

Table IX

Distances (Å) of Selected Atoms from the Allyl Plane through C1, C2, and C3 in 1a and 2a

atom	dist from the allyl plane	
	1a	2a
C4	0.210 (9)	0.240 (4)
M	1.7313 (7)	1.7037 (6)
H1s	0.20 (6)	0.15 (3)
H1a	-0.42 (7)	-0.41 (3)
H3a	-0.33 (7)	-0.37 (3)
H3s	0.13 (7)	0.21 (3)

Dihedral Angles (deg) of Selected Planes with the Allyl Plane through C1, C2, and C3 in 1a and 2a

plane	dihedral angle with the allyl plane	
	1a	2a
H1s,C1,C2	12 (3)	11 (1)
H1a,C1,C2	34 (5)	34 (2)
H3a,C3,C2	25 (5)	31 (1)
H3a,C3,C2	9 (3)	14 (1)
C4,C2,C3	9.6 (7)	10.7 (3)
C4,C2,C1	9.5 (7)	10.8 (3)

<sup>a</sup> Esd's in parentheses.

difference maps and refined. In each structure a single average thermal parameter was refined for the three methyl hydrogens, and a second averaged temperature factor was obtained for the five phenyl hydrogens. For the other hydrogen atoms individual isotropic temperature factors were refined.

Table IX shows distances of the  $\pi$ -allyl protons from the plane defined by C1, C2, and C3, as well as some dihedral angles relative to the  $\pi$ -allyl plane. As expected<sup>19</sup> the syn protons move from the plane toward the metal, while the anti protons bend away from the metal.

The complete lists of anisotropic temperature factors (Table S1 for 1a and Table S2 for 2a), bond angles (Table S3 for 1a and Table S4 for 2a), values of  $10F_o$  vs  $10F_c$  (Table S5 for 1a and Table S6 for 2a), least-squares planes (Table S7 for 1a and Table S8 for 2a), together with a list of selected torsion angles and angles between least-squares planes for the two complexes (Table S9), have been deposited as supplementary material.

Routine <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured by using WP-200 and WM-250 MHz Bruker spectrometers. The <sup>119</sup>Sn spectra were measured on the WM-250 MHz spectrometer. Solvents and temperatures are given in the tables. For 1a the <sup>1</sup>H and <sup>13</sup>C and <sup>195</sup>Pt "reverse" NMR spectra<sup>36</sup> were measured by using a 400-MHz spectrometer. The 2-D NOESY and COSY spectra were measured by using standard pulse sequences.<sup>37</sup>

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**Registry No.** 1a (isomer 1), 115419-84-6; 1a (isomer 2), 115509-05-2; 1b, 115419-82-4; 1c, 115419-83-5; 2a, 115419-85-7; 2b, 115419-81-3; 2c, 115436-77-6; SnCl<sub>2</sub>, 7772-99-8; [PdCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>], 12081-18-4; [PtCl(C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>], 35770-44-6.

**Supplementary Material Available:** Tables containing anisotropic temperature factors (Tables S1 and S2), bond angles (Tables S3 and S4), least-squares planes (Tables S7 and S8), and selected torsion angles (Table S9) (11 pages); listings of structure factors (Tables S5 and S6) (28 pages). Ordering information is given on any current masthead page.

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## Synthesis and Structures of Bimetallic Titanium and Chromium Carbene Complexes of the Type Cp<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub>

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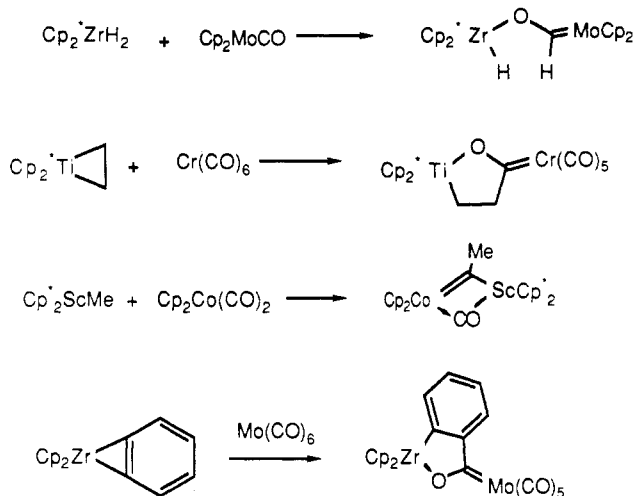
$\beta,\beta$ -Dimethyltitanocene metallacyclobutane 1 reacts with M(CO)<sub>5</sub> (M = Cr, Mo) in toluene to yield a titanocene ketene adduct and M(CO)<sub>5</sub>. This reaction produces two intermediates, 3 and 4, with the formula Cp<sub>2</sub>Ti(O)CH<sub>2</sub>CM(CO)<sub>5</sub>. Independent synthesis of 3 and 4 (M = Cr) was achieved by the reaction of Cp<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub> (9) and NaN(TMS)<sub>2</sub>. Complexes 3 and 4 are formed in a 1:1 ratio, with this ratio changing to 1.3:1 when the methylene group is deuteriated. The fluxional behavior of intermediates 3 and 4 was studied by using variable-temperature <sup>1</sup>H NMR. In contrast, reaction of NaN(TMS)<sub>2</sub> and Cp\*<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) (preparation from Cp\*<sub>2</sub>TiCl<sub>2</sub> and LiO(CH<sub>3</sub>)CCr(CO)<sub>5</sub>) does not yield complexes analogous to 3 and 4 but instead yields Cp\*<sub>2</sub>Ti(Cl)O(CH<sub>2</sub>)CCr(CO)<sub>5</sub>Na. Cp\*<sub>2</sub>Ti(Cl)O(CH<sub>3</sub>)CCr(CO)<sub>5</sub> exists as two rotational isomers, 11 and 12. The X-ray crystal structure of 11 reveals that the methyl group is wedged between the two permethylcyclopentadienyl ligands. Crystals of 11 are monoclinic, P2<sub>1</sub>/c, with *a* = 12.490 (2) Å, *b* = 13.472 (33) Å, *c* = 17.791 (4) Å,  $\beta$  = 109.83 (2)°, and *Z* = 4. The reaction of Cp\*<sub>2</sub>TiCl<sub>2</sub> and 2LiO(CH<sub>3</sub>)CCr(CO)<sub>5</sub> yields Cp\*<sub>2</sub>Ti(O(CH<sub>3</sub>)CCr(CO)<sub>5</sub>)<sub>2</sub> (13). The X-ray crystal structure of 13 reveals that the methyl group of each Fischer carbene moiety is wedged between the permethylcyclopentadienyl ligands. Crystals of 13 are monoclinic, P2<sub>1</sub>/n, with *a* = 9.958 (2) Å, *b* = 32.226 (8) Å, *c* = 11.998 (3) Å,  $\beta$  = 108.21 (2)°, and *Z* = 4.

### Introduction

Insertion reactions are some of the most common and important reactions in organometallic chemistry. Aside

from being mechanistically interesting, they have proven useful in organic synthesis and have been postulated in catalytic cycles. A subset of the broad group of insertion reactions is the insertion of carbon monoxides of group VIB metal carbonyl complexes into early-transition-metal alkyl, aryl and hydride bonds.<sup>1,2</sup> Several examples of this

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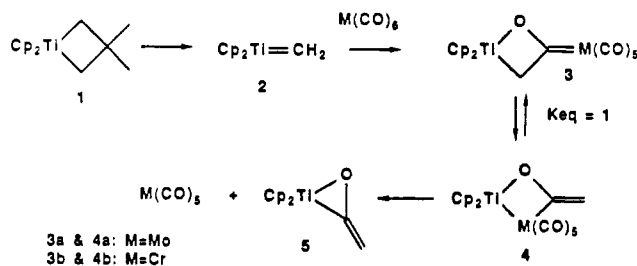


**Figure 1.** Early-transition-metal insertions of bound carbon monoxide.

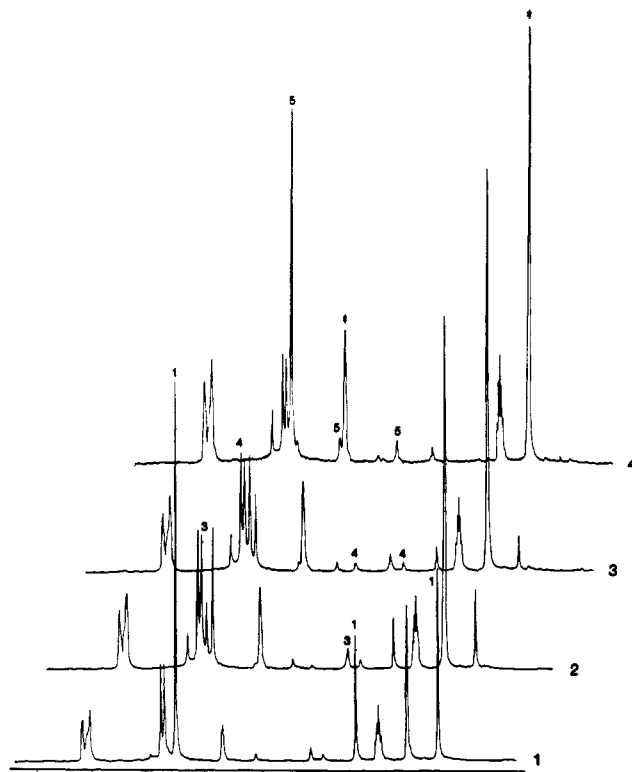
specific insertion reaction are shown in Figure 1. These reactions are often viewed as the nucleophilic attack of an alkyl, aryl, or hydride ligand on the electrophilic carbon of a coordinated carbon monoxide. Furthermore, the reactions are strikingly similar to the preparative reactions for generating Fischer carbene<sup>3</sup> complexes from alkyl- or aryllithium reagents and metal carbonyls. In the past several years, many new routes to Fischer carbenes have been reported. Specifically, Erker<sup>4</sup> has used  $\eta^2$ -bound olefins of early transition metals to effect the synthesis of metallocyclic carbenes, and Petz has reported the insertion of metal carbonyls into the Ti-N bond of  $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$  to give Fischer carbenes.<sup>5</sup>

These insertion reactions form carbon-carbon and/or metal-carbon bonds and thus can be viewed as one of the primary steps in building small organic fragments from carbon monoxide. In addition, synthetic utility can be envisioned by using the metal-carbon bonds for other insertion reactions or by taking advantage of the Fischer carbene moiety for Diels-Alder reactions,<sup>6</sup> quinone formation,<sup>7</sup> or several other recently developed synthetic methods using Fischer carbenes as synthons.<sup>8,9</sup>

To our knowledge, there are no examples of metal-bound carbon monoxide inserting into early-transition-metal alkylidenes. Furthermore, the reaction of metal alkylidenes with carbonyl complexes is surprisingly rare, even though organic and inorganic carbonyls do react with other organic and inorganic carbenes. Herrmann has extensively



**Figure 2.** Reaction of " $\text{Cp}_2\text{Ti}=\text{CH}_2$ " with  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}$ ).



