244(4)], Zr1–N2 2.232(2) [2.240(3)], Zr1–N3 2.246(4) [2.245(3)], Zr1–N4 2.228(3) [2.243(2)]; N3-Zr1-N4 78.8(1) [84.4(1)], N2-Zr1-N4 136.8(1) [138.4(1)], N2-Zr1-N3 85.5(1) [81.2(1)], N1-Zr1-N4 85.7(1) [80.6(1)], N1-Zr1-N3 137.5(1) [137.5(1)], N1-Zr1-N2 79.3(1) [84.2(1)].

The two Zr–porphyrinogen moieties are arranged in an eclipsed sandwich structure that contains the Li_4H_4 plane, which is parallel to the N_4 cores (dihedral angles 2.0° [1.6°]) and perpendicular to the Zr···Zr axis (dihedral angle 1.5°). The two N_4 cores are planar, and parallel to each other (dihedral angle 0.5(1)°). The Zr ions are displaced by 0.817(1) [0.805(1)] Å from the N_4 plane (values in square brackets refer to molecule B). The Zr···Zr separation is 3.058(1) Å. Each hydride ion bridges two Zr atoms at distances ranging from 1.96 to 2.08 and two Li atoms at distances from 2.11 to 2.27 Å; the Li–H distance in lithium hydride is 2.04 Å.[11a] Both porphyrinogens assume a saddle-shaped conformation, with all the pyrrolyl anions η^1-bonded to Zr (Zr–N distances range from 2.228(3) to 2.246(3) Å) and η^5-bonded to lithium (Li-η^5(C_4H_2N), 2.152(12) Å).

The reaction of **1** with active proton sources should produce a variety of salts that are bifunctionally complexed. Among them a very significant one is lithium oxide, which is derived from the controlled hydrolysis of **3** and **4** in toluene. Complexes **5** and **6** have been obtained as pale yellow crystalline solids. The structure of **5** is shown in Figure 2.[10] In the centrosymmetric complex **5** the two eclipsed Zr–porphyrinogen moieties sandwich the Li_4O_2 plane that is parallel to the N_4 cores (dihedral angle 0.6(1)°) and perpendicular to the Zr···Zr′ axis (dihedral angle 0.4(1)°). The N_4 core is planar; the Zr atom protrudes by 0.798(1) Å towards the oxygen anion. The Zr···Zr′ and O···O′ separations are 3.315(1) and 2.470(3) Å, respectively. The oxygen atom bridges two Zr atoms and two Li atoms at distances of

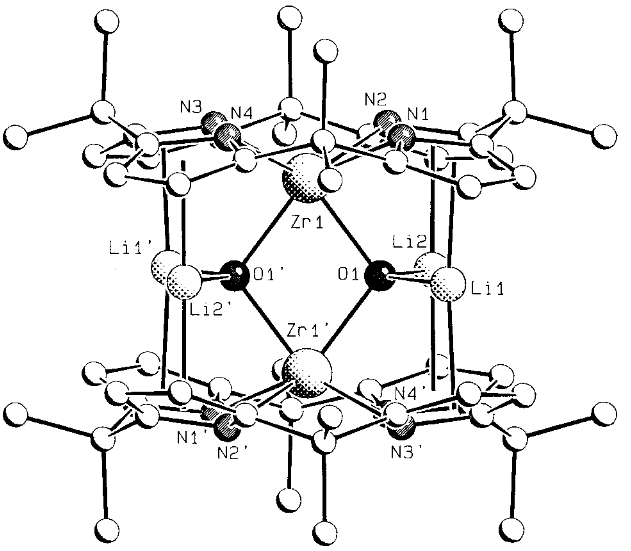


Figure 2. SCHAKAL drawing of complex **5**. Selected bond lengths [Å] and angles [°]: Zr1–O1 2.066(2), Zr1–O1′ 2.068(2), Zr1–N1 2.248(2), Zr1–N2 2.252(2), Zr1–N3 2.249(2), Zr1–N4 2.248(2), Li1–O1 1.994(6), Li2–O1 1.967(5); O1-Zr1-O1′ 73.4(1), Li1-O1-Li2 119.7(2), Zr1-O1-Zr1′ 106.6(1). Prime denotes a transformation of $0.5-x$, $0.5-y$, $-z$.

2.067(2) and 1.978(13) Å, respectively; the Li–O distance in lithium oxide is 1.98 Å.[11b] The rather long Zr–O bond length is expected owing to the absence of a π interaction (see the narrow Zr-O-Zr angle, 73.4(1)°). The porphyrinogen has a saddle-shaped conformation with all the pyrrolyl anions η^1-bonded to Zr (av Zr–N 2.249(1) Å) and η^5-bonded to lithium (Li–η^5(C_4H_2N) 2.181(4)).

