(η^6-Acetophenone)Cr(CO)$_3$ Enolates Complexed to Bis(cyclopentadienyl)titanium(IV) and -zirconium(IV)

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This is a synthetic and structural report on substituted acetophenone−Cr(CO)$_3$ enolate complexes of titanium(IV) and zirconium(IV). The deprotonation of [(η^6-2,4,6-R′R″R‴C$_6$H$_2$-COMe)Cr(CO)$_3$] [R′ = R″ = R‴ = H, **1**; R′ = Me, R″ = R‴ = H, **2**; R′ = R″ = Me, R‴ = H, **3**, R′ = R″ = R‴ = Me, **4**] with KH in the presence of 18-crown-6 in THF gave the ion-pair enolates [{η^6-2,4,6-R′R″R‴C$_6$H$_2$−C(CH$_2$)O$\cdots$K(18-crown-6)}Cr(CO)$_3$] [R′ = R″ = Me, R‴ = H, **5**; R′ = R″ = R‴ = Me, **6**]. When the deprotonation of **1−4**, carried out using LiNPr$^i_2$ in THF, was followed by reaction with (cp)$_2$MCl$_2$ [M = Ti, Zr], dimetallic enolates were isolated and characterized [η^6-2,4,6-R′R″R‴C$_6$H$_2$−C(CH$_2$)O−M(Cl)(cp)$_2$] [R′ = R″ = R‴ = H, M = Ti, **7**; R′ = Me, R″ = R‴ = H, M = Zr, **8**; R′ = R″ = Me, R‴ = H, M = Zr, **9**; R′ = R″ = R‴ = Me, M = Ti, **10**; R′ = R″ = R‴ = Me, M = Zr, **11**]. In all of these complexes, the enolato functionality is O-bonded to the oxophilic [(cp)$_2$M(Cl)] fragment. Complexes **10** and **11** have been isolated as an 85:15 diastereoisomeric mixture with a significant diastereoselection for the most hindered form. The two diastereoisomers cannot be interconverted thermally because of the very high barrier to free rotation around the phenyl−C(enolate) bond, as from our calculations. An X-ray crystallographic analysis has been carried out on the most hindered diastereoisomer of **11** and compared with that of the starting complex **4**, where the oxygen is directed to the opposite face of the arene ring. In order to clarify the mechanism of the diastereoisomerization, the protolysis of the potassium and lithium enolates, including that of the pyridine adduct **12** [{η^6-2,4,6-Me$_3$C$_6$H$_2$-C(CH$_2$)OLiPy$_2$}Cr(CO)$_3$], has been carried out. The protolysis, which produces exclusively the starting diastereoisomer of **4** having the oxygen syn to the [Cr(CO)$_3$] group, supports strongly the fact that there is no change in the conformation at the level of the enolato formation. Then the comparison between results from the reaction of the lithium enolate of **4** and **12** with Me$_3$SiCl, MeBu$^t_2$SiCl, Me$_3$SiOSO$_2$-CF$_3$, and (cp)$_2$ZrCl$_2$ shows that the diastereoselection depends mostly on steric, rather than on electronic, factors. Further support for the steric argument comes when some steric hindrance has been introduced in the starting ketone, *i.e.* using [(η^6-2,4,6-R′R″R‴C$_6$H$_2$COCH$_2$-CH$_3$)Cr(CO)$_3$]. The corresponding lithium enolate reacted with (cp)$_2$ZrCl$_2$ gave a diastereoselection with a 67:33 ratio. The only plausible hypothesis for explaining the diastereoisomerization occurring at the stage of the reaction of the enolate with the electrophile is an intermolecular migration of the [Cr(CO)$_3$] fragment from the more to the less hindered face of the arene ring. Crystallographic details: **4** is monoclinic, space group $P2_1/c$, a = 6.858(1) Å, b = 13.977(2) Å, c = 14.557(2) Å, $\alpha = \gamma$ = 90°, β = 94.46(1)°, Z = 4, and R = 0.034; **11** is monoclinic, space group $P2_1/c$, a = 11.238(1) Å, b = 14.144(1) Å, c = 14.808(1) Å, $\alpha = \gamma$ = 90°, β = 95.12(1)°, Z = 4, and R = 0.033.

Introduction

The [(η^6-C$_6$R$_6$)Cr(CO)$_3$] complexes[1] have experienced important applications in organic synthesis[2] due to their electronic,[3−5] steric,[6] and stereochemical characteristics.[7−9] These [arene−Cr(CO)$_3$] fragments have been scarcely used for supporting the enolato functionality in combination with other transition metals.[10,11] In this context, we report herein a synthetic and structural study on substituted [acetophenone−Cr(CO)$_3$] enolates and their complexation by [(cp)$_2$MCl]$^+$ [M = Ti,Zr] cations occurring with diastereoisomerization.

Results and Discussion

The syntheses of the starting materials **1−4** have been carried out following slight modifications of the original procedure.[12] The deprotonation can be carried out using either KH or LiNPr$^i_2$, the former one being used in the synthesis of ion-pairs **5** and **6**.

