Bifunctional Carriers of Alkali-Metal Enolates: The Use of Zirconium *meso*-Octaethylporphyrinogen in Aldol Condensation Reactions

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Summary: The (meso-octaethylporphyrinogenato)zirconium(IV) species [(Et_8N_4)Zr(thf)] (**1**) *binds the acetophenone potassium enolate [$PhCOCH_2K$]* (**2**) *in its ion-pair form, [(η^5:η^1:η^1:η^1-Et_8N_4)Zr{PhC(CH_2)O}K($thf)_3$]* (**3**), *and thus drives the aldol condensation reaction with acetophenone. The resulting aldolate, which occurs in a metallacyclic form due to the solvation of potassium by a phenyl ring, remains η^1 (O)-bonded to zirconium, [(η^5:η^1:η^1:η^1-Et_8N_4)Zr{PhC(CH_2)OC(O)C(Me)Ph}K]$_n$* (**4**).

Bifunctional coordination compounds, which have as a part of their structure two complementary (*i.e.* electron-poor and electron-rich) reactive sites, display the ability to carry polar functionalities in their tight or separated ion-pair form. This unique behavior is exemplified by organocuprates,[1] which act as carriers of lithium organometallics and exhibit a bifunctional nature, by which both copper and lithium can intervene in the reaction with a substrate. Only a few other examples can be mentioned, such as the alkyl and aryl derivatives of transition metals in their "ate" form.[2] We should emphasize the relevance of using "carriers" [$L_nM-R^-Li^+$] rather than neutral organometallic functionalities [L_nM-R], since the former is more likely to convert a stoichiometric into a catalytic metal-promoted reaction.

The bifunctional (*meso*-octaethylporphyrinogenato)-zirconium species [Et_8N_4Zr(THF)] (**1**), which displays carrier properties toward alkali-metal alkyls, aryls, and hydrides,[3,4] has been engaged in reactions with potassium enolates and in the aldol condensation reaction, as reported in Scheme 1.

The employment of early transition metals to influence the reactivity of enolates is a commonly used strategy in organic synthesis.[5] Although mediation by titanium(IV)[6] and, in some cases, zirconium(IV)[7] is commonly encountered,[8] very rarely have these intermediates been isolated and characterized.[9] In addition, they have never been identified as zirconium−alkali-metal enolate adducts. To this end we wish to report a zirconium complex acting as a carrier of the alkali-metal enolate and the derived alkali-metal aldolate in their ion-pair forms.

Complex **1** displays its bifunctional character by binding the potassium enolate **2** in the tight ion-pair

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[10] Procedure for **3**: KH (0.232 g, 5.79 mmol) was added at room temperature to a colorless THF (150 mL) solution of freshly distilled CH_3COPh (0.69 g, 5.8 mmol). At the end of the gas evolution, the suspension of a white solid in a pale yellow solution was warmed to 50 °C for 2 h. **1** (4.06 g, 5.79 mmol) was added, yielding a yellow solution. The solvent was removed *in vacuo*, toluene was added to the residue, and the product, **3**, was collected and dried *in vacuo* (3.2 g, 70%). Crystals suitable for X-ray analysis were grown in a mixture of toluene and THF. Anal. Calcd for $C_{52}H_{75}KN_4O_3Zr$: C, 67.09; H, 7.63; N, 6.02. Found: C, 67.82; H, 7.20; N, 6.43. ^1H NMR (pyridine-d_5, 200 MHz, 298 K): δ 7.91 (m, 2H, Ar H), 7.22 (m, 3H, Ar H), 6.45 (s, 8H, C_4H_2N), 5.00 (s, 1H, C=CH_2), 4.51 (s, 1H, C=CH_2), 2.24 (q, J = 7.31 Hz, 8H, CH_2), 2.04 (q, J = 7.25 Hz, 8H, CH_2), 0.96 (t, J = 7.31 Hz, 12H, CH_3), 0.86 (t, J = 7.25 Hz, 12H, CH_3). The crystals used for the X-ray analysis contain a THF molecule of crystallization.