**Figure 3.**  $^1\text{H}$  NMR spectra of the reaction of 1 with  $\text{Mo}(\text{CO})_6$ . Spectrum 1 is labeled to indicate the resonances of compound 1. Spectrum 2 is labeled to indicate the resonances of compound 3. Spectrum 3 is labeled to indicate the resonances due to compound 4. Spectrum 4 is labeled to indicate the resonances of compound 5 and isobutylene ( $\neq$ ).

studied the addition of organic carbenes to inorganic carbonyl complexes,<sup>10</sup> and the reactions of carbon monoxide with inorganic alkylidene complexes.<sup>11</sup>

In only one case has the attack of a metal alkylidene on a metal carbonyl been documented. This reaction involves the insertion of a carbon monoxide ligand of  $\text{CpMn}(\text{CO})_3$  into an uranium alkylidene<sup>12</sup> (eq 1). The bonding in the product can be described by two canonical forms—an enolate and a Fischer carbene.

Although the coupling of metal alkylidenes with metal carbonyl complexes is rare in monometallic systems, such coupling is frequently postulated in heterogeneous Fischer-Tropsch systems<sup>13</sup> to yield surface-bound ketene frag-

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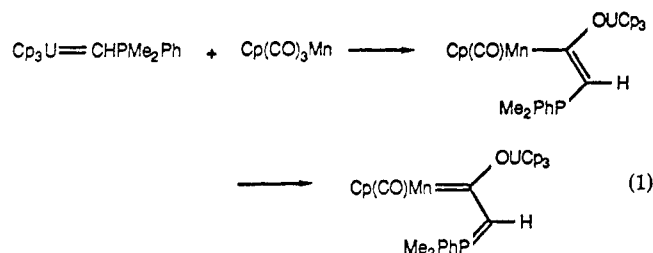
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ments. The formation of bound ketene in bimetallic and cluster complexes has been documented.<sup>14</sup> Herein we report the coupling of titanocene methylidene with  $\text{Cr}(\text{CO})_6$  to yield a titanocene ketene complex.

### Results and Discussion

The reaction of titanocene metallacyclobutane with a group VIB metal carbonyl proceeds at a rate proportional to the rate of cleavage of the titanocene metallacyclobutane to form titanocene methylidene. The reaction proceeds at 5 °C when the metallacycle is  $\beta,\beta$ -dimethyltitanocene metallacyclobutane 1. At this temperature, this reaction produces two intermediates which rearrange to form titanocene ketene 5 (Figure 2). These intermediates are formulated to be a  $\beta$ -*exo*-alkylidene,  $\alpha$ -oxatitanocene metallacyclobutane 3, and a titanocene-group VIB metal-bridged ketene adduct 4. The rearrangement of 3 and 4 to 5 proceeds before total consumption of the titanocene metallacyclobutane.

Figure 3 shows the  $^1\text{H}$  NMR spectra for the reaction of 1 and  $\text{Mo}(\text{CO})_6$ . Initially 1 cleaves to form titanocene methylidene and isobutylene. The titanocene methylidene then reacts with  $\text{Mo}(\text{CO})_6$  to form 3 and 4. The intermediates 3 and 4 are formed in a 1:1 equilibrium mixture over the temperature range -50 to +15 °C (the cyclopentadienyl ligand resonances of 3 and 4 have the same intensity, Figure 3). This one-to-one ratio of cyclopentadienyl ligand resonances is consistent with one intermediate with diastereotopic cyclopentadienyl ligands or with the two intermediates shown in Figure 2. The  $^1\text{H}$  NMR spectrum suggests the presence of a methylene group with a chemical shift in the correct region for an  $\alpha$ -methylene of a titanocene metallacyclobutane, but this shift is also indicative of a Fischer carbene moiety. The resonance for 3a was at  $\delta$  3.17 (Figure 3, spectrum 2), which is at slightly lower field than is normally found for titanocene metallacyclobutanes<sup>15</sup> (typically in the range of  $\delta$  1.8–2.7). This small downfield shift is a consequence of the location of the methylene group  $\alpha$  to the double bond of the Fischer carbene. For example, the chemical shift of the methyl group bound to the carbene carbon of  $(\text{C}_5\text{O})_5\text{CrC}(\text{CH}_3)\text{OCH}_3$  is  $\delta$  3.05.<sup>16</sup>

The geminal coupling of  $J_{\text{HH}} = 1.5$  Hz is also suggestive of a ketene adduct. However, the olefin resonances of titanocene and zirconocene ketene adducts are typically in the range of 4–5 ppm,<sup>17</sup> while the resonances found for 4a are  $\delta$  2.97 and 4.13 (Figure 3, spectrum 3).

The insertion of a carbon monoxide ligand of  $\text{Mo}(\text{CO})_6$  into the titanocene methylidene Ti–C double bond is presumed to proceed by initial coordination of the carbonyl oxygen to the titanium, followed by nucleophilic attack of the methylidene carbon on the electrophilic carbonyl carbon. This proposed insertion mechanism is supported

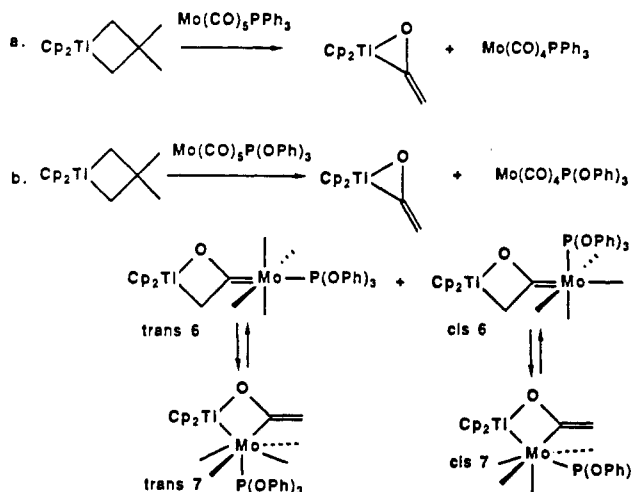
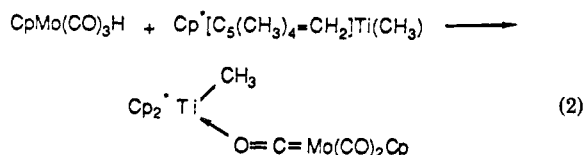


Figure 4. (a) Reaction of " $\text{Cp}_2\text{Ti}=\text{CH}_2$ " with  $\text{Mo}(\text{CO})_4\text{PPh}_3$ . (b) Reaction of " $\text{Cp}_2\text{Ti}=\text{CH}_2$ " with  $\text{Mo}(\text{CO})_4\text{P}(\text{OPh})_3$ .

by Stucky et al.,<sup>18</sup> who were successful in isolating the oxygen-coordinated titanocene complex shown below (eq 2), which is clearly analogous to the complex invoked in our mechanism.



The complex  $\text{Cp}^*_2\text{Ti}(\text{CH}_3)(\text{OC})_3\text{MoCp}$  was isolated from the reaction of  $\text{CpMo}(\text{CO})_3\text{H}$  with  $\text{Cp}^*[\text{C}_5(\text{CH}_3)_4=\text{CH}_2]\text{Ti}(\text{CH}_3)$ . This complex exhibits a donor–acceptor interaction between one of the carbonyl oxygens and the titanium center, and this interaction increases the C–O bond length of the coordinated carbonyl.<sup>18</sup> Thus, the donor–acceptor interaction between the oxygen of a CO ligand on  $\text{Mo}(\text{CO})_6$  and the titanium of  $\text{Cp}_2\text{TiCH}_2$  should also increase the electrophilicity of the carbonyl carbon and promote attack by the titanocene methylidene. Similar interactions have been observed between molecular Lewis acids and metal-coordinated carbon monoxide. Shriver has extensively studied the Lewis acid promoted migration of alkyl and aryl moieties to coordinated CO.<sup>19</sup> The initial coordination of the CO ligand of  $\text{Mo}(\text{CO})_6$  to the titanium center can be viewed as Lewis acid promoted migration of the methylidene to the carbonyl.