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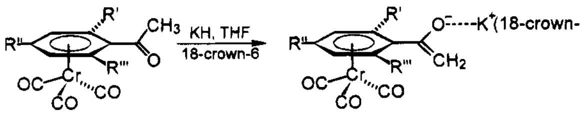
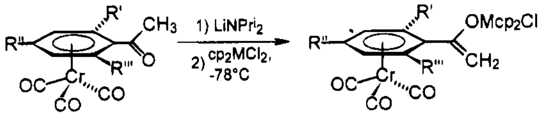


(1)

R' = R'' = Me, R''' = H, **3**
R' = R'' = R''' = Me, **4**

R' = R'' = Me, R''' = H, **5**
R' = R'' = R''' = Me, **6**

The enolates **5** and **6** have been isolated in quantitative yield, although their insolubility prevented solution characterization. When the deprotonation carried out either with KH at 25 °C or, better yet, at −78 °C with LiNPr$^{i}_{2}$ followed by reaction with (cp)$_2$MCl$_2$ [M = Ti, Zr, cp = η^5-C$_5$H$_5$] at −78 °C, we were able to isolate complexes **7**−**11**.



(2)

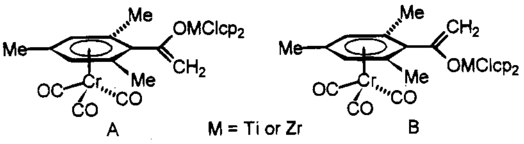
R' = R'' = R''' = H, **1**
R' = Me, R'' = R''' = H, **2**
R' = R'' = Me, R''' = H, **3**
R' = R'' = R''' = Me, **4**

R' = R'' = R''' = H, M = Ti, **7**
R' = Me, R'' = R''' = H, M = Zr, **8**
R' = R'' = Me, R''' = H, M = Zr, **9**
R' = R'' = R''' = Me, M = Ti, **10**
R' = R'' = R''' = Me, M = Zr, **11**

Although we encountered some difficulties in the preparation of **7**−**11**, all of these complexes have been isolated as crystalline solids. The methyl substituents have a very beneficial effect on the yield, **10** and **11** being obtained in *ca.* 70% and on a multigram scale. The ^{1}H NMR spectra of the isolated solids **7** and **8** exhibited a pair of doublets for the olefinic CH$_2$ group, as expected. In **9**, however, this signal appeared as two singlets. In all three cases, one singlet was observed for the two cyclopentadienyl rings. Further, the spectra of **10** and **11** consist of pairs of all the resonances, indicative of the presence of two species. The two components are believed to be two diastereoisomers, which can be formally related by a simple rotation around the phenyl−C(enolate) bond, present in an 85:15 ratio. As expected, we did not observe any change in the diastereoisomeric ratio by varying the temperature at which the NMR spectrum was recorded.

The reason for this is that the diastereoisomeric ratio is established at the temperature at which the synthesis is carried out. It depends on the nature of the metal and of the substituents in the phenyl ring and has nothing to do with a formal rotation around the phenyl−C(enolate) bond. The reported ratio of 85:15 is that observed for the collected crude solid of **10** and **11**.

Chart 1



The two diastereoisomers of **10** and **11** are shown in Chart 1.

We can, however, improve the diastereoisomeric ratio by crystallization. In the case of **11**, a recrystallization from toluene led to a 96:4 ratio, with a significant increase in the less soluble diastereoisomer. This observation suggests that the two diastereoisomers may also be present in the reactions leading to the formation of **7**−**9**, although because of their low yield and relative solubilities, they may not be detected. The quantitative ratio can be easily established for **10** and **11** and checked *via* the intensity of the peaks of different groups. A significant change from **4** to **10** and from **4** to **11** is observed in the chemical shifts of the *o*-methyl groups, downfield 0.15 and 0.10 ppm, respectively, which are significantly affected by the presence of the [(cp)$_2$MCl] fragment.

Using steric arguments, one can foresee a far greater stability for the less hindered A diastereoisomer. However, a problem arises when we compare the solid state structure of the precursor **4** with that of **11** (the less soluble diastereoisomer) shown in Figures 1 and 2, respectively. The two complexes are the opposite diastereoisomers. The question which should be answered concerns the stage and the mechanism of such an inversion.

In order to clarify this major stereochemical aspect, we had to support the fact that the diastereoisomeric interconversion is not the consequence of any free rotation around the phenyl−C(enolate) or phenyl−C(ketone) bond in complexes **4** and **11**. A calculation of the potential energy as a function of the torsional angle about the C11−C20 vector[13] was carried out for both complexes. Such a rotation has been found to be energetically forbidden. In particular for complex **4**, two potential energy maxima greater than 420 kJ/mol were found for rotations of *ca.* 70° and −90°, while such

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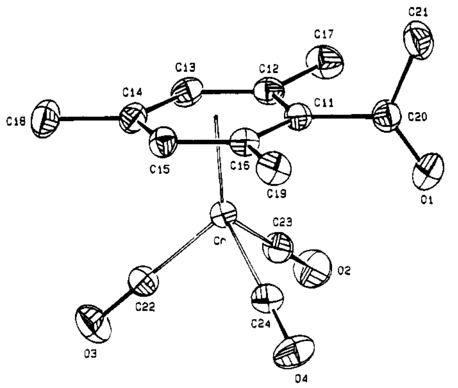


Figure 1. ORTEP view of complex **4** (30% probability ellipsoids).

