Reaction of Metal Carbonyls with Naked Enolates To Make a Metallocarbene Enolate and Alkylcarbonylmetalates

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The KH-mediated deprotonation of acetophenone and propiophenone in THF led to the ion-pair and naked forms of the following crystalline enolates in good yield: $\mathrm{ArC(CH_2)O\cdots K(18\text{-}crown\text{-}6)}$ [Ar = Ph, **4**; $\mathrm{2\text{-}MeOC_6H_4}$, **5**; $\mathrm{1,3,5\text{-}Me_3C_6H_2}$, **6**], $\mathrm{[PhC(CH_2)O][K(kryptofix\text{-}2,2,2)]}$, **7**, and $\mathrm{[PhC({=}CHMe)O\cdots K(18\text{-}crown\text{-}6)]}$, **8**. The reaction of ion-pair **4** with $\mathrm{[Cr(CO)_5(THF)]}$ led to the isolation of an alkylcarbonylmetalate, **9**, $\mathrm{[PhC(O)CH_2Cr(CO)_4CO\cdots K(18\text{-}crown\text{-}6)]_n}$, a crystalline polymer in which the $\mathrm{[PhC(O)CH_2Cr(CO)_5]^-}$ anion is bridged by $\mathrm{[K(18\text{-}crown\text{-}6)]^+}$ *via* the oxygen of the enolate and one of the carbonyl oxygens. The protonation of the Fischer carbene $\mathrm{[(CO)_5Cr{=}C(OMe)Me]}$, **10**, led to an alkylcarbonylmetalate analogue of **9**. The X-ray analysis of $\mathrm{[CH_2(OMe)CCr(CO)_4CO\cdots K(18\text{-}crown\text{-}6)]}$, **11**, revealed a decrease in the Cr–C(carbene) bond distance, and electron transfer from the anionic carbene to the *trans* CO. The *trans* Cr–C–O has an increased Cr–C bond length, a decreased C–O bond length, and a Cr–C–O angle of 159.7(6)°. The reaction of **4** with $\mathrm{[Cr(CO)_6]}$ led to a Fischer-type metallacarbene, **12**, from attack of the enolate on carbon monoxide; **12** was deprotonated by starting material to a dianionic metallacarbene enolate $\mathrm{[(CO)_5Cr{=}C(O^-)CH{=}C(O^-)Ph]}$, **13**. The alkylation and silylation of **13** led to the corresponding alkylated and silylated forms of **13**, $\mathrm{[(CO)_5Cr{=}C(OMe){-}CH{=}C(OMe)Ph]}$, **16**, and $\mathrm{[(CO)_5Cr{=}C(OSiR_2R'){-}CH{=}C(OSiR_2R')Ph]}$ [R = R′ = Me, **17**; R = Me, R′ = $\mathrm{Bu^t}$, **18**]. An analogous metallacarbene enolate and its silylated form have been obtained for tungsten, $\mathrm{[(CO)_5W{=}C(O^-)CH{=}C(O^-)Ph\cdots\{K(18\text{-}crown\text{-}6)\}_2]}$, **19**, and $\mathrm{[(CO)_5W{=}C(OSiMe_3){-}CH{=}C(OSiMe_3)Ph]}$, **20**. The reaction of the naked enolate **7** and $\mathrm{[Cr(CO)_6]}$ led to a metallacarbene enolate which, due to the absence of stabilization by ion-pair formation, is much less stable than **13** or **19**. Crystallographic details are as follows: **4** is monoclinic, space group $P2_1/n$, a = 10.109(1) Å, b = 9.041(1) Å, c = 24.935(2) Å, β = 96.94(1)°, Z = 4, and R = 0.053; **7** is monoclinic, space group $P2/n$, a = 17.473(2) Å, b = 10.615(1) Å, c = 16.133(2) Å, β = 99.75(1)°, Z = 4, and R = 0.040; **8** is monoclinic, space group $P2_1/c$, a = 14.285(3) Å, b = 16.714(2) Å, c = 10.381(4) Å, β = 107.88(2)°, Z = 4, and R = 0.0 51; **9** is triclinic, space group $P\bar{1}$, a = 10.649(1) Å, b = 14.122(1) Å, c = 10.635(1) Å, α = 94.64(1)°, β = 98.04(1)°, γ = 108.81(1)°, Z = 2, and R = 0.031; **11** is triclinic, space group $P\bar{1}$, a = 14.029(1) Å, b = 12.355(1) Å, c = 8.995(1) Å, α = 91.82(1)°, β = 91.17(1)°, γ = 91.89(1)°, Z = 2, and R = 0.051.

Introduction

Many reactions involving the enolato functionality[1] are driven by the metal ion to which it is bonded.[2,3] In this paper, we are mainly interested in the nature of naked or weakly ion-pair bonded enolates[4-6] and their reactivity with metal carbonyls.

The use of highly nucleophilic naked enolates in reactions with metal carbonyls led to the isolation of some

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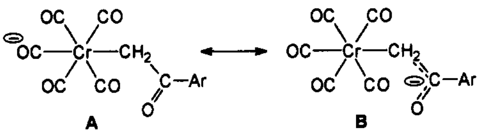
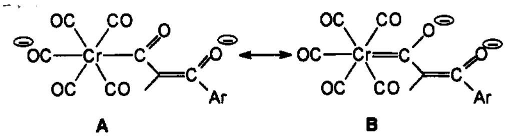
unprecedented classes of metal-bonded enolates. In order to make a straightforward comparison between related species bonded to a metal, we employed the same metallic fragment [Cr(CO)$_5$] for all of our studies. We report the synthesis, structure, chemical properties, and literature precedents of the following related classes of compounds:

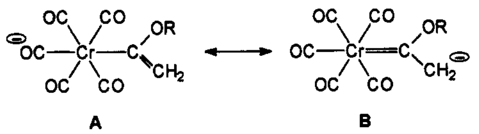
(i) α-ketoalkylcarbonylmetalates



(ii) metallacarbene enolates derived from enolates



(iii) metallacarbene enolates derived from metallacarbenes



The electron-withdrawing properties of [Cr(CO)$_5$] affect the relative contribution by forms **A** and **B**.

Some important precedents have been reported for class i by Bergman and Heathcock with the chemistry of the neutral [Re(CO)$_5$CH$_2$COR] and derivatives, though the carbonylmetalated form was not considered.[3] The generation of a metallacarbene *via* the nucleophilic attack of an enolate on a metal–CO bonded group[7] has no precedent in the literature. Class ii contains an interesting organic synthon. Class iii metallacarbene enolates derived from the deprotonation of Fischer-type carbene compounds have numerous precedents,[8–12] and we report the structure of the naked form. Some preliminary results have already been communicated.[13]

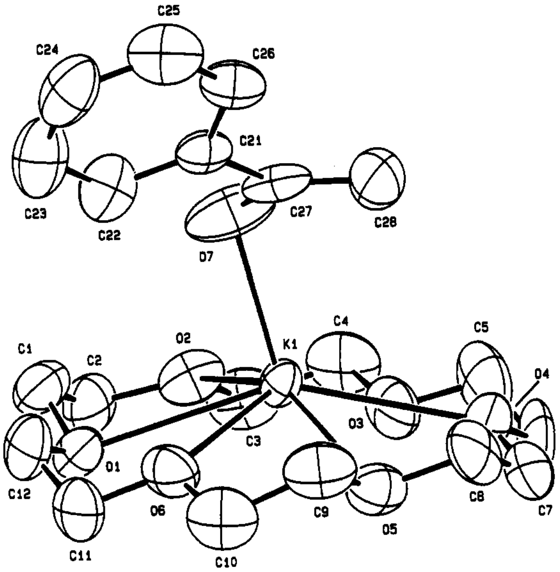
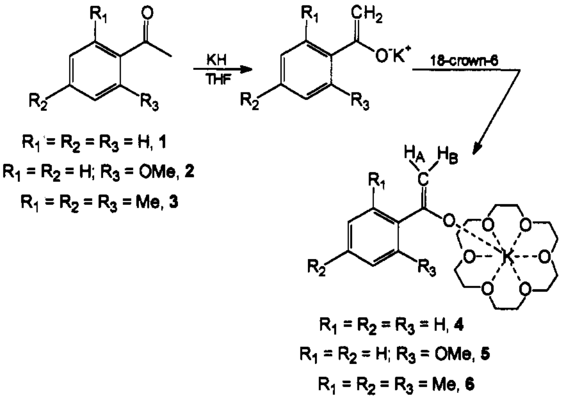


Figure 1. ORTEP drawing for complex **4** (30% probability ellipsoids).