Complex 4 possesses a  $\mu_2,\eta^2$ -ketene ligand. In order to determine whether 3 and 4 were actually one complex with diastereotopic cyclopentadienyl ligands or two separate complexes, we designed several studies to perturb the equilibrium between 3 and 4 away from a value of unity. In the first attempt, the group VIB metal carbonyl was substituted with triphenylphosphine and triphenyl phosphite. The reaction of 1 with  $\text{Mo}(\text{CO})_5\text{PPh}_3$  yielded only the titanocene ketene complex 5 (Figure 4a) without any detectable intermediates. In contrast, the reaction of 1 with  $\text{Mo}(\text{CO})_5\text{P}(\text{OPh})_3$  did result in formation of intermediates 6 and 7 in a trans to cis ratio of 1.6:1 (Figure 4b). However, the equilibrium between oxametallacycle 6 and

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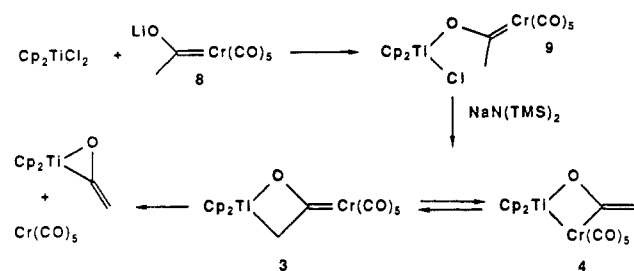


Figure 5. Alternative synthesis of 3b and 4b.

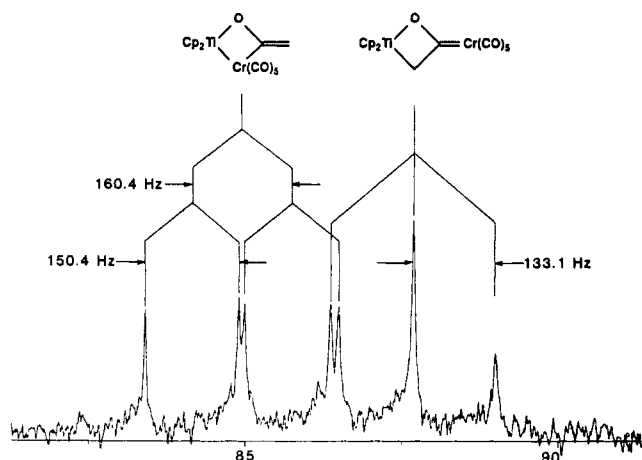


Figure 6.  $^{13}\text{C}$  ( $^1\text{H}$ -coupled) spectrum of  $^{13}\text{C}$ -enriched 3b and 4b.

bridging ketene adduct 7 was still approximately unity for both the cis and trans complexes. The  $^{31}\text{P}$  NMR shows three signals (one peak is twice as large and presumably is two overlapping signals) with the correct integrated intensities for the four intermediates.

Further attempts at perturbing the equilibrium away from unity by reacting 1 with non-group VIB carbonyl complexes failed. Facile addition of titanocene methylene is observed only when carbonyl complexes of group VIB are the electrophilic complexes. Using other carbonyl complexes as the electrophiles results in decomposition of the titanocene methylene. This lack of reactivity with late metal carbonyl complexes is probably due to the decreased electrophilicity of the bound carbon monoxide. In fact, generation of the Fischer carbenes from late-transition-metal complexes is difficult, as these complexes do not react efficiently with alkyl- or aryllithium reagents.

Independent synthesis of the proposed intermediates 3 and 4 provided additional structural proof and a facile method for shifting the equilibrium of 3 and 4 away from a value of unity. The reaction of titanocene dichloride with the Fischer carbene salt 8 forms compound 9<sup>21</sup> (Figure 5). Deprotonation of 9 at low temperature with sodium hexamethyldisilamide yields the same intermediates formed in the reaction of 1 and  $\text{Cr}(\text{CO})_6$ . This intramolecular alkylation and oxametallacyclobutane formation can be accomplished at  $-50^\circ\text{C}$ . At temperatures below  $-10^\circ\text{C}$ , the intermediates do not rearrange to titanocene ketene at a perceptible rate.

The synthetic route shown in Figure 5 allowed facile isotopic enrichment of the methylene group of 3b and 4b. Thus,  $^{13}\text{C}$ -labeled 9,  $\text{Cp}_2\text{Ti}(\text{Cl})\text{O}(\text{*CH}_3)\text{CCr}(\text{CO})_5$ , was synthesized and allowed to react with  $\text{NaN}(\text{TMS})_2$ . The proton-coupled  $^{13}\text{C}$  NMR spectrum is displayed in Figure 6. The CH coupling constant for the methylene group of 3b was found to be 133.1 Hz, well within the range normally observed for the  $\alpha$ -carbons of titanocene metalla-

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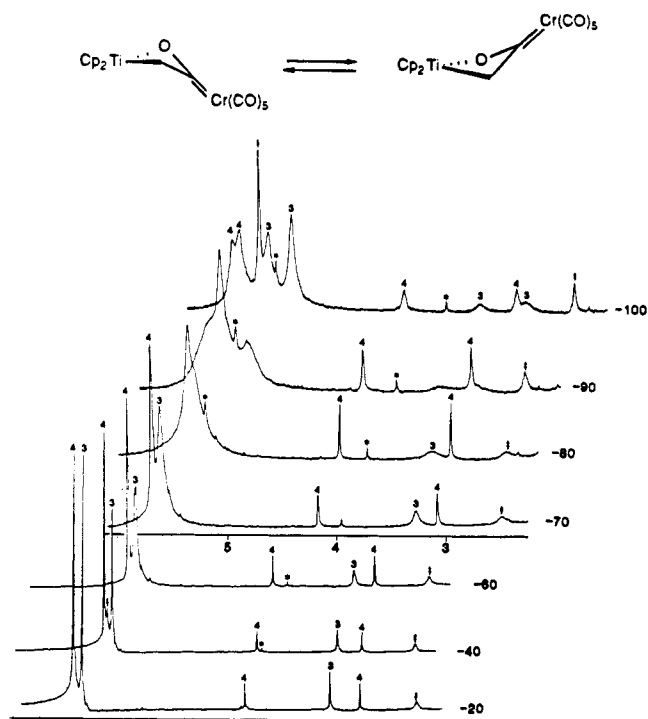
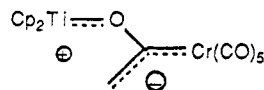


Figure 7. Variable-temperature  $^1\text{H}$  spectra of 3b and 4b. All resonances are labeled according to their compound number:  $\star$ , impurity;  $\dagger$ , starting material (9).

cyclobutanes ( $J_{\text{CH}}$  is typically in the range of 130–140 Hz). Two coupling constants for the methylene group of 4 were found, with values of 160.4 and 150.4 Hz. These values are typical of  $\text{sp}^2$ -hybridized carbons (normally 150–170 Hz).<sup>22</sup> Thus, compound 4 does contain olefinic protons even though the  $^1\text{H}$  NMR chemical shifts are at a slightly higher field than usual.

Deuterium-enriched 9 ( $\text{Cp}_2\text{Ti}(\text{Cl})\text{O}(\text{CD}_3)\text{CCr}(\text{CO})_5$ ) was also synthesized and allowed to react with  $\text{NaN}(\text{TMS})_2$ . The reaction mixture afforded the intermediates 3 and 4 in a 1.3:1 ratio with the oxametallacycle favored over the bridging ketene complex. This simple isotopic substitution finally broke the degeneracy of the equilibrium ratio and establishes the existence of two intermediates with the structures displayed in Figure 2.

The interconversion of 3 and 4 presumably occurs through a zwitterionic form analogous to  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{-OCMo}(\text{CO})_2\text{Cp}$ .<sup>23</sup> This zwitterionic form is stabilized through delocalization of the anionic charge<sup>24</sup> and the donation from oxygen to titanium.



This resonance stabilization is evident from the low  $\text{p}K_a$  of typical Fischer carbenes. For example, the aqueous  $\text{p}K_a$  of the methyl group bound to the carbene carbon of  $(\text{CO})_5\text{Cr}(\text{Me})\text{OMe}$  is 8.0.<sup>25</sup>

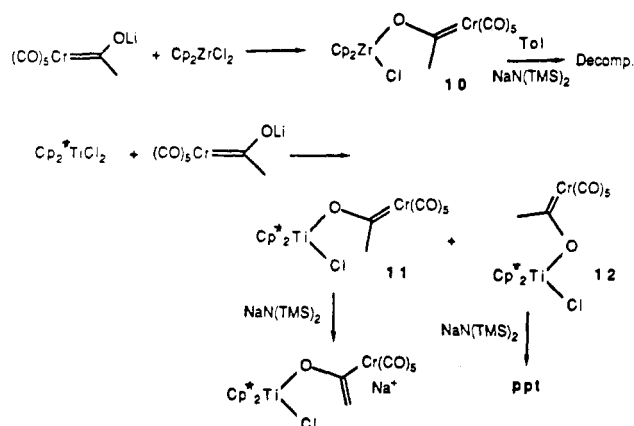
Variable-temperature  $^1\text{H}$  NMR spectra of intermediates 3b and 4b revealed a fluxional process similar to other oxametallacyclobutanes and metallacyclopentenes (Figure

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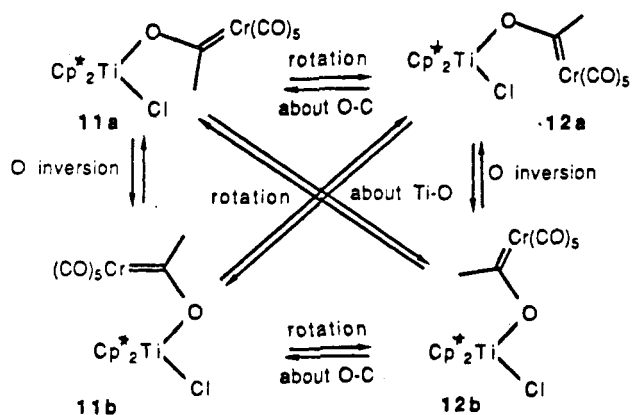