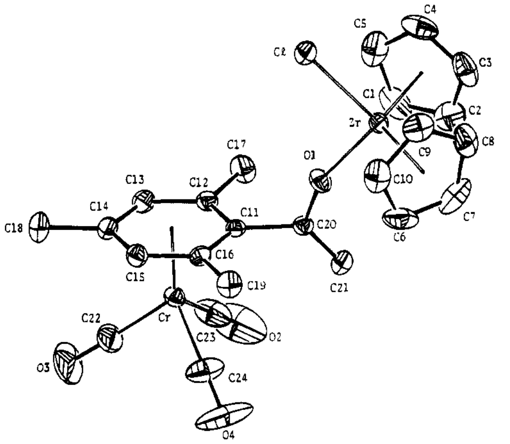
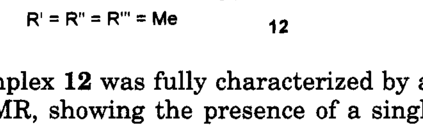


Figure 2. ORTEP view of complex **11** (30% probability ellipsoids).

energy barriers are of about 430 kJ/mol for rotations of *ca.* +70° and −100° in the case of complex **11**. We should point out that the stereochemical results from the enolato reaction on an analogous model substrate,[10] [(η^6-2-OMeC$_6$H$_4$COCH$_3$)Cr(CO)$_3$], are hardly comparable because when the same calculations as mentioned above were carried out based on its structural data,[14] showing the coplanarity between the acetyl and the methoxy group, we found no potential energy barrier for the free rotation around the phenyl−C(ketone) bond. With the assumption of the forbidden free rotation mentioned above for our complexes, we inspected at which stage the diastereoisomerization might occur. For this purpose we studied the protolysis of the potassium and lithium enolates derived from **4**. The lithium enolate is insoluble, thus hardly characterizable in solution. It has been, however, recrystallized from hot pyridine to form an orange crystalline solid, **12**, though the crystals were not suitable for an X-ray analysis.



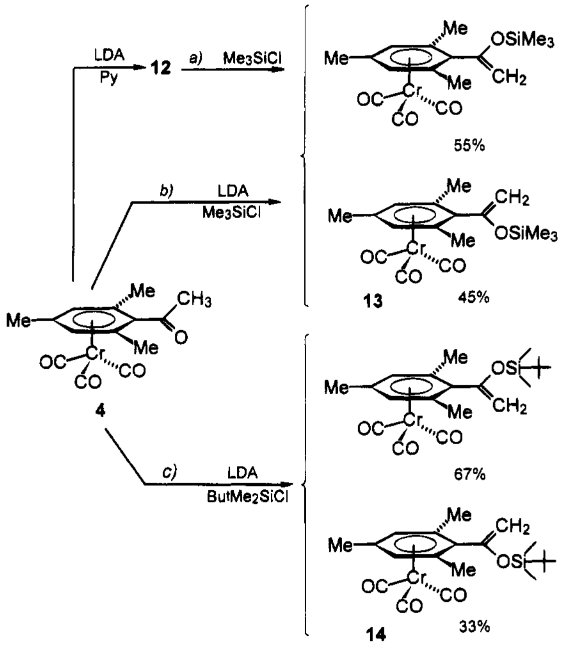
12

(3)

Complex **12** was fully characterized by analysis and ^{1}H NMR, showing the presence of a single diastereoisomer. The protolysis of the potassium and lithium enolates of **4**, including the pyridine derivative with acetic acid at −78 °C, **12**, gave exclusively the starting diastereoisomer of **4**. The prevented free rotation around the C11−C20 bond along with the results of the protolysis of the lithium and potassium enolates of **4** support strongly the hypothesis that there is no change in conformation at the level of the enolate formation, and the oxygen is still *syn* to the [Cr(CO)$_3$] group. This automatically leads to the hypothesis that it is the steric and/or electronic properties of the electrophile reacting with the enolate which affect the diastereoisomeric ratio.

We addressed this latter issue by studying the reaction of the lithium enolate derived from **4** and its pyridine adduct with Me$_3$SiCl and Bu$^t{}_2$MeSiCl. The reaction was carried out using some general procedures reported for the synthesis of silyl enol ethers.[15] In order to improve the electrophilicity of Bu^{t}Me$_2$SiCl, we used the cosolvent following the suggestion in a recent report.[16]

In reactions 4a, 4b, and 4c we obtained **13** and **14** in a roughly 60:40 diastereoisomeric ratio, assuming that the most abundant diastereoisomer is the less hindered one.



(4)

A comparison between the results obtained from the reactions of the lithium enolate of **4** reacting with [(cp)$_2$MCl$_2$] (reaction 2), Bu^{t}Me$_2$SiCl, and Me$_3$SiCl (reaction 4) shows that the diastereoselection depends mostly upon steric factors. The negligible electronic influence on such a diastereoselection has been proved using Me$_3$SiOSO$_2$CF$_3$, which gave the same stereoselection as Me$_3$SiCl.