S0276-7333(96)00932-6 CCC: $14.00

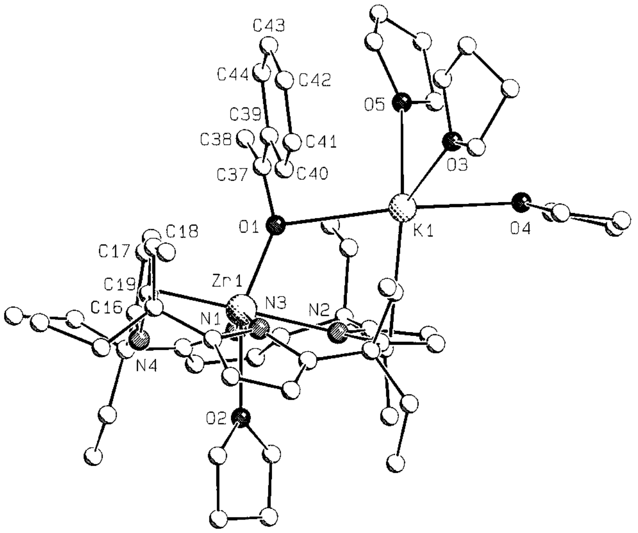
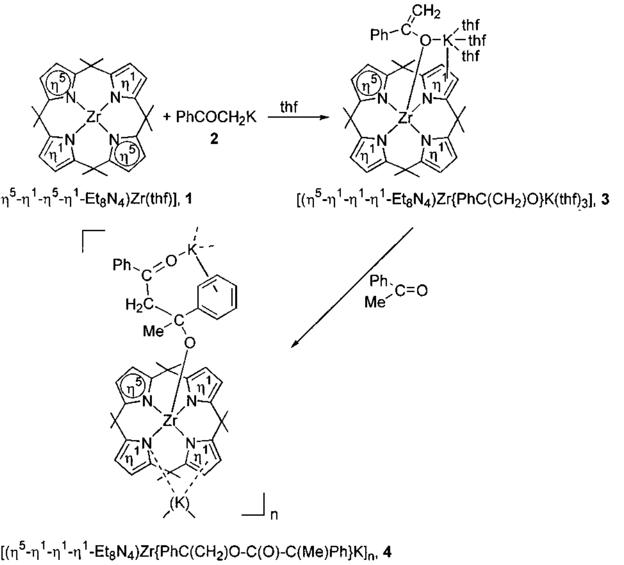


Figure 1. SCHAKAL drawing of complex **3**. Selected bond distances (Å) are as follows: Zr1−O1, 2.041(3); Zr1−O2, 2.400(3); Zr1−N1, 2.239(5); Zr1−N2, 2.255(4); Zr1−N3, 2.233(5); Zr1−N4, 2.429(4); Zr1−Cp4, 2.249(4); K1−O1, 2.886(4); K1−O3, 2.760(4); K1−O4, 2.795(6); K1−O5, 2.772(4); K1−Cp2, 2.907(4); O1−C37, 1.337(5); C37−C38, 1.346(8); C37−C39, 1.494(8). Cp2 and Cp4 refer to the centroids of the pyrrole rings containing N2 and N4, respectively.

form, with zirconocene taking care of the oxygen, while potassium is η^5-bonded to one of the N2, C6, ..., C9 pyrrolyl anions (see complex **3**[10] in Scheme 1 and Figure 1[11]); K−N and K−C distances range from 3.122(5) to 3.255(5) Å. During this reaction the porphyrinogen changes its bonding mode from $\eta^5{:}\eta^1{:}\eta^5{:}\eta^1$ to $\eta^5{:}\eta^1{:}\eta^1{:}\eta^1$, having the pyrrolyl ring (N4, C16, ..., C19) nearly perpendicular to the N_4 core; the dihedral angle is 81.0(2)°. The $\eta^5{:}\eta^1{:}\eta^1{:}\eta^1$ bonding mode of the porphyrinogen cannot be revealed in solution, because of its very low solubility in solvents allowing NMR experiments at low temperature. The N_4 core shows tetrahedral distortions (from −0.075(4) to +0.079(1) Å), Zr protruding by 0.519(2) Å in the O1 direction. The porphyrinogen assumes a flattened saddle-shaped conformation, which consequently allows a suitable binding site for the K cation. The structural parameters of the enolato functionality, with significant C═C double-bond character (C37−C38 = 1.346(8) Å) and a C−O single bond (O1−C37 = 1.337(5) Å), are quite close to those we observed in other η^1-(O)-bonded zirconium enolates.

