Zirconium *meso*-Octaethylporphyrinogen as a Carrier for Sodium Hydride in Toluene: Zirconium–Sodium Bimetallic Hydride and Alkyls[†]

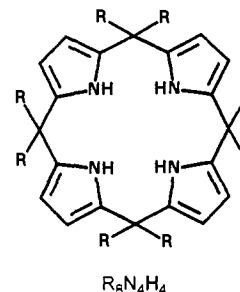**Denis Jacoby,[‡] Carlo Floriani,*,[‡] Angiola Chiesi-Villa,[§] and Corrado Rizzoli[§]**

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Abstract: The reaction of the tetralithium *meso*-octaethylporphyrinogen Et$_8$N$_4$Li$_4$(THF)$_4$ (**2**) with ZrCl$_4$(THF)$_2$ led to the formation of [(η^5-η^1-η^5-η^1-Et$_8$N$_4$)Zr(THF)] (**3**), containing two η^5 and two η^1 pyrrolyl anions bonded to zirconium. Such a complex acts as a bifunctional acid–base system able to dissolve ionic salts in their monomeric or dimeric form in hydrocarbon solution. The reaction of **3** with NaH in toluene led to the complexation of NaH via the interaction of the hydride with the Lewis acid Zr and the η^5 complexation of Na by the pyrrolyl anions in [{(η^5-η^1-η^1-η^1-Et$_8$N$_4$)-Zr}$_2$(μ-NaH)$_2$] (**4**). Complex **4** reacts with terminal olefins in toluene by inserting the C=C double bond in the Zr–H functionality and so forming, in the case of ethylene, [{(η^5-η^1-η^1-η^1-Et$_8$N$_4$)Zr(CH$_2$CH$_3$)}$_2$(μ-Na)$_2$] (**5**) and, in the case of 1-hexene, [{(η^5-η^1-η^1-η^1-Et$_8$N$_4$)Zr(CH$_2$(CH$_2$)$_4$CH$_3$)}$_2$(μ-Na)$_2$] (**6**). Similarly, **4** adds to PhC≡CH, which leads to the corresponding vinyl complex [(η^5-η^1-η^1-η^1-Et$_8$N$_4$)Zr-*trans*-(CH=CHPh)]$_2$ (**7**). The dimeric structure of **4** remains intact after the reaction giving **5–7**, however, in these products, major differences in the Na–porphyrinogen interaction modes can be seen. The reaction of **4** with C$_2$H$_4$ in THF led to a Zr–H porphyrinogen monomeric species identical to that formed from dissolving **5** in THF, [{(η^5-η^1-η^1-η^1-Et$_8$N$_4$)Zr(CH$_2$CH$_3$)}{Na(THF)$_2$}] (**8**). Crystallographic details: **3** orthorhombic, space group *Pbcn*, $a = 12.935(3)$ Å, $b = 12.704(3)$ Å, $c = 21.649(3)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $R = 0.037$; **4** monoclinic, space group *C2/c*, $a = 24.272(3)$ Å, $b = 12.640(4)$ Å, $c = 21.886(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 101.75(1)°$, $Z = 4$, $R = 0.053$; **5** triclinic, space group $P\bar{1}$, $a = 11.565(2)$ Å, $b = 12.598(2)$ Å, $c = 14.327(2)$ Å, $\alpha = 100.30(1)°$, $\beta = 103.65(1)°$, $\gamma = 113.73(1)°$, $Z = 1$, $R = 0.034$; **7** monoclinic, space group $P2_1/c$, $a = 13.815(2)$ Å, $b = 24.619(2)$ Å, $c = 13.981(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 108.73(1)°$, $Z = 2$, $R = 0.047$; **8** monoclinic, space group $P2_1/c$, $a = 11.264(1)$ Å, $b = 19.646(4)$ Å, $c = 20.609(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 101.18(2)°$, $Z = 4$, $R = 0.042$.

Introduction

Although porphyrinogen is a well-known precursor of porphyrin, its chemistry has never been explored. This is mainly due to its instability since it spontaneously aromatizes to give porphyrin.[1–3] This oxidation reaction is facile due to the presence of hydrogen atoms in the meso positions. However, a stable form of porphyrinogen has been known for more than a century, which is the form having two alkyl groups in each meso portion.[4]

R$_8$N$_4$H$_4$

Our recent investigations on the use of *meso*-octaalkylporphyrinogen in coordination and organometallic chemistry led us to discover some of its peculiar characteristics: (i) the tetraanionic form of the *meso*-octaalkylporphyrinogen stabilizes high-valent metals;[5] (ii) the conformational flexibility allows for close proximity between the peripheral aliphatic chains and the metal;[5,6] (iii) the *meso*-octaalkylporphyrinogen undergoes a reversible redox process involving the formation and cleavage of cyclopropane units.[7] What are of particular interest in the case of R$_4$N$_4$H$_4$ are the following: (i) the four independent and conformationally

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† Dedicated to Professor Gian Paolo Chiusoli on the occasion of his 70th birthday.

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flexible pyrrolyl anions can bind the metal η^1, η^3, or η^5 providing $4(n + 2)$ electrons ($0 \leq n \leq 4$) to the metal (considering the following contribution for each pyrrolyl anion: η^1, $n = 0$; η^3, $n = 0.5$; η^5, $n = 1$) depending on its requirement along the reaction pathway;[8] (ii) the pyrrolyl anions σ-bonded to the central metal atom maintain the ability to bind η^3 or η^5 to another metal ion on the periphery of ligand **1** (vide infra).[6]
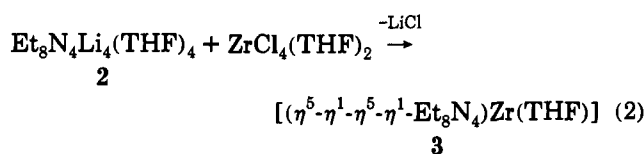
Contrary to the case of porphyrin, porphyrinogen is able to use also the periphery for binding either metals or substrates. The porphyrinogen used in this study is the *meso*-octaethyl derivative [$Et_8N_4H_4$] (**1**). The structure of **3** has been briefly communicated.[8]

Results and Discussion

Complexation of metals by *meso*-octaethylporphyrinogen was carried out in aprotic solvents using the lithiated form obtained by treating **1** with LiBu^n, as exemplified in reaction 1.

1, Et$_8$N$_4$H$_4$ →(LiBu^n / THF)   **2, Et$_8$N$_4$Li$_4$(THF)$_4$**   (1)
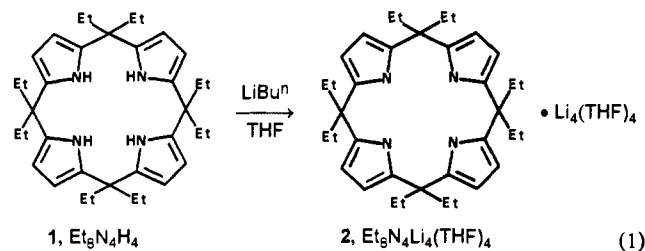
The lithiated form **2**, which is, structurally, a very complex aggregate,[9] is highly soluble in hydrocarbon solutions. The reaction of **2** with ZrCl$_4$ (reaction 2) gave almost quantitatively **3** as light-yellow crystals.