The only plausible hypothesis for explaining the diastereoisomerization occurring at the stage of the reaction of the enolate with the electrophile is an intermolecular migration of the [Cr(CO)$_3$] fragment from the more to the less hindered face of the arene ring.[17]

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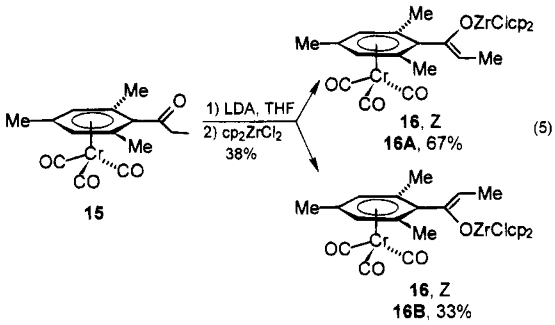
Complex **4** has the usual three-legged piano stool conformation (Figure 1). A selection of the structural parameters is listed in Table 4b and compared with those of complex **11**. The acetyl group is nearly perpendicular to the aromatic ring, the dihedral angle being 86.7(1)°. The acetyl oxygen points in the $Cr(CO)_3$ direction as indicated by the torsional angles Cr−C11−C20−O1, 4.3(1)°, and Cr−C11−C20−C21, −176.9(1)°. The acetyl group has normal structural parameters: C20−O1, 1.196(2) Å; C20−C21, 1.496(3) Å; C11−C20−O1, 122.1(2)°; C11−C20−C21, 116.0(1)°, C21−C20−O1, 121.9(2)°.

Although the acetyl group is affected by some high thermal motion or disorder, no exchange is observed between C21 and O1. This is in agreement with a forbidden rotation around the C11−C20 bond as a consequence of the steric hindrance with *o*-methyl groups. A calculation of the potential energy as a function of the torsional angle around the C11−C20 vector was carried out.[13] The results agree with an energetically forbidden rotation. The clockwise and counterclockwise twists of 90° showed two potential energy barriers corresponding to the coplanarity of the acetyl group with the aromatic ring. In such a conformation, the C17⋯C21 and C21⋯C19 distances are too short, 2.47 Å, to allow unhindered rotation.

The structure of **11** is shown in Figure 2, with selected structural parameters reported in Table 4. The comparison of the data of **4** and **11** shows that the arene−$Cr(CO)_3$ skeleton is almost identical in both compounds. In complex **11**, the phenyl ring is perpendicular to the enolato plane O1⋯C20⋯C21, with the dihedral angle being 79.1(1)°, but with the opposite diastereoisomer present since the CH_2 moiety is in the $Cr(CO)_3$ direction (contrary to what is observed in **4**). As discussed above, the interconversion between the two diastereoisomers by a simple rotation around C11−C20 is again prevented by significant steric hindrance. A calculation of the potential energy as a function of the torsional angle around C11−C20 in **11** gave two maxima of energy barriers corresponding to a rotation of *ca.* −100° (clockwise) and 70° (counterclockwise).[13] The conversion of the acetyl function in **4** into the enolate occurs with a shortening of the C20−C21 bond, and a lengthening of C20−O1 bonds, which converge in the enolato form (Table 4). The "CH_2" nucleophile is *trans* to the Cl substituent at Zr, the torsional angle Zr⋯C20⋯C21 being 178.5(6)°. The equatorial plane of the $[(cp)_2ZrCl]$ fragment is almost coplanar with the enolate, with the dihedral angle between Cl, Zr, O1, and O1⋯C20⋯C21 planes of 8.0(2)°.

The diastereoisomer interconversion was observed to a lesser degree when we reacted the lithium enolate derived from **15** with $(cp)_2ZrCl_2$, as reported in eq 5.



(5)

For the crystalline solid **15**, which we assume to be the *Z* isomer, based on comparisons to the propiophenone enolate reported recently and to the literature data,[18] we observed in the NMR spectrum the presence of two diastereoisomers in a 2:1 ratio. We assume that this ratio is dictated by sterics, so that the less hindered A diastereoisomer should be the predominant one, as was found for **11**. Contrary to **11**, however, the steric selection of the reaction is not so important, because of the introduction of the methyl group which reduces the steric preference for the $[(cp)_2ZrCl]$ fragment.

Conclusions

We have reported the synthetic method leading to the isolation of the ion-pair and complexed forms of the substituted acetophenone−$Cr(CO)_3$-based enolates generated as lithium or potassium derivatives. An oxygen-type complexation has been achieved using oxophilic metals such as zirconium(IV) and titanium(IV). A significant diastereoselection has been observed in the formation of the dimetallic enolates, essentially determined by steric factors. A number of experiments have been performed focused toward an understanding of the diastereoselection.

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. Complexes **1**−**4** and **15** have been prepared according to the reported procedures.[12]

Synthesis of 5. To a solution of **3** (0.75 g, 2.64 mmol) in THF (50 mL) was added KH (0.17 g, 4.14 mmol). The mixture was stirred until hydrogen evolution stopped; then 18-crown-6 (0.70 g, 2.64 mmol) was added at −20 °C. Immediately after the addition of the crown ether, a light-yellow solid formed, which solubilized at room temperature. The solution was evaporated to dryness, and the residue was washed with Et_2O, filtered, and dried (94%). IR (THF): ν(CrC=O) 1951 (m), 1868 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{35}CrKO_{10}$: C, 51.19; H, 6.01. Found: C, 50.01; H, 6.49.