The aldol condensation has been performed by reacting **3** with acetophenone in THF at room temperature. The reaction led to **4**[12] as a yellow crystalline solid in good yield. Zirconium drives the reaction by assisting the formation of a metallacyclic structure derived from the complexation of the aldolate by the potassium cation (see Scheme 1 and Figure 2[13]). Such a metallacycle formation mimics, at least structurally, the various proposed cyclic transition states for the aldol condensation reaction.[9,14] The present metallacycle has, in addition, some peculiarities when it is compared to the early reports on the use of transition metals in enolate chemistry.[9] First of all, the transition metal is not part of the metallacycle but is supporting a unique structurally identified alkali-metal metallacycle. Second, one

Scheme 1



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(11) Crystal data for **3**: $C_{60}H_{87}KN_4O_5Zr{\cdot}C_4H_8O$, M_r = 1146.8, triclinic, space group $P\bar{1}$, a = 14.189(3) Å, b = 19.264(4) Å, c = 12.724(2) Å, α = 103.84(3)°, β = 115.56(3)°, γ = 94.08(2)°, V = 2985.5(15) Å^3, Z = 2, ρ_{calcd} = 1.276 g cm^{-3}, F(000) = 1228, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 25.60 cm^{-1}: crystal dimensions 0.18 × 0.25 × 0.44 mm. The structure was solved by the heavy-atom method and anisotropically refined for all non-hydrogen atoms. All the hydrogen atoms were located from difference Fourier maps and introduced as fixed contributors in the last stage of refinement (U_{iso} = 0.08 Å^2). For 8755 unique observed reflections ($I > 2\sigma(I)$) collected at T = 138 K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140°$) and corrected for absorption, the final R value is 0.063 (wR2 = 0.172 for the 10 471 reflections having $I > 0$ used in the refinement). All calculations were carried out on a Quansan personal computer equipped with an Intel Pentium processor. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. See the Supporting Information for more details.

(12) Procedure for **4**: Freshly distilled $PhCOCH_3$ (0.52 g, 4.3 mmol) was added dropwise to a pale yellow THF (200 mL) solution of **3** (3.4 g, 4.3 mmol). The resulting light yellow solution was stirred at room temperature for 12 h. After removal of the solvent, toluene was added to the residue and a yellow solid, **4**, was collected (3.04 g, 77%). Recrystallization from THF/toluene gave crystals suitable for X-ray analysis. They contain a toluene molecule of crystallization. Anal. Calcd for $C_{52}H_{63}KN_4O_2Zr$: C, 68.91; H, 7.01; N, 6.18. Found: C, 68.49; H, 7.19; N, 6.00. ^{1}H NMR (pyridine-d_5, 200 MHz, 298 K): δ 8.15 (dd, J_o = 8 Hz, J_m = 1.6 Hz, 2H, O═CAr H), 7.85 (dd, J_o = 8 Hz, J_m = 0.8 Hz, 2H, −OCAr H), 7.35 (m, 3H, Ar H), 7.21 (m, 2H, Ar H), 7.07 (t, J_o = 8 Hz, 1H, −OCAr H), 6.40−6.36 (two singlets overlapping with a pair of doublets, 8H, C_4H_2N), 4.04 (d, J = 16.4 Hz, 1H, CH_2), 3.77 (d, J = 16.4 Hz, 1H, CH_2), 2.37 (m, 4H, CH_2), 2.29 (m, 4H, CH_2), 2.22 (s, 3H, CH_3), 2.08 (q, J = 7.2 Hz, 8H, CH_2), 1.03 (t, J = 7.2 Hz, 12H, CH_2), 0.95 (t, J = 7.2 Hz, 12H, CH_3).

(13) Crystal data for **4**: $C_{52}H_{63}KN_4O_2Zr{\cdot}C_7H_8$, M_r = 998.6, monoclinic, space group $P2_1/n$, a = 15.015(4) Å, b = 20.844(6) Å, c = 16.489(3) Å, β = 102.13(2)°, V = 5045(2) Å^3, Z = 4, ρ_{calcd} = 1.315 g cm^{-3}, F(000) = 2112, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 29.02 cm^{-1}; crystal dimensions 0.23 × 0.25 × 0.58 mm. The structure was solved by the heavy-atom method and anisotropically refined for all the non-H atoms. All the hydrogen atoms were located from difference Fourier maps, introduced as fixed contributors in the last stage of refinement (U_{iso} = 0.05 Å^2). For 5350 unique observed reflections ($I > 2\sigma(I)$) collected at T = 138 K on a Rigaku AFC6S diffractometer ($5 < 2\theta < 140°$) and corrected for absorption, the final R value is 0.054 (wR2 = 0.144 for the 8080 reflections having $I > 0$ used in the refinement). All calculations were carried out on a Quansan personal computer equipped with an Intel Pentium processor. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. See the Supporting Information for more details.