Results and Discussion

A monomeric ion-pair form of acetophenone enolate was generated in THF using KH as a deprotonating agent followed by the addition of 18-crown-6



(1)

The potassium enolate is soluble in the case of **3**, while it is insoluble in the case of **1** and **2**. The addition of 18-crown-6 reverses the solubility trend, making **4** and **5** very soluble and **6** insoluble. The enolates **4–6** are thermally stable but very air-sensitive. They were obtained in high yield as yellow crystalline solids. The ^{1}H NMR spectra show a pair of doublets for the enolate protons, with the proton *cis* to the phenyl group (H$_A$) upfield.[14] The ^{13}C NMR spectrum shows a resonance for the enolic carbon at 125.8 ppm, in contrast to the 83–97 ppm range observed for several Li, Mg, and Zn derivatives.[15] The ion-pair structure of **4** is reported in Figure 1 and will be discussed with complex **8**. There are some precedents in the literature on the isolation of weak ion-pair enolates[4–6] and some rare structural characterizations.[4,6]

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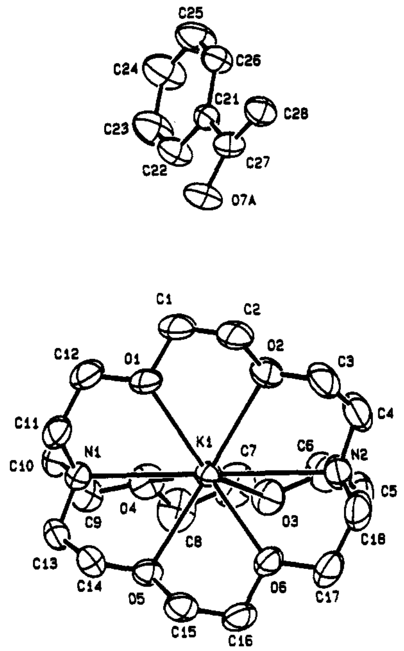
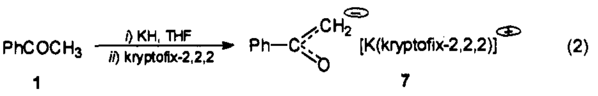


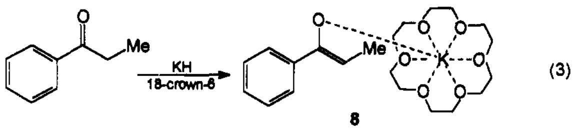
Figure 2. ORTEP drawing for complex 7 (30% probability ellipsoids). Only the A position is given for the disordered O7 atom.

The ion separated form[5] of the enolato 1 was obtained by adding kryptofix-2,2,2 to the THF solution of deprotonated 1:



$$\underset{1}{PhCOCH_3} \xrightarrow[ii)\ kryptofix\text{-}2,2,2]{i)\ KH,\ THF} \underset{7}{Ph{-}C(=CH_2)O^{-}\ [K(kryptofix\text{-}2,2,2)]^{+}} \quad (2)$$

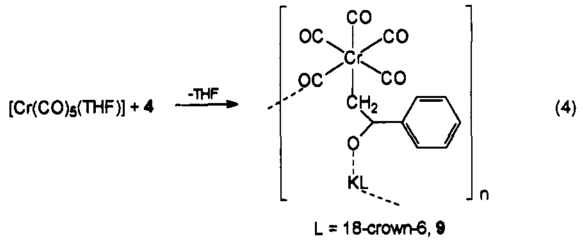
The crystal structure of 7 in Figure 2 shows no interaction between the countercation and the enolato anion, except for some hydrogen bonding between the basic enolate oxygen and the periphery of the kryptofix-2,2,2, leading to a dimeric structure in the solid state. The oxygen atom is statistically distributed over two positions (A and B) symmetrically arranged with respect to the plane running through the rest of the ion (out of plane distance: −0.337(10) Å and 0.354(10) Å, respectively). The C27 and C28 atoms lie on the plane of the phenyl ring and do not show any disorder, as indicated by the rather low values of their U_{ij} parameters (Table SVIII). Thus, the disorder of the oxygen atom is not correlated to free rotation of the enolato around the C21–C27 bond but is probably a consequence of crystal packing effects. As observed in complexes 4, 8, and 9, the conformation of the enolato ion seems to be determined by an intramolecular contact involving the oxygen and hydrogen atom of the α carbon atom (Table 9-(d)). The enolato functionality shows a significant bond delocalization over the C–C–O fragment, with similar C7–O7 and C27–C28 bond distances (Table 7). The deprotonation of propiophenone using the same method as in reaction 1 gave the corresponding ion-pair enolate with an *E*:*Z* isomer ratio of 2:98.[16] The *Z* isomer was the only one isolated (88%) as a solid and structurally characterized:



The ^{1}H NMR of enolate 8 shows a quartet at 5.18 ppm for the enolic proton and a doublet for the Me group at 2.47 ppm with a J_{HH} = 6.25 Hz. The structure of 8 shown in Figure 3 is similar to that of 4 and shows the *Z* conformation of the propiophenone enolate. A selection of structural parameters for 4 and 8 are reported in Tables 7–9. In both compounds the enolato fragment is mainly in the ketonic form with a C27–O7 [1.291(13) Å, 4; 1.298(5) Å, 8] shorter than the C27–C28 bond (1.393(16) Å, 4; 1.340(5) Å, 8), while in the ion-separated 7, the two bond distances are closer in value (Table 7).

Metal carbonyls undergo two major kinds of transformations on reactions with nucleophiles,[17] they are carbon monoxide substitution, which serves to bind the nucleophile at the metal,[18] and reaction at the metal-bonded electrophilic carbon monoxide. The later reaction leads to the synthesis of α-metallacarbenes.[7] No reactions of metal carbonyls, however, have been explored so far using alkali-metal enolates as nucleophiles, which are very important synthons in organic synthesis. We report here results on both classes of reactions using 4 as unprecedented nucleophile.

The substitution reaction was carried out by replacing the labile THF in [Cr(CO)$_5$(THF)] by the enolato ligand.



[Cr(CO)$_5$] is a typical carbophilic fragment, preferring the CH$_2$ rather than the oxygen donor atom, resulting in the conversion of enolato functionality to an M–C σ bond; this restores the ketonic form as shown by a band at 1690 cm^{-1} in the IR spectrum. Such binding of the enolate transforms a typical nucleophilic carbon into a conventional M–C σ bond, which is expected to perform insertion reactions rather than additions to electrophilic carbons.[3] The structure of 9 reported in Figure 4 shows a polymer where the complexed enolato anions are bridged by the [K(18-crown-6)]$^+$ cations. Potassium interacts with the oxygen of the enolate O7 and the oxygen from one of the CO *cis* to the enolato group of an adjacent anion. The potassium links the anions in chains running parallel to the [100] axis. The K···O29′ line is nearly perpendicular to the mean plane of the oxygens, the dihedral angle it forms with the normal to this plane being 9.7(1)°. The K···O7 and K···O29′ interactions are weak (Table 7).

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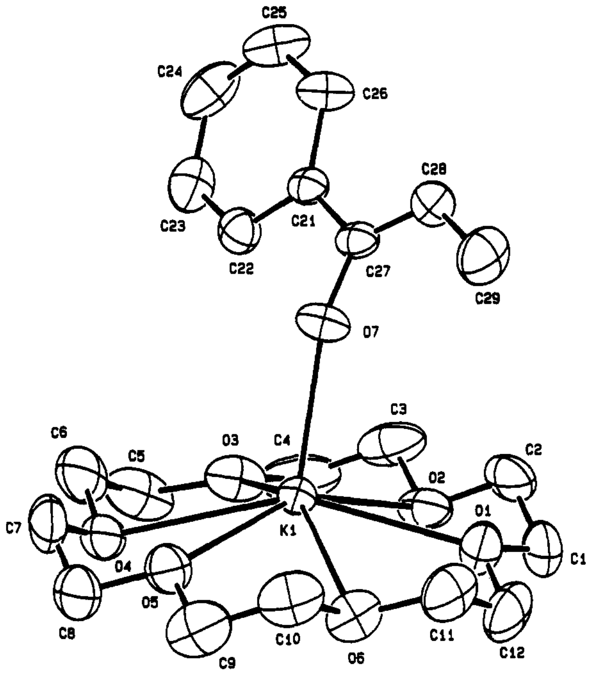


Figure 3. ORTEP drawing for complex 8 (30% probability ellipsoids).