Synthesis of 6. To a solution of **4** (0.91 g, 3.00 mmol) in THF (50 mL) was added KH (0.15 g, 3.7 mmol). The mixture was stirred until hydrogen evolution stopped, then 18-crown-6 (0.80 g, 3.00 mmol) was added at −20 °C. After a few minutes, a light-yellow solid formed and after standing overnight at 0 °C, the solid was filtered and dried (90%). IR (THF): ν(CrC=O) 1949 (m), 1866 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{37}CrKO_{10}$: C, 51.99; H, 6.21. Found: C, 51.18; H, 6.21.

Synthesis of 7. A solution of **1** (1.80 g, 12.00 mmol) in THF (30 mL) was added dropwise to a THF (30 mL) suspension of KH (0.49 g, 12.00 mmol). The mixture was stirred until hydrogen evolution stopped; then $(cp)_2TiCl_2$ (1.70 g, 11.00

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mmol) was added at −78 °C. The reaction mixture was allowed to slowly reach room temperature and stirred overnight. The THF was evaporated, and the red oil treated with toluene (50 mL) yielding a red suspension which was filtered. Red crystals grew slowly from the filtrate (21%). IR (THF): ν(CrC=O) 1968 (s), 1894 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{17}ClCrO_4Ti$: C, 49.97; H, 3.96. Found: C, 50.32; H, 3.99.

Synthesis of 8. A solution of **2** (0.55 g, 2.00 mmol) in THF (30 mL) was added to a LDA solution (THF, 30 mL; Pr$^i_2$NH, 0.30 mL, 2.1 mmol; Bu^{n}Li, 1.30 mL, 1.6 M, 5.1 mmol) at −78 °C. The enolate precipitated after a few minutes, and the mixture was stirred for 1 h. Upon addition of $(cp)_2ZrCl_2$ (0.57 g, 1.90 mmol) at -78 °C, the solid disappeared and the solution turned dark yellow. The solution was stirred for 2 h at −60 °C and was then evaporated to dryness. The yellow solid was treated with CH_2Cl_2 (50 mL) and filtered. Once again, the solvent was evaporated and the yellow crystalline residue was washed with Et_2O, filtered, and dried (37%). IR (THF): ν(CrC=O) 1965 (m), 1891 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{19}ClCrO_4Zr$: C, 50.23; H, 3.64. Found: C, 50.23; H, 3.79.

Synthesis of 9. A solution of **3** (0.84 g, 2.97 mmol) in THF (30 mL) was added to a LDA solution (THF, 30 mL; Pr$^i_2$NH, 0.35 g, 3.46 mmol; Bu^{n}Li, 1.90 mL, 1.6 M, 3.04 mmol) at −78 °C. The enolate precipitated after a few minutes, and the mixture was stirred for 1 h. Upon addition of $(cp)_2ZrCl_2$ (0.83 g, 2.82 mmol) at −78 °C, the solid disappeared and the solution turned dark yellow. The solution was stirred for 2 h at −60 °C and was then evaporated to dryness. The yellow solid was treated with CH_2Cl_2 (50 mL) and filtered. Once again the solvent was evaporated and the remaining yellow crystalline residue was washed with Et_2O, filtered and dried. (20%). IR (THF): ν(CrC=O) 1963 (m), 1887 (s) cm^{-1}. Anal. Calcd for $C_{23}H_{21}ClCrO_4Zr$: C, 51.15; H, 3.92. Found: C, 49.55; H, 4.09.

Synthesis of 10. A solution of **4** (1.77 g, 5.90 mmol) in THF (30 mL) was added to a LDA solution (THF, 30 mL; Pr$^i_2$NH, 0.60 g, 5.9 mmol; Bu^{n}Li, 3.75 mL, 1.6 M, 6.0 mmol) at −78 °C. The enolate precipitated after a few minutes, and the mixture was stirred for 1 h. $(cp)_2TiCl_2$ (1.40 g, 5.60 mmol) was then added at the same temperature, but it reacted very slowly. The reaction was complete after stirring for 3 h at −25 °C. The reaction mixture was allowed to warm very slowly to room temperature and was then evaporated to dryness. The red solid obtained was treated with CH_2Cl_2 (50 mL) and filtered. The solvent was evaporated slowly, and the red crystalline residue was washed with Et_2O, filtered, and dried (70%). IR (THF): ν(CrC=O) 1957 (m), 1884 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{23}ClCrO_4Ti$: C, 56.43; H, 4.54. Found: C, 55.77; H, 4.62. ^{1}H NMR (CD_2Cl_2): 2 isomers *ca.* 85:15: *1*, δ 2.17 (s, Me, 3H), 2.32 (s, Me, 6H), 4.23 (large peak, =CH_2, 2H), 4.93 (s, PhCr, 2H), 6.44 (s, (cp)Ti, 10H); *2*, δ 2.17 (s, Me, 6H), 2.20 (s, Me, 3H), 4.23 (large peak, =CH_2, 2H), 4.89 (s, PhCr, 2H), 6.57 (s, (cp)Ti, 10H). The isomeric ratio is that obtained for both the crude solid and the crystalline form.