**Figure 8.** Attempted extension of the deprotonation and intramolecular alkylation presented in Figure 5.

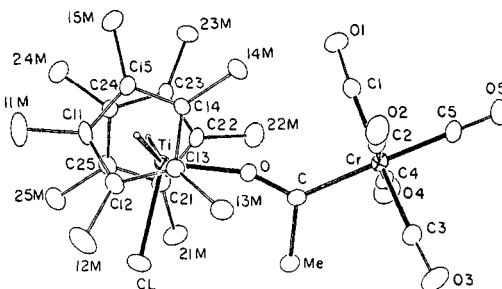
7).<sup>26</sup> At  $-40\text{ }^{\circ}\text{C}$ , a 400-MHz  $^1\text{H}$  NMR spectrum shows initial broadening of the resonance attributed to the methylene group of **3b**. Further cooling of the toluene solution to  $-80\text{ }^{\circ}\text{C}$  results in complete collapse of the methylene resonance of **3b**. Concurrent with this coalescence, the cyclopentadienyl ligand resonance of **3b** begins to broaden. Finally at  $-100\text{ }^{\circ}\text{C}$ , both the methylene and cyclopentadienyl ligand resonances sharpen into two separate peaks apiece. The low-temperature limit was never reached due to freezing of the solvent. All attempts at attaining the slow-exchange limit in freon solvents were unsuccessful due to the insolubility of compounds **3b** and **4b**. The fluxional processes observed are attributed to a puckering of the ring of the oxametallacyclobutane in **3b**. The extent of puckering due to  $\pi$ -donation is the subject of current theoretical debate.<sup>27</sup> At  $0\text{ }^{\circ}\text{C}$ , the rate of interconversion of the two ring puckered structures shown in Figure 7 is rapid on the NMR time scale, and thus, the methylene and cyclopentadienyl resonances appear as singlets. Upon cooling, the interconversion rate decreases, and correspondingly, the  $^1\text{H}$  NMR resonances broaden. This puckering is also possible for **4b**, and thus the cyclopentadienyl ligand resonances of **4b** are also observed to broaden and then separate into two separate signals at  $-100\text{ }^{\circ}\text{C}$  (Figure 7).

Extensions of the deprotonation and intramolecular alkylation sequence of Figure 5 resulted in limited success. Although  $\text{Cp}_2\text{Zr}(\text{ketene})$  is a known compound,<sup>17</sup> the zirconocene complex **10** does not cleanly undergo intramolecular alkylation in toluene to form analogues of **3** and **4** (Figure 8a). The reaction of **8** with  $\text{Cp}^*_2\text{TiCl}_2$  forms rotomers **11** and **12**. Neither **11** nor **12** react with  $\text{NaN}(\text{TMS})_2$  to form analogues to **3** or **4**; instead these reactions produce stable anions (Figure 8b). The anion formed from **11** is soluble in toluene whereas the anion formed from **12** immediately precipitates as its sodium salt. These results are consistent with extensive delocalization of the anionic charge, as well as steric inhibition of the closure reaction to form analogues to **3** and **4**.

The two rotomers (**11** and **12**, Figure 9) cannot be interconverted by heating in toluene to  $110\text{ }^{\circ}\text{C}$ . Instead, the complexes begin to decompose at about  $90\text{ }^{\circ}\text{C}$  probably through loss of CO. Interconversion is restricted because the permethylcyclopentadienyl wedge sterically inhibits



**Figure 9.** Interconversion of **11** and **12**.



**Figure 10.** ORTEP diagram of compound **11** with numbering scheme.

rotation. Compounds **11** and **12** can also exist in two isomeric forms due to inversion at oxygen (**11a,b**, **12a,b**). This inversion at oxygen does not interconvert rotomers **11** and **12**; instead, the inversion forces either the methyl groups or the  $\text{Cr}(\text{CO})_5$  fragment into the wedge formed by the permethylcyclopentadienyl ligands. These isomers most likely exist predominantly as **11a** and **12b** due to the large steric bulk of the  $\text{Cr}(\text{CO})_5$  fragment.

The X-ray crystal structure of **11** was determined, and an ORTEP diagram is shown in Figure 10. There are several unique features about the structure of **11**. The Ti-O-C angle is  $158.3(4)^\circ$  and the O-Ti-Cl angle is  $97.2(1)^\circ$ . In a similar compound,  $\text{Cp}^*_2\text{TiCl}_2$ ,<sup>28</sup> the Cl-Ti-Cl angle was found to be  $92.9^\circ$ . The larger angle of  $97.2^\circ$  in **11** is most likely due to steric nonbonded interactions between the Cl and the Fischer carbene methyl group. The proximity of these two groups in the permethylcyclopentadienyl wedge increases the bond angle separating the Cl and the O substituents. For comparison, a similar complex  $[\text{Cp}_2\text{ZrOC}(\text{Ph})\text{Mo}(\text{CO})_5]_2\text{O}$  with two Fischer-type molybdenum zirconoxyphenylcarbene moieties has been structurally characterized.<sup>2</sup> The O-Zr-O bond angle in this compound was found to be  $99.4(1)^\circ$ . This angle is similar to the observed Cl-Ti-O angle of **11** and again results from large steric interactions within the cyclopentadienyl wedge. In addition, the Ti-O-C angle of  $158.3(4)^\circ$  in **11** is larger than that found in an analogous alkoxytitanocene chloride complex,  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$ .<sup>29</sup> In this complex, the Ti-O-C angle was found to be  $133.2(2)^\circ$ . Therefore, the larger Ti-O-C bond angle in **11** is due to steric interactions and not the result of increased O lone-pair donation to the Ti center. The longer Ti-O bond in **11** ( $2.00(4)\text{ \AA}$ ) relative to the Ti-O bond on the analogous complex  $\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}$  ( $1.855\text{ \AA}$ ) is also consistent with steric factors instead of  $\pi$ -bonding increasing the bond angle. Further

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(27) (a) Tatsumi, K.; Yasuda, H.; Nakamura, A. *Isr. J. Chem.* **1983**, *23*, 145. (b) Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.

(28) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457.

(29) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

**Table I. Summary of Crystal Data and Intensity Collection Information for 11**

formula	C <sub>27</sub> H <sub>33</sub> O <sub>6</sub> ClCrTi
fw	588.91/amu
cryst system	monoclinic
space group	P2 <sub>1</sub> /c
a, Å	12.490 (2)
b, Å	13.472 (3)
c, Å	17.791 (4)
β, deg	109.83 (2)
V, Å <sup>3</sup>	2816 (2)
Z	4
D <sub>calcd</sub> , g/cm <sup>3</sup>	1.39
λ, Å	0.710 733
μ, cm <sup>-1</sup>	8.31
scan range	1.0° above Kα <sub>1</sub> , 1.0° below Kα <sub>2</sub>
reflections collected	±h, ±k, ±l 11 168, 4101 > 0
R(F)	0.139
R(F) [F <sub>o</sub> <sup>2</sup> > 3σ(F <sub>o</sub> <sup>2</sup> )]	0.056
goodness of fit	1.12

**Table II. Selected Bond Distances (Å) for 11**

Cr-C	2.089 (6)	C-O	1.269 (7)
Cr-C(1)	1.880 (7)	C-Me	1.528 (10)
Cr-C(2)	1.897 (7)	Cl-Me	3.502 (7)
Cr-C(3)	1.876 (7)	C(1)-O(1)	1.146 (9)
Cr-C(4)	1.892 (7)	C(2)-O(2)	1.138 (8)
Cr-C(5)	1.844 (7)	C(3)-O(3)	1.151 (9)
Cr-Me	3.316 (7)	C(4)-O(4)	1.136 (9)
Ti-O	2.007 (4)	C(5)-O(5)	1.166 (9)
Ti-Cl	2.347 (2)	C(11)-C(11M)	1.492 (10)
Ti-C(11)	2.460 (7)	C(12)-C(12M)	1.487 (10)
Ti-C(12)	2.477 (7)	C(13)-C(13M)	1.498 (9)
Ti-C(13)	2.402 (6)	C(14)-C(14M)	1.503 (9)
Ti-C(14)	2.390 (6)	C(15)-C(15M)	1.500 (9)
Ti-C(15)	2.435 (7)	C(21)-C(21M)	1.489 (10)
Ti-C(21)	2.458 (7)	C(22)-C(22M)	1.489 (10)
Ti-C(22)	2.437 (7)	C(23)-C(23M)	1.499 (9)
Ti-C(23)	2.406 (7)	C(24)-C(24M)	1.498 (10)
Ti-C(24)	2.437 (7)	C(25)-C(25M)	1.510 (10)
Ti-C(25)	2.438 (7)		

**Table III. Selected Bond Angles (deg) for 11**

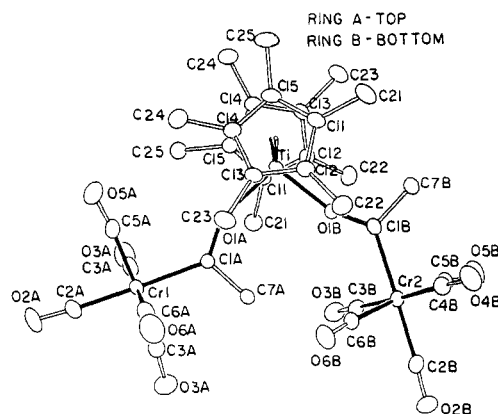
C-Cr-C(1)	91.5 (3)	C(3)-Cr-C(5)	88.1 (3)
C-Cr-C(2)	95.3 (3)	C(4)-Cr-C(5)	91.1 (3)
C-Cr-C(3)	91.7 (3)	Cr-C(1)-O(1)	177.2 (6)
C-Cr-C(4)	86.0 (3)	Cr-C(2)-O(2)	176.9 (6)
C-Cr-C(5)	177.1 (3)	Cr-C(3)-O(3)	176.3 (6)
C(1)-Cr-C(2)	89.5 (3)	Cr-C(4)-O(4)	178.8 (6)
C(1)-Cr-C(3)	176.1 (3)	Cr-C(5)-O(5)	179.5 (6)
C(1)-Cr-C(4)	91.5 (3)	Cr-C-O	129.2 (5)
C(1)-Cr-C(5)	88.8 (3)	Cr-C-Me	119.4 (5)
C(2)-Cr-C(3)	88.1 (3)	O-C-Me	111.3 (5)
C(2)-Cr-C(4)	178.4 (3)	C-O-Ti	158.3 (4)
C(2)-Cr-C(5)	87.6 (3)	O-Ti-Cl	97.2 (1)
C(3)-Cr-C(4)	90.8 (3)		

evidence of the steric crowding in the permethylcyclopentadienyl wedge is provided by the near planarity of Cl, Ti, O, C, Cr, and Me moieties. The slight displacement of the Me group from the plane by 7° is again most likely due to steric repulsion between Cl and Me. However, crystals packing forces cannot be ruled out as the cause of this distortion. If the Me group was locked symmetrically between the permethylcyclopentadienyl ligands and felt no steric repulsion from the Cl, then all the atoms and groups would be expected to lie in the same plane. Tables II and III present selected bond lengths and bond angles for 11. Table IV lists the atomic coordinates for 11.

