The Structure of the 1,3-Diphenyl-2-azaallyl Anion–Potassium Ion Pair and its Oxidative Coupling by Zirconium(IV)

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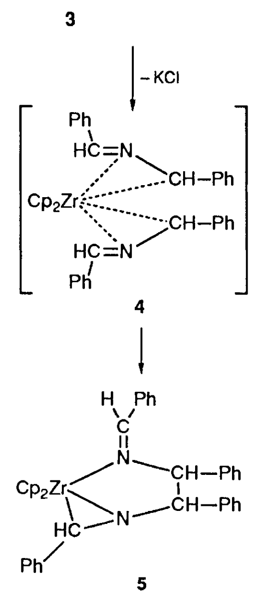
Deprotonation of $PhCH{=}N{-}CH_2Ph$ by KH in tetrahydrofuran in the presence of 18-crown-6 led to the isolation of the 2-azaallyl anion–potassium ion pair [PhCH$\overset{-}{=}$N$\overset{-}{=}$CHPh]···[K(18-crown-6)] which was oxidatively coupled to a diimino ligand by Cp_2ZrCl_2 to form $[Cp_2Zr(\eta^2\text{-}PhCH{-}N{-}CH(Ph)CH(Ph){-}N{=}CHPh\text{-}\eta^1)]$.

In spite of the ubiquitous presence of the allyl ligand in organometallic chemistry,[1] the reactions of the isoelectronic 2-azaallyl ligand,[2,3] where the central CH group of the allyl fragment is replaced by a nitrogen atom, with transition metals[4] are not so common; this particular ligand has been studied mainly by Young.[2] With such a perspective we decided to isolate the title anion in the solid state and to study its reaction with transition metals. Some preliminary results are reported in this communication.

The imine $PhCH{=}N{-}CH_2Ph$, **1**, was refluxed for 12 h in the presence of KH and then the 18-crown-6 was added. The solid residue obtained from the evaporation of tetrahydrofuran (THF), followed by extraction with Et_2O gave **2** as violet crystals (94%),† [see eqn. (1)].

$$\underset{\mathbf{1}}{PhCH{=}N{-}CH_2Ph} \xrightarrow[\text{18-crown-6}]{\text{KH}} \underset{\mathbf{2}}{[Ph{-}CH{\overset{-}{=}}N{\overset{-}{=}}CH{-}Ph]^-[K(18\text{-crown-6})]^+} \quad (1)$$



Scheme 1

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† Analytical data are in agreement with the proposed formula.

The solid state structure‡ is shown in Fig. 1 for the two enantiomeric 2-azaallyl forms *A* and *B* interacting with the [K(18-crown-6)]$^+$ cation, both forms have a very close structure.

In each case the azaallyl plane defined by C(17)–N(1)–C(18) is almost parallel to the plane through O(1)···O(6) of the 18-crown-6, the dihedral angle being 4.3(5)° (molecule *A*) and 9.1(6)° (molecule *B*). The azaallyl has the *cis* conformation. The K···azaallyl interaction is mainly localized at N(1) and C(17) in the *A* form [K···N(1) 3.105(6); K···C(17) 3.044(7) Å] and at N(1) and C(18) in the *B* form [K···N(1) 3.017(7); K···C(18) 3.263(9) Å]. The C(17)–N(1)–C(18)–C(21) and C(18)–N(1)–C(17)–C(11) torsional angles have very close values for the two forms [172.3(7) and −178.5(7)° (*A*); 176.4(7) and −173.1(8)° (*B*)]. The C(17)–N(1) and C(18)–N(1) bond distances are very similar to each other and in both forms (see caption for Fig. 1). While the structure of **2** represents the first example of a 2-azaallyl ion pair, significant examples of 1-azaallyl ion pairs appeared recently in the literature.[5]