Synthesis of 11. A solution of **4** (1.62 g, 5.50 mmol) in THF (30 mL) was added to a LDA solution (THF, 30 mL; Pr$^i_2$NH, 0.80 mL, 5.5 mmol; Bu^{n}Li, 3.40 mL, 1.6 M, 5.5 mmol) at −78 °C. The enolate precipitated after a few minutes, and the mixture was stirred for 1 h. Upon addition of $(cp)_2ZrCl_2$ (1.51 g, 5.0 mmol) at −78 °C, the solid disappeared and the solution turned dark yellow. The solution was stirred for 2 h at −60 °C and was then evaporated to dryness. The yellow solid obtained was treated with CH_2Cl_2 (50 mL) and filtered. The solvent was evaporated slowly, and the yellow crystalline residue was washed with Et_2O, filtered, and dried (75%). Crystal suitable for X-ray analysis were obtained by recrystallization from toluene. IR (THF): ν(CrC=O) 1960 (m), 1884 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{23}ClCrO_4Zr$: C, 52.02; H, 4.18. Found: C, 52.19; H, 4.16. ^{1}H NMR (CD_2Cl_2): 2 isomers *ca.* 85:15: *1*, δ 2.18 (s, Me, 3H), 2.31 (s, Me, 6H), 4.31 and 4.36 (2s, =CH_2, 2H), 4.93 (s, PhCr, 2H), 6.40 (s, (cp)Zr, 10H); *2*, δ 2.17 (s, Me, 3H), 2.20 (s, Me, 6H), 4.20 and 4.21 (2s, =CH_2, 2H), 4.85 (s, PhCr, 2H), 6.30 (s, (cp)Zr, 10H). The isomeric ratio is that obtained for both the crude solid and the crystalline form. Crystallization from toluene gave a 96:4 diastereoisomeric ratio.

Synthesis and Reactions of 12. BuLi (3.2 mL, 1.6 M in hexane, 5.12 mmol) was added to a THF (10 mL) solution of diisopropylamine (0.7 mL, 5.44 mmol) cooled to 0 °C. A THF (20 mL) solution of **4** (1.45 g, 4.90 mmol) was then added at −78 °C. The resulting suspension was warmed to room temperature and the solvent removed. The yellow powder was recrystallized from hot pyridine to afford an orange microcrystalline solid (41%). ^{1}H NMR (Py-d_5): δ 4.70 (s, 2 H, H Arom), 4.18 (s, 2H, =CH_2), 2.24 (s, 6H, Me); 1.99 (s, 3H, Me). Anal. Calcd for $C_{24}H_{23}CrLiN_2O_4$: C, 70.24; H, 5.61; N, 6.83. Found: C, 61.99; H, 5.59; N, 5.72.

Me_3SiCl (0.050 mL, 0.421 mmol) was added to a THF (10 mL) solution of **12** (0.164 g, 0.388 mmol) cooled to −78 °C. When the solution was warmed to room temperature and the solvent evaporated, an orange oil was obtained. The ^{1}H NMR of the crude oil showed that the corresponding silyl ether **13** was obtained in quantitative yield and in a 55:45 diastereoisomeric ratio.

Acetic acid (0.070 mL, 0.25 mmol) was added to a stirred THF (10 mL) solution of **12** (0.22 g, 0.513 mmol) cooled to −78 °C. The solution was warmed to room temperature, Et_2O (40 mL) was added, and 5% HCl (15 mL) was used to wash the organic layer. The ether solution gave **4** (95%) after drying over Na_2SO_4 and evaporating the solvent.

Synthesis of 13. To a solution of diisopropylamine (0.480 mL, 3.443 mmol) in THF (10mL) was added a solution of Bu^{n}Li (1.5 M in *n*-hexane, 2.1 mL) at 0 °C. The solution was stirred for 5 min and then cooled to −78 °C. A solution of (2,4,6-trimethylacetophenone)chromium tricarbonyl (0.923 g, 3.13 mmol) in THF (20 mL) was slowly added to this mixture. After a few minutes, the enolate started to precipitate and the resulting mixture was stirred at −78 °C for 1 h. Trimethylchlorosilane (0.4 mL, 3.13 mmol) was added by syringe, and the mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed *in vacuo*, and an orange solid was obtained. The ^{1}H NMR confirmed the presence of two diastereoisomers in a 55:45 ratio. The crude product was recrystallized from pentane (15 mL) after 1 day at −20 °C (20%). ^{1}H NMR ($CDCl_3$) (purified product): δ 4.88 (s, 2 H, H Arom), 4.62 and 4.61 (s, 2 H, =CH_2, 55%), 4.54 and 4.53 (s, 2 H, =CH_2, 45%); 2.30−2.21 (m, 9H, CH_3, two isomers); 0.30 (s, 9H, $SiMe_3$). Anal. Calcd for $C_{17}H_{22}CrO_4Si$: C, 55.12; H, 5.99. Found: C, 55.07; H, 6.23.