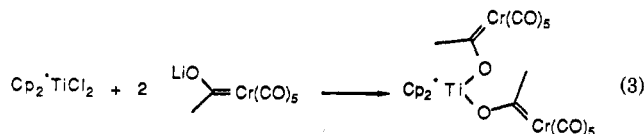
In order to determine if isomer 12 is a rotomer of 11 (with the methyl group wedged along one side of the titanium center) as depicted in Figure 10, an X-ray crystal structure was desired. Suitable crystals of 12 were not

**Table IV. Atom Coordinates (×10<sup>4</sup>) and U<sub>eq</sub>'s for 11**

atom	x	y	z	U <sub>eq</sub> , Å <sup>2</sup>
Cr	482.2 (9)	115.8 (8)	3471.1 (6)	398 (3)
Ti	3188.8 (9)	231.9 (8)	1920.8 (7)	338 (3)
Cl	4353.3 (15)	-1161.7 (13)	2387.2 (11)	596 (6)
O	2245 (3)	86 (3)	2630 (2)	352 (11)
C	1878 (5)	-297 (5)	3147 (4)	388 (18)
Me	2656 (6)	-1134 (6)	3602 (4)	692 (23)
C(1)	369 (6)	1343 (5)	2946 (4)	468 (20)
O(1)	254 (5)	2093 (3)	2624 (3)	741 (19)
C(2)	-627 (6)	-415 (5)	2545 (4)	439 (20)
O(2)	-1329 (4)	-716 (4)	2002 (3)	697 (17)
C(3)	488 (5)	-1108 (5)	3977 (4)	474 (21)
O(3)	437 (4)	-1842 (4)	4293 (3)	783 (19)
C(4)	1564 (6)	634 (5)	4413 (4)	444 (21)
O(4)	2226 (5)	933 (4)	4977 (3)	812 (20)
C(5)	-699 (6)	503 (5)	3806 (4)	488 (21)
O(5)	-1444 (4)	742 (4)	4021 (3)	724 (17)
C(11)	2796 (5)	-93 (5)	491 (4)	398 (18)
C(12)	2581 (5)	-994 (5)	819 (4)	419 (20)
C(13)	1699 (5)	-840 (5)	1122 (4)	334 (19)
C(14)	1325 (5)	159 (5)	942 (3)	302 (16)
C(15)	1995 (5)	623 (5)	557 (4)	356 (21)
C(11M)	3558 (6)	-5 (6)	5 (4)	779 (24)
C(12M)	3083 (6)	-1970 (5)	731 (4)	710 (26)
C(13M)	1185 (5)	-1637 (5)	1478 (4)	484 (21)
C(14M)	297 (5)	616 (5)	1063 (4)	446 (20)
C(15M)	1682 (5)	1570 (5)	89 (4)	527 (22)
C(21)	4802 (6)	971 (5)	2985 (4)	425 (21)
C(22)	3848 (6)	1562 (5)	2899 (4)	375 (18)
C(23)	3482 (5)	1991 (5)	2130 (4)	343 (18)
C(24)	4252 (5)	1682 (5)	1749 (4)	360 (19)
C(25)	5040 (5)	1040 (5)	2266 (4)	438 (22)
C(21M)	5520 (6)	464 (5)	3729 (4)	646 (25)
C(22M)	3413 (6)	1826 (5)	3555 (4)	621 (23)
C(23M)	2607 (5)	2796 (5)	1867 (4)	507 (21)
C(24M)	4439 (5)	2166 (5)	1046 (4)	564 (22)
C(25M)	6076 (5)	607 (5)	2133 (4)	656 (25)

**Figure 11. ORTEP diagram of compound 13 with numbering scheme.**

obtained; instead, compound 13 was prepared by treatment of Cp\*<sub>2</sub>TiCl<sub>2</sub> and 2 equiv of 8 (eq 3).



13

The <sup>1</sup>H NMR spectrum of 13 revealed two different methyl resonances at δ 2.28 and 3.48, indicating that the two Fischer carbene moieties are not bonded symmetrically to Cp\*<sub>2</sub>Ti.

Figure 11 shows an ORTEP diagram of 13. The same general features evident in the X-ray structure of 11 are present, and the methyl group of the second Fischer carbene unit is also sandwiched between the two per-

Table V. Summary of Crystal Data and Intensity Collection Information for 13

formula	C <sub>34</sub> H <sub>36</sub> O <sub>12</sub> Cr <sub>2</sub> Ti
fw	788.55
cryst system	monoclinic
space group	P2 <sub>1</sub> /n
a	9.958 (2)
b	32.226 (8)
c	11.998 (3)
β	108.21 (2)
V	3657 (3) Å <sup>3</sup>
Z	4
D <sub>calc'd</sub> , g/cm <sup>3</sup>	1.43 (1)
λ, Å	0.710733 Å
μ, cm <sup>-1</sup>	8.92
scan range collected	1.0° above Kα <sub>1</sub> , 1.0° below Kα <sub>2</sub> ~14 000, 5860 > 0
R(F)	0.0662
R(F) [F <sub>o</sub> <sup>2</sup> > 3σ(F <sub>o</sub> <sup>2</sup> )]	0.046
goodness of fit	1.96

Table VI. Selected Bond Distances (Å) for 13

Ti-O(1A)	2.051 (2)	C(13A)-C(23A)	1.509 (5)
Ti-O(1B)	1.973 (2)	C(14A)-C(15A)	1.410 (5)
Ti-C(11A)	2.477 (4)	C(14A)-C(24A)	1.510 (5)
Ti-C(12A)	2.462 (4)	C(15A)-C(25A)	1.505 (6)
Ti-C(13A)	2.405 (4)	C(11B)-C(12B)	1.410 (5)
Ti-C(14A)	2.389 (4)	C(11B)-C(15B)	1.412 (5)
Ti-C(15A)	2.486 (4)	C(11B)-C(21B)	1.496 (5)
Ti-C(11B)	2.420 (3)	C(12B)-C(13B)	1.413 (5)
Ti-C(12B)	2.458 (4)	C(12B)-C(22B)	1.500 (5)
Ti-C(13B)	2.411 (4)	C(13B)-C(14B)	1.417 (5)
Ti-C(14B)	2.434 (4)	C(13B)-C(23B)	1.507 (5)
Ti-C(15B)	2.425 (4)	C(14B)-C(15B)	1.409 (5)
Cr(1)-C(1A)	2.107 (4)	C(14B)-C(24B)	1.511 (5)
Cr(1)-C(2A)	1.847 (4)	C(15B)-C(25B)	1.509 (5)
Cr(1)-C(3A)	1.874 (5)	C(1A)-O(1A)	1.270 (4)
Cr(1)-C(4A)	1.873 (5)	C(1B)-O(1B)	1.268 (4)
Cr(1)-C(5A)	1.851 (4)	O(1A)-C(1A)	1.270 (4)
Cr(1)-C(6A)	1.897 (5)	C(1A)-C(7A)	1.501 (5)
Cr(2)-C(1B)	2.096 (4)	O(2A)-C(2A)	1.150 (6)
Cr(2)-C(2B)	1.862 (4)	O(3A)-C(3A)	1.146 (6)
Cr(2)-C(3B)	1.887 (4)	O(4A)-C(4A)	1.149 (6)
Cr(2)-C(4B)	1.886 (4)	O(5A)-C(5A)	1.152 (6)
Cr(2)-C(5B)	1.872 (5)	O(6A)-C(6A)	1.131 (7)
Cr(2)-C(6B)	1.884 (4)	O(1B)-C(1B)	1.268 (4)
C(1A)-C(7A)	1.501 (5)	O(2B)-C(2B)	1.151 (5)
C(1B)-C(7B)	1.524 (5)	O(3B)-C(3B)	1.145 (5)
C(11A)-C(12A)	1.413 (5)	O(4B)-C(4B)	1.142 (5)
C(11A)-C(15A)	1.401 (5)	O(5B)-C(5B)	1.141 (6)
C(11A)-C(21A)	1.508 (6)	O(6B)-C(6B)	1.138 (5)
C(12A)-C(13A)	1.404 (5)		
C(12A)-C(22A)	1.503 (6)		
C(13A)-C(14A)	1.417 (5)		

methylcyclopentadienyl ligands. This methyl group resides along the side of the permethylcyclopentadienyl wedge and not in the face of the wedge as does the other Fischer carbene unit. An additional interesting feature of the structure of 13 is the orientation of the carbene π-bonds with respect to the carbonyls. The Fischer carbene moiety, which has its methyl group (C7B) along the side of the permethylcyclopentadienyl wedge, has its Cr-C π-bond between two different carbonyl groups. This is one of the few examples of a metal-carbene π-bond that is positioned between two donor-acceptor ligands.<sup>30</sup> This arrangement results from the steric demand of the methyl group (C(7A)) on the second Fischer carbene, which forces the rotation of the carbonyls away from their normal positions. Tables VI and VII present selected bond lengths and angles for 13, and Table VIII lists the atom coordinates for 13.