$$Et_8N_4Li_4(THF)_4 + ZrCl_4(THF)_2 \xrightarrow{-LiCl}$$
2

$$[(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)Zr(THF)] \quad (2)$$
3

Complex **3** is very air-sensitive. It is soluble even in aliphatic solvents. We did not succeed in removing the THF molecule bonded to zirconium. The reported bonding mode for the porphyrinogen to the metal corresponds to the structure observed in the solid state (Figure 1). The ^{1}H NMR spectrum in solution at room temperature is in agreement with the solid-state structure and shows two sets of different 3,4-pyrrolic protons. By raising slightly the temperature of the solution, the two singlets are collapsed to a unique one, indicating that the η^1 and η^5 pyrrolyl anions are fluxional. Relevant bond distances and angles of complex **3** are quoted in Table II. The structure consists of [(Et$_8$N$_4$)Zr(THF)] discrete monomeric units having an imposed C_2 symmetry. The η^5-bonding mode of the pyrrolyl anions is indicated by the narrow range of the zirconium–pyrrolyl ring distances which vary from 2.446(2) to 2.552(2) Å. The two η^5-bonded pyrrolyl rings are bent to make a cavity in the equatorial plane to accomodate the two σ-bonded pyrrolyl anions. The overall geometry resembles the structure of bis(cyclopentadienyl)zirconium derivatives. The Zr–η^5-pyrrolyl distance [2.214(2) Å] and the angle between zirconium and the centroids of the two η^5-bonded rings [142.6(1)°] are very close to the values found in [η^5-(C$_5$H$_5$)$_2$Zr(σ-NC$_4$H$_4$)$_2$][10] for the η^5-cyclopentadienyl ligands. A relevant difference concerns the N1–Zr–N1' angle involving the two σ-bonded pyrrolyl anions which is 164.5(1) vs

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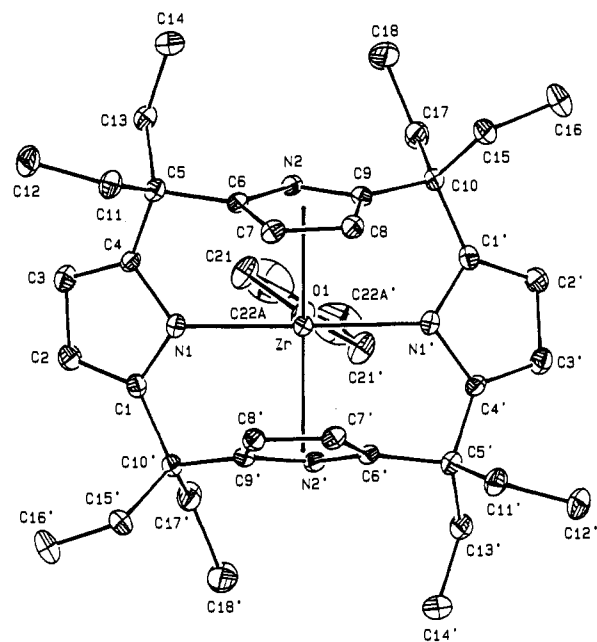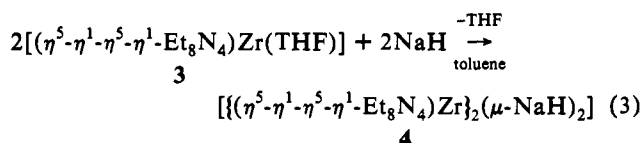

Figure 1. An ORTEP drawing of complex **3** (30% probability ellipsoids). For clarity, only one position is given for the disordered atoms. Primes indicate a transformation of $1 - x, y, 0.5 - z$.

95.68(8)° in the bis(cyclopentadienyl) derivative.[10] The widening of the N1–Zr–N1' angle leads to coordinative unsaturation of the metal, which is made up for by the oxygen atom of the THF molecule. The N1, N1', and O1 σ-bonded atoms lie in a plane perpendicular to that containing the zirconium atom and the centroids of the η^5-bonded rings [dihedral angle 90.8(1)°]. The overall coordination geometry can be described as a pseudo trigonal bipyramid, with N1 and N1' occupying the axial position. The Zr–N σ-bond distance falls in the usual range, i.e. in [(tmtaa)Zr(Cl)$_2$][11] 2.166(4) Å, in [(tmtaa)$_2$Zr][11] 2.332(5) Å (tmtaa = dibenzotetramethyltetraaza[14]annulene dianion), and in [(η^5-C$_5$H$_5$)$_2$Zr(σ-NC$_4$H$_4$)$_2$][10] at a mean Zr–N distance of 2.169(2) Å. The [(Et$_8$N$_4$)Zr] moiety has a saddle-shape conformation. In Table VII, there is a comparison between the most relevant parameters concerning the conformation of the [(Et$_8$N$_4$)Zr] moieties in complexes **3, 4, 5, 7**, and **8**. The four nitrogen atoms show small but significant tetrahedral distorsion from planarity (Table VII); the out-of-plane distance of Zr from the σ-bonded pyrrole ring is 0.764(1) Å in the direction opposite that of the THF oxygen. The two σ-bonded pyrrole rings form dihedral angles of 151.4(1)° with the N$_4$ plane, while the η^5-bonded rings are tilted by 106.4(1)° with respect to the same plane. The η^5-η^1-η^5-η^1-bonding mode of the porphyrinogen provides 16 valence electrons to zirconium, which achieves a closed shell configuration with the addition of a THF molecule.

Complex **3** exemplifies a rather unusual bifunctional system, acting as a Lewis acid via the metal center and as an electron-rich site at the periphery. In this view, we should expect complexation of ion pairs and their dissolution in nonpolar solvents. This was clearly observed in the case of **3** reacting with NaH in toluene.

$$2[(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)Zr(THF)] + 2NaH \xrightarrow[\text{toluene}]{-THF}$$
3

$$[\{(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)Zr\}_2(\mu\text{-NaH})_2] \quad (3)$$
4

The ^{1}H NMR spectrum of **4** in C$_6$D$_6$ at 293 and 340 K agrees with the solid-state structure which contains two different pairs

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Zirconium meso–Octaethylporphyrinogen

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds **3**, **4**, **5**, **7**, and **8**

compound	3	4	5	7	8
chemical formula	$C_{36}H_{48}N_4Zr \cdot C_4H_8O$	$C_{72}H_{98}N_8Na_2Zr_2$	$C_{76}H_{106}N_8Na_2Zr_2$	$C_{88}H_{110}N_8Na_2Zr_2 \cdot 2(C_7H_8)$	$C_{46}H_{69}N_4NaO_2Zr$
a (Å)	12.935(3)	24.272(3)	11.565(2)	13.815(2)	11.264(1)
b (Å)	12.704(3)	12.640(4)	12.598(2)	24.619(2)	19.646(4)
c (Å)	21.649(3)	21.886(3)	14.327(2)	13.981(2)	20.609(3)
α (deg)	90	90	100.30(1)	90	90
β (deg)	90	101.75(1)	103.65(1)	108.73(1)	101.18(2)
γ (deg)	90	90	113.73(1)	90	90
V (Å³)	3557.5(13)	6573.9(24)	1766.8(5)	4503.3(10)	4474.1(12)
Z	4	4	1	2	4
fw	700.1	1304.0	1360.2	1692.6	792.3
space group	$Pbcn$ (No. 60)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 1)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
t (°C)	22	22	22	22	22
λ (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
ρ_{calcd} (g cm^{-1})	1.307	1.318	1.278	1.248	1.176
μ (cm^{-1})	3.38	3.70	3.47	2.85	2.82
transmn coeff	0.987–1.000	0.907–1.000	0.943–1.000	0.875–1.000	0.894–1.000
R^a	0.037	0.053	0.034	0.043	0.042
R_w^b	0.041	0.054	0.036	0.046	0.044

$^a R = \sum|\Delta F|/\sum|F_o|.$ $^b R_w = \sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|.$

Table II. Selected Bond Distances (Å) and Angles (deg) for Complex **3**^{a}

Zr–N1	2.261(3)	Zr–C8	2.535(2)
Zr–N2	2.446(2)	Zr–C9	2.494(2)
Zr–C6	2.531(2)	Zr–Cp2	2.214(2)
Zr–C7	2.552(2)	Zr–O1	2.235(3)
N1–Zr–N1′	164.5(1)	O1–Zr–N1	82.3(1)
N1–Zr–N2	84.8(1)	O1–Zr–N2	80.2(1)
N1–Zr–N2′	92.6(1)	O1–Zr–Cp2	108.7(1)
N1–Zr–Cp2	93.2(1)	Cp2–Zr–Cp2′	142.6(1)
N1–Zr–Cp2′	91.7(1)	Zr–N1–C1	123.7(2)
N2–Zr–Cp2′	170.0(1)	Zr–N1–C4	125.7(2)
N2–Zr–N2′	160.3(1)	C1–N1–C4	107.0(2)

^{a} Primes indicate a transformation of $1 - x, y, 0.5 - z$. Cp2 refers to the centroid of the pyrrolic ring containing N2.

