The O-bonded Monometallic and O- and C-bonded Dimetallic Form of N,N-Diphenylacetamide Enolate with Transition Metals: X-Ray Structure of [Ph₂N–C(CH₂)OZr(η⁵-C₅H₅)₂(Cl)] and [Ph₂N–C{CH₂Cr(CO)₅}OZr(η⁵-C₅H₅)₂(Cl)]

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The N,N-diphenylacetamide enolato anion oxygen bonded to zirconium in [Ph₂N–C(CH₂)OZr-(η⁵-C₅H₅)₂(Cl)] has been synthesised, which, when reacted with [Cr(CO)₅(thf)], led to the dimetallic form of the amide enolato O-bonded to zirconium and C-bonded to chromium.

The amide enolates have a relevant role in synthetic chemistry.[1] Although it is well known that the metallated form is responsible for the stereochemical control in their reactions,[2] we did not find any indication of isolation and structural characterisation of transition metal amide enolates. In this context we report here the derivatisation of a very simple amide enolate in a mono- (**A**) and di-metallic (**B**) form: in the latter form both nucleophilic sites, C and O, are engaged in binding two different M and M' transition metals.

Deprotonation of **1** was carried out in thf by the use of LiNPr$^i_2$ followed by reaction with zirconocene dichloride, see eqn. (1).

Complex **3**†‡ was isolated in high yield (80%) as a yellow crystalline solid. The lithium form of the amide enolate, **2**,†‡ was obtained as a white crystalline solid. We do not know its structure, a single example being reported for a lithium amide

enolate.[3] The structure of **3**,§ shown in Fig. 1 with some selected structural parameters, will be discussed jointly with that of **4**.

The soft nucleophilicity of the methylene carbon in the enolate **3** was engaged in binding a low-valent transition metal.

Compound **4** was obtained by adding a tetrahydrofuran (thf) solution of [Cr(CO)₅(thf)] to a diethyl ether solution of **3**, see eqn. (2). The oily compound formed was crystallised from diethyl ether to give **4**†‡ as a crystalline solid. This reaction, which was not observed with the analogous zirconium keto-enolates,[4] emphasizes the good nucleophilicity of the
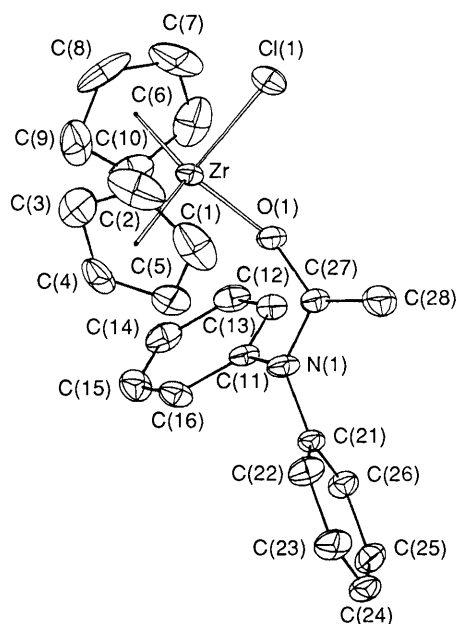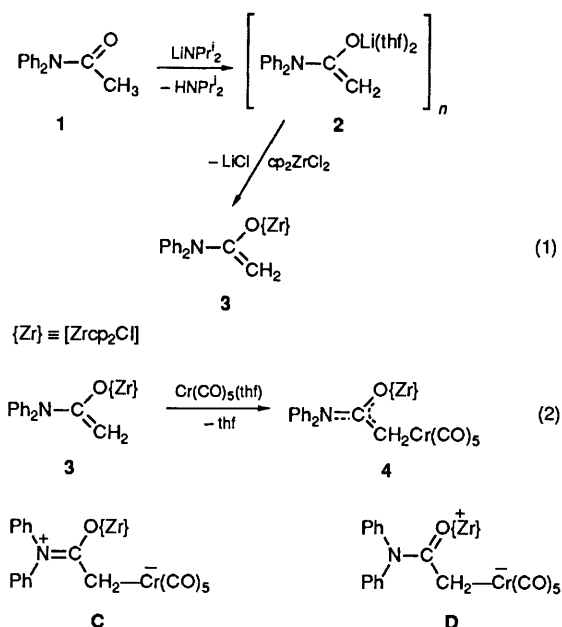
A   B

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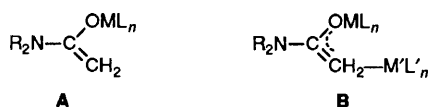
† Satisfactory analytical and spectroscopic data have been obtained.

‡ *NMR data*: complex **2**: ¹H NMR (δ, C₆D₆): 1.40 (m, 8H, thf), 3.42 (s, 1H, CH₂), 3.63 (m, 9H, thf + CH₂), 6.85 (m, 2H, Ph), 7.1–7.3 (m, 8H, Ph). Complex **3**: ¹H NMR (δ, CD₂Cl₂): 3.64 (s, 2H, CH₂), 6.22 (s, 10H, cp), 7.0–7.4 (m, 10H, Ph). ¹³C NMR (δ, CD₂Cl₂): 78.1 (s, CH₂), 115.1 (s, cp), 123.5–129.7 (5s, Ph), 147.1 (s, Ph), 163.9 (s, C–O). Complex **4**: ¹H NMR (δ, CD₂Cl₂): 1.72 (q, 2H, CH₂–Cr), 6.28 (s, 5H, cp), 6.31 (s, 5H, cp), 7.3–7.5 (m, 10H, Ph). ¹³C NMR (δ, C₆D₆): 13.8 (s, CH₂–Cr), 115.4 (t, cp), 130 (Ph), 191.3 (s, N–C–O), 219.8 (s, Cr–CO), 225.2 (s, Cr-CO). IR ν/cm⁻¹ (nujol), Cr(CO)₅: 2051w, 1938s, 1916s, 1840s.