The bonding in Fischer carbenes is often viewed in two different manners. The first is a singlet carbene donating

Table VII. Selected Bond Angles (deg) for 13

O(1A)-Ti-O(1B)	99.6 (1)	C(14A)-C(13A)-C(12A)	108.1 (3)
Ti-O(1A)-C(1A)	150.1 (2)	C(23A)-C(13A)-C(12A)	125.2 (3)
Ti-O(1B)-C(1B)	161.2 (2)	C(23A)-C(13A)-C(14A)	126.2 (3)
O(1A)-C(1A)-C(7A)	114.1 (3)	C(15A)-C(14A)-C(13A)	107.6 (3)
O(1B)-C(1B)-C(7B)	113.5 (3)	C(24A)-C(14A)-C(13A)	125.7 (3)
O(1A)-C(1A)-Cr(1)	127.8 (2)	C(24A)-C(14A)-C(15A)	126.1 (3)
O(1B)-C(1B)-Cr(2)	127.5 (3)	C(14A)-C(15A)-C(11A)	108.1 (3)
C(7A)-C(1A)-Cr(1)	118.0 (2)	C(25A)-C(15A)-C(11A)	123.3 (3)
C(7B)-C(1B)-Cr(2)	119.0 (2)	C(25A)-C(15A)-C(14A)	126.2 (3)
C(1A)-Cr(1)-C(2A)	178.0 (2)	C(15B)-C(11B)-C(12B)	108.0 (3)
C(1A)-Cr(1)-C(3A)	91.6 (2)	C(21B)-C(11B)-C(12B)	125.2 (3)
C(1A)-Cr(1)-C(4A)	87.2 (2)	C(21B)-C(11B)-C(15B)	125.8 (3)
C(1A)-Cr(1)-C(5A)	91.8 (2)	C(13B)-C(12B)-C(11B)	108.0 (3)
C(1A)-Cr(1)-C(6A)	92.3 (2)	C(22B)-C(12B)-C(11B)	124.0 (3)
C(2A)-Cr(1)-C(3A)	89.3 (2)	C(22B)-C(12B)-C(13B)	127.4 (3)
C(2A)-Cr(1)-C(4A)	92.1 (2)	C(14B)-C(13B)-C(12B)	107.8 (3)
C(2A)-Cr(1)-C(5A)	86.3 (2)	C(23B)-C(13B)-C(12B)	125.1 (3)
C(2A)-Cr(1)-C(6A)	89.5 (2)	C(23B)-C(13B)-C(14B)	125.3 (3)
C(3A)-Cr(1)-C(4A)	176.8 (2)	C(15B)-C(14B)-C(13B)	107.9 (3)
C(3A)-Cr(1)-C(6A)	91.3 (2)	C(24B)-C(14B)-C(13B)	127.4 (3)
C(3A)-Cr(1)-C(6A)	88.5 (2)	C(24B)-C(14B)-C(15B)	122.2 (3)
C(4A)-Cr(1)-C(5A)	91.7 (2)	C(14B)-C(15B)-C(11B)	108.1 (3)
C(4A)-Cr(1)-C(6A)	88.6 (2)	C(25B)-C(15B)-C(11B)	126.3 (3)
C(5A)-Cr(1)-C(6A)	175.8 (2)	C(25B)-C(15B)-C(14B)	125.1 (3)
C(1B)-Cr(2)-C(2B)	178.1 (2)	C(7A)-C(1A)-O(1A)	114.1 (3)
C(1B)-Cr(2)-C(3B)	88.9 (2)	C(7B)-C(1B)-O(1B)	113.5 (3)
C(1B)-Cr(2)-C(4B)	88.7 (2)	C(15A)-C(11A)-C(12A)	108.2 (3)
C(1B)-Cr(2)-C(5B)	92.0 (2)	C(21A)-C(11A)-C(12A)	125.5 (3)
C(1B)-Cr(2)-C(6B)	92.8 (2)	C(21A)-C(11A)-C(15A)	124.4 (3)
C(2B)-Cr(2)-C(3B)	91.4 (2)	C(13A)-C(12A)-C(11A)	107.8 (3)
C(2B)-Cr(2)-C(4B)	91.1 (2)	C(22A)-C(12A)-C(11A)	126.7 (3)
C(2B)-Cr(2)-C(5B)	89.8 (2)	C(22A)-C(12A)-C(13A)	124.7 (3)
C(2B)-Cr(2)-C(6B)	85.3 (2)		
C(3B)-Cr(2)-C(4B)	176.0 (2)		
C(3B)-Cr(2)-C(5B)	88.2 (2)		
C(3B)-Cr(2)-C(6B)	94.4 (2)		
C(4B)-Cr(2)-C(5B)	88.6 (2)		
C(4B)-Cr(2)-C(6B)	89.0 (2)		
C(5B)-Cr(2)-C(6B)	174.6 (2)		

a pair of electrons via an sp<sup>2</sup>-hybrid orbital, and a filled metal d orbital back-donating into an empty p orbital on carbon.<sup>31</sup> A second description is a covalent alkylidene σ- and π-bond.<sup>32,33</sup> The introduction of a heteroatom substituent, however, has been found to stabilize the donor singlet carbene state.<sup>34</sup> In either of the two bonding descriptions, a p orbital on carbon interacts with a dπ orbital on chromium. A dπ symmetric orbital can be built at any angle with respect to the carbonyl ligands by a linear combination of d<sub>xz</sub> and d<sub>yz</sub> orbitals (taking the Cr=C axis as the z axis).<sup>35</sup> Thus, rotation along the Cr-C bond axis only slightly perturbs the Cr-C double bond. In fact, the C(1)-C(1A) bond distance in the rotated Fischer carbene moiety of 13 is essentially the same (0.02 Å shorter) as the C(2)-C(1B) bond distance of the other Fischer carbene moiety.

In summary, the intramolecular alkylation of 11 and 12 (in the presence of NaN(TMS)<sub>2</sub>) does not occur due to steric hindrance between the permethylcyclopentadienyl ligands and the bulky Cr(CO)<sub>5</sub> fragment. This steric crowding is evident from the barrier to rotation of the Fischer carbene moiety of 11 and 12 with respect to the Cp\*<sub>2</sub> TiCl fragment. Thus 11 and 12 cannot be used as compounds to enter a model Fischer-Tropsch system. Compound 9, however, when reacted with NaN(TMS)<sub>2</sub> does produce models for a Fischer-Tropsch system. Compounds 3 and 4 can be produced either by the intra-

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Table VIII. Atom Coordinates ( $\times 10^4$ ) and  $U_{eq}$ 's for 13

atom	x	y	z	$U_{eq}, \text{\AA}^2$
Ti	4525.9 (7)	3892.1 (2)	2803.0 (5)	337 (1)
Cr(1)	1240.7 (7)	4116.5 (2)	-1369.8 (5)	508 (2)
Cr(2)	1531.7 (7)	2760.8 (2)	3565.4 (5)	448 (1)
O(1A)	3159 (2)	3969 (1)	1138 (2)	362 (6)
C(1A)	2096 (4)	3847 (1)	303 (3)	390 (9)
O(2A)	102 (4)	4545 (1)	6308 (3)	1064 (12)
C(2A)	507 (5)	4371 (1)	-2812 (4)	709 (13)
O(oA)	3469 (4)	3730 (1)	-2265 (3)	996 (11)
C(3A)	2632 (5)	3869 (1)	-1900 (3)	638 (12)
O(4A)	-1081 (4)	4464 (1)	-515 (3)	1219 (14)
C(4A)	-189 (5)	4334 (2)	-832 (4)	752 (15)
O(5A)	2977 (4)	4892 (1)	-721 (3)	983 (11)
C(5A)	2332 (5)	4589 (1)	-913 (3)	589 (11)
O(6A)	-664 (5)	3383 (1)	-2340 (3)	1430 (16)
C(6A)	68 (6)	3650 (2)	-1947 (4)	864 (17)
C(7A)	1361 (5)	3476 (1)	596 (3)	668 (12)
O(1B)	3582 (2)	3428 (1)	3333 (2)	391 (6)
C(1B)	3288 (4)	3157 (1)	3985 (3)	430 (9)
O(2B)	-1070 (4)	2221 (1)	2906 (3)	892 (10)
C(2B)	-66 (5)	2424 (1)	3173 (3)	578 (11)
O(3B)	2271 (3)	2472 (1)	1424 (3)	796 (9)
C(3.3)	1975 (4)	2591 (1)	2216 (3)	526 (10)
O(4B)	1027 (4)	3014 (1)	5832 (3)	958 (11)
C(4B)	1220 (4)	2921 (1)	4976 (4)	587 (11)
O(5B)	3225 (4)	2037 (1)	4865 (3)	1189 (13)
C(5B)	2622 (5)	2317 (1)	4373 (4)	677 (12)
O(6B)	-535 (3)	3428 (1)	2348 (2)	777 (9)
C(6B)	287 (5)	3184 (1)	2783 (3)	497 (10)
C(7B)	4369 (4)	3132 (1)	5206 (3)	584 (11)
C(11A)	4720 (4)	4263 (1)	4656 (3)	467 (10)
C(12A)	3265 (4)	4230 (1)	4025 (3)	454 (9)
C(13A)	3016 (4)	4454 (1)	2977 (3)	409 (9)
C(14A)	4317 (4)	4627 (1)	2958 (3)	444 (9)
C(15A)	5351 (4)	4521 (1)	4024 (3)	476 (10)
C(21A)	5398 (5)	4140 (1)	5921 (3)	741 (13)
C(22A)	2130 (5)	4054 (1)	4468 (3)	615 (11)
C(23A)	1577 (4)	4545 (1)	2119 (3)	587 (11)
C(24A)	4510 (5)	4922 (1)	2042 (4)	624 (11)
C(25A)	6732 (4)	4742 (1)	4572 (4)	692 (13)
C(11B)	5521 (4)	3422 (1)	1698 (3)	397 (9)
C(12B)	6113 (4)	3301 (1)	2880 (3)	454 (9)
C(13B)	6920 (4)	3637 (1)	3500 (3)	442 (10)
C(14B)	6911 (4)	3954 (1)	2678 (3)	433 (10)
C(15B)	6033 (4)	3822 (1)	1570 (3)	420 (9)
C(21B)	4722 (4)	3143 (1)	718 (3)	570 (10)
C(22B)	6055 (4)	2868 (1)	3318 (3)	598 (11)
C(23B)	7912 (4)	3617 (1)	4739 (3)	647 (13)
C(24B)	7957 (4)	4305 (1)	2818 (3)	592 (12)
C(25B)	5848 (4)	4047 (1)	429 (3)	563 (10)

molecular alkylation reaction of 9 or by the CO insertion of  $\text{Cr}(\text{CO})_6$  into the Ti-C double bond of 2.