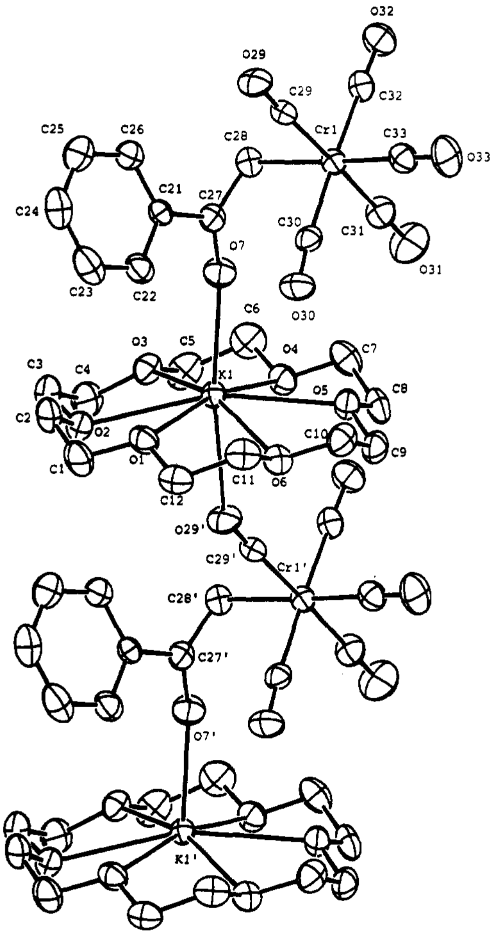
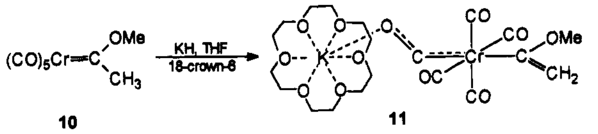


Figure 4. ORTEP drawing for complex 9 (30% probability ellipsoids). Prime denotes a transformation of $1 + x, y, z$.

The long K–O7 distance (2.606(3) Å) is in agreement with the negative charge of the enolate delocalized on the [Cr(CO)$_4$] fragment rather than on the C═O bond, as a consequence of the Cr—C σ bond formation. The CO *trans* to the Cr—CH$_2$ bond is the one mainly affected by this back donation, with a significant shortening of the Cr—C33 bond and a lengthening of the C33—O33 bond (Table 8). The enolato moiety is approximately perpendicular to the C28,C30,C32,C33 and C28,C33,C29,C31 angles, the dihedral angles they form being 87.4(1)° and 106(1)°, respectively. The structural parameters of the Cr—enolato fragment are particularly relevant, and reveal a short C27—O7 (1.240(4) Å), a long C27—C28 bond (1.421(5) Å), and a Cr—C28 bond length in agreement with other Cr—C σ bonds. These data support the formation of an alkylcarbonylmetalate of Cr(0) from the reaction between [Cr(CO)$_5$(THF)] and the enolate 4. It is not surprising that this compound does not display the conventional reactivity associated with carbonyl compounds.[19]

The functionalized enolates resulting from the binding of the enolato group to metal carbonyls can be compared with the enolates derived from the deprotonation of Fischer-type carbenes.[8-12] 10 was chosen as starting material, because it has the same [Cr(CO)$_5$] fragment used for other reactions in the present study. The generation of an enolate from an ester equivalent like a Fischer-carbene has been known for long time, though there is no structural evidence to confirm the low nucleophilicity of such an enolate relative to the enolate derived from an ester. The high acidity of the methyl group in 10[8b] allows an easy deprotonation by KH in THF.



10 11 (5)

Complex 11 was obtained in high yield (88%) as a crystalline solid. The ^{1}H NMR spectrum is similar to that reported by Casey for the same fragment in the same solvent (but with [(PPh$_3$)$_2$N]$^+$ as cation)[8b] and the enolate proton resonances are at 3.76 and 4.51 ppm, while the methoxy protons are at 3.35 ppm *vs* 3.78, 4.52, and 3.29 for the same protons in the Casey compound. A significant shift was observed for the ^{13}C NMR of the carbenic carbon, moving from 360.4 in 10 to 204.1 ppm in 11, and also a decrease in the CO stretching frequencies (see Experimental Section) down to 2030, 1900, and 1852 cm^{-1}. These data, together with the structural data, support that the Cr(CO)$_5$ fragment absorbs the negative charge of the enolate, which loses its nucleophilicity. The structure of 11 reported in Figure 5 shows that the complexed cation [K(18-crown-6)]$^+$ interacts with the O33 of the CO *trans* to the carbene-enolato group. Owing to a charge delocalization on C33–O33 carbon monoxide, the Cr–C33 and C33–O33 bonds are much shorter and longer, respectively (Table 8), than the corresponding bond lengths for the other Cr–C–O groups. The bent orientation of the Cr–C33–O33 fragment (159.7(6)°) gives further support to the presence of the negative charge on that group. On comparison of the carbene enolate parameters in 11 with those of the starting fragment in [(CO)$_5$CrC(OEt)Me][20] (the only difference being the ethoxy group), there is a lengthening of the Cr–C(carbene) bond from 2.053(1) to 2.126(5) Å, a shortening of the C–C bond from 1.511(1) to 1.340(8) Å, and a slight lengthening of the C–O bond from 1.314(1) to 1.366(7) Å.

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[19] We did not observe any reaction with aldehydes and ketones.
[20] See ref 7, p 94.

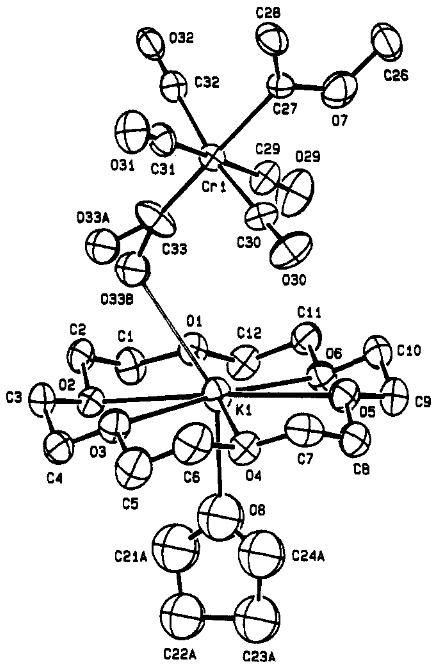


Figure 5. ORTEP drawing for complex 11 (30% probability ellipsoids).

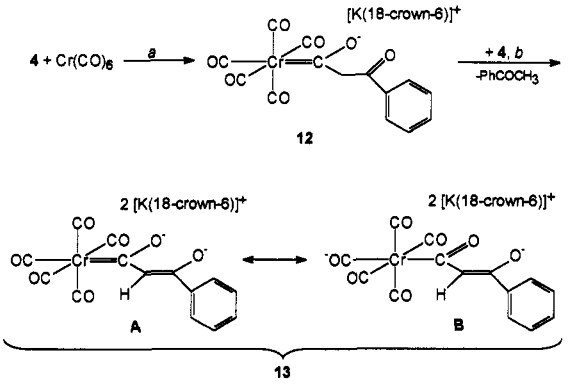
The Cr–C27 bond length in 11 lies between the Cr—C pure σ bond in 9 and that of an authentic carbene in $[(CO)_5CrC(OEt)Me]$.[20] The deprotonation of the Fischer carbene leads to a considerable loss of M═C double bond character. The C28, C27, O7, and C26 atoms define a plane which is nearly coplanar and perpendicular to the C27,C29,C31,C33 and C27,C30,C32,C33 mean plane, the dihedral angles they form being 15.1(2)° and 75.1(2)°, respectively. The Cr atom lies 0.072(1) Å out from the C28, C27, O7, C26 plane.

In Table 9 we compare the structural parameters of complexes 4, 7, 8, 9, and 11 for the common fragment.

(1) The $[K(18\text{-crown-}6)]^+$ cation in complexes 4, 8, 9, and 11 shows similar geometries. The most significant differences concern the out-of-plane distances of potassium from the mean plane through the six oxygen atoms of 18-crown-6, which decrease from 4 to 11 (Table 9(a)); the largest out-of-plane distances correspond to the strongest K···O7 interactions (complexes 4, 8; Table 7). The smallest out-of-plane distance is found in complex 11, where potassium weakly interacts with the oxygen of a THF molecule (K–O8 = 2.728(6) Å) and even more weakly with the oxygen atom of a disordered carbonyl group (K···O33B = 3.185(8) Å). In complex 9, the K out-of-plane distance is intermediate, corresponding to a K···O7 interaction weaker than those observed in complexes 4 and 8. Crystal packing effects could also play a role, and in complexes 4 and 8, for example, there is no simple correlation between the K out-of-plane and K···O7 distances. In these two complexes, however, the K out-of-plane distances are similar to each other and are longer than those found in 9 and 11. In all the complexes, the K···O7 line is approximately perpendicular to the oxygen mean plane (Table 9(b)). The K···O7—C27 angles (Table 7) are all different, but the values observed for complex 4 might imply an interaction different from that observed in complexes 8 and 11 and could be related to the shortening of the K···O7 distance. Thus, while complexes 4 and 8 might be expected to be conformationally comparable, they show a different orientation of the enolato ligand with respect to the $[K(18\text{-crown-}6)]$, as shown in Figures 1 and 3.