{Zr} ≡ [Zrcp₂Cl]

Fig. 1 An ORTEP view of complex 3. Bond distances (Å) and angles (°): Zr–cp(1) 2.206(5), Zr–cp(2) 2.215(5), Zr–Cl(1), 2.461(1), Zr–O(1) 1.976(3), O(1)–C(27) 1.337(5), N(1)–C(27) 1.414(6), C(27)–C(28) 1.323(7); cp(1)–Zr–cp(2) 128.9(2), O(1)–Zr–Cl(1) 98.3(1), Zr–O(1)–C(27) 147.3(3).

methylene carbon in such an amide enolate. In addition, it represents a quite unique use of an enolate as a nucleophile towards organometallic substrates. The Cr(CO)₅ fragment introduces significant changes in the amide enolate skeleton. The bonding scheme proposed for the dimetallic form derives from the structural data summarised in the caption of Fig. 2, showing the structure of 4§ (vide infra). The torsional angles Cl(1)–Zr · · · C(27)–C(28) [18.4(4), 3 and 23.2(3)°, 4] and Cl(1)–Zr · · · C(27)–N(1) [176.7(3), 3 and 178.4(4)°, 4] show in both complexes the CH₂ nucleophile being cis and N(1) trans oriented referring to the Cl ligand at zirconium.

The dihedral angles of the C(11) · · · C(16) and C(21) · · · C(26) phenyl planes with respect to the enolato O(1), N(1), C(27), C(28) plane are very close in both complexes: 112.5(1) and 109.5(2)° for complex 3, 109.8(1) and 102.0(1)° for complex 4 respectively. The binding of Cr(CO)₅ by 3 induced a significant rotation around the Zr–O bond, as exemplified in comparing the following torsional angles: Cl(1)–Zr–O(1)–
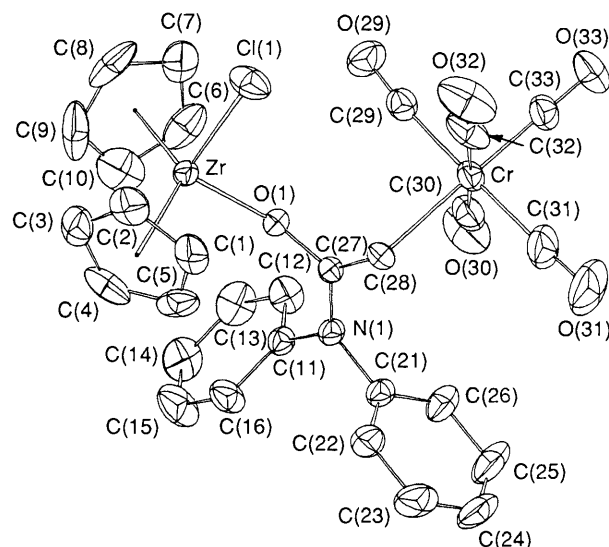
Fig. 2 An ORTEP view of complex 4. Bond distances (Å) and angles (°): Zr–cp(1) 2.206(5), Zr–cp(2) 2.206(7), Zr–Cl(1) 2.415(2), Zr–O(1) 2.045(3), O(1)–C(27) 1.311(5), N(1)–C(27) 1.360(6), C(27)–C(28) 1.388(7), Cr–C(28) 2.329(5), Cr–C(29) 1.894(6), Cr–C(30) 1.895(8), Cr–C(31) 1.896(8), Cr–C(32) 1.908(9), Cr–C(33) 1.815(6); cp(1)–Zr–cp(2) 130.1(3), O(1)–Zr–Cl(1) 97.3(1), Zr–O(1)–C(27) 141.2(3), Cr–C(28)–C(27) 107.7(3).

C(27) [95.9(5), 3; 76.1(5)°, 4], Zr–O(1)–C(27)–C(28) [−87.4(7), 3; −61.0(7)°, 4]; Zr–O(1)–C(27)–C(21) [90.6(6), 3; 119.2(5)°, 4]. The attack of the methylene carbon on Cr(CO)₅ led to the formation of an alkylcarbonylmetallate.⁵ The C-end of the enolate binds Cr at the normal distance for a Cr–C σ bond [2.329(5) Å] in a metallate derivative.⁶ The CO trans to it takes care of the major amount of the charge transferred by the enolate to the metal, the Cr–C(33) and C(33)–O(33) distances being significantly shorter and longer respectively than those for the other four Cr–C–O groups (see caption of Fig. 2). Lengthening of the C(27)–C(28) and Zr–O(1) bonds, shortening of the C(27)–O(1) and N(1)–C(27) bonds were observed moving from 3 to 4, as we expect every time the methylene carbon is engaged into a nucleophilic attack on some electrophile. In addition N(1) has a significant degree of pyramidality in 3, being 0.169(4) Å out of the plane C(11), C(21), C(27), while N(1) is almost coplanar in 4 [0.019(4) Å]. According to these facts a simple picture for charge separation is shown in the limiting structures C and D of 4.

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