Table III. Selected Bond Distances (Å) and Angles (deg) for Complex **4**^{a}

Zr–N1	2.250(7)	Zr–C19	2.546(8)
Zr–N2	2.457(6)	Zr–Cp2	2.231(8)
Zr–N3	2.274(6)	Zr–Cp4	2.240(8)
Zr–N4	2.491(7)	Zr–H1	1.95
Zr–C6	2.498(8)	Na–N1′	2.971(8)
Zr–C7	2.565(9)	Na–N3	2.817(8)
Zr–C8	2.576(10)	Na–Cp1′	2.658(7)
Zr–C9	2.527(9)	Na–Cp3	2.658(11)
Zr–C16	2.526(8)	Na–H1	2.11
Zr–C17	2.552(10)	Na–H1′	2.54
Zr–C18	2.557(8)		
N1–Zr–N2	91.6(2)	Cp4–Zr–N3	92.9(3)
N1–Zr–N3	158.9(3)	Cp4–Zr–H1	109.5
N1–Zr–N4	85.9(2)	Zr–N1–C4	123.3(5)
N1–Zr–H1	87.1	Zr–N1–C1	123.3(5)
N2–Zr–N3	83.4(2)	Zr–N3–C11	125.5(6)
N2–Zr–N4	156.6(3)	Zr–N3–C14	123.7(5)
N2–Zr–H1	74.9	C1–N1–C4	106.4(6)
N3–Zr–N4	90.6(3)	Zr–N2–C9	76.8(5)
N3–Zr–H1	71.8	Zr–N2–C6	75.6(4)
N4–Zr–H1	81.8	C6–N2–C9	106.3(7)
Cp2–Zr–N1	92.5(3)	H1–Na–H1′	69.5
Cp2–Zr–N3	93.0(3)	H1–Na–Cp1′	149.7
Cp2–Zr–N4	174.1(3)	H1–Na–Cp3	82.8
Cp2–Zr–H1	103.9	H1′–Na–Cp1′	86.0
Cp2–Zr–Cp4	146.3(3)	H1′–Na–Cp3	148.2
Cp4–Zr–N1	93.8(3)	Cp1′–Na–Cp3	124.9(3)
Cp4–Zr–N2	173.1(3)		

^{a} Primes indicate a transformation of $1 - x, y, 0.5 - z$. Cp1, Cp2, Cp3, and Cp4 refer to the centroids of the pyrrolic rings containing N1, N2, N3, and N4, respectively.

III. This sandwich-type complexation of sodium[12] is rather unusual, as is the binding of the Na–H ion pair. The high stability of the η^5-pyrrolyl–Na interaction is shown by the fact that **3** forms even in THF. The hydrido ligand is triply bridging to one Zr and two Na cations (Zr–H1, 1.95 Å;[13] Na–H1, 2.11 Å; Na⋯H′, 2.54 Å). The last two distances should be compared with the Na–H distance (2.44 Å) in solid NaH.[14] Neutral[15] or cationic[16] hydrido complexes of zirconium(IV) are not comparable to complex **4**, with the exception of those containing Y[17a] or Al.[17b]
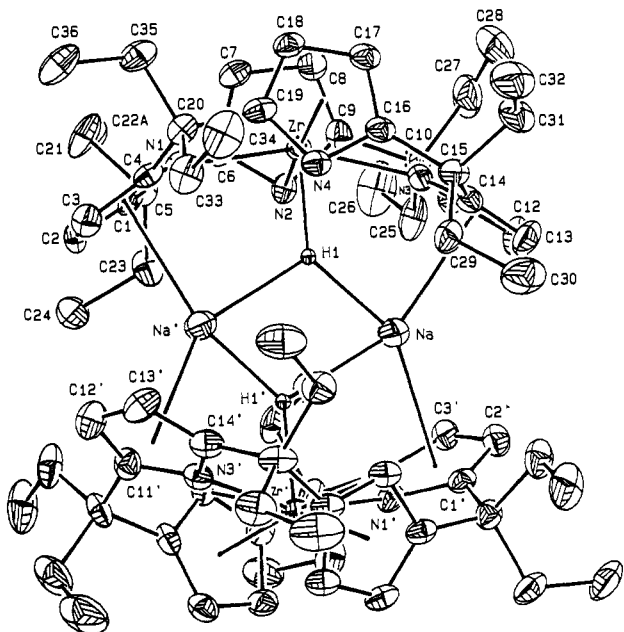

Figure 2. An ORTEP drawing of complex **4** (30% probability ellipsoids). For clarity, only one position is given for the disordered C30 methyl carbon atom. Primes indicate a transformation of $1 - x$, y, $0.5 - z$.

of pyrrolyl anions, as shown in Figure 2. The peripheral ethyl groups are well differentiated as four quartets for CH$_2$ and two triplets for CH$_3$. The structure of the dimer **4** is self-explanatory with regard to the complexation mode of the Na–H pair by **3**. Zirconium is η^5-bonded to two opposite pyrrolyl anions and σ-bonded to the other two, which function as binding sites for sodium cations. Relevant structural parameters are given in Table
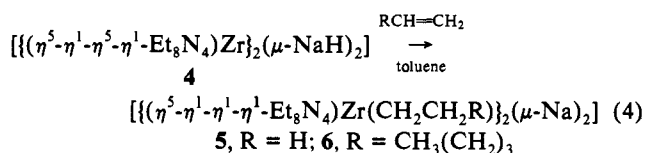
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The zirconium σ-bonded atoms N1, N3, and H1 (complex **4**) are in a plane perpendicular to that containing Zr and the centroids of the η⁵-bonded rings, the dihedral angle being 89.6°. The Zr atom is displaced by 0.982(1) and 0.667(1) Å from the σ-bonded pyrrole planes containing N1 and N3. Bond distances and angles within the [(Et₈N₄)Zr] moiety are not significantly affected by the formation of the dimer (Table III), and the molecule maintains a saddle-shape conformation, though some differences are observed in the dihedral angles (Table VII). The metal is significantly more out of the N₄ plane in **4** than **3** (Table VII), as a consequence of the bond to the hydrido ligand.

Hydrozirconation[15,16,18] is an important organometallic reaction, so a preliminary test of reactivity was the reaction of **4** with olefins:

$$[\{(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)Zr\}_2(\mu\text{-}NaH)_2] \xrightarrow[\text{toluene}]{RCH=CH_2}$$
$$\mathbf{4}$$

$$[\{(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}Et_8N_4)Zr(CH_2CH_2R)\}_2(\mu\text{-}Na)_2] \quad (4)$$
$$\mathbf{5}, R = H; \mathbf{6}, R = CH_3(CH_2)_3$$

Only terminal olefins insert into these Zr–H bonds. We did not observe any reaction with internal olefins, such as 2-butene, 2-hexene, cyclohexene, etc. The proposed bonding mode of the octaethylporphyrinogen to zirconium in **5** and **6**[19] is based on the solid-state structures. Details are reported for complex **5** only. The ¹H NMR spectrum suggests, however, the η⁵-η¹-η⁵-η¹-bonding mode is the same in both **5** and **6**. For the latter, the ¹H NMR spectrum was unchanged from 293 down to 200 K. The insertion reaction with ethylene resulted in some major changes to the structure of the dimer. The dimeric structure remains (see Figure 3), but the ethyl groups are pointing outside the cavity. They form, however, by insertion of an ethylene molecule into a Zr–H bond within the cavity.