The 2-azaallyl anion prepared *in situ* in dimethoxyethane by using either LiBu or KH was reacted with Cp_2ZrCl_2 (Cp = η^5-C_5H_5). The solution was evaporated to dryness and the solid recrystallized from Et_2O gave red-brown crystals of **5**.†‡§

The structure is supported by an X-ray analysis‡ (Fig. 2) and spectroscopic data. The ligand around zirconium is a bidentate diimine formally derived from the condensation of benzaldehyde and 1,2-diphenylethylenediamine. One of the imino groups is η^1 N-bonded and the other one is η^2 C,N-bonded to zirconium. It may come from the oxidative coupling of two azaallyls *via* an intermediate like **4** and the oxidative addition of one of the imino groups to zirconium(II). The Zr–N, Zr–C, and C–N bond distances (see caption for Fig. 2) allow a significant comparison for the η^1 and η^2 bonding mode of the same functionality within the same ligand. The η^2 bonding of an imino group has never been structurally identified in zirconium(IV) chemistry.[6] Some interesting structural com-

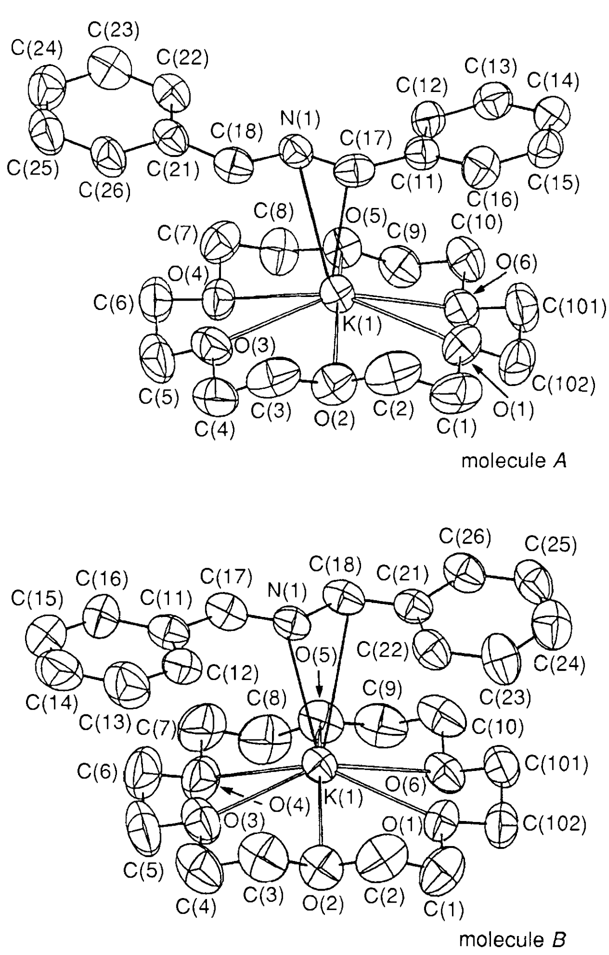

Fig. 1 An ORTEP drawing for compound **2** (molecule *A*, values for *B* in square brackets) (30% probability ellipsoids). Bond distances (Å): K–O$_{av}$, 2.818(6) [2.852(7)]; K(1)–N(1), 3.105(6) [3.017(7)]; K(1)–C(17), 3.044(7) [3.554(9)]; K(1)–C(18), 3.647(8) [3.263(9)]; N(1)–C(17), 1.340(10) [1.326(11)]; N(1)–C(18), 1.350(10) [1.349(11)]; C(17)–C(11), 1.455(9) [1.430(10)]; C(18)–C(21), 1.450(10) [1.437(10)]. Bond angles (°): C(17–N(1)–C(18), 122.3(7) [123.5(7)]; N(1)–C(17)–C(11), 120.8(6) [124.3(8)]; N(1)–C(18)–C(21), 122.3(7) [121.7(7)].