Complex **5** reveals how a multicenter interaction led to the complexation of a molecular form of lithium oxide. The synthetic potential of these carrier properties of complexes of high-valent metal centers with *meso*-octaalkylporphyrinogens towards a variety of salts and polar organometallic compounds is currently under investigation.[2]

Experimental Section

1: $ZrCl_4$ (14.0 g, 37.0 mmol) was added to a suspension of $[Me_8N_4Na_4(thf)_2]$[12] (24.5 g, 37.0 mmol) in THF (200 mL). The mixture was stirred at room temperature for 15 h, then at 60 °C for 4 h. The white fine NaCl powder was filtered off and the orange THF solution was evaporated to dryness. The resulting yellow solid was collected in *n*-hexane, filtered, and dried (79 %). Elemental analysis calcd for **1** ($C_{32}H_{40}N_4OZr$): C 65.37, H 6.85, N 9.53; found: C 65.67, H 6.79, N 9.59. ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): $\delta = 6.18$ (s, 4H; C_4H_2N), 6.01 (s, 4H; C_4H_2N), 3.16 (m, 4H; THF), 1.86 (s, 12H; CH_3), 1.59 (s, 12H; CH_3), 0.89 (m, 4H; THF).

3: LiH (1.0 g, 125 mmol) was added to a suspension of **1** (7.33 g, 12.48 mmol) in toluene (50 mL) and the resulting mixture refluxed for 24 h. A dark blue suspension was obtained, which was then evaporated to dryness and the solid residue was extracted with freshly distilled toluene. A pale green crystalline, light-sensitive solid was collected (49 %). Elemental analysis calcd for **3** ($C_{56}H_{68}Li_4N_8Zr_2$): C 63.25, H 6.40, N 10.54; found: C 62.90, H 6.57, N 10.14. X-ray quality crystals were grown by slow cooling of a hot toluene solution of **3**. The low solubility of **3** and **4** in innocent solvents prevented their characterization in solution by NMR spectroscopy.

4: Compound **2** (6.52 g, 9.32 mmol) was heated up to 80 °C in the presence of an excess of LiH (0.30 g, 37.5 mmol) in toluene (200 mL) and stirred for two days. A green solution was obtained with a small amount of undissolved solid, which was filtered off. The solvent was evaporated to dryness and the solid collected with *n*-hexane (100 mL) (75 %). It was recrystallized from hot toluene. Elemental analysis calcd for **4** ($C_{72}H_{100}Li_4N_8Zr_2$): C 67.09, H 7.77, N 8.70; found: C 66.87, H 8.02, N 8.81.

5: A controlled hydrolysis reaction was carried out by allowing a solution of toluene (300 mL) and water (0.10 g, 5.56 mmol) to diffuse through a glass joint into a flask containing a suspension of **3** (3.00 g, 2.82 mmol) in toluene (50 mL). After two days a pale yellow solid was collected (73 %). Elemental analysis calcd for **5** ($C_{56}H_{64}Li_4O_2N_8Zr_2$): C 61.57, H 5.86, N 10.26; found; C 62.00, H 5.93, N 10.14. X-ray quality crystals were grown in a mixture of toluene and *n*-hexane. ^{1}H NMR ([D$_6$]benzene, 200 MHz, 298 K): $\delta = 5.93$ (s, 8H; C_4H_2N), 1.38 (s, 24H; Me). Complex **6** was prepared following the same procedure.

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[10] Crystal structure analysis of **4**: $C_{72}H_{100}Li_4N_8Zr_2$, $M_r = 1287.8$, triclinic, space group $P\bar{1}$, $a = 14.248(4)$, $b = 19.105(2)$, $c = 11.760(3)$ Å, $\alpha = 99.46(1)$, $\beta = 94.72(2)$, $\gamma = 89.32(1)°$, $V = 3146.9(13)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.359$ g cm^{-3}, $F(000) = 1360$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $\mu(Mo_{K\alpha}) = 3.73$ cm^{-1}; crystal dimensions $0.28 \times 0.35 \times 0.41$ mm. For 6922 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 295$ K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 50°$) the conventional R value is 0.036 ($wR2 = 0.101$ for the 9724 unique reflections having $I > 0$ used in the refinement). Crystal structure analysis of **5**: $C_{56}H_{64}Li_4N_8O_2Zr_2$, $M_r = 1091.4$, monoclinic, space group $C2/c$, $a = 21.691(2)$, $b = 12.911(1)$, $c = 18.942(2)$ Å, $\beta = 98.91(1)°$, $V = 5240.7(9)$ Å^3, $Z = 4$,

$\rho_{calcd} = 1.383$ g cm^{-3}, $F(000) = 2256$, Mo$_{K\alpha}$ ($\lambda = 0.71069$ Å, μ(Mo$_{K\alpha}$) = 4.38 cm^{-1}: crystal dimensions $0.23 \times 0.29 \times 0.34$ mm. For 2505 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 295$ K on a Rigaku AFC6S diffractometer ($6 < 2\theta < 50°$) the conventional R value is 0.026 ($wR2 = 0.043$ for the 4570 unique reflections having $I > 0$ used in the refinement). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101526 . Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] The synthesis and structure of [Me$_8$N$_4$Na$_4$(thf)$_2$] will be reported in a forthcoming paper. The alternative use of the sodium instead of the lithium porphyrinogen is dictated by easier separation of NaCl from the reaction mixture.

