every 100 measurements, showed no diminution.

The structures were solved using MULTAN 80.[36] Non-hydrogen atoms were refined, first isotropically and subsequently anisotropically, by using full-matrix least squares using unique reflections with $I \geq 2\sigma(I)$. Hydrogen atoms for **6** were all refined isotropically. For **3e:7** all hydrogen atoms except those on C(10), C(11), C(16), C10′), and C(11′) were refined isotropically. Each unrefined hydrogen atom was assigned an isotropic temperature factor based on the thermal parameters of the carbon atom to which it is bonded. Some disorder was apparent at the end of each butanamide chain. Atomic scattering factors for non-hydrogen atoms were taken from ref 37, those for hydrogen atoms from ref 38. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights w, were determined as follows: $w^{1/2} = 1$ when $|F_o| \leq X$ and $w^{1/2} = X/|F_o|$ > X. For **6** $X = 14.0$ and for **3e:7** $X = 9.0$.[39]

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(38) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(39) All calculations were carried out on a VAZ 11/780 computer. The least-squares refinement program was based on FMLS (Ganzel, P. L.; Sparks, R. A.; Trueblood, K. N.), UCLA, and modified by McPhail, A. T.; Duke University. Figures 5 and 6 were drawn with ORTEP, crystallographic illustration programs, Johnson, C. K., Oak Ridge, ORNL-3794.

Carbonylation of Titanocene Cyclobutenes. Synthesis and Characterization of a Titanocene–Vinylketene Complex

James D. Meinhart, Bernard D. Santarsiero, and Robert H. Grubbs*

Contribution No. 7164 from the Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125. Received August 12, 1985

Abstract: Carbonylation of several titanocene metallacyclobutene complexes yields the corresponding titanocene–vinylketene complex. The ketene complexes have been isolated as the trimethylphosphine adduct, one of which has been characterized by X-ray diffraction: $Cp_2Ti(C,O-\eta^2\text{-}OCC(C_6H_5)C(Si(CH_3)_3)CH_2)\cdot P(CH_3)_3$; space group $P2_1/c$; $Z = 4$; 6717 reflections; R_f 0.084, $I > 0$; $a = 9.625$ (2) Å, $b = 16.217$ (2) Å, $c = 16.917$ (4) Å; $\beta = 101.28$ (10)°; $V = 2589.5$ (9) Å^3. Mechanistic studies of the reaction by NMR indicate the presence of an intermediate acyl complex which has been isolated. The experimental evidence suggests that the insertion of carbon monoxide occurs into the less sterically encumbered sp^3 bond rather than the sp^2 bond of the metallacyclobutene. The rearrangement of the acyl complex to the vinylketene product may occur via a titanocene–cyclobutenone complex.

Mediation of complex organic transformations by organometallic catalysts and reagents is an important area of organic chemistry. The potential for both regio- and stereoselectivity in such reactions by the appropriate metal–ligand combinations, in addition to the ability of many organometallic systems to incorporate small organic molecules into larger more complex structures, has prompted a great deal of study in this area.[1] In particular, "Fischer" carbene complexes of Cr and Fe react with a variety of alkynes and carbon monoxide to form hydroquinones,[2]

Table I. Titanocene–Vinylketene–Trimethylphosphine Complexes

compd	R	R′	yield, %
2a	Ph	Ph	82
2b	Ph	Me$_2$Si	92
2c	Ph	CH$_3$	80
2d	CH$_3$	CH$_3$	77
2e	CH$_2$CH$_3$	CH$_2$CH$_3$	70

naphthols,[2] naphthoquinones,[3] or pyrones[4] and with imines to yield β-lactams.[5] The mechanistic details of these complex tranfor-
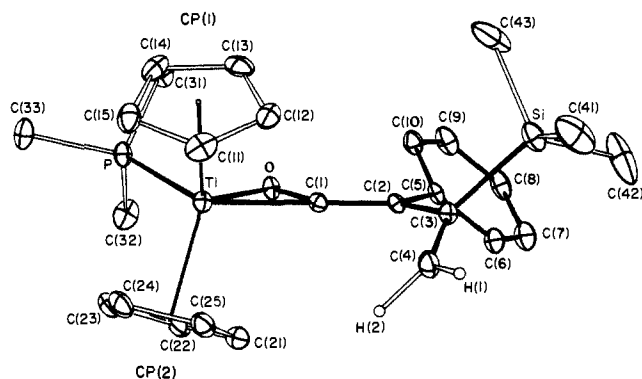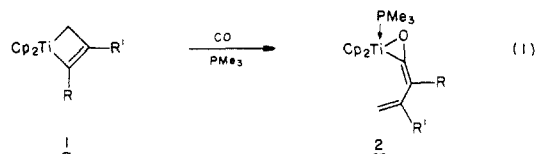
(1) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(2) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689–1706.