(2) The enolato ligands assume a conformation resulting in torsion angles around the C21–C27 bond which are close to each other (Table 9(c)) in complexes 4, 8, and 9. In complex 7, there is no rotation around this bond. This feature seems to be a consequence of a strong intramolecular O···H—C hydrogen bonding, involving the O7 basic oxygen and the H22 atom attached to the C22 α-carbon (Table 9(d)).

We took advantage of the high nucleophilicity of the naked enolate in the reaction with a metal-bonded CO. This is similar to the classic Fischer-carbene synthesis usually performed using lithium alkyls.[7,8a,21] The reaction between 4 and $Cr(CO)_6$ was carried out in Et_2O at room temperature, and although complex 13 has limited thermal stability in THF, it can be recrystallized from that solvent at less than 0 °C. The isolation of 13 is the result of a two-step reaction: (a) the nucleophilic attack on CO by the enolate, followed by (b) the deprotonation of the intermediate carbene-enolate 12 by the starting enolate 4.



(6)

The deprotonation is probably faster than step a, so even with a 1:1 stoichiometry the only identifiable compounds were 13, the excess $Cr(CO)_6$ and $PhCOCH_3$. Complex 13, though extremely reactive, was obtained in high yield (>90%) as a crystalline solid. It was completely characterized by analytical and spectroscopic means. The IR spectrum shows four CO bands from 2012 to 1850 cm^{-1}, in agreement with an important electron delocalization from the carbene enolate on the $Cr(CO)_5$ fragment; it does not show any carbonylic band. A single enolic proton is seen in the ^1H NMR spectrum at 6.58 ppm, and the enolic ^{13}C appears as a doublet at 118.1 ppm with a J_{HC} = 152.7 Hz. The ^{13}C NMR spectrum shows a resonance at 244.7 ppm for the carbenic carbon, suggesting some contribution by form **B**, which contains a Cr–C σ bond and electron delocalization on the $Cr(CO)_5$ fragment (see complex 11).

Several years ago Casey[9b,22] reported the acylation of a Fischer carbene leading to the acylated–alkylated form of a metallacarbene enolate very similar to 13.

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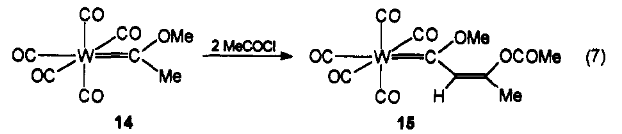
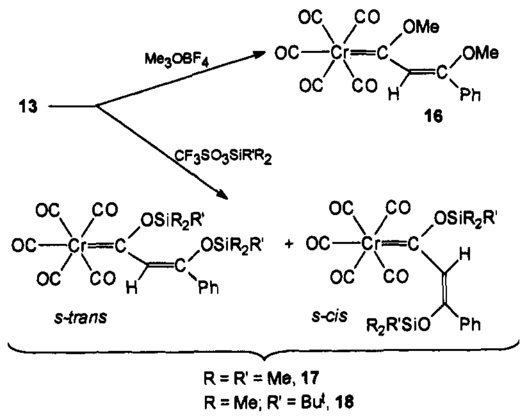
(21) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645. Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. Fischer, E. O. *Pure Appl. Chem.* **1972**, *30*, 353.

(22) Casey, Ch. P.; Boggs, R. A.; Marten, D. F.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1973**, 243.



(7)

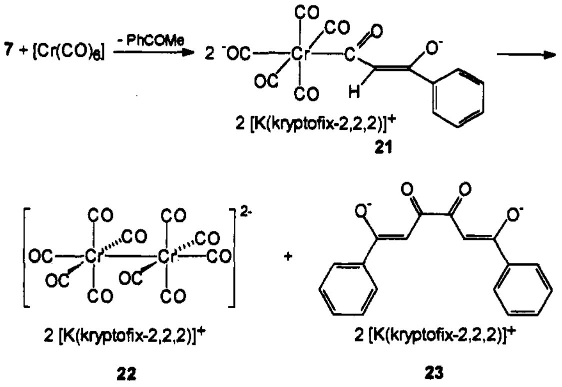
Such an alkylated form was obtained by reacting **13** with an alkylating agent.[23] This reaction is extremely sensitive to the alkylating agent,[12,24] with the yield varying in a wide range, and the product of interest is difficult to separate from {[K(18-crown-y)]Cl}, which is very soluble even in pentane. The results are summarized in reaction 8.



(8)

Complexes **16**, **17**, and **18** have common spectroscopic characteristics: they show three active IR CO bands corresponding to a pseudo C_{4v} symmetry.[25] The ^{1}H NMR spectrum of **16** shows two methyl resonances, while **17** showed four resonances for the two $SiMe_3$ groups. The same kind of spectrum was observed for **18**. Both **17** and **18** show the presence of two isomers due to the steric hindrance of the $SiMe_3$ and $SiMe_2Bu^t$ groups. We believe that the two isomers form during the alkylation process, with a significant preference for the less hindered one, in a 4:1 ratio. Such isomers have been observed in case of α,β unsaturated carbenes.[26] The NMR spectra are temperature independent. The existence of two isomers is further supported by the ^{13}C spectrum, which shows two close peaks for the carbenic carbon at 347.2 and 353.8 ppm (complex **17**) and at 353.5 and 362.4 ppm (complex **18**); the CO groups show a pair of two singlets for the carbonyls *cis* and *trans* to the carbene-enolato fragment.[26] Reactions 6 and 8 have been extended to $W(CO)_6$, and very similar results have been obtained with the isolation of $\{[(CO)_5WC(O^-)CH{=}C(O^-)Ph][K(18\text{-crown-}6)]_2\}$, **19**, and $[(CO)_5W{=}C(OSiMe_3)CH{=}C(OSiMe_3)Ph]$, **20**.

Compounds like **13** and **19**, though thermally labile, can be used in chemical reactivity study. Their relative stability may be associated to the ion-pair formation with the $[K(18\text{-crown-}6)]^+$ cations. This became clear when we tried to use the naked enolate **7** instead of **4** in the reaction with $Cr(CO)_6$.



(9)

The reaction carried out at 0 °C in THF gave **22** quantitatively;[27] it was isolated and fully characterized, including an X-ray analysis. Reaction 9 should follow the same pathway as reaction 6; however, the metallacarbene enolate **21**, which is not stabilized by ion-pair formation, decomposes with a homolytic Cr–C cleavage leading to **22** and an unidentified organic material, which may well be **23**, although we did not pursue it.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of purified nitrogen using modified Schlenk techniques or in a Braun drybox. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer and NMR spectra on a Bruker AC 200 instrument. The synthesis of $[(CO)_5Cr{=}C(OMe)Me]$ has been performed as reported in the literature.[28]

Synthesis of 4. Distilled acetophenone **1** (5.70 g, 47 mmol) was added to a THF (300 mL) suspension of KH (2.10 g, 52 mmol) with a syringe, and then the mixture was stirred over 4–5 h. A white fluffy precipitate formed after several minutes, which dissolved as soon as 18-crown-6 (12.54 g, 47 mmol) was added. Excess KH was filtered off, the solvent evaporated, ether (200 mL) added, and the yellow microcrystalline product collected by filtration and dried (92%). Crystals suitable for X-ray analysis were obtained by extraction with ether. 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_6D_6): δ 3.29 (s, OCH_2, 24 H), 4.01 (d, $=CH_2$, 1 H, J = 1.9 Hz), 4.63 (d, $=CH_2$, 1 H, J = 1.9 Hz), 7.2–7.5 and 8.5 (m, Ph, 5 H). ^{13}C NMR (C_6D_6): δ 70.7 (OCH_2), 125.8 ($=CH_2$), 127.4–128.9 (Ph), 149.1 (Ph).

Synthesis of 5. 2-Methoxyacetophenone (**2**) (1.00 g, 6.7 mmol) was added to a THF (50 mL) suspension of KH (0.27 g, 6.7 mmol) with a syringe, and the mixture was stirred over 3–4 h. After several minutes a white fluffy precipitate formed, which dissolved as soon as 18-crown-6 (1.77 g, 6.7 mmol) was added. Excess KH was filtered off, the solvent evaporated, Et_2O (50 mL) added, and the yellow microcrystalline product collected by filtration and dried (87%). Anal. Calcd for $C_{21}H_{33}KO_8$: C, 55.73; H, 7.35. Found: C, 55.85; H, 7.52. ^{1}H NMR (C_6D_6): δ 3.45 (s, OCH_2, 24 H), 3.86 (s, OMe, 3 H), 4.16 (d, $=CH_2$, 1 H, J = 2.7 Hz), 4.42 (d, $=CH_2$, 1 H, J = 2.7 Hz), 6.85 (m, Ph, 1 H), 7.10 (m, Ph, 2 H), 8.3 (m, Ph, 1 H).