Synthesis of 14. To a solution of diisopropylamine (0.38 mL, 2.69 mmol) in THF (8 mL) at 0 °C was added a solution of Bu^{n}Li (1.5 M in *n*-hexane, 1.7 mL). The solution was stirred for 5 h and cooled to −78 °C, and a solution of (2,4,6-trimethylacetophenone)chromium tricarbonyl (0.72 g, 2.44 mmol) in THF (18 mL) was then slowly added. The enolate precipitated as a yellow solid, and the mixture was stirred at −78 °C for 1 h. *tert*-Butyldimethylsilyl chloride was then added in one portion. The mixture was stirred for 1 h; then dimethylpropyleneurea (9 mL) was added over 5 min. The resulting yellow solution was allowed to warm to room temperature and stirred for 10 h. The THF was removed, and the red solution was diluted with pentane (50 mL) and extracted in air with ice water (2 × 40mL). The pentane was evaporated under low pressure, and an orange-yellow oil was obtained as a mixture of two diastereoisomers in a 67:33 ratio (27%). ^{1}H NMR ($CDCl_3$) (crude product): δ 4.87 (s, 2H, H Arom), 4.62 (s, 2 H, =CH_2, major diastereoisomer), 4.60 (br s, 2H, =CH_2, minor diastereoisomer), 2.30−2.22 (m, 9 H,CH_3), 0.95 (s, 9H, Bu^t), 0.11 (s, 6 H, CH_3).

Synthesis of 16. A solution of **14** (1.46 g, 4.67 mmol) in THF (30 mL) was added to a LDA solution (THF, 30 mL; Pr$^i_2$NH, 0.70 mL, 4.94 mmol; Bu^{n}Li, 2.95 mL, 1.6 M, 4.67 mmol) at −78 °C. The solution turned orange-red and was stirred for 1 h. Upon addition of $(cp)_2ZrCl_2$ (1.30 g, 4.44 mmol) at −78 °C, the solution color remained unchanged. The solution was

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 4 and 11[a]

compound	**4**	**11**
mol. form.	$C_{14}H_{14}CrO_4$	$C_{24}H_{23}ClCrO_4Zr$
a, Å	6.858(1)	11.238(1)
b, Å	13.977(2)	14.144(1)
c, Å	14.557(2)	14.808(1)
α, deg	90	90
β, deg	94.46(1)	95.12(1)
γ, deg	90	90
V, Å^3	1391.1(3)	2344.3(3)
Z	4	4
form. wt	298.3	554.1
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
t, °C	22	22
λ, Å	0.71069	0.71069
ϱ_{calc}, g cm^{-3}	1.424	1.570
μ, cm^{-1}	8.07	10.31
transmissn coeff	0.892−1.000	0.702−1.000
R	0.034	0.033
R_w	0.037	
wR2		0.075

[a] $R = \sum|\Delta F|/\sum|F_o$. $R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$. $wR2 = [\sum(w\delta F^2)^2/\sum(wF_o^2)^2]^{1/2}$.

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

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cr1	227.6(4)	48.8(2)	2194.9(2)
O1	−612(2)	1623(1)	4106(1)
O2	2843(2)	1716(1)	1922(1)
O3	2800(2)	−1109(1)	1068(1)
O4	2856(2)	−486(1)	3844(1)
C11	−2199(2)	676(1)	2913(1)
C12	−2262(2)	1070(1)	2018(1)
C13	−2344(3)	455(1)	1255(1)
C14	−2355(2)	−546(1)	1354(1)
C15	−2319(2)	−927(1)	2252(1)
C16	−2240(2)	−337(1)	3035(1)
C17	−2259(3)	2145(1)	1871(2)
C18	−2427(3)	−1192(2)	525(2)
C19	−2198(3)	−781(2)	3979(1)
C20	−2122(3)	1324(1)	3751(1)
C21	−4050(3)	1583(2)	4097(2)
C22	1795(3)	−666(1)	1502(1)
C23	1830(3)	1070(1)	2026(1)
C24	1849(3)	−274(1)	3208(2)

Table 3. Fractional Atomic Coordinates (×10^4) for Complex 11

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
Zr	97.2(2)	407.6(2)	2664.2(2)	C10	−1178(4)	743(3)	3943(2)
Cr	4819.0(4)	2633.5(3)	4418.5(3)	C11	3330(2)	1706(2)	3853(2)
Cl	536.5(7)	−1082.0(5)	3488.6(6)	C12	4406(2)	1414(2)	3497(2)
O1	1463(2)	1163(1)	3200(1)	C13	5405(2)	1190(2)	4109(2)
O2	5346(5)	3740(3)	2808(3)	C14	5365(2)	1254(2)	5046(2)
O3	7074(3)	3373(3)	5358(4)	C15	4294(2)	1548(2)	5384(2)
O4	3546(4)	4353(2)	4975(4)	C16	3281(2)	1774(2)	4798(2)
C1	1262(4)	650(4)	1316(3)	C17	4503(3)	1303(3)	2498(2)
C2	135(4)	938(3)	1075(3)	C18	6460(3)	1002(3)	5672(3)
C3	−594(3)	182(4)	1032(2)	C19	2153(3)	2072(2)	5188(2)
C4	52(4)	−608(3)	1282(3)	C20	2226(2)	1891(2)	3235(2)
C5	1248(4)	−310(4)	1470(3)	C21	2017(3)	2687(2)	2781(2)
C6	−1002(3)	1601(3)	3546(4)	C22	6180(4)	3096(3)	5004(3)
C7	−1556(4)	1580(3)	2681(3)	C23	5158(4)	3301(3)	3439(3)
C8	−2104(3)	711(4)	2563(3)	C24	4036(4)	3679(2)	4767(3)
C9	−1873(3)	203(3)	3319(3)				