The reaction of 2 with  $\text{Cr}(\text{CO})_6$  is the first homogeneous example of a metal-bound carbene coupling with a metal-bound carbon monoxide to form bound ketene. The postulated coupling of a bound carbon monoxide and a bound carbene on transition-metal surfaces<sup>39</sup> could be viewed to proceed as shown in Figure 12. The steps shown are analogous to the proposed mechanism by which 2 and  $\text{Cr}(\text{CO})_6$  react to yield 5. In step A, the carbonyl oxygen interacts with the metal surface, and consequently there is an increase in the electrophilicity of the carbonyl carbon. In step B, the carbene migrates to the carbonyl carbon, and finally in step C, rearrangement of the strained carbon fragment 16 yields surface-bound ketene 17. In our system, 3 and 4 are analogues to 16 and 17 and subsequently expel the  $\text{Cr}(\text{CO})_5$  fragment to form 5. Thus, the reaction of  $\text{Cr}(\text{CO})_5$  with 2 can be viewed as a possible homogeneous analogue to heterogeneous Fischer-Tropsch chemistry.

### Experimental Section

**General Considerations.** All manipulations were performed by using glovebox or standard Schlenk line techniques. Argon was purified by passage through Chemalog R3-11 and activated

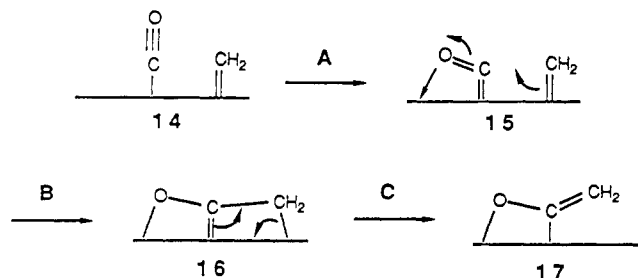


Figure 12. Fischer-Tropsch analogy.

4-Å molecular sieves. Deuteriated solvents were purchased from Cambridge Isotope Laboratories and purified by vacuum transfer from sodium benzophenone ketyl.  $\text{CH}_2\text{Cl}_2$  was purified by vacuum distillation from  $\text{CaH}_2$ . THF was predried over  $\text{CaH}_2$  and then vacuum distilled from sodium benzophenone ketyl. Preparative chromatography was performed by using the method of Still.<sup>38</sup>  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  were purchased from Alfa and used as received.

Metallacyclobutanes,<sup>15</sup> titanocene ketene,<sup>17</sup>  $\text{Cp}_2\text{Ti}(\text{Cl})\text{O}(\text{CH}_3)\text{CCr}(\text{CO})_5$ ,<sup>21</sup>  $\text{LiO}(\text{CH}_3)\text{CCr}(\text{CO})_5$ ,<sup>21</sup>  $\text{Mo}(\text{CO})_5\text{PPh}_3$ ,<sup>36</sup>  $\text{Mo}(\text{CO})_5\text{P}(\text{OPh})_3$ ,<sup>36</sup> and  $\text{Cp}^*\text{TiCl}_2$ <sup>37</sup> were synthesized as previously described. Deuteriated or  $^{13}\text{C}$ -enriched 9 was synthesized from the deuteriated or  $^{13}\text{C}$ -enriched  $\text{CH}_3\text{I}$ .

$^1\text{H}$  NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz  $^1\text{H}$ , 13.76 MHz  $^2\text{H}$ , 36.2 MHz  $^{31}\text{P}$ , 22.5 MHz  $^{13}\text{C}$ ) and/or JEOL GX-400 (399.65 MHz  $^1\text{H}$ , 100.67 MHz  $^{13}\text{C}$ ). Spectra were taken in benzene- $d_6$  or toluene- $d_6$  solutions, and resonances were referenced to residual protons on the solvent. All NMR tube experiments were prepared in a drybox, and the NMR tube was capped with a rubber septum.

**Synthesis of  $\text{Cp}^*\text{Ti}(\text{Cl})\text{O}(\text{CH}_3)\text{Cr}(\text{CO})_5$  (11 and 12).** A 300-mL three-necked flask was equipped with reflux condenser and charged with 2.7 g ( $4.5 \times 10^{-3}$  mol) of  $\text{Cp}^*\text{TiCl}_2$ , 1.6 g of  $\text{LiO}(\text{CH}_3)\text{CCr}(\text{CO})_5$  ( $6.6 \times 10^{-3}$  mol), and 100 mL of  $\text{CH}_2\text{Cl}_2$ . The reaction was refluxed for 7 h and cooled to room temperature. The solution was then filtered through a 1-in. plug of Celite on a glass frit. The solvent was removed on a rotary evaporator and the red solid dissolved in the minimum amount of  $\text{CH}_2\text{Cl}_2$ . A preparative column was run with 200 g of silica gel with a 2/1 pentane/ $\text{CH}_2\text{Cl}_2$  eluent. The first red band 11 ( $R_f$  0.53), second red band 13 ( $R_f$  0.35), and third red band 12 ( $R_f$  0.12) were collected. Each fraction was dried by a rotary evaporator and recrystallized from a 2/1 petroleum ether/ $\text{CHCl}_3$  solution. Compound 11: yield 0.92 g (22%);  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.72 (s, 30 H), 2.87 (s, 3 H);  $^{13}\text{C}$  (100.1 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  352.2, 223.8, 219.4, 128.5, 50.9, 12.69. Anal. Calcd for  $\text{C}_{26}\text{H}_{33}\text{O}_6\text{CrTi}$ : C, 55.07; H, 5.64. Found: C, 54.90; H, 5.59. Compound 12: yield 0.42 g, 11%;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.64 (s, 30 H), 2.58 (s, 3 H);  $^{13}\text{C}$  (100.1 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  344.7, 224.2, 219.9, 125.3, 50.5, 11.7.

**Crystal Structure Determination of  $\text{Cp}^*\text{Ti}(\text{Cl})\text{O}(\text{CH}_3)\text{CCr}(\text{CO})_5$ .** A single crystal of  $\text{Cp}^*\text{Ti}(\text{Cl})\text{O}(\text{CH}_3)\text{CCr}(\text{CO})_5$  was obtained from slow cooling of a solution of petroleum ether/ $\text{CHCl}_3$  (1/2) and was mounted in air. The crystal was then optically centered on an Enraf-Nonius CAD 4 diffractometer equipped with a graphite monochromator and  $\text{Mo K}\alpha$  radiation. The space group was  $P2_1/c$ . A total of 11 168 reflections were collected. After equivalent ( $2/m$  symmetry) reflections were merged 4942 remained, of which 4101 had  $F_o^2 > 0$  and 1827 had  $F_o^2 > 3\sigma(F_o^2)$ . These reflections,  $1 \leq \theta \leq 25^\circ$ , were collected in the hemisphere ( $\pm h, \pm k, +$ ). Crystal decay was monitored by three check reflections, and the intensities did not significantly decrease over 2 days of exposure to X-rays. The crystal data parameters are summarized in Table I.

The positions of the titanium and chromium atoms were determined from a Patterson map, and the Fourier map phased on

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(39) (a) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* 1980, 102, 6181. (b) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* 1981, 103, 1287.



the two heavy atoms revealed the remainder of the structure. All hydrogen atoms were placed at idealized positions with fixed coordinates and isotropic Gaussian amplitudes. All other atoms were refined with anisotropic  $U_{ij}$  parameters.

All calculations were performed on a VAX 11/750 computer using the CRYM system of programs.

**Synthesis of  $Cp^*_2Ti(O(CH_3)CCr(CO)_5)_2$ .** A medium Schlenk tube was loaded with 500 mg ( $1.2 \times 10^{-3}$  mol) of  $Cp^*_2TiCl_2$  and 615 mg ( $2.5 \times 10^{-3}$  mol) of  $LiO(CH_3)CCr(CO)_5$ . The reactants were suspended in 10 mL of THF and stirred at room temperature for 72 h. The solvent was removed under vacuum and the red solid dissolved in  $CH_2Cl_2$  and filtered through a 1-in. plug of Celite on a glass frit. The red solution was chromatographed on silica gel with a 2/1 pentane/ $CH_2Cl_2$  eluent. The major product **13** ( $R_f$  0.35) was collected and dried on a rotary evaporator: yield 270 mg, 35%;  $^1H$  NMR (90 MHz,  $C_6D_6$ )  $\delta$  1.51 (s, 30 H), 2.28 (s, 3 H), 3.48 (s, 3 H);  $^{13}C$  (100.1 MHz,  $C_6D_6$ )  $\delta$  223.32, 223.42, 218.93, 219.17, 346.47, 350.56, 58.39, 57.41, 129.59, 12.84.