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[23] Alkylation with $[Me_3O]BF_4$: Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Organic Syntheses*, Coll. Vol. VIII, p 216. Auman, R.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 879. Alkylation with $[Et_3O]BF_4$: Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *68*, P15. Alkylation with $SiMe_3Cl$: Fischer, E. O.; Moser, E. *J. Organomet. Chem.* **1968**, *12*, P1–P2. Fischer, E. O.; Selmayr, T.; Kreissl, F. R.; Schubert, U. *Chem. Ber.* **1977**, *110*, 2574. Alkylation with $CF_3SO_3SiMe_3$: Voran, S.; Blau, H.; Malisch, W.; Schubert, U. *J. Organomet. Chem.* **1982**, *232*, C33.

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Synthesis of 6. 2,4,6-Trimethylacetophenone (**3**) (0.75 g, 4.6 mmol) was added to a THF (50 mL) suspension of KH (0.20 g, 5 mmol) with a syringe; the mixture was stirred over 3–4 h and filtered to eliminate excess KH. In this case, no precipitate formed, but when 18-crown-6 (1.22 g, 4.6 mmol) was added, the naked enolate formed immediately (86%). Anal. Calcd for $C_{23}H_{37}KO_7$: C, 59.46; H, 8.03. Found: C, 58.42; H, 7.99. ^1H NMR (C_6D_6): δ 2.96 (s, Me, 9 H), 3.18 (s, OCH_2, 24 H), 3.85 (d, $=CH_2$, 1 H, J = 2.6 Hz), 4.22 (d, $=CH_2$, 1 H, J = 2.6 Hz), 6.98 (m, Ph, 2 H).

Synthesis of 7. Distilled acetophenone (**1**) (0.31 g, 2.56 mmol) was added to a THF (50 mL) suspension of KH (0.135 g, 3.40 mmol) with a syringe, and the mixture was stirred over 4–5 h. A white fluffy precipitate formed after several minutes, which dissolved as soon as Kryptofix-2,2,2 (0.96 g, 2.56 mmol) was added. Excess KH was filtered off, the solvent evaporated, and the residue light-yellow oil redissolved in Et_2O (50 mL). Yellow crystals, suitable for X-ray analysis formed on standing several hours at 0 °C (88%). Anal. Calcd for $C_{26}H_{43}KN_2O_7$: C, 58.40; H, 8.11; N, 5.24. Found: C, 58.23; H, 8.27; N, 5.20. ^1H NMR (C_6D_6): δ 2.37 (t, NCH_2, 12 H), 3.36 (t, OCH_2, 12 H), 3.43 (s, OCH_2, 12 H), 4.03 (d, $=CH_2$, 1 H, J = 2.4 Hz), 4.67 (d, $=CH_2$, 1 H, J = 2.4 Hz), 7.1–7.5 and 8.55 (m, Ph, 5 H). ^{13}C NMR (C_6D_6): δ 55.9 (s, NCH_2, Kryptofix-2,2,2), 68.8 (s, OCH_2, Kryptofix-2,2,2), 71.0 (s, OCH_2, Kryptofix-2,2,2), 125.2 (s, $=CH_2$), 127.2–128.9 (s, Ph), 150.7 (s, Ph), 170.5 (s, $C-O^-$).

Synthesis of 8. Distilled propiophenone (5.52 g, 41.10 mmol) was added to a THF (50 mL) suspension of KH (1.65 g, 41.10 mmol) with a syringe, and the mixture was stirred over 4–5 h. After several minutes a white fluffy precipitate formed, which dissolved as soon as 18-crown-6 (10.81 g, 40.9 mmol) was added. Excess KH was filtered off, and the solvent evaporated to 30 mL. To the resulting light-yellow microcrystalline product was added Et_2O (100 mL), and then the product was collected by filtration and dried (88%). Anal. Calcd for $C_{21}H_{33}KO_7$: C, 57.77; H, 7.62. Found: C, 58.21; H, 8.29. ^1H NMR (C_6D_6): δ 2.47 (d, Me, 3 H, J = 6.25 Hz), 3.26 (s, OCH_2, 24 H), 5.18 (q, $=CH$, 1 H, J = 6.25 Hz), 7.2 (m, Ph, 1 H), 7.45 (m, Ph, 2 H), 8.40 (m, Ph, 2 H).

Synthesis of 9. A THF (250 mL) solution of $[Cr(CO)_5]$, prepared *in situ* by photolysis of $Cr(CO)_6$ (0.57 g, 2.58 mmol), was added dropwise at –90 °C to a THF (40 mL) solution of **4** (1.09 g, 2.58 mmol). The red solution was evaporated to dryness and the oily residue redissolved in ether (50 mL) to give a yellow microcrystalline solid (35%). Crystals suitable for X-ray analysis were obtained by extraction with Et_2O. IR (THF): $\nu(CrC=O)$ 2036 (w), 1908 (w), 1864 (w) cm^{-1}; $\nu(C=O)$ 1690 cm^{-1}. 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 (wide peak, CH_2-Cr, 2 H), 3.08 (s, OCH_2, 24 H); 7.1–7.4 and 8.25 (m, Ph, 5 H). ^{13}C NMR (CD_2Cl_2): δ 18.0 (s, CH_2-Cr), 70.8 (s, OCH_2), 128.1–130.1 (2s, Ph), 141.1 (s, Ph), 196.0 (s, PhCO), 222.8 and 228.6 (2s, Cr–CO).

Synthesis of 11. To a THF (50 mL) suspension of KH (0.30 g, 7.48 mmol) at –20 °C was added the Fischer carbene **10** (1.35 g, 5.40 mmol). The solution was stirred for 2 h at –20 °C. 18-Crown-6 (1.43 g, 5.40 mmol) was then added, the solution concentrated to dryness, Et_2O (50 mL) added, and the light-yellow product collected by filtration and dried (88%). Crystals suitable for X-ray analysis were obtained recrystallizing from THF/Et_2O 1/2. IR(THF): $\nu(CrC=O)$ 2030 (w), 1900 (s), 1852 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{29}CrKO_{12}$: C, 43.48; H, 5.29. Found: C, 44.03; H, 5.41. ^1H NMR (CD_2Cl_2): δ 3.45 (s, OMe, 3 H), 3.63 (s, OCH_2, 24 H), 3.87 (s, $=CH$, 1 H), 4.65 (s, $=CH$, 1 H). ^1H NMR (THF-d_8): δ 3.35 (s, OMe, 3 H), 3.65 (s, OCH_2, 24 H), 3.76 (s, $=CH$, 1 H), 4.51 (s, $=CH$, 1 H). ^{13}C NMR (THF-d_8): δ 55.2 (s, OMe), 72.4 (s, OCH_2), 93.9 (s, $=CH_2$), 204.1 (s, Cr–C), 226.6 and 229.8 (2s, CrCO).

Synthesis of 13. The enolate **4** (5.20 g, 12.3 mmol) was added to an Et_2O (150 mL) suspension of $Cr(CO)_6$ (1.38 g, 6.25 mmol), and the mixture was stirred for 3–4 h at room temperature. An orange, microcrystalline solid formed slowly, which was collected by filtration, washed with Et_2O (3 × 50 mL), and dried (90%). It could be recrystallized from THF, but at a temperature lower than 0 °C (thermally unstable). IR (THF): $\nu(CrC=O)$ 2012 (w), 1913 (m), 1884 (s), 1850 (m) cm^{-1}. Anal. Calcd for $C_{38}H_{54}CrK_2O_{19}$: C, 48.30; H, 5.76. Found: C, 48.40; H, 5.86. ^1H NMR (THF-d_8, 273 K): δ 3.60 (s, OCH_2, 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 72.4 (s, CH_2-O, 18-crown-6), 118.1 (s, $=CH$), 128.0–130.7 (m, Ph), 150.5 (s, Ph), 163.4 (s, $C-O^-$), 230.7–232.9 (2s, Cr–CO), 244.7 (2s, $Cr-CO^-$). ^{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 (s, $C-O^-$), 230.3–232.6 (2s, Cr–CO), 244.7 (2s, $Cr-CO^-$).

Synthesis of 16. To a THF (100 mL) suspension of **13** (6.27 g, 6.63 mol) at –20 °C was added Me_3OBF_4 (1.96 g, 13.27 mmol), and the mixture was stirred for 5–6 h as the temperature rose. THF was evaporated and the residue redissolved in *n*-hexane (100 mL) and filtered. An orange oil was obtained which was purified by flash chromatography, with a mixture of heptane–Et_2O (10:1), yielding a red crystalline solid (9%). IR (THF): $\nu(CrC=O)$ 2055 (m), 1973 (w), 1939 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{12}CrO_7$: C, 52.18; H, 3.28. Found: C, 53.38; H, 3.42. ^1H NMR (CD_2Cl_2): δ 3.91 (s, OMe, 3 H), 4.17 (s, OMe, 3 H), 6.99 (s, $=CH$, 1 H), 7.2–7.6 (m, Ph, 5 H).

