Naked Enolates and Their Reactions with Metal Carbonyls Leading to Metallocarbene Enolates and Alkylcarbonylmetalates

Patrick Veya and Carlo Floriani*

Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

Angiola Chiesi-Villa and Carlo Guastini

Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR,
Università di Parma, I-43100 Parma, Italy

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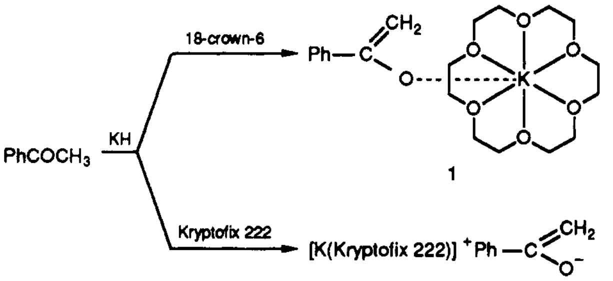
Summary: Preparations of the acetophenone ion pair [PhC(CH$_2$)O···K(18-crown-6)] (**1**) and the ion-separated potassium enolate [PhCOCH$_2$]$^-$[K(Kryptofix 222)]$^+$ (**2**) are reported. Such starting materials have been characterized by ^{1}H and ^{13}C NMR spectroscopy and X-ray analysis. The reaction of the highly nucleophilic enolate **1** with Cr(CO)$_6$ led to attack at carbon monoxide with the formation of the potassium metallocarbene enolate [(CO)$_5$Cr=C(O)CH=C(Ph)O]$^{2-}$([K(18-crown-6)]$^+$)$_2$ (**4**). The enolate **1** reacts with [Cr(CO)$_5$(THF)], binding the metal through the carbon end and forming the alkylcarbonylmetalate–potassium ion pair [(CO)$_5$CrCH$_2$C(Ph)O···K(18-crown-6)] (**6**).

The interaction of ketone enolates with main-group or electron-poor transition metals is a subject of wide interest.[1] Much less attention has been directed to reaction of metal enolates on electron-rich metals or on functionalities attached to them.[2] Within this context we decided to look at the reactivity of highly nucleophilic naked enolates on transition-metal carbonyls. The synthesis of naked or ion-pair monomeric enolates[3] has been achieved by forming the potassium enolate as reported in reaction 1 and complexing the potassium cation with 18-crown-6 or Kryptofix 222.[4,5]



1 (1)

2

Compounds **1**[4] and **2**[3b,5] have been obtained in very good yield and in crystalline form. The ^{1}H NMR spectra (C$_6$D$_6$) show two fine doublets at 3.29 and 4.01 ppm (J = 1.9 Hz) for **1** and at 4.03 and 4.67 ppm (J = 2.4 Hz) for **2**. The ^{13}C NMR spectra show the enolic carbon at 125.8 ppm, in agreement with a carbon–carbon double bond. The X-ray structure has been determined for both compounds. Details are given in Figure 1 for **2**.[6] The [K(Kryptofix 222)] fragment does not deserve any special comment. The enolate anion is weakly bonded in the solid state via the basic oxygen to the peripheral hydrogens of Kryptofix (A refers to one of the two portions over which the enolato oxygen is statistically distributed). The naked anion is in

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* To whom correspondence and reprint requests should be addressed.

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(3) For investigations of potassium enolates with crown ethers or cryptands see the following. (a) Structure of ethyl acetoacetate potassium enolate with 18-crown-6: Riche, C.; Pascard-Billy, C.; Cambillau, C.; Bram, G. *J. Chem. Soc., Chem. Commun.* **1977**, 183. Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *Can. J. Chem.* **1982**, *60*, 2554. Structure with Kryptofix 222: Cambillau, C.; Bram, G.; Corset, J.; Riche, C. *New J. Chem.* **1979**, *3*, 9. (b) Cyclohexanone, propanone, and acetophenone potassium enolates with Kryptofix 222 have been reported without any structural characterization: Pierre, J.-L.; Le Goeller, R.; Handel, H. *J. Am. Chem. Soc.* **1978**, *100*, 8022. These authors saw an intriguing behavior for complex **2**, reaction with Et$_2$O. We have never observed such a reaction with Et$_2$O. **2** behaves correctly if Et$_2$O is well dried. (c) Pinacolone potassium enolate structure: Williard, P.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462.