A plausible explanation for such an "inversion" between the hydrido and the ethyl groups is the possible rupture of the dimer into two monomers in toluene solution. This should not be very surprising since we isolated Zr–K porphyrinogen complexes where K is η⁶-bonded to a toluene molecule.[19] Details of the structure of **5** are given in Figure 3, showing the centrosymmetric dimer, and in Figure 4, which shows the η⁵-η¹-η¹-η¹-bonding mode of the porphyrinogen to zirconium in the monomeric moiety, while a selection of the structural parameters are listed in Table IV. The [(Et₈N₄)Zr] moiety in **5** has a saddle-shaped conformation with an orientation of the pyrrole rings remarkably different from
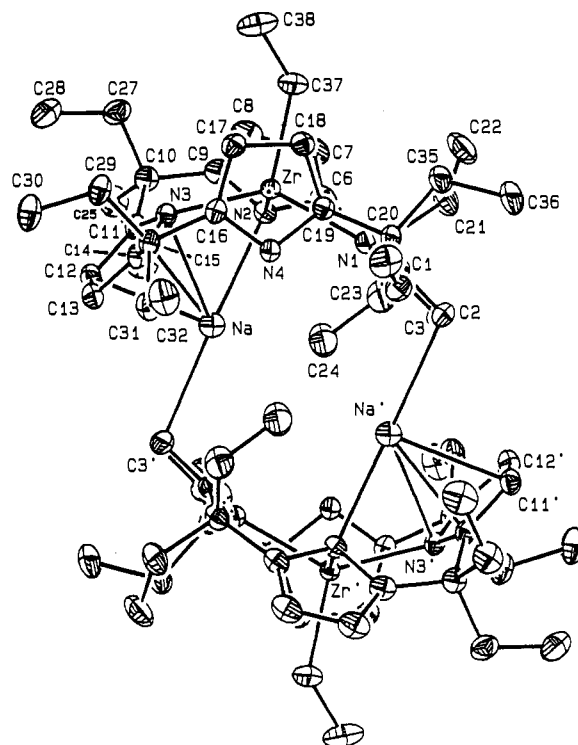

Figure 3. An ORTEP drawing of complex **5** (30% probability ellipsoids). Primes indicate a transformation of −x, −y, −z.
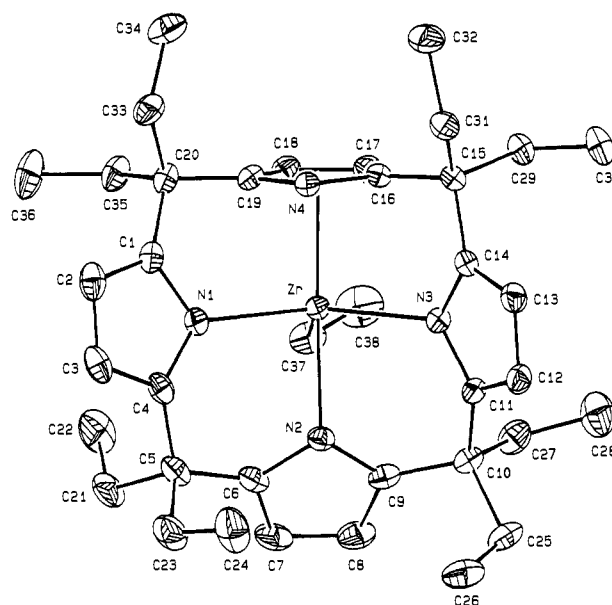

Figure 4. An ORTEP drawing of the [Zr(Et₈N₄)] moiety of complex **5** (30% probability ellipsoids).

those present in complexes **3** and **4**. This is a consequence of the different interactions between zirconium and porphyrinogen. In particular, the σ-bonded pyrrole rings are bent with respect to the N₄ plane such that they are nearly midway between being parallel and perpendicular to the plane (Table VII), while the η⁵-bonded ring is perpendicular to the plane. The distances of Zr from the mean planes of the pyrroles containing N1, N2, and N3 are 0.574(1), 1.859(1), and 1.103(1) Å, respectively. The sodium cation is σ-bonded to N2 and η³ (N3, C11, and C12) and η² (C2′ and C3′) bonded to opposite pyrroles of the dimer, and its coordination sphere is completed by using the hydrogens from the methyl groups at C24 and C26 [Na⋯C24, 2.928(4) Å; Na⋯C26, 3.216(6) Å; Na⋯H242, 2.53 Å; Na⋯H243, 2.40 Å; Na⋯H261, 2.55 Å; Na⋯H242–C24, 104°; Na⋯H243–C24, 108°;

(15) (a) For a survey of group IV and V hydrides, see: Toogood, G. E.; Wallbridge, M. G. H. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 267. (b) Carlin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: Chichester, U.K., 1986. (c) Cardin, D. J.; Lappert, M. F.; Raston, C. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1981; Vol. 3, Chapter 23.2, p 45. (d) Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (e) Labinger, J. A. *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: Weinheim, Germany, 1992. Buchwald, S. L.; La Maire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

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Zirconium meso-Octaethylporphyrinogen

J. Am. Chem. Soc., Vol. 115, No. 9, 1993 3599

Table IV. Selected Bond distances (Å) and Angles (deg) for Complex **5**[a]

Zr–C37	2.235(3)	Na–N2	2.543(3)
Zr–N1	2.233(3)	Na–N3	2.996(2)
Zr–N2	2.274(2)	Na–C11	2.606(3)
Zr–N3	2.230(2)	Na–C12	2.780(3)
Zr–N4	2.395(2)	Na–C2′	2.927(3)
Zr–C16	2.520(2)	Na–C3′	2.605(4)
Zr–C17	2.632(2)	Na–C24	2.928(4)
Zr–C18	2.625(3)	Na–C26	3.216(6)
Zr–C19	2.481(3)	C37–C38	1.526(5)
Zr–Cp4	2.238(2)		
N1–Zr–N2	80.4(1)	N4–Zr–C37	131.6(1)
N1–Zr–N3	135.0(1)	Cp4–Zr–C37	102.7(1)
N1–Zr–N4	81.1(1)	Zr–N1–C4	129.0(2)
N1–Zr–C37	105.5(1)	Zr–N1–C1	122.5(2)
N1–Zr–Cp4	96.4(1)	C1–N1–C4	106.3(2)
N2–Zr–N3	78.1(1)	Zr–N2–C9	109.8(1)
N2–Zr–N4	136.6(1)	Zr–N2–C6	112.1(1)
N2–Zr–C37	91.3(1)	C6–N2–C9	105.2(3)
N2–Zr–Cp4	166.0(1)	Zr–N3–C14	119.4(2)
N3–Zr–N4	88.1(1)	Zr–N3–C11	125.6(2)
N3–Zr–C37	114.0(1)	C11–N3–C14	106.3(2)
N3–Zr–Cp4	95.2(1)		

[a] Primes indicate a transformation of −x, −y, −z. Cp4 refers to the centroid of the pyrrolic ring containing N4.

Na···H261–C26, 126°]. In agreement with the solid-state structure, the ^{1}H NMR spectra for both **5** and **6** show two distinct sets of ethyl groups. Two methylene groups are different from the other six, while the methyls are grouped into two sets of equal intensity. The forced geometry around the methylene carbons is felt more by the protons than is any sodium–methyl interaction.