Synthesis of 17. To an Et_2O (150 mL) suspension of **13** (12.20 g, 12.91 mol) was added trimethylsilyl triflate (5.0 g, 25.82 mmol) dropwise at –78 °C with a syringe. The suspension suddenly turned dark red and was stirred for 30 min. The ether was evaporated and the residue redissolved in *n*-pentane (200 mL) and filtered. The potassium salt was washed with *n*-pentane (50 mL). The potassium triflate 18-crown-6 is slightly soluble in *n*-pentane. The pentane was eliminated yielding a red solid (73%). IR (THF): $\nu(CrC=O)$: 2054 (w), 1983 (s), 1945 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{24}CrO_7Si_2$: C, 49.57; H, 4.99. Found: C, 51.36; H, 6.07. ^1H NMR (C_6D_6): two isomers 4/1: δ *1* 0.0 (s, $SiMe_3$, 9 H), 0.27 (s, $SiMe_3$, 9 H), 6.9–7.0 (m, Ph, 3 H), 7.4 (m, Ph, 2 H), 7.58 (s, $=CH$, 1 H). *2* –0.08 (s, $SiMe_3$, 9 H), 0.14 (s, $SiMe_3$, 9 H), 7.55 (s, $=CH$, 1 H). ^1H NMR (CD_2Cl_2): two isomers 4/1: δ *1* 0.12 (s, $SiMe_3$, 9 H), 0.43 (s, $SiMe_3$, 9 H), 7.3–7.4 (m, Ph, 3 H), 7.49 (s, $=CH$, 1 H), 7.60 (m, Ph, 2 H). *2* 0.01 (s, $SiMe_3$, 9 H), 0.36 (s, $SiMe_3$, 9 H), 7.31 (s, $=CH$, 1 H), 7.4–7.6 (m, Ph, 5 H). ^{13}C NMR (CD_2Cl_2, not coupled): δ 1.3 and 0.6 (2s, $SiMe_3$), 128.4–138.6 (m, Ph), 145.0 (s, $=CH$), 154.4 (s, $=COSi$), 218.3 and 226.6 (2s, CrCO), 347.2 and 353.8 (2s, $Cr=C$).

Synthesis of 18. To an Et_2O (60 mL) suspension of **13** (1.74 g, 1.84 mol) was added dimethyl *tert*-butylsilyl triflate (0.85 mL, 3.68 mmol) dropwise at –78 °C with a syringe. The suspension suddenly turned dark red and was stirred for 30 min. Ether was evaporated and the residue redissolved in *n*-pentane (200 mL) and filtered. The potassium salt was washed with cold *n*-pentane (50 mL). Pentane was eliminated yielding a red liquid (84%). IR (THF): $\nu(CrC=O)$ 2054 (w), 1983 (s), 1945 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ –0.03 to +0.038 (5s, $SiMe_2$, 12 H), 0.87–1.13 (7s, Si–Bu^t, 18 H), 6.96 and 7.02 (2s, CH, 1 H), 7.35–7.6 (m, Ph, 5 H). ^{13}C NMR (CD_2Cl_2): δ –4.0, –3.0, and 1.5 (3s, $SiMe_2$), 26.0 (m, Si–Bu^t), 127.0–139.5 (m, Ph), 145.4 (s, $=CH$), 154.1 (s, $=COSi$), 218.0 and 226.1 (2s, CrCO), 353.6 and 362.4 (2s, $Cr=C$).

Synthesis of 19. The enolate **4** (2.68 g, 6.34 mmol) was added to an Et_2O (60 mL) suspension of $W(CO)_6$ (1.12 g, 3.17 mmol); then, the mixture was stirred for 3–4 h at room temperature. An orange microcrystalline solid formed slowly, which was collected by filtration, washed with Et_2O (3 × 20 mL), and dried (89%). IR (THF): $\nu(WC=O)$ 2028 (w), 1929 (m), 1888 (s), 1852 (m) cm^{-1}. Anal. Calcd for $C_{38}H_{54}K_2O_{19}W$: C, 42.38; H, 5.05. Found: C, 41.72; H, 5.35.

Synthesis of 20. To an ether (60 mL) suspension of **19** (2.93 g, 2.72 mol) was added trimethylsilyl triflate (1.0 mL, 5.45 mmol) dropwise at –78 °C with a syringe. The suspension suddenly turned dark red and was stirred for 30 min. The ether was evaporated and the residue redissolved in *n*-pentane (200 mL) and filtered. The potassium salt was washed with cold *n*-pentane (50 mL). Pentane was eliminated yielding a red liquid (73%). IR (THF): $\nu(WC=O)$ 2063 (w), 1977 (s), 1942 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): two isomers 69/31: δ *1* 0.16 and 0.47 (2s, $SiMe_3$, 18 H),

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 4, 7, 8, 9 and 11

compound	**4**	**7**	**8**	**9**	**11**
chem formula	$C_{20}H_{31}KO_7$	$C_{26}H_{43}KN_2O_7$	$C_{21}H_{33}KO_7$	$C_{25}H_{31}CrKO_{12}$	$C_{24}H_{37}CrKO_{13}$
a, Å	10.109(1)	17.473(2)	14.285(3)	10.649(1)	14.029(1)
b, Å	9.041(1)	10.615(1)	16.714(2)	14.122(1)	12.355(1)
c, Å	24.935(2)	16.133(2)	10.381(4)	10.635(1)	8.995(1)
α, deg	90	90	90	94.64(1)	91.82(1)
β, deg	96.94(1)	99.75(1)	107.88(2)	98.04(1)	91.17(1)
γ, deg	90	90	90	108.81(1)	91.89(1)
V, Å^3	2262.3(4)	2949.1(6)	2358.9(11)	1485.4(3)	1557.1(2)
Z	4	4	4	2	2
fw	422.6	534.7	436.6	614.6	624.6
space group	$P2_1/n$ (No. 14)	$P2/n$ (No. 10)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	22	22	22	22	22
λ, Å	0.71069	1.54178	1.54178	0.71069	0.71069
ρ_{calc}, g cm^{-3}	1.241	1.204	1.229	1.374	1.332
μ, cm^{-1}	2.65	19.31	22.85	5.70	5.46
transm coeff	0.949–1.000	0.884–1.000	0.809–1.000	0.875–1.000	0.876–1.000
$R = \sum\|\Delta F\|/\sum\|F_o$	0.053	0.040	0.051	0.031	0.051
$R_w = \sum w^{1/2}\|\Delta F\|/\sum w^{1/2}\|F_o\|$	0.054	0.050	0.051	0.031	0.057

Table 2. Fractional Atomic Coordinates (×10^4) for Complex 4

atom	x/a	y/b	z/c
K1	4563(1)	−71(2)	3090(1)
O1	6770(5)	1899(6)	2892(3)
O2	5381(7)	296(7)	2043(2)
O3	2718(7)	−272(7)	2111(3)
O4	1768(6)	−541(7)	3102(3)
O5	3180(7)	944(6)	3971(2)
O6	5848(6)	1706(6)	3905(3)
O7	6036(8)	−2221(8)	3422(3)
C1	7394(9)	1178(11)	2502(5)
C2	6548(11)	1175(11)	1995(4)
C3	4482(14)	335(12)	1604(4)
C4	3384(13)	−662(12)	1646(4)
C5	1684(14)	−1102(15)	2168(5)
C6	912(9)	−528(14)	2592(7)
C7	1170(10)	−60(12)	3520(7)
C8	2105(13)	−49(12)	4025(4)
C9	4121(13)	959(12)	4415(4)
C10	5134(12)	2104(12)	4356(3)
C11	6819(11)	2687(11)	3804(5)
C12	7596(9)	2075(11)	3385(5)
C21	6923(6)	−2933(9)	4294(2)
C22	7985(6)	−1954(9)	4279(2)
C23	9097(6)	−2049(9)	4667(2)
C24	9146(6)	−3123(9)	5071(2)
C25	8084(6)	−4101(9)	5086(2)
C26	6973(6)	−4006(9)	4697(2)
C27	5716(11)	−2849(10)	3853(4)
C28	4503(11)	−3397(11)	3979(5)

7.3–7.7 (m, Ph + =CH, 6 H); 2 0.05 and 0.37 (2s, $SiMe_3$, 18 H), 7.3–7.7 (m, Ph + =CH, 6 H). ^{13}C NMR (CD_2Cl_2): δ 1.3 (m, $SiMe_3$), 128.2–138.7 (m, Ph), 150.1 (s, =CH), 160.1 (s, =COSi), 199.8 and 206.9 (2s, CrCO), 323.1 and 313.5 (2s, Cr=C).