(4) Procedure for **1**: Acetophenone (5.70 g, 47.4 mmol) was slowly added to a THF (300 mL) suspension of KH (2.10 g, 52.3 mmol). The resulting white fluffy suspension was stirred for 4–5 h. It dissolved by addition of freshly distilled 18-crown-6 (12.54 g, 47.4 mmol), giving a brown-red solution. The solution was evaporated to dryness and the residue extracted with Et$_2$O (18.8 g, 92% of a white-yellow crystalline solid very sensitive to air). **1** can also be recrystallized from a THF/Et$_2$O solution. Anal. Calcd for C$_{20}$H$_{31}$KO$_7$: C, 56.85; H, 7.39; K, 9.25. Found: C, 56.71; H, 7.32; K, 9.02. ^{1}H NMR (C$_6$D$_6$): δ 3.29 (s, CH$_2$—O 18-crown-6, 24 H), 4.01 (d, =CH, 1 H, J 1.9 Hz), 4.63 (d, =CH, 1 H, J 1.9 Hz), 7.2–7.5 and 8.5 (m, Ph, 5 H). ^{13}C NMR (C$_6$D$_6$): δ 70.7 (s, 18-crown-6), 125.8 (s, =CH$_2$), 127.4–128.9 (m, Ph), 149.1 (s, Ph).

(5) Procedure for **2**: The same procedure as for **1** was used for **2**, which, being more soluble, was crystallized after extraction as the Et$_2$O solution was cooled to 0 °C (88%). Anal. Calcd for C$_{26}$H$_{43}$KN$_2$O$_7$: C, 58.29; H, 8.27; N, 5.22. Found: C, 58.23; H, 8.27; N, 5.20. ^{1}H NMR (C$_6$D$_6$): δ 2.37 (t, CH$_2$—N, 12 H), 3.36 (t, CH$_2$—O, 12 H), 3.43 (s, CH$_2$—O, 12 H), 4.03 (d, =CH, 1 H, J 2.4 Hz), 4.67 (d, =CH, 1 H, J 2.4 Hz), 7.1–7.5 and 8.55 (m, Ph, 5 H). ^{13}C NMR (C$_6$D$_6$): δ 55.9 (s, N—CH$_2$, Kryptofix 222), 68.8 (s, O—CH$_2$, Kryptofix 222), 71.0 (s, O—CH$_2$, Kryptofix 222), 125.2 (s, =CH$_2$), 127.2–128.9 (s, Ph), 150.7 (s, Ph), 170.5 (s, C—O$^-$).

(6) Structure of **2**: C$_{26}$H$_{43}$KN$_2$O$_7$, M_r = 534.7, monoclinic, space group $P2/n$, a = 17.473 (2) Å, b = 10.615 (1) Å, c = 16.133 (2) Å, β = 99.75 (1)°, V = 2949.1 (6) Å^3, Z = 4, ρ_{calcd} = 1.204 g cm^{-3}, λ(Cu Kα) = 1.541 78 Å, μ(Cu Kα) = 19.31 cm^{-1}, crystal dimensions 0.35 × 0.40 × 0.48 mm^3; 3474 unique observed structure amplitudes ($I > 2\sigma(I)$) collected at room temperature on a Siemens AED diffractometer in the range 6° < 2θ < 140°. The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least squares anisotropically except for the disordered atoms of the two butyl groups. The enolate oxygen atom was found to be disordered over two positions (A and B) symmetrically distributed with respect to the plane running through the rest of the ion. The hydrogen atoms, partly located in a difference Fourier map and partly geometrically calculated, were introduced as fixed contributors in the final stage of refinement. All calculations were carried out with use of SHELX-76.