Complex **4** reacts equally well with PhC≡CH as reported in eq 5. The reaction with PhC≡CH was carried out in toluene and gave the cis addition of Zr and H to phenylacetylene:[18]

$$[\{(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-Et}_8N_4)Zr\}_2(\mu\text{-NaH})_2] \xrightarrow{\text{PhC≡CH}}$$

4

$$\left(\begin{array}{c}(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-Et}_8N_4)Zr\\ \end{array}\text{C}=\text{C}\begin{array}{c}H\\Ph\end{array}\right)_2 (\mu\text{-Na})_2 \quad (5)$$

7
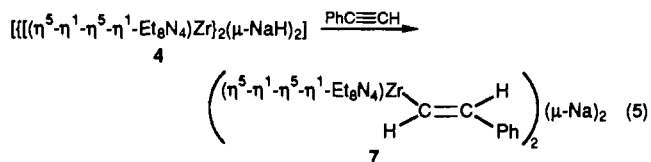
The bonding mode of the porphyrinogen in solution, as shown by the ^{1}H NMR spectrum at room temperature, is $\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1$ and differs from that found in the solid state (Figure 5), where one of the pyrrolyl anions is η^5-bonded and three are σ-bonded via the nitrogen atoms to zirconium. The out-of-plane distances of Zr from the mean planes of the pyrrole rings containing N1, N2, and N3 are 0.898(1), 1.720(1), and 0.512(1) Å, respectively. The four nitrogen atoms lie in a perfect plane from which zirconium is displaced by 0.821(1) Å toward the vinyl ligand, which is pointed outward with respect to the cavity of the dimer. The interaction of sodium with the porphyrinogen is like that in **5**, with Na interacting with N2′, η^3-bonded to N1′, C3′, and C4′, and η^2-bonded to C12 and C13 (Table V). In addition, relatively short contacts between Na, C28′, and C24′ should be emphasized (Figure 5): Na···C24′, 3.144(11) Å; Na···C28′, 2.936(11) Å; Na···H242′, 2.60 Å; Na···H243′, 2.88 Å; Na···H281′, 2.46 Å; Na···H282′, 2.52 Å; Na···H242′–C24′, 109°; Na···H243′–C24′, 91°; Na···H281′–C28′, 108°; Na···H282′–C28′, 106°. Selected bond distances and angles are in Table V. The ^{1}H NMR spectrum, though in agreement with some differences in the ethyl groups, does not show a clear differentiation between the two different kinds of ethyl groups.

Reaction 4 carried out in THF leads to the monomeric form, **8**, of the Zr–Na–ethyl complex **5**. The same compound has been obtained by solubilization of **5** in THF. A number of Li–Zr alkyl derivatives similar to **8** have been obtained by addition of LiR to **3** in THF solutions.[19] The sodium cation is again bonded to
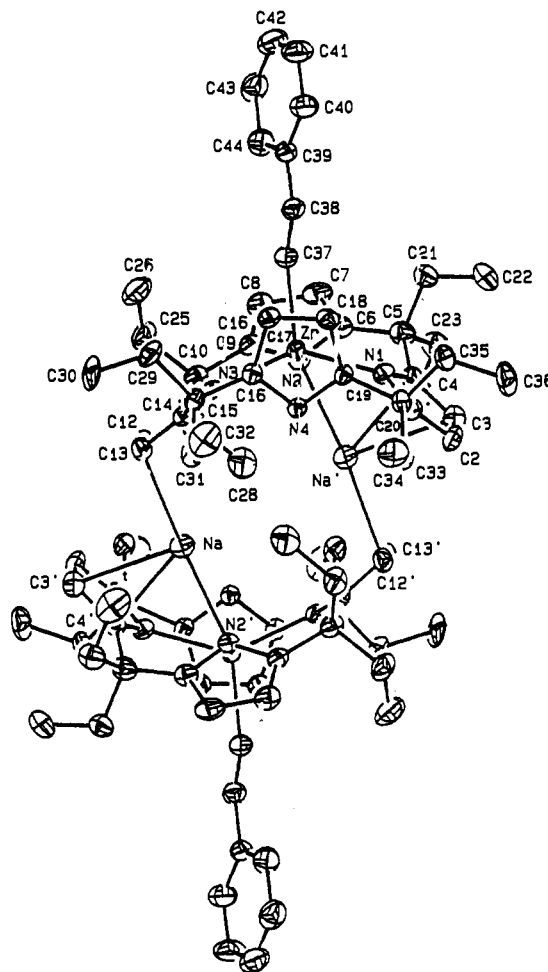

Figure 5. An ORTEP drawing of complex **7** (30% probability ellipsoids). The toluene solvent molecule and the C30B disordered methyl carbon are omitted for clarity. Primes indicate a transformation of −x, −y, −z.

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex **7**[a]

Zr–C37	2.227(7)	Na–N1′	3.006(6)
Zr–N1	2.207(5)	Na–N2′	2.560(6)
Zr–N2	2.273(6)	Na–C3′	2.903(8)
Zr–N3	2.234(5)	Na–C4′	2.602(7)
Zr–N4	2.395(6)	Na–C12	2.599(9)
Zr–C16	2.496(8)	Na–C13	2.830(8)
Zr–C17	2.596(8)	Na–C24′	3.144(11)
Zr–C18	2.616(7)	Na–C28′	2.931(10)
Zr–C19	2.499(8)	C37–C38	1.310(9)
Zr–Cp4	2.225(8)	C38–C39	1.483(9)
N1–Zr–N2	78.9(2)	Cp4–Zr–N3	96.3(2)
N1–Zr–N3	136.7(2)	Cp4–Zr–C37	104.9(3)
N1–Zr–N4	87.2(2)	Zr–N1–C4	126.4(4)
N1–Zr–C37	109.2(2)	Zr–N1–C1	122.2(4)
N2–Zr–N3	81.4(2)	C1–N1–C4	106.0(6)
N2–Zr–N4	138.4(2)	Zr–N2–C9	115.3(4)
N2–Zr–C37	87.3(2)	Zr–N2–C6	112.4(4)
N3–Zr–N4	82.7(2)	C6–N2–C9	105.4(5)
N3–Zr–C37	107.8(3)	Zr–N3–C14	123.2(5)
N4–Zr–C37	134.2(2)	Zr–N3–C11	128.9(4)
Cp4–Zr–N1	95.1(2)	C11–N3–C14	106.2(5)
Cp4–Zr–N2	167.6(2)		

[a] Primes indicate a transformation of −x, −y, −z. Cp4 refers to the centroid of the pyrrolic ring containing N4.

porphyrinogen but in this case completes its coordination sphere with THF instead of using weak interactions with methyl groups (Figure 6).

Relevant bond distances and angles are listed in Table VI. The structure of **8** consists of discrete monomers of [(Et₈N₄)-
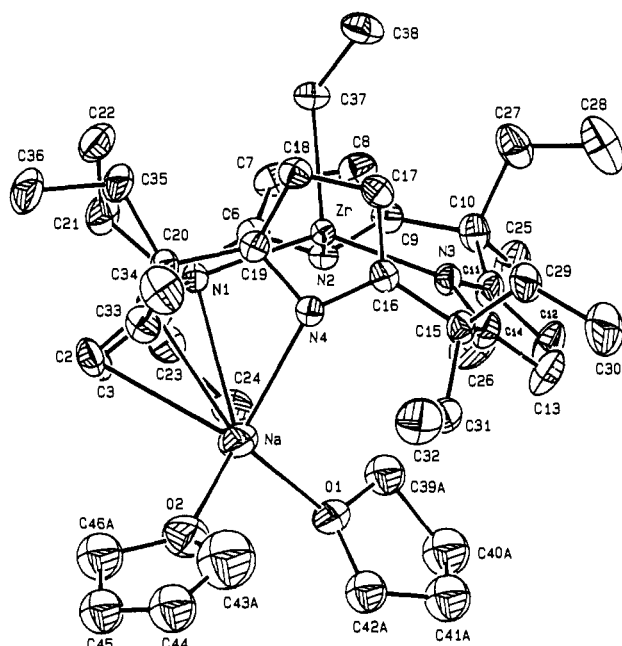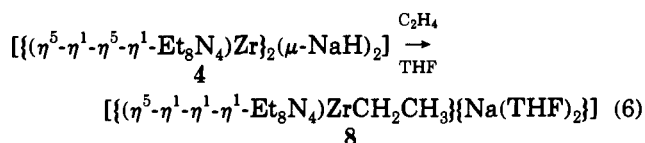
Figure 6. An ORTEP drawing of complex 8 (30% probability ellipsoids). For clarity, only one position is given for the disordered atoms of the THF molecule.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex 8[a]