Reaction of 7 with [Cr(CO)$_6$], Synthesis of 22. To a THF (40 mL) solution of $Cr(CO)_6$ (0.25 g, 1.13 mmol) at 0 °C was added 7 (1.21 g, 2.26 mmol). The mixture was stirred for a few minutes and turned orange-red. A yellow microcrystalline solid formed, which was collected by filtration and dried (100%). The product is sparingly soluble in THF. IR (THF): ν(CrC=O) 1911 (w), 1877 (s), 1839 (w) cm^{-1}. Anal. Calcd for $C_{46}H_{72}Cr_2K_2N_4O_{22}$: C, 45.46; H, 5.97; N, 4.61. Found: C, 45.00; H, 6.25; N, 4.34. ^1H NMR (CD_3COCD_3): δ 2.59 (t, NCH_2, 12 H), 3.59 (t, OCH_2, 12 H); 3.62 (t, OCH_2, 12 H).

X-ray Crystallography for Complexes 4, 7, 8, 9, and 11. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[29] Crystal data and details associated with data collection are given in Tables 1 and SI. Data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background the profile measurement technique[30] was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[31] and the absolute scale was established by the Wilson method.[32] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected for complexes 4, 9, and 11. Data for complexes

Table 3. Fractional Atomic Coordinates (×10^4) for Complex 7[a]

atom	x/a	y/b	z/c
K1	5679.5(3)	1708.6(5)	3361.3(3)
O1	4098(1)	912(2)	3191(1)
O2	4755(1)	2532(2)	4520(1)
O3	6575(1)	3901(2)	3254(2)
O4	5677(1)	2804(2)	1804(1)
O5	6355(1)	−529(2)	2845(1)
O6	6901(1)	548(2)	4434(1)
O7A	7842(6)	7659(8)	5501(7)
O7B	7619(6)	7177(7)	5274(7)
N1	4938(1)	356(2)	1795(1)
N2	6423(2)	3023(3)	4948(2)
C1	3654(2)	1755(4)	3617(3)
C2	4029(2)	1878(4)	4491(2)
C3	5129(3)	2708(4)	5351(2)
C4	5814(3)	3571(4)	5356(3)
C5	6939(3)	4054(5)	4730(3)
C6	6618(3)	4722(4)	3947(3)
C7	6362(3)	4529(4)	2463(3)
C8	6302(3)	3624(4)	1772(3)
C9	5463(2)	2088(4)	1048(2)
C10	4783(2)	1278(3)	1117(2)
C11	4200(2)	−216(4)	1945(2)
C12	3711(2)	650(5)	2361(2)
C13	5448(2)	−635(3)	1579(2)
C14	5838(2)	−1361(3)	2338(2)
C15	6847(2)	−1183(3)	3502(2)
C16	7359(2)	−279(4)	4014(2)
C17	7370(2)	1248(5)	5076(2)
C18	6864(3)	2090(5)	5501(2)
C21	8561(1)	5738(2)	5875(1)
C22	8252(2)	5704(3)	6601(2)
C23	8512(3)	4842(4)	7233(2)
C24	9065(3)	3978(4)	7130(3)
C25	9381(2)	4002(4)	6414(3)
C26	9130(2)	4860(3)	5785(2)
C27	8254(1)	6695(2)	5209(2)
C28	8553(2)	6733(3)	4490(2)

[a] The site occupation factor for the disordered O7 atom is 0.5 for A and B positions.

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Table 4. Fractional Atomic Coordinates (×10⁴) for Complex 8

atom	*x*/*a*	*y*/*b*	*z*/*c*
K1	8242.5(6)	–921.7(5)	5795.3(8)
O1	6942(2)	–2169(2)	4818(3)
O2	6464(2)	–1007(2)	6519(3)
O3	7915(3)	111(2)	7694(3)
O4	9869(3)	–149(2)	7893(3)
O5	10218(2)	–1289(2)	6086(4)
O6	8877(3)	–2509(2)	5047(3)
O7	7407(2)	77(2)	4087(3)
C1	6055(4)	–2161(4)	5158(6)
C2	5785(3)	–1331(4)	5323(7)
C3	6233(4)	–206(4)	6765(8)
C4	7012(7)	105(4)	7968(7)
C5	8715(6)	519(4)	8681(6)
C6	9518(6)	598(4)	8125(7)
C7	10681(4)	–122(4)	7346(6)
C8	10971(4)	–940(4)	7148(6)
C9	10485(4)	–2069(4)	5749(8)
C10	9695(5)	–2384(4)	4626(6)
C11	8058(5)	–2858(3)	4023(5)
C12	7243(5)	–2942(3)	4563(6)
C21	6636(3)	1347(2)	3802(4)
C22	7169(3)	1551(3)	5120(4)
C23	7121(4)	2305(3)	5645(5)
C24	6544(5)	2883(3)	4830(7)
C25	6028(4)	2700(3)	3546(6)
C26	6057(4)	1944(3)	3031(4)
C27	6722(3)	518(2)	3294(4)
C28	6111(3)	272(3)	2104(4)
C29	6182(4)	–548(3)	1574(5)

Table 5. Fractional Atomic Coordinates (×10⁴) for Complex 9

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cr1	–5151.6(5)	2385.1(4)	8533.4(5)
K1	–266.4(6)	2555.1(5)	6452.7(6)
O1	–1412(2)	1268(2)	4151(2)
O2	473(2)	3173(2)	4089(2)
O3	1426(2)	4531(2)	6380(2)
O4	1427(2)	3720(2)	8697(2)
O5	–283(2)	1755(2)	8746(2)
O6	–1237(2)	428(2)	6438(2)
O7	–2323(2)	3107(2)	6778(2)
O29	–7628(2)	2305(2)	6695(2)
O30	–4732(3)	742(2)	6813(3)
O31	–2628(3)	2501(3)	10332(3)
O32	–5594(3)	3944(2)	10389(2)
O33	–6843(3)	728(2)	9771(3)
C1	–945(4)	1586(4)	3026(3)
C2	–642(4)	2685(3)	3092(3)
C3	938(4)	4229(3)	4113(4)
C4	1996(4)	4700(3)	5271(4)
C5	2379(4)	5018(3)	7506(4)
C6	1723(4)	4759(3)	8627(4)
C7	904(4)	3414(3)	9794(4)
C8	719(4)	2320(3)	9798(3)
C9	–539(4)	712(3)	8680(4)
C10	–1660(4)	171(3)	7595(4)
C11	–2257(4)	–61(3)	5352(4)
C12	–1708(4)	225(3)	4173(4)
C21	–4273(3)	2966(2)	5340(3)
C22	–4077(4)	2261(3)	4492(4)
C23	–4788(5)	2020(3)	3253(4)
C24	–5695(5)	2467(4)	2844(4)
C25	–5903(5)	3155(4)	3668(4)
C26	–5203(4)	3407(3)	4916(3)
C27	–3404(3)	3275(2)	6656(3)
C28	–3848(3)	3720(3)	7676(3)
C29	–6676(3)	2351(2)	7378(3)
C30	–4871(3)	1394(3)	7436(3)
C31	–3568(4)	2463(3)	9651(3)
C32	–5409(3)	3371(3)	9679(3)
C33	–6176(3)	1377(3)	9300(3)

Table 6. Fractional Atomic Coordinates (×10⁴) for Complex 11[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cr1	2593.8(5)	1994.7(6)	3710.2(8)
K1	2278.9(7)	–1840.9(10)	1255.3(13)
O1	871(2)	–1174(3)	–701(4)
O2	378(2)	–2345(3)	1848(4)
O3	1806(3)	–2663(3)	4015(4)
O4	3704(3)	–2642(3)	3063(4)
O5	4210(2)	–1472(3)	563(4)
O6	2789(2)	–1236(3)	–1647(4)
O7	4012(3)	3466(3)	2337(5)
O8	2076(5)	–3820(4)	–170(9)
O29	2679(3)	1674(4)	377(5)
O30	4369(3)	724(4)	4021(5)
O31	2595(3)	2170(4)	7050(5)
O32	1089(3)	3669(4)	3469(5)
O33A	1089(7)	233(8)	4046(11)
O33B	1398(6)	–54(6)	3404(9)
C1	–51(4)	–1643(5)	–466(7)
C2	–241(3)	–1615(5)	1140(7)
C3	183(4)	–2447(5)	3385(7)
C4	900(5)	–3177(5)	4034(7)
C5	2542(6)	–3292(6)	4647(8)
C6	3457(5)	–2714(6)	4569(8)
C7	4635(5)	–2163(5)	2884(8)
C8	4834(4)	–2170(5)	1279(8)
C9	4412(4)	–1362(5)	–969(7)
C10	3693(4)	–684(5)	–1681(7)
C11	2081(4)	–656(4)	–2403(6)
C12	1141(4)	–1242(5)	–2221(6)
C21A	1168(12)	–4474(15)	–646(20)
C22A	1497(11)	–5564(15)	–744(22)
C23A	2592(11)	–5414(18)	–1029(25)
C24A	2960(9)	–4309(15)	–288(23)
C21B	1742(16)	–4699(20)	670(26)
C22B	2089(28)	–5565(28)	–267(29)
C23B	1727(12)	–5090(14)	–1756(20)
C24B	2576(13)	–4269(15)	–1342(22)
C26	4632(5)	4381(5)	2159(8)
C27	3552(3)	3361(4)	3651(6)
C28	3747(4)	4097(5)	4750(7)
C29	2659(4)	1828(5)	1622(7)
C30	3695(4)	1190(4)	3892(5)
C31	2584(4)	2125(4)	5785(6)
C32	1656(4)	3027(4)	3563(6)
C33	1782(4)	831(5)	3707(7)

[a] The site occupation factor for the disordered O33 and C21–C24 atoms is 0.5 for A and B positions.