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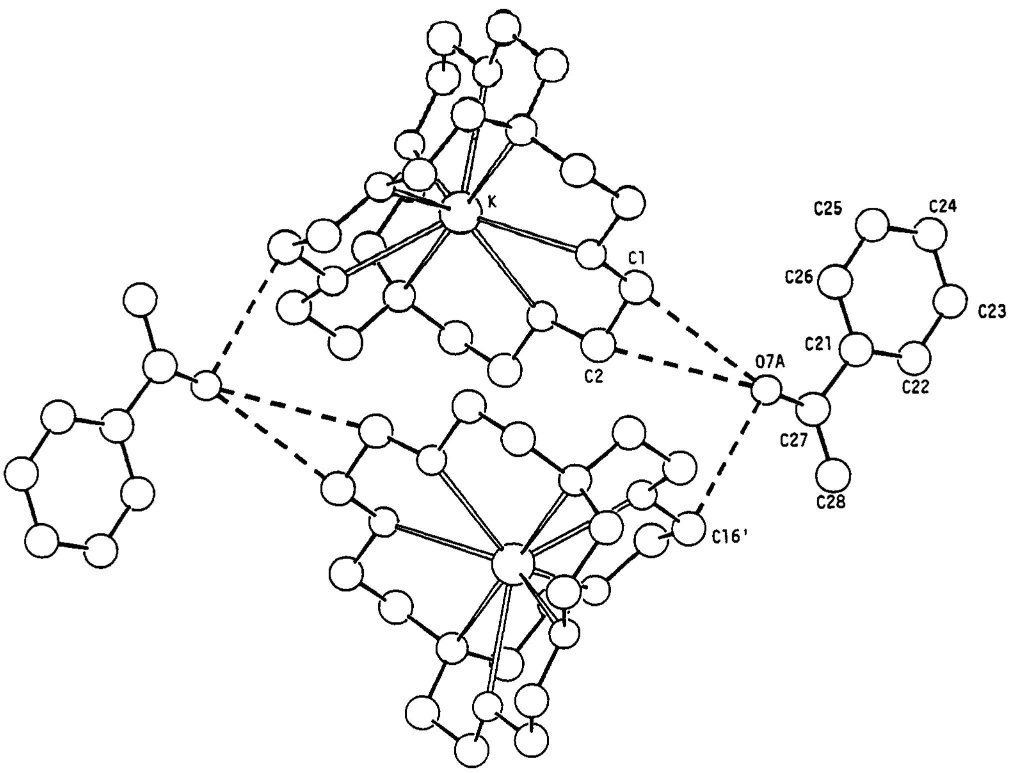
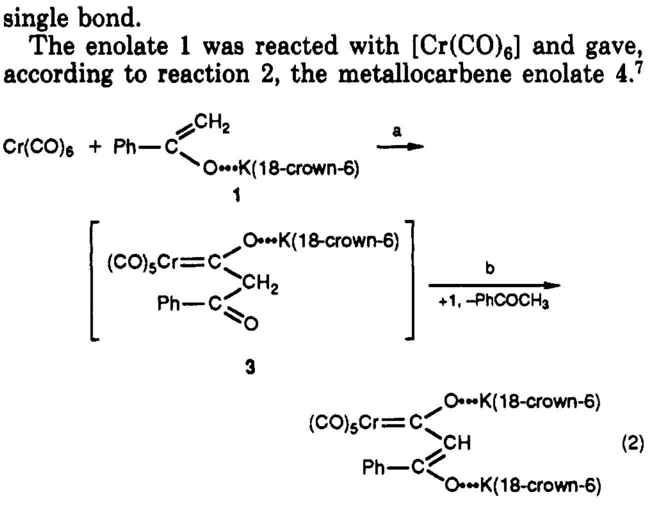


Figure 1. View of the packing in complex **2**. Selected bond distances (Å) and angles (deg) include the following: K–O1 = 2.854 (2), K–O2 = 2.809 (4), K–O3 = 2.821 (3), K–O4 = 2.768 (3), K–O5 = 2.838 (2), K–O6 = 2.793 (3), K–N1 = 3.004 (3), K–N2 = 3.007 (3), O7A–C1 = 3.237 (20), O7A–C2 = 3.301 (18), O7A–C16′ = 3.246 (17), O7A–C27 = 1.393 (17), C21–C27 = 1.508 (4), C27–C28 = 1.348 (5); O7A–C27–C21 = 113.7 (8), C21–C27–C28 = 119.5 (3), O7A–C27–C28 = 124.5 (7). The prime denotes a transformation of 1 − *x*, −*y*, 1 − *z*.

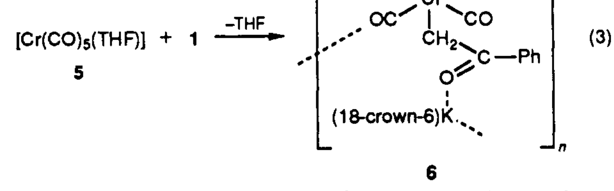
the enolato form with a C═C double bond and a C—O single bond.