**Crystal Structure Determination of  $Cp^*_2Ti(O(CH_3)CCr(CO)_5)_2$ .** A single crystal of  $Cp^*_2Ti(O(CH_3)CCr(CO)_5)_2$  was obtained from slow cooling of a 1/2 solution of petroleum ether/ $CHCl_3$  and was mounted in air. The crystal was then optically centered on a Enraf-Nonius CAD 4 diffractometer equipped with a graphite monochromator and Mo  $K\alpha$  radiation. The space group was  $P2_1/n$ . A total of approximately 14 000 reflections were collected; after space group absences were deleted and duplicates merged, 6401 reflections remained, of which 5860 had  $F_o^2 > 0$  and 4309 had  $F_o^2 > 3\sigma(F_o^2)$ . The data were collected in the hemisphere ( $\pm h, \pm k, +l$ ),  $2\theta = 2-50$ , and in the quadrant ( $\pm h, +k, +l$ ),  $2\theta = 50-55^\circ$ . Crystal decay was monitored by three check reflections, whose intensities decreased negligibly over the approximate 3 days of exposure. The crystal parameters are in Table V.

The positions of the titanium and the two chromium atoms were determined from a Patterson map, and a Fourier map phased on these heavy atoms revealed the remainder of the structure. All hydrogen atoms were placed at idealized positions with fixed coordinates and isotropic Gaussian amplitudes. All other atoms were refined with anisotropic  $U_{ij}$  parameters.

All calculations were performed on a VAX 11/750 computer using the CRYM system of programs.

**Reaction of **1** with  $M(CO)_6$  ( $M = Cr, Mo$ ).** In a drybox, a 5-mm NMR tube was loaded with 10 mg ( $4.0 \times 10^5$  mol) of **1** and 1 equiv of  $M(CO)_6$ . A small flask was filled with 0.6 mL of toluene- $d_8$  and capped with a rubber septum. The solvent and NMR tube were cooled to  $-10^\circ C$ . The NMR probe was precooled to  $5^\circ C$ , and 0.4 mL of cooled toluene- $d_8$  was added by syringe to the NMR tube. The reaction was monitored by  $^1H$  NMR. Identification of the final product, titanocene ketene, was done by comparison of published  $^1H$  and  $^{13}C$  NMR data.<sup>30</sup>  $^1H$  NMR (90 MHz, toluene- $d_8$ ): intermediate **3a** ( $M = Mo$ ),  $\delta$  5.68 (s, 10 H), 3.17 (s, 2 H); intermediate **4a** ( $M = Mo$ ),  $\delta$  5.75 (s, 10 H), 2.97 (d, 1 H,  $J_{HH} = 1.5$  Hz), 4.13 (d, 1 H,  $J_{HH} = 1.5$  Hz); intermediate **3b** ( $M = Cr$ ),  $\delta$  5.67 (s, 10 H), 3.35 (s, 2 H); intermediate **4b** ( $M = Cr$ ),  $\delta$  5.75 (s, 10 H), 3.04 (d, 1 H,  $J_{HH} = 1.5$  Hz), 4.11 (d, 1 H,  $J_{HH} = 1.5$  Hz).

**Reaction of **1** with  $Mo(^{13}CO)_5P(OPh)_3$ .** A 5-mm NMR tube was charged with 18 mg of **1** ( $7.26 \times 10^{-5}$  mol) and 46 mg of  $Mo(^{13}CO)_5P(OPh)_3$  ( $8.42 \times 10^{-5}$  mol). A small flask was loaded with 0.6 mL of toluene- $d_8$ . The solvent and the NMR probe were cooled to  $0^\circ C$ , and the solvent was added by syringe to the tube. The reaction was monitored by  $^1H$  NMR. *trans*-**6**:  $^1H$  NMR (90 MHz, toluene- $d_8$ )  $\delta$  5.69 (s, 10 H), 3.29 (s, 2 H);  $^{13}C$  NMR (22.5 MHz, toluene- $d_8$ )  $\delta$  338.6 ( $J_{CP} = 29.3$  Hz). *cis*-**6**:  $^1H$  NMR (90 MHz, toluene- $d_8$ )  $\delta$  5.81 (s, 10 H), 3.47 (s, 2 H);  $^{13}C$  NMR (22.5 MHz, toluene- $d_8$ )  $\delta$  342.5 ( $J_{CP} = 12.2$  Hz). *trans*-**7**:  $^1H$  NMR (90

MHz, toluene- $d_8$ )  $\delta$  5.79 (s, 10 H), 3.02 (s, 1 H), 4.18 (s, 1 H). *cis*-**7**:  $^1H$  NMR (90 MHz, toluene- $d_8$ )  $\delta$  5.92 (s, 10 H), 3.09 (s, 1 H), 4.23 (s, 1 H).

**Reaction of  $Cp_2Ti(Cl)O(CH_3)CCr(CO)_5$  (**9**) and  $NaN(TMS)_2$ .** A 5-mm NMR tube was loaded with 20 mg of **9** ( $4.5 \times 10^{-5}$  mol) and 7 mg ( $3.8 \times 10^{-5}$  mol) of  $NaN(TMS)_2$ . A small flask was loaded with 0.6 mL of toluene- $d_8$ . The solvent was cooled to  $-50^\circ C$  along with the NMR probe. The solvent was added to the NMR tube at  $-50^\circ C$ . The reaction yielded intermediates **3** and **4** instantaneously. The reaction was slowly warmed to room temperature in the NMR probe, and isomerization to the titanocene ketene adduct **5** was observed.

**Reaction of  $Cp_2Ti(Cl)O(^{13}CH_3)CCr(CO)_5$  and  $NaN(TMS)_2$ .** A 5-mm NMR tube was loaded with 10 mg ( $2.2 \times 10^{-5}$  mol) of  $Cp_2Ti(Cl)O(^{13}CH_3)CCr(CO)_5$  and 4 mg ( $2.1 \times 10^{-5}$  mol) of  $NaN(TMS)_2$ . A small flask was loaded with 0.6 mL of toluene- $d_8$ . The solvent and the NMR probe were cooled to  $-50^\circ C$ . Toluene (0.4 mL) was syringed into the NMR tube at  $-50^\circ C$ : **3b** ( $^{13}C$ , toluene- $d_8$ ),  $\delta$  87.3 (t,  $J_{CH} = 133.1$  Hz); **4b** ( $^{13}C$ , toluene- $d_8$ ),  $\delta$  90.1 (dd,  $J_{CH} = 150.4$  and 160.4 Hz).

**Reaction of  $Cp_2Ti(Cl)O(CD_3)CCr(CO)_5$  and  $NaN(TMS)_2$ .** Two 5-mm NMR tubes were loaded with 10 mg ( $2.2 \times 10^{-5}$  mol) of  $Cp_2Ti(Cl)O(CD_3)CCr(CO)_5$  and 4 mg ( $2.1 \times 10^{-5}$  mol) of  $NaN(TMS)_2$ . A small flask was loaded with 0.6 mL of toluene- $d_8$  and another small flask loaded with 0.6 mL of protiotoluene. The solvent flasks were cooled to  $-50^\circ C$ , and 0.4 mL of each solvent was syringed into one of the NMR tubes. A  $^2H$  NMR spectra was recorded for the sample in the protio solvent, and a  $^1H$  NMR spectra was recorded for the sample in the deuterio solvent. Integration of the  $^2H$  or  $^1H$  resonances revealed a 1.3:1 ratio of **3b** to **4b**.

**Synthesis of  $Cp_2Zr(Cl)O(CH_3)CCr(CO)_5$ .** A 250-mL three-necked flask was charged with 2.5 g ( $1.02 \times 10^{-2}$  mol) of  $LiO(CH_3)CCr(CO)_5$ , 3 g ( $1.03 \times 10^{-2}$  mol) of  $Cp_2ZrCl_2$ , and 100 mL of  $CH_2Cl_2$ . The reaction was stirred for 1 h. A fine white suspension of  $LiCl$  precipitated, and the solution turned orange. The solution was filtered through a 1-in. plug of Celite on a glass frit. The  $CH_2Cl_2$  solvent was removed under vacuum until an orange precipitate started to form. The solution was then cooled to  $-50^\circ C$  for 24 h. Yellow-orange crystals were collected by filtration and washed with pentane at  $-50^\circ C$ . The crystals were then dried in vacuo: yield 3.1 g, 60%;  $^1H$  NMR (90 MHz,  $C_6D_6$ )  $\delta$  5.87 (s, 10 H), 2.52 (s, 3 H);  $^{13}C\{^1H\}$  NMR (22.5 MHz,  $C_6D_6$ )  $\delta$  367.3, 224.4, 218.1, 115.3, 52.3. Anal. Calcd for  $C_{17}H_{13}O_6ZrCrCl$ : C, 41.51; H, 2.66. Found: C, 41.27; H, 2.66.

**Reaction of **11** or **12** with  $NaN(TMS)_2$ .** A 5-mm NMR tube was charged with 10 mg ( $1.7 \times 10^{-5}$  mol) of **11** or **12**, 3 mg of  $NaN(TMS)_2$  ( $1.6 \times 10^{-5}$  mol), and 0.4 mL of toluene- $d_8$ . The NMR tube was shaken and allowed to stand for 4 h. A  $^1H$  NMR spectra showed formation of an anion from **11**, but a precipitate from **12** was formed. Anion from **11**:  $^1H$  NMR (90 MHz, toluene- $d_8$ )  $\delta$  1.68 (s, 30 H), 5.72 (s, 1 H), 5.02 (s, 1 H);  $^{13}C$  (100.1 MHz, toluene- $d_8$ )  $\delta$  129.4, 105.6, 182.7, 11.6.

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**Supplementary Material Available:** Tables of Gaussian amplitudes and H-atom positions (4 pages); listings of calculated and observed structure factors (45 pages). Ordering information is given on any current masthead page.