stirred for 2 h at −60 °C, and was then evaporated to dryness. The solid obtained was treated with CH_2Cl_2 (50 mL) and filtered. The solvent was removed, and the crystalline residue was washed with Et_2O, filtered, and dried (38%). IR (THF): *ν*(CrC=O) 1959 (m), 1883 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{25}ClCrO_4Zr$: C, 52.85; H, 4.44. Found: C, 54.55; H, 4.78. ^{1}H NMR (CD_2Cl_2): 2 isomers *E*:*Z* = 1:2, *δ* 1.40 and 1.71 (2d, CH=Me, 3H, *J* = 7.0 Hz), 2.19 and 2.28 (2s, Me, 9H), 4.82 (q, =CH, 1H, *J* = 7.0 Hz), 4.94 (s, PhCr, 2H), 6.31 (s, (cp)Zr, 10H).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complexes 4 and 11[a]

(a) In the Zirconium Coordination Sphere of Complex **11**

Zr−Cl	2.463(1)	Zr−Cp1	2.205(5)
Zr−O1	1.977(2)	Zr−Cp2	2.224(4)
Cp1−Zr−Cp2	128.0(2)	Cl−Zr−Cp1	107.6(1)
O1−Zr−Cp2	107.5(1)	Cl−Zr−O1	98.6(1)
O1−Zr−Cp1	106.2(1)	Zr−O1−C20	154.6(2)
Cl−Zr−Cp2	105.1(1)		

(b) In the Chromium Coordination Sphere

	complex **4**	complex **11**
Cr−C22	1.827(2)	1.812(4)
Cr−C23	1.830(2)	1.800(5)
Cr−C24	1.833(2)	1.819(4)
Cr−Cb1	1.720(2)	1.716(3)
O1−C20	1.196(2)	1.338(3)
C20−C21	1.496(3)	1.322(4)
C11−C20	1.517(2)	1.497(3)
O2−C23	1.156(2)	1.157(6)
O3−C22	1.151(2)	1.159(6)
O4−C24	1.150(3)	1.156(5)
C24−Cr−Cb1	125.8(1)	127.3(1)
C23−Cr−Cb1	126.4(1)	127.4(2)
C23−Cr−C24	88.1(1)	86.8(2)
C22−Cr−Cb1	127.7(1)	125.5(2)
C22−Cr−C24	87.9(1)	88.8(2)
C22−Cr−C23	88.1(1)	88.0(2)
O1−C20−C11	122.1(2)	112.5(2)
C11−C20−C21	116.0(1)	124.0(2)
O1−C20−C21	121.9(2)	123.5(2)
Cr−C22−O3	179.2(2)	177.5(4)
Cr−C23−O2	179.8(1)	178.2(4)
Cr−C24−O4	179.3(1)	178.7(4)

[a] Cp1, Cp2, and Cb1 refer to the centroids of the aromatic rings C1...C5, C6...C10, and C11...C16, respectively.

X-ray Crystallography. The compounds **4** and **11** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[19] Crystal data and details associated with structure refinement are given in Table 1. Data were collected at room temperature (295 K) on a single-crystal diffractometer (Philips PW1100 and Enraf-Nonius CAD4 for **4** and **11**, respectively). For intensities and background reflections, individual reflection profiles were analyzed.[20] The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[21] Intensity data were corrected for absorption using ABSORB.[22] During the least-squares refinements, the functions minimized were $\Sigma w|\Delta F|^2$ for **4** and $\Sigma w(\Delta F^2)^2$ for **11**. The weighting schemes $\{w = k/\sigma^2(F_o) + g|F_o|^2\}$[23a] and $\{w = 1/[\sigma^2(F_o^2) + (0.0130P)^2]\}$[23b] (with $P = (F_o^2 + 2F_c^2)/3$) based on a counting statistic were applied for **4** and **11**, respectively. Anomalous scattering corrections were included in all structure factor calculations.[24b] Scattering factors for neutral atoms were taken from ref 24a for non-hydrogen atoms and from ref 25 for H atoms. Among the low-angle reflections, no correction for secondary extinction was deemed necessary. All calculations were carried out on an IBM-AT personal computer equipped with an INMOS T800

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Transputer using SHELX-76[23a] for **4** and on an Encore 91 computer using SHELXL-92[23b] for **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. Refinement was first done isotropically and then anisotropically by full-matrix least-squares for non-H atoms. The hydrogen atoms, located from a difference Fourier map, were introduced in calculations prior the final cycles of refinement as fixed contributors (isotropic *U*s fixed at 0.10 Å^2) for **4**. For **11** they were successfully refined. The final difference maps showed no unusual features, with no significant peak above the general background. Final atomic coordinates are listed in Tables 2 and 3 for non-H atoms and in Tables SII–SIII for hydrogen atoms. Thermal parameters are given in Tables SIV–SV, and bond distances and angles in Tables SVI–SVII.[26]

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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 (9 pages). Ordering information is given on any current masthead page.

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(26) See paragraph at the end of the paper regarding supplementary material.