The enolate **1** was reacted with $[Cr(CO)_6]$ and gave, according to reaction 2, the metallocarbene enolate **4**.[7]



Complex **4**[7] was obtained in 90% yield in crystalline form regardless of the stoichiometric ratio. Deprotonation of **3** (step b) is much faster than step a. Actually, if a 1/1 stoichiometry is used, 50% of the $Cr(CO)_6$ is recovered by sublimation and acetophenone is regenerated. The IR spectrum does not show any ketone band related to **3**, but only a $M(CO)_5$ pattern. Complex **4** is rather thermally labile, and it has to be handled at a temperature lower than 0 °C in solution. It was analytically and spectroscopically fully characterized. The ^1H NMR spectrum of complex **4** shows a singlet at 6.58 ppm, for the methine proton, and the absence of any methylenic proton. The ^{13}C NMR spectrum gives hints: the enolic carbon exhibits a doublet at 118.5 ppm (J_{CH} = 152.7 Hz). The carbene carbon is at 330.1 ppm. Some difficulties have been encountered thus far in the X-ray analysis of **4**, due to its thermal lability. The reaction of **2** with $Cr(CO)_6$ is more complex and is still under investigation.

The use of electron-rich unsaturated metals can reverse the normal enolate–transition-metal interaction, which normally occurs through the oxygen.[1,2] We chose to also examine the reaction of **1** with $[Cr(CO)_5(THF)]$, as a source of the soft 16e⁻ $Cr(CO)_5$. The nucleophilic attack of the enolate proceeds at the metal rather than at the CO as observed for $Cr(CO)_6$:



The metal prefers the softer CH_2 site of the enolate,

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[7] Procedure for **4**: **1** was added as a solid (5.20 g, 12.30 mmol) to an Et_2O (150 mL) solution of $Cr(CO)_6$ (1.38 g, 6.25 mmol); this mixture was then stirred for 3–4 h at room temperature. A microcrystalline solid slowly formed (5.10 g, 90%). It was recrystallized from THF at a temperature lower than 0 °C. The solid is thermally stable. Anal. Calcd for $C_{38}H_{54}CrKO_{19}$: C, 48.30; H, 5.76. Found: C, 48.40; H, 5.86. ^1H NMR (THF-d_8, 273 K): δ 3.60 (s, CH_2—O 18-crown-6, 48 H), 6.58 (s, ═CH, 1 H), 7.1–7.2 (m, Ph, 3 H), 8.00 (m, Ph, 2 H). ^{13}C NMR (THF-d_8, 273 K, not coupled): δ 72.2 (s, CH_2—O 18-crown-6), 118.5 (s, ═CH enolic), 126.6–130.0 (m, Ph), 150.1 (s, Ph), 163.4 (impurities), 170.6 (s, C—O⁻), 230.3–232.6 (s, Cr–CO), 330.1 (s, Cr═C). ^{13}C NMR (THF-d_8, 273 K, coupled): δ 72.2 (t, CH_2—O, J_{CH} 141.3 Hz), 118.5 (d, ═CH, J_{CH} 152.7 Hz), 126.6–131.7 (m, Ph), 150.2 (m, Ph), 163.4 (impurities), 170.6 (s, C—O⁻), 230.3 and 232.6 (2 s, OC—Cr), 330.1 (very weak). IR (THF solution): 2012 (w), 1983 (w), 1913 (m), 1884 (s), 1850 (m) cm^{-1}.

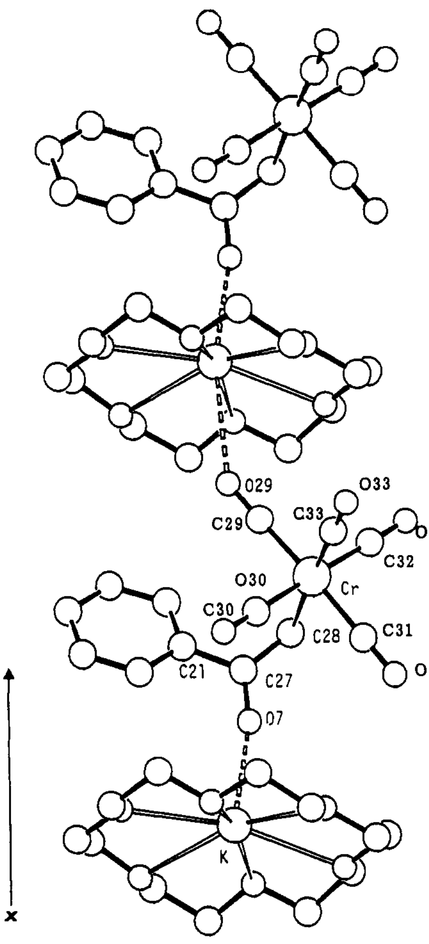

Figure 2. View of the polymeric chain running along x in complex **6**. Selected bond distances (Å) include the following: Cr–C28 = 2.293 (4), Cr–C29 = 1.877 (3), Cr–C30 = 1.872 (4), Cr–C31 = 1.889 (4), Cr–C32 = 1.887 (4), Cr–C33 = 1.821 (4), O7–C27 = 1.238 (5), C21–C27 = 1.514 (4), C33–O33 = 1.163 (5), K–O29′ = 2.922 (4), K–O7 = 2.607 (3). The prime denotes a transformation of $1 + x, y, z$.