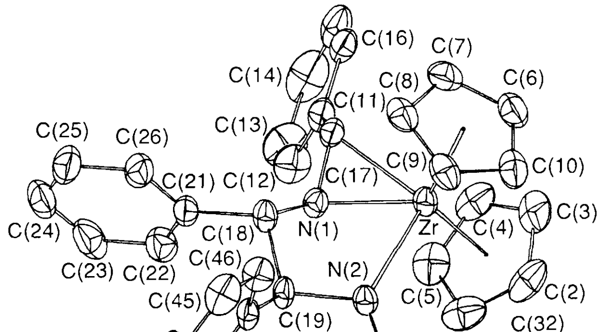

Fig. 2 An ORTEP drawing for complex **5** (30% probability ellipsoids). Bond distances (Å): Zr–Cp(1), 2.236(5); Zr–Cp(2), 2.251(6); Zr–N(1), 2.091(4); Zr–C(17), 2.331(6); Zr–N(2), 2.449(4); N(1)–C(17), 1.418(8); N(1)–C(18), 1.462(7); N(2)–C(19), 1.528(7); N(2)–C(20), 1.269(8). Bond angles (°); Cp(1)–Zr–Cp(2), 129.7(2); N(1)–Zr–N(2), 69.3(2); N(1)–Zr–C(17), 36.9(2); N(2)–Zr–C(17), 104.8(2).

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‡ *Crystal data* for **2**: $C_{26}H_{36}NO_6K$, M = 497.7, monoclinic, space group Pc, a = 10.875(1), b = 17.401(2), c = 14.569(1) Å, β = 97.14(1)°, U = 2735.6(5) Å^3, Z = 4, D_c = 1.208 g cm^{-3}, Cu-Kα radiation (λ = 1.54178 Å); crystal dimensions 0.32 × 0.42 × 0.48 mm^3. The structure was solved by direct methods (SHELX-86) and refined by full-matrix least-squares. For 2878 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 140°$, the R values is 0.049. Since the space group is polar, the chirality of the crystals was tested by inverting all the coordinates and refining to convergence once again. The resulting R values indicated the previous choice should be considered the correct one (R = 0.0539, R_G = 0.0517 for the 'inverted' structure *vs.* R = 0.0493, R_G = 0.0471 for the original choice.

For **5**: $C_{38}H_{34}N_2Zr$, M = 609.9, monoclinic, space group $P2_1/n$, a = 16.280(1), b = 20.981(2), c = 18.396(1) Å, β = 106.46(1)°, U = 6026.0(8) Å^3, Z = 8, D_c = 1.345 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å); crystal dimensions 0.25 × 0.28 × 0.48 mm^3. The structure was solved by direct methods (SHELX-86) and refined by full-matrix least-squares. For 4418 unique observed structure amplitudes [$I > 2\sigma(I)$] collected at room temperature on a Philips diffractometer in the range $6 < 2\theta < 46°$, the R value is 0.042.

For both compounds refinement was by full-matrix least-squares anisotropically for all the non-hydrogen atoms. All the hydrogen atoms were directly located from difference maps and introduced in the refinement as fixed contributors (U = 0.082 Å^2). During the refinement the phenyl rings were considered as rigid hexagons (C–C = 1.395 Å). All calculations were carried out using SHELX76. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ ^{1}H NMR for complex **5** (δ, C_7D_8, 243 K): 3.85 (s, 1 H, η^2-C,N); 4.15 (d, 1 H, CH–CH); 5.92 (d, 1 H, CH–CH, J_{HH} 10 Hz); 5.45 (s, 5 H, Cp); 6.03 (s, 5 H, Cp); 6.9–7.8 (m, 20 H, Ph); 8.48 (s, 1 H, η^1-C,N).

parisons can be made with η^2-imine[7] and Schiff base[8] derivatives.

Scheme 1 shows that even in the presence of a metal, which is difficult to reduce, the azaallyl ligand undergoes an oxidative coupling. The use of the azaallyl anion in transition metal chemistry has to overcome the difficulty derived from its reducing properties, as we are currently exploring.

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