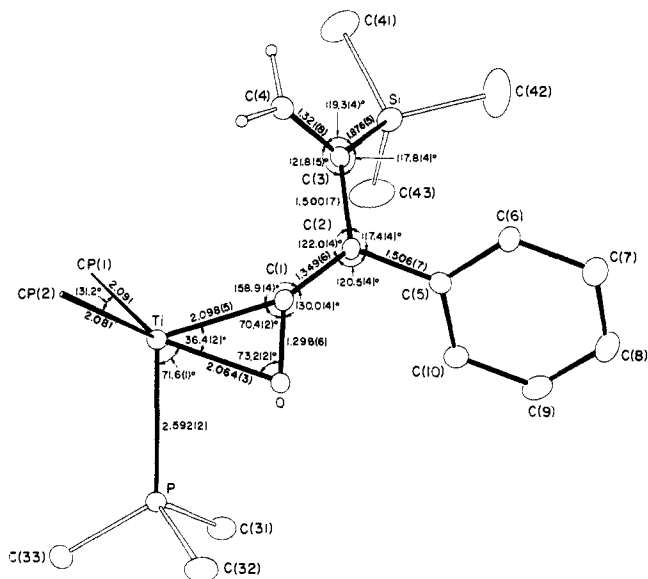**Figure 1.** Ortep diagram of **2b** with atom labeling.

mations have yet to be determined with any degree of certainty, and further understanding of the mechanism will surely provide insight into the scope and limitations of this reaction. Several proposed mechanisms suggest the formation of a metallacyclobutene complex derived from the carbene and the alkyne, followed by carbon monoxide insertion and rearrangement.[2,4] However, no metallacyclobutenes or acyl complexes have been isolated and characterized from these systems. One report of trapping experiments suggests vinylketenes to be intermediates,[6] and a vinylketene has been isolated and structurally characterized as a Cr–arene complex.[7] In light of the complexity and potential utility of these annulation reactions and our longstanding interest in titanocene–methylene chemistry, we have undertaken a study of the titanacyclobutene system.

Reaction of a toluene solution of the titanacyclobutene[8] I with carbon monoxide in the presence of 1 equiv of trimethylphosphine (eq 1) affords the titanium–vinylketene complex[9] **2**. The car-
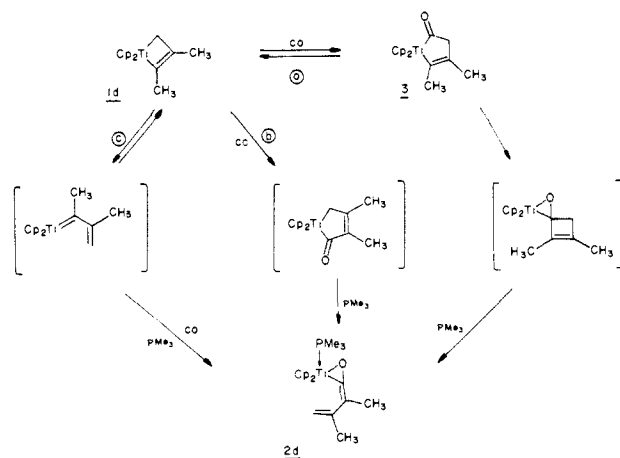

bonylation proceeds with a variety of titanacyclobutenes to yield the corresponding ketene complex in good yield (Table I). Notably, bis(trimethylsilyl)titanacyclobutene does not react to yield an analogous product even under forcing conditions (80 °C, 3 days).[10] The use of ^{13}C-enriched CO (90% ^{13}C) followed by ^{13}C NMR analysis shows exclusive incorporation of the ^{13}C at the metal-bound ketene carbon.[9] In the absence of a Lewis base, the carbonylation proceeds to give a sparingly soluble, oligomeric ketene adduct which may be solubilized by the addition of a ligand such as trimethylphosphine, pyridine, or THF.[9b]

In order to more completely characterize the vinylketene complex and determine the regiochemistry of the rearrangement,

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(3) Wulff, W. D.; Tang, P.-C. *J. Am. Chem. Soc.* **1984**, *106*, 434–6.
(4) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363–4.
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(6) Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765–69.
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(8) (a) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149–51. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584–6. (c) The synthesis of titanacyclobutenes 1c–1e were accomplished via titanocyclobutanes. Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876–8.
(9) For other titanium ketene complexes see: (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499–5500. (b) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–70. (c) Fachinetti, G.; Biran, C.; Floriani, C.; Ghiesi-Villa, A.; Guastini, G. *Ibid.* **1978**, *100*, 1921–2.
(10) The crystal structure of the bis(trimethylsilyl)titanacyclobutene (see **4b**) shows a distortion toward a carbene–acetylene complex and free bis(trimethylsilyl)acetylene is observed during carbonylation.

Figure 2. Ortep drawing of **2b** with selected bond lengths and angles.

Scheme I

crystals of **2b** suitable for an X-ray diffraction analysis were obtained, and the refined structure is shown in Figures 1 and 2.[11] The η^2 coordination of the ketene group places the atoms Ti, O, C(1), C(3), and C(5) in a plane (maximum deviation from Ti–O–C(1) plane 0.13 Å). The only other structurally characterized titanocene–ketene complex is the bridged diphenylketene dimer