Zr–C37	2.249(3)	Zr–Cp4	2.273(4)
Zr–N1	2.248(2)	Na–O1	2.250(3)
Zr–N2	2.199(2)	Na–O2	2.317(5)
Zr–N3	2.215(2)	Na–N1	2.949(3)
Zr–N4	2.427(2)	Na–N4	2.680(3)
Zr–C16	2.549(4)	Na–C1	2.649(4)
Zr–C17	2.653(4)	Na–C2	2.826(4)
Zr–C18	2.650(4)	C37–C38	1.513(6)
Zr–C19	2.516(2)		
N1–Zr–N2	81.5(1)	Cp4–Zr–N2	167.1(1)
N1–Zr–N3	139.2(1)	Cp4–Zr–N3	93.9(1)
N1–Zr–N4	79.7(1)	Cp4–Zr–C37	102.5(1)
N1–Zr–C37	103.2(1)	Zr–N2–C9	113.0(2)
N2–Zr–N3	81.0(1)	Zr–N2–C6	116.2(2)
N2–Zr–N4	137.9(1)	C6–N2–C9	106.0(3)
N2–Zr–C37	90.4(1)	Zr–N3–C14	124.4(2)
N3–Zr–N4	89.3(1)	Zr–N3–C11	126.1(2)
N3–Zr–C37	113.5(1)	C11–N3–C14	105.7(3)
N4–Zr–C37	130.5(1)	Zr–C37–C38	128.0(3)
Cp4–Zr–N1	95.0(1)		

[a] Cp4 refers to the centroid of the pyrrolic ring containing N4.

$$[\{(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)Zr\}_2(\mu\text{-}NaH)_2] \xrightarrow[THF]{C_2H_4}$$
$$\mathbf{4}$$

$$[\{(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}Et_8N_4)ZrCH_2CH_3\}\{Na(THF)_2\}] \quad (6)$$
$$\mathbf{8}$$

$Zr(C_2H_5)Na(THF)_2]$. The geometry of the $[(Et_8N_4)Zr(Et)]^-$ anion is very close to that observed in complex 5 and is shown in Figure 4. The four nitrogen atoms lie on a plane from which Zr is displaced by 0.800(1) Å toward the ethyl ligand. The out-of-plane distances of Zr from the mean planes of the σ-bonded pyrroles containing N1, N2, and N3 are 0.759(1), 1.628(1), and 0.683(1) Å, respectively. The Na cation is linked to the anion through an η^3 interaction involving the N1, C1, and C2 atoms and through a σ interaction involving the N4 nitrogen atom. A difference between the solid and solution states is again seen for 8, since the ¹H NMR spectrum shows an η^5-η^1-η^5-η^1-bonding mode vs the η^5-η^1-η^1-η^1 mode observed in the solid state (Figure 6).

The η^5 to η^1 bonding mode change in one of the pyrrolyl anions

moving from complexes 3 and 4 to the alkylated forms 5, 7, and 8 deserves some comments. Three factors can affect this change: (i) the electron requirements of the central metal atom; (ii) the bonding requirements of the alkali cation; (iii) steric effects. In the context of this last point, we observed that in complexes 5–8 one of the hydrogens from the carbon bonded to zirconium points toward the pyrrolyl ring σ-bonded to Zr and facing the η^5-bonded one. In all of these compounds, the H···pyrrolyl centroid distances range from 2.56 to 2.68 Å. The structural parameters reported for all the compounds show clearly thtat the pyrrolyl anion assumes either the η^5- or the η^1-bonding mode, though we reported recently some examples in which it is η^3-bonded.[6]

We should emphasize that the σ-bonding mode of the pyrrolyl anion requires a pyramidal geometry around the N atom with zirconium significantly displaced from the pyrrole plane. This displacement for complexes 5, 7, and 8 ranges from 0.430(1) to 0.982(1) Å for the opposite σ-pyrroles and from 1.628(1) to 1.859(1) Å for the σ-pyrroles opposite the η^5-bonded ones. Additional proof for the η^1-bonding mode of the pyrrole and the pyramidal geometry of the nitrogen atoms derives from: (i) the C–C bond distances within the σ-bonded pyrroles which show a significant bond localization; (ii) the distance of the nitrogen from the planes through the three bonded atoms, which has the following trend: N1 from the C1–C4–Zr plane, 0.135(2) Å in complex 5, 0.218(7) Å in complex 7, 0.179(2) Å in complex 8; N3 from the C11–C14–Zr plane, 0.273(2) Å in complex 5, 0.125(5) Å in complex 7, 0.180(2) Å in complex 8; N2 from the C6–C9–Zr plane, 0.550(2) Å in complex 5, 0.493(6) Å in complex 7, 0.469(2) Å in complex 8.

Conclusions

We should emphasize a number of unprecedented characteristics of this prophyrinogen–zirconium system in organometallic chemistry: (i) The ability of 3 to carry in hydrocarbon solvents alkali and other alkali-organometallic ion pairs is due to its bifunctional nature, acting as a Lewis acid at the metal center and as a base at its electron-rich periphery. (ii) In the reaction of 3, the porphyrinogen adapts its bonding mode to the metal depending on the metal's electron needs and steric constraints when it is binding a substrate. (iii) The chemistry so far reported for Zr-porphyrinogen in toluene shows the essential role of the periphery in binding alkali cations in different positions and its action as a sort of internal solvent. This suggests that energetic and steric factors in the organometallic chemistry of Zr may be controlled as a function of the solvent. This may serve as a way to fine-tune reaction energetics in organometallic chemistry.

Experimental Section

General Methods. All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly distilled prior to use. NMR spectra were recorded on a 200-AC Bruker instrument. $ZrCl_4(THF)_2$ was prepared as reported.[20]

Synthesis of 1. The synthesis of 1 is a modification of the so-called "acetone-pyrrole" synthesis.[4] Pyrrole (50 mL, 720 mmol), 3-pentanone (77 mL, 720 mmol), and methanesulfonic acid (4 mL) were mixed in ethanol (200 mL), and the mixture was allowed to reflux under stirring for 4 h, then cooled in the freezer until a white crystalline solid precipitated. The solid was filtered off, washed five times with small amounts of ethanol, and dried under vacuum at 50 °C (67%). Anal. Calcd for $C_{36}H_{52}N_4$: C, 80.00; H, 9.63; N, 10.37. Found: C, 79.41; H, 10.51; N, 10.42. ¹H NMR (CD_2Cl_2): δ 0.57 (t, CH_3, 24 H), 1.78 (m, CH_2, 16 H), 5.89 (s, C_4H_2N, 4 H), 5.91 (s, C_4H_2N, 4 H), 6.94 (s, 4 NH). IR(Nujol) (N–H): 3440 cm⁻¹.

Synthesis of 2. BuLi (200 mL, 1.6 M, 320 mmol) was added dropwise to a THF (200 mL) solution of 1 (43.0 g, 80.0 mmol). The mixture was stirred at 50 °C for 1 h, until gas evolution stopped. The yellow solution was evaporated to dryness and the white residue dissolved in n-hexane (200 mL), affording a white suspension, which was filtered off, washed

(20) Manzer, L. E. *Inorg. Synth.* **1982,** *21,* 135.