7 and 8 were corrected for absorption using the program ABSORB[33] for complex 7 and a semiempirical method[34] for complex 8. The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. A weighting scheme based on counting statistics[31] was applied for complexes 4, 7, and 11. Unit weights were used for complexes 8 and 9 since these gave a satisfactory analysis of variance and the best agreement factors.[31] Anomalous scattering corrections were included in all structure factor calculations.[35b] Scattering factors for neutral atoms were taken from ref 35a for non-hydrogen atoms and from ref 36 for H. Among the low-angle reflections a correction for secondary extinction was carried out for complex 8,[37] while no correction was deemed necessary for 4, 7, 9, and 11.

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map for complexes 7, 8, and 9. For 4 and 11 the structures were solved using SHELX86.[38]

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Table 7. Selected Bond Distances (Å) and Angles (deg) for Complexes 4, 7, 8, 9, and 11

	4	7	8	9	11
(a) In the K$^+$ Coordination Sphere					
K1–O1	2.943(6)	2.858(2)	2.769(3)	2.793(2)	2.781(4)
K1–O2	2.852(6)	2.809(2)	2.865(3)	2.858(2)	2.785(3)
K1–O3	2.893(7)	2.826(2)	2.766(4)	2.806(2)	2.796(4)
K1–O4	2.861(6)	2.768(2)	2.950(3)	2.811(2)	2.779(4)
K1–O5	2.892(6)	2.839(2)	2.812(3)	2.769(2)	2.818(3)
K1–O6	2.786(7)	2.796(2)	2.983(4)	2.842(3)	2.837(4)
K1–O7	2.526(8)		2.461(3)	2.606(3)	
K1–O8					2.728(6)
K1–O29′[a]				2.922(3)	
K1–N1		3.003(2)			
K1–N2		3.010(3)			
(b) In the Enolato Ligand					
O7–C27	1.291(13)	1.379(10) [1.242(10)][c]	1.298(5)	1.240(4)	1.366(7)
C21–C27	1.543(11)	1.510(3)	1.501(5)	1.511(4)	
C27–C28	1.393(16)	1.351(5)	1.340(5)	1.421(5)	1.340(8)
C28–C29			1.492(7)		
O7–C26					1.419(8)
K1–O7–C27	114.5(6)	161.2(3)	166.0(2)		
O7–C27–C21	111.0(8)	113.5(5) [115.6(5)][b]	115.4(3)	116.4(3)	
C21–C27–C28	117.6(8)	119.3(2) [120.4(3)][b]	120.1(3)		
O7–C27–C28	131.3(10)	124.8(5) [122.8(5)][b]	124.2(4)	123.6(3)	
C26–O7–C27					118.9(4)

[a] Prime denotes a transformation of $x + 1, y, z$. [b] The values in brackets refer to the B position of the O7 disordered atom.

Table 8. Selected Bond Distances (Å) and Angles (deg) for Complexes 9 and 11 Involving the Cr Coordination Sphere

	9	11		9	11
Cr1–C27		2.126(5)	C29–O29	1.142(4)	1.131(8)
Cr1–C28	2.293(4)		C30–O30	1.151(5)	1.129(7)
Cr1–C29	1.879(3)	1.888(6)	C31–O31	1.134(5)	1.137(7)
Cr1–C30	1.874(4)	1.872(6)	C32–O32	1.144(5)	1.146(7)
Cr1–C31	1.889(4)	1.869(5)	C33–O33	1.162(5)	1.250(11)[a]
Cr1–C32	1.888(4)	1.868(5)			
Cr1–C33	1.821(4)	1.804(6)			
C32–Cr1–C33	91.0(2)	96.1(2)	C28–Cr1–C29	90.0(1)	
C31–Cr1–C33	91.6(2)	91.5(2)	C27–Cr1–C33		178.5(2)
C31–Cr1–C32	89.9(2)	90.7(2)	C27–Cr1–C32		83.9(2)
C30–Cr1–C33	88.2(2)	94.8(2)	C27–Cr1–C31		90.1(2)
C30–Cr1–C32	178.4(2)	169.0(2)	C27–Cr1–C30		85.2(2)
C30–Cr1–C31	88.6(2)	88.1(2)	C27–Cr1–C29		89.6(2)
C29–Cr1–C33	91.1(2)	88.9(3)	Cr1–C27–C28		127.1(4)
C29–Cr1–C32	90.4(2)	92.0(2)	Cr1–C28–C27	105.0(2)	
C29–Cr1–C31	177.3(2)	177.3(2)	Cr1–C29–O29	177.7(3)	176.4(6)
C29–Cr1–C30	91.1(1)	89.1(2)	Cr1–C30–O30	175.7(3)	178.4(5)
C28–Cr1–C33	176.6(1)		Cr1–C31–O31	179.0(4)	177.5(5)
C28–Cr1–C32	85.7(2)		Cr1–C32–O32	177.8(3)	179.2(5)
C28–Cr1–C31	87.3(2)		Cr1–C33–O33	178.9(3)	159.7(6)[b]
C28–Cr1–C30	95.0(1)				

[a] 1.223(10) for C33–O33B. [b] 162.1(6) for Cr1–C33–O33B.

Table 9. Most Relevant Conformational Parameters for Complexes 4, 7, 8, 9, and 11

(a) Distances (Å) of Atoms from the Mean Plane through the Six Oxygen Atoms of 18-Crown-6

	4	8	9	11
O1	−0.174(6)	0.168(3)	0.265(2)	0.220(4)
O2	0.231(6)	−0.131(3)	−0.233(2)	−0.186(4)
O3	−0.210(7)	0.117(3)	0.160(2)	0.173(4)
O4	0.163(6)	−0.138(3)	−0.120(2)	−0.195(4)
O5	−0.127(6)	0.257(4)	0.150(2)	0.227(4)
O6	0.157(6)	−0.192(3)	−0.221(2)	−0.239(4)
K	0.758(2)	0.692(1)	0.406(1)	0.114(1)

(b) Dihedral Angles (deg) between the KO Lines and the Normal to the Oxygen Mean Plane

	4	8	8	11
K···O7	15.8(1)	20.6(1)	6.4(1)	
K···O8				6.0(1)
K···O29′			9.7(1)	

(c) Torsion Angles (deg) around the C21–C27 Bond of the Enolato Ligand

4	8	9
24.1(3)	10.2(2)	22.8(1)

(d) Geometry of the Intramolecular C–H···O Interactions

	4	7	8	9
O7···C22 (Å)	2.737(9)	2.746(10) [2.729(10)][a]	2.749(6)	2.765(4)
O7···H22 (Å)	2.31	2.42 [2.45]	2.28	2.42
O7···H22-C22 (deg)	100	100 [97]	109	103

[a] The values in brackets refer to O7B.

Refinement was done by full-matrix least-squares first isotropically and then anisotropically for non-H atoms, except for the O33 and C21–C24 disordered atoms in complex 11. In complex 7 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. A disorder affecting the O33 carbonyl and the THF molecule was found in complex 11. It was solved considering the O33 carbonyl oxygen and the C21–C24 carbons distributed over two positions (A and B) refined with a site occupation factor of 0.5.

For 4, 7, 9, and 11 the hydrogen atoms were located from difference Fourier maps. For 8 they were put in geometrically calculated positions. They were introduced in the subsequent refinements as fixed atom contributions with isotropic U's fixed at 0.15 Å^2 for 4 and 7 and 0.12, 0.09, and 0.10 Å^2 for 8, 9, and 11 respectively. In complex 4, the methylenic H atoms bonded to C28, which could not be located from difference Fourier maps, were ignored. In complex 11, the H atoms associated to disordered THF molecule were ignored. During the refinement of complex 4 the Ph ring was constrained to be a regular hexagon (C–C = 1.395 Å).

The final difference maps showed no unusual feature, with no significant peak above the general background. Final atomic coordinates are listed in Tables 2–6 for non-H atoms and in Tables SII–VI for hydrogens. Thermal parameters are given in Tables SVII–XI, selected bond distances and angles in Tables 7 and 8.[39]

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (20 pages). Ordering information is given on any current masthead page.

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(38) Sheldrick, G. *SHELX-86: a FORTRAN-77 Program for the solution of Crystal Structure from Diffraction Data*; University of Cambridge: Cambridge, England, 1986.

(39) See paragraph at the end regarding supplementary material.