resulting in the formation of an alkylcarbonylmetalate ion pair (**6**).[8] The CH_2 gives a large peak at 2.69 ppm and at 18.0 ppm in the ^1H and ^{13}C NMR spectra. Furthermore, the IR spectrum has a ketone band at 1690 cm^{-1}, showing that all the enolic charge has been transferred to the metal. The proposed structure was equally well supported by analytical and X-ray data.[9] Figure 2 shows that the solid-state structure of **6** is polymeric, due to the bridging interaction mode of the unsaturated [K(18-crown-6)]$^+$ cation.

Potassium interacts at a short distance with the enolate oxygen O7 and at a rather long distance with a carbonylic oxygen. By the interaction with the $Cr(CO)_5$ unit the enolato anion is frozen in the unusual ketonic form (C27–C28, 1.424 (6) Å; C27–O7, 1.240 (5) Å) in contrast to the case for **1** and **2** and mainly to those complexes obtained with an oxophilic metal attached to the oxygen.[10] The C end of the enolate binds Cr at the normal distance for a Cr–C σ bond (2.293 (4) Å) in a metalate derivative.[11] The CO trans to it takes care of the major amount of the charge transferred by the enolate to the metal, the Cr–C33 and C33–O33 distances being significantly shorter and longer, respectively, than those for the other four Cr–C–O groups (see the caption for Figure 2). Complex **6** should be considered as an alkylcarbonylmetalate anion in the ion-pair form.[12] The extension of enolate reactivity to metal carbonyls is under investigation, as well as the chemistry of complexes **4** and **6**.

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Supplementary Material Available: Tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters and ORTEP views of compounds **2** and **6** (13 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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(8) Procedure for **6**: A THF (50 mL) solution of **1** (1.09 g, 2.58 mmol) was added at −90 °C to a THF solution (250 mL) of $[Cr(CO)_5(THF)]$ generated in situ by the photolysis of $Cr(CO)_6$ (0.57 g, 2.58 mmol). The resulting red solution was evaporated to dryness. The solid was extracted with use of Et_2O (50 mL) to give a yellow crystalline solid (0.55 g, 35%). Anal. Calcd for $C_{25}H_{31}CrKO_{12}$: C, 48.86; H, 5.08. Found: C, 48.74; H, 5.10. ^1H NMR (C_6D_6): δ 2.69 (broad peak, CH_2—Cr, 2 H), 3.08 (s, CH_2—O, 24 H), 71.–7.4 and 8.25 (m, Ph, 5 H). ^{13}C NMR (CD_2Cl_2): δ 18.00 (s, CH_2—Cr), 70.8 (s, CH_2—O), 128.1–130.1 (2 s, Ph), 141.1 (s, Ph), 199.6 (s, Cr—$CH_2C(O)Ph$), 222.8 and 228.6 (2 s, Cr—CO). IR (THF solution): $\nu_{C=O}$ 2036 (w), 1942 (w), 1908 (s), 1864 (w) cm^{-1}; $\nu_{C=O}$ (Cr—$CH_2C(O)Ph$) 1690 (m) cm^{-1} (compare with a rhenium(I) enolate,[2c] 1669–1672 cm^{-1}).

(9) Structure of **6**: $C_{25}H_{31}CrKO_{12}$, $M_r = 614.6$, triclinic, space group $P\bar{1}$, $a = 10.649$ (1) Å, $b = 14.122$ (1) Å, $c = 10.635$ (1) Å, $\alpha = 94.64$ (1)°, $\beta = 98.04$ (1)°, $\gamma = 108.81$ (1)°, $V = 1485.4$ (3) Å^3, $Z = 2$, $\rho_{calcd} = 1.374$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 5.70 cm^{-1}, crystal dimensions 0.32 × 0.45 × 0.50 mm^3; 3229 unique observed structure amplitudes ($I > 2\sigma(I)$) collected at room temperature on a Philips PW 1100 diffractometer in the range $6° < 2\theta < 50°$ with the use of $\omega/2\theta$ scanning technique. The structure was solved as above and refined by full-matrix least squares anisotropically for all the non-hydrogen atoms. All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. All calculations were carried out with use of SHELX-76.

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(11) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3, Chapter 26.1, p 930.

(12) Alkylcarbonylmetalate anions for group 6 metals have been reported: Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357.