Table VII. Comparison of Structural Parameters within the [Zr(Et$_8$N$_4$)] Units

complex	3	4	5	7	8
distance of Zr from the N$_4$ plane,^{a} Å	0.361(1)	0.457(1)	0.855(1)	0.821(1)	0.800(1)
distance of N1 from the N$_4$ plane, Å	–0.057(3)	–0.042(7)	–0.008(2)	–0.008(5)	0.024(2)
distance of N2 from the N$_4$ plane, Å	0.057(3)	0.043(7)	0.008(2)	0.008(5)	–0.025(2)
distance of N3 from the N$_4$ plane, Å		–0.043(7)	–0.007(2)	–0.008(5)	0.022(2)
distance of N4 from the N$_4$ plane, Å		0043(8)	0.007(2)	0.007(5)	–0.021(2)
dihedral angle A–C,^{b} deg	122.9(1)	115.3(3)	90.1(1)	99.5(3)	99.9(1)
dihedral angle B–D, deg	32.8(1)	28.9(3)	55.6(1)	59.2(3)	61.7(1)
dihedral angle, N$_4$–A, deg	151.4(1)	143.2(2)	141.7(1)	134.4(2)	138.1(1)
dihedral angle N$_4$–B, deg	106.4(1)	103.7(3)	147.0(1)	151.8(2)	153.4(1)
dihedral angle N$_4$–C, deg		152.1(3)	127.8(1)	144.7(2)	141.1(1)
dihedral angle N$_4$–D, deg		105.2(2)	91.8(1)	93.2(2)	92.4(1)

^{a} N$_4$ refers to the least-squares mean-plane defined by N1, N2, N3, and N4. ^{b} A, B, C, and D refer to the least-squares mean-planes defined by the pyrrolic rings containing N1, N2, N3, and N4, respectively.

with *n*-hexane (100 mL), and dried. A white microcrystalline solid was obtained (65 g, 95%). Anal. Calcd for Et$_8$N$_4$Li$_4$(THF)$_4$, C$_{52}$-H$_{80}$Li$_4$N$_4$O$_4$: C, 73.23; H, 9.39; N, 6.57. Found: C, 73.04; H, 10.08; N, 6.88. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 1.09 (t, CH$_3$, 24 H), 1.19 (t, THF, 16 H), 2.17 (q, CH$_2$, 16 H), 3.23 (t, THF, 16 H), 6.31 (s, C$_4$H$_2$N, 8 H).

Synthesis of 3. ZrCl$_4$(THF)$_2$ (3.80 g, 7.90 mmol) was added to a toluene (150 mL) solution of **2** (6.70 g, 7.86 mmol). The mixture was stirred at room temperature for 15 h, then at 60 °C for ¹/₂ h. The white fine LiCl powder was filtered off and the yellow toluene solution evaporated to dryness. The yellow crystalline residue was dissolved in *n*-hexane. A microcrystalline yellow solid formed, which was filtered off and dried (5.20 g, 95%). The method is reproductible on larger quantities. Large yellow cubic crystals suitable for X-ray analysis were obtained by recrystallizing from hexane/toluene. Anal. Calcd for [(Et$_8$N$_4$)Zr(THF)], C$_{40}$H$_{56}$N$_4$OZr: C, 68.57; H, 8.00; N, 8.00. Found: C, 68.23; H, 8.03; N, 8.19. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.90 (THF, 4 H), 0.90 (t, CH$_3$, 12 H), 1.08 (t, CH$_3$, 12 H), 1.97 (m, CH$_2$, 12 H), 2.53 (m, CH$_2$, 4 H), 3.06 (THF, 4 H), 6.03 (s, C$_4$H$_2$N, 4 H), 6.20 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$D$_8$, 293 K): δ 6.23 (s, C$_4$H$_2$N, 4 H), 6.30 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$D$_8$, 313 K): δ 6.26 (s, C$_4$H$_2$N, 4 H), 6.28 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$D$_8$, 320 K): δ 6.27 (s, C$_4$H$_2$N, 8 H). We report only the pyrrole resonances at different temperatures, since the other signals are almost unchanged.

Synthesis of 4, Method A. **3** (5.75 g, 8.22 mmol) and NaH (0.40 g, 16.66 mmol) were mixed in toluene (200 mL), and the mixture was allowed to reflux at 80 °C while stirring for 20 h, then filtered while hot to remove a light suspension. The solvent was evaporated to ³/₄ volume, and *n*-hexane (100 mL) was added, yielding a pale-yellow microcrystalline solid (78%). This solid can be recrystallized in toluene affording pale-yellow crystals. Anal. Calcd for [{(Et$_8$N$_4$)Zr}$_2$(NaH)$_2$], C$_{72}$H$_{98}$N$_8$Na$_2$Zr$_2$: C, 66.35; H, 7.52; N, 8.60. Found: C, 65.58; H, 7.56; N, 8.52. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.93 (t, CH$_3$, 12 H), 1.08 (t, CH$_3$, 12 H), 1.49 (s, hydride, 1 H), 1.61 (q, CH$_2$, 4 H), 1.72 (q, CH$_2$, 4 H), 2.08 (q, CH$_2$, 4 H), 2.60 (q, CH$_2$, 4 H), 5.98 (s, C$_4$H$_2$N, 4 H), 6.12 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_6$D$_6$, 340 K): δ 5.93 (s, C$_4$H$_2$N, 4 H), 6.16 (s, C$_4$H$_2$N, 4 H).

When **4** (0.8 g, 10.00 mmol) was dissolved in THF (50 mL) and heated at 50 °C over a few hours, after evaporation to dryness, the starting material was recovered.

Synthesis of 4, Method B. **3** (1.73 g, 2.4 mmol) and NaH (60 mg, 2.5 mmol) were mixed in THF (200 mL), and the mixture was allowed to reflux while stirring for 12 h, then filtered while hot. After evaporation of the solvent and addition of *n*-hexane (100 mL), a yellow microcrystalline solid was obtained, whose NMR spectrum is identical to the product obtained in toluene.

Synthesis of 5. A toluene (50 mL) suspension of **4** (1.20 g, 1.8 mmol) was stirred at room temperature under an ethylene atmosphere over 4 days. The suspension slowly dissolved to form a limpid yellow solution. The solvent was evaporated and the residue dissolved in *n*-hexane (50 mL). After addition of a few drops toluene and filtration, colorless crystals were obtained. Another crop of identical product was obtained after evaporating the mother liquor to dryness (80%). Anal. Calcd for [{Et$_8$N$_4$)Zr(C$_2$H$_5$)}$_2$(μ-Na)$_2$], C$_{76}$H$_{106}$N$_8$Na$_2$Zr$_2$: C, 67.06; H, 7.79; N, 8.24. Found: C, 67.59; H, 7.79; N, 8.26. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.11 (q, CH$_2$Zr, 4 H), 0.63 (t, CH$_3$, 12 H), 0.82 (t, CH$_3$, 12 H), 1.42 (t, C*H$_3$*CH$_2$Zr, 3 H), 1.90 (q, CH$_2$, 12 H), 2.18 (q, CH$_2$, 4 H), 6.03 (s, C$_4$H$_2$N, 4 H), 6.62 (s, C$_4$H$_2$N, 4 H).

When **5** is dissolved in THF and stirred a few hours at room temperature, evaporation to dryness affords **8**.

Synthesis of 6. Complex **4** (1.40 g, 2.15 mmol) was mixed with 1-hexene (0.3 mL, *d* = 0.673, 2.50 mmol) in toluene (50 mL). Refluxing this suspension at 80–90 °C afforded a solution, which was refluxed over 72 h. A limpid pale-yellow solution was obtained, which was evaporated to dryness, and *n*-hexane (50 mL) added. A white solid was filtered off (65%) and recrystallized in hexane, yielding white cubic crystals. Anal. Calcd for [{(Et$_8$N$_4$)Zr(CH$_2$(CH$_2$)$_4$CH$_3$)}$_2$(μ-Na)$_2$], C$_{84}$H$_{122}$N$_8$Na$_2$Zr$_2$: C, 68.49; H, 8.28; N, 7.61. Found: C, 68.76; H, 8.43; N, 7.66. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.14 (q, CH$_2$Zr, 2 H), 0.64 (t, CH$_3$, 12 H), 0.79 (t, CH$_3$, 12 H), 0.90 (t, C*H$_3$*(CH$_2$)$_5$Zr, 3 H), 1.25 (m, (CH$_2$)$_4$, 8 H), 1.66–1.97 (m, CH$_2$, 12 H), 2.18 (q, CH$_2$ 4 H), 6.02 (s, C$_4$H$_2$N, 4 H), 6.66 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$H$_8$, 293 K): δ 6.20 (s, C$_4$H$_2$N, 4 H), 6.84 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$H$_8$, 230 K): δ 6.07 and 6.11 (2s, C$_4$H$_2$N, 4 H), 6.71 and 6.73 (2s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$H$_8$, 200 K): δ 5.70, 5.98, 6.05, and 6.21 (4s, C$_4$H$_2$N, 4 H), 6.52, 6.67, 6.78, and 6.90 (4s, C$_4$H$_2$N, 4 H).

Synthesis of 7. Complex **4** (0.66 g, 1.02 mmol) was mixed with phenylacetylene (0.12 mL, *d* = 0.93, 1.09 mmol) in toluene (50 mL). After refluxing this suspension at 80–90 °C for 8 h, a limpid orange solution was obtained which was allowed to cool slowly. Large yellow crystals formed (66%). Anal. Calcd for [{(Et$_8$N$_4$)Zr(CH=CHPh)}$_2$(μ-Na)$_2$]·2C$_7$H$_8$, C$_{102}$H$_{126}$N$_8$Na$_2$Zr$_2$: C, 72.42; H, 7.45; N, 6.63. Found: C, 72.02; H, 7.48; N, 6.71. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.62–0.99 (t, CH$_3$, 24 H), 1.92 (m, CH$_2$, 16 H), 2.11 (s, C$_7$H$_8$, 3 H), 5.89–7.46 (m, CH=CHPh, 7 H), 6.06 (s, C$_4$H$_2$N, 4 H), 6.77 (s, C$_4$H$_2$N, 4 H), 7.20 (m, C$_7$H$_8$, 5 H).

Synthesis of 8. A THF (100 mL) suspension of **4** (2.27 g, 3.48 mmol) was stirred at room temperature under an ethylene atmosphere over 96 h. The solvent was evaporated and the residue dissolved in *n*-hexane (100 mL). A yellow microcrystalline solid was obtained (87%), which can be recrystallized into hexane/toluene affording yellow crystals. Anal. Calcd for [{(Et$_8$N$_4$)Zr(C$_2$H$_5$)}{Na(THF)$_2$}], C$_{46}$H$_{69}$N$_4$NaO$_2$Zr: C, 69.69; H, 8.71; N, 7.07. Found: C, 69.09; H, 8.28; N, 6.91. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.28 (q, CH$_2$Zr, 2 H), 0.81 (t, CH$_3$, 12 H), 0.91 (t, CH$_3$, 12 H), 1.29 (THF, 8 H), 1.47 (t, C*H$_3$*CH$_2$Zr, 3 H), 2.00 (m, CH$_2$, 16 H), 3.16 (THF, 8 H), 6.08 (s, C$_4$H$_2$N, 4 H), 6.72 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$D$_8$, 293 K): δ 6.25 (s, C$_4$H$_2$N, 4 H), 6.89 (s, C$_4$H$_2$N, 4 H). ^{1}H NMR (C$_7$D$_8$, 180 K): δ 6.32 (s, C$_4$H$_2$N, 4 H), 6.78 and 6.97 (2s, C$_4$H$_2$N, 4 H).

X-ray Crystallography for Complexes 3, 4, 5, 7, and 8. The crystals selected for study were mounted in glass capillaries that were sealed under nitrogen. Crystal data and details are given in Table I. The reduced cells were obtained with use of TRACER.[21] The data were collected at room temperature on a single-crystal four-circle diffractometer. For intensities and background, individual reflection profiles were analyzed.[22] The structure amplitudes were obtained after the usual Lorentz and polarization corrections[23] and the absolute scale was established by the Wilson method.[24] Intensity data were corrected for absorption using ABSORB[25] for complexes **3, 5, 7,** and **8** and a semiempirical method[26]

(21) Lawton, S. L.; Jacobson, R. A. *TRACER*. A cell reduction program. Ames Laboratory, Iowa State University of Science and Technology, 1965.

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(23) Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer: Sheldrick, G. *SHELX-76, System of Crystallographic Computer Programs*; University of Cambridge: Cambridge, England, 1976.

(24) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151.

(25) Ugozzoli, F. ABSORB. A program for F_o absorption correction. In *Comput. Chem.* **1987**, *11*, 109.

based on ψ scan for complex **4**. The function minimized during the full-matrix least-squares refinement was $\Delta w |\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. Scattering factors for neutral atoms were taken from ref 27a for non-hydrogen atoms and from ref 28 for H. Anomalous scattering corrections were included in all structure factor calculations.[27b] Among the low-angle reflections, no correction for secondary extinction was deemed necessary.

For all complexes, solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from three-dimensional Patterson maps. Refinement was first done isotropically, then anisotropically, for all non-H atoms except for the C51–C57 of the toluene solvent molecule in complex **7** and the C39–C46 atoms of the THF molecule in complex **8**. The methyl carbon atoms C22, C24 (complex **4**), and C30 (complex **7**) were found to be statistically distributed over two positions (A and B). In addition, the C57 methyl carbon of toluene solvent was found distributed over four positions (A, B, C, and D) about the c glide. In complex **3**, the C22 carbon atom of the THF molecule was found to be statistically distributed over three positions (A, B, and C). The two THF molecules of complex **8** showed very high thermal motion. It was interpreted as disorder by splitting the C39, C40, C41, C42, C43, and C46 carbon atoms in two positions (A and B). For all the disordered atoms, the site occupation factors, deduced from an electron density map, are quoted in supplementary Tables SII–SVI. During the refinement, the aromatic rings C39–C44, C51–C56 (complex **7**), and C51–C56 (complex **8**) were constrained to be regular

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(28) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965,** *42,* 3175.

hexagons (C–C, 1.39(1) Å). Besides a constraint (C–C = 1.52(1) Å) was applied to the four C–C distances involving the four positions of the C57 methyl carbon (complex **7**). Most of the hydrogen atoms were located from difference maps, the remainder put in geometrically calculated positions. They were introduced in calculations as fixed contributors (isotropic U's fixed at 0.08 Å^2). The H atoms associated to the ethyl groups (complexes **4** and **7**), to the THF molecule (complexes **3** and **8**), and to the toluene solvent molecule (complex **7**) were ignored. The final R factors are given in Table I.

Final atom coordinates are listed in Tables SII–SVI for non-H atoms and in Tables SVII–SXI. for hydrogens. Thermal parameters are given in Tables SXII–SXVI, selected bond distances and angles in Tables SXVII–SXXI.[29]

Supplementary Material Available: Experimental details associated with data collection (Table SI), fractional atomic coordinates (Tables SII–SVI), unrefined hydrogen coordinates (Tables SVII–SXI), thermal parameters (Tables SXII–SXVI), and bond distances and angles (Tables SXVII–SXXI) for complexes **3, 4, 5, 7,** and **8**, and Schakal drawings for complexes **4, 5,** and **7** (32 pages); listings of observed and calculated structure factors (71 pages). Ordering information is given on any current masthead page.

(29) See the paragraph at the end of the paper regarding supplementary material.