Rhodium-Catalyzed Intermolecular [4+2] Cycloaddition of Unactivated Substrates[**]

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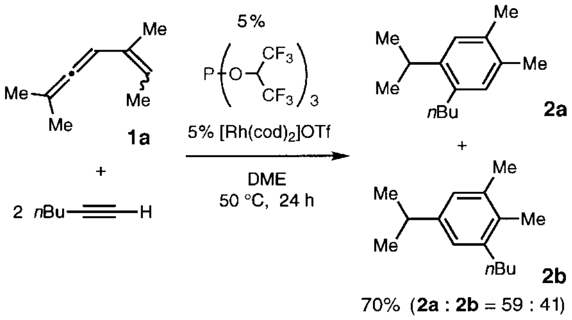
Cycloaddition reactions have played a prominent role in the construction of complex cyclic compounds.[1] In particular, [4+2] Diels–Alder cycloaddition is arguably the most important synthetic tool for the preparation of six-membered rings.[2] Virtually the only requirement for [4+2] cycloaddition reactions to be effective is that the two components have complementary electronic properties. This is typically achieved by employing an electron-rich 1,3-diene and an electron-deficient dienophile. In fact, 1,3-dienes and dienophiles in which the multiple bonds are not activated by electron-withdrawing or electron-releasing substituents fail to undergo cycloaddition except under the most severe conditions. The use of transition metal catalysts has proven to be a valuable solution to this limitation. Complexation of unactivated substrates to such catalysts promotes both inter-[3] and intramolecular[4] [4+2] cycloadditions. Recently, we developed new [4+1] and [4+2] cycloaddition reactions of unactivated vinylallenes based on our study of their bonding interactions with transition metals.[5–7] Here we report a rhodium-catalyzed intermolecular [4+2] cycloaddition reaction between a vinylallene and an ordinary alkyne which proceeds under mild conditions without the need for electron-withdrawing or electron-releasing substituents. With this method, 1,3,5-trisubstituted benzene derivatives can be synthesized in a highly regioselective manner.

We first examined the reaction of vinylallene **1a** with the unactivated dienophile 1-hexyne in the presence of [Rh(dppe)(cod)]PF$_6$ (dppe = 1,2-bis(diphenylphosphanyl)ethane, cod = (Z,Z)-1,5-cyclooctadiene), a potent catalyst for the [4+1] cycloaddition of vinylallene with carbon monoxide.[5a] However, [4+2] cycloaddition failed to occur even under forcing conditions,[8] which led us to examine the electronic perturbation of the catalyst.[9] Screening of various combinations of catalyst precursors and phosphorus ligands under different reaction conditions revealed that a complex prepared in situ from [Rh(cod)$_2$]OTf and P[OCH(CF$_3$)$_2$]$_3$, one of the most strongly electron-accepting ligands available, efficiently catalyzed the [4+2] cycloaddition.[10] 1,2-Dimethoxyethane (DME) was the solvent of choice. Thus, a mixture of **1a**, 1-hexyne (2 equiv), [Rh(cod)$_2$]OTf (5 mol %), and P[OCH(CF$_3$)$_2$]$_3$ (5 mol %) in DME was heated at 50 °C for 24 h (Scheme 1). Isomerization (i.e. aromatization) ensued after cycloaddition to afford the corresponding tetrasubstituted benzene in 70 % yield as a mixture of regioisomers (**2a** and **2b**).



Scheme 1. [4+2] Cycloaddition of vinylallene **1a** with 1-hexyne.

A variety of substrates were allowed to react under the standard reaction conditions to produce the corresponding aromatic compounds (Table 1).[11] It is noteworthy that synthetically useful results were obtained with substrates lacking directive heteroatom functionalities. For example, ethyne was found to be a reactive dienophile. Furthermore, when a terminal alkyne and a vinylallene lacking substituents at the vinylic terminus were used, 1,3,5-trisubstituted benzene derivatives (**2d**, **2f–j**) were produced in a highly regioselective manner.[12] Hydroxyl and chloro functionalities are compatible with the present reaction conditions (**2h**, **2i**). In the case of 1,7-octadiyne, a tethered bis-benzene derivative (**2j**) was obtained in 82 % yield, without formation of the [2+2+2] cycloadduct.[13] An internal alkyne could also be employed in the reaction. Vinylallenes in which the allenic terminus is monosubstituted (**1d**) and nonsubstituted (**1e**) gave lower yields of the corresponding cycloadducts (**2l**, **2m**). These results can be explained in terms of the preference for η^2 over η^4 coordination. With **1d** and **1e**, η^2 coordination at the allenic π bond distal to the vinyl group would be favored over η^4 coordination owing to steric reasons.[5a, 14]

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