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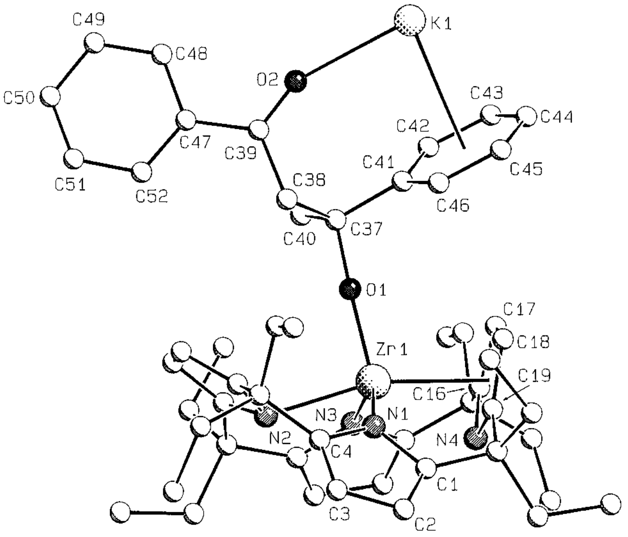

Figure 2. SCHAKAL drawing of complex **4**. Selected bond distances (Å) are as follows: Zr1−O1, 1.917(4); Zr1−N1, 2.243(4); Zr1−N2, 2.262(4); Zr1−N3, 2.227(4); Zr1−N4, 2.349(5); Zr1−Cp4, 2.305(7); K1−O2, 2.628(4); K1−Cp1′, 2.845(5); K1−N2′, 3.128(4); K1−Cb41, 3.055(6); O1−C37, 1.430(7); O2−C39, 1.225(7); C37−C38, 1.533(9); C37−C40, 1.529(9); C37−C41, 1.541(10); C38−C39, 1.518(8); C39−C47, 1.499(10). The prime denotes a transformation of $-0.5 + x$, $0.5 - y$, $-0.5 + z$. Cp1′ and Cp4 refer to the centroids of the pyrrole rings containing N1′ and N4, respectively. Cb41 refers to the centroid of the C41, ..., C46 aromatic ring.

of the arene rings solvates the potassium cation, the K···C distance ranging from 3.148(6) to 3.547(6) Å for the C41−C46 ring (K···C41−C46(centroid) = 3.055(6) Å].[15]

In addition, the K^+ cation acts as a bridge with an adjacent anion symmetry-related by the crystallographic *n* glide plane. The cation interacts in an η^1 fashion with the N2′ nitrogen atom (the prime indicates the symmetry transformation $-0.5 + x$, $0.5 - y$, $-0.5 + z$) and in an η^5 fashion with the N1′, C1′, ..., C4′ pyrrole ring, as indicated by the narrow range of the K−N and K−C distances ranging from 2.981(5) to 3.180(5) Å. In the crystal the bridging role of potassium gives rise to infinite chains running along the [101] crystallographic axis (Figure S1, Supporting Information). The bonding mode and geometry of the $[Zr(Et_8N_4)]$ moiety is close to that observed in **3**, the major difference being the out-of-plane distance of zirconium from the planar N_4 core (0.886(1) *vs* 0.519(2) Å), which can be attributed to the stronger Zr−O(alkoxide) interaction. The Zr−O1 line forms a dihedral angle of 20.3(1)° with the normal to the N_4 core.

Among the structural parameters of the cyclic potassium aldolate, we should mention the very short Zr−O1 [1.917(4) Å; Zr−O1−C37 = 169.4(4)°) and the long O1−C37 (1.430(7) Å) distance and the C=O double bond (C39−O2 = 1.225(7) Å). In the aldol compound the ^1H NMR spectrum at room temperature reveals the same η^5:η^1:η^1:η^1 bonding mode of the porphyrinogen observed in the solid state. We are extending this work by using **1** as a carrier for both the starting enolates as well as for the final alkali-metal aldolate along with investigations into the removal of the potassium aldolate from **4** to give **1**, which can then act as a catalyst in the metal-assisted aldol condensation reactions.

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Supporting Information Available: Figure S1, giving a SCHAKAL drawing of complex **4**, and tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for complexes **3** and **4** (16 pages). Ordering information is given on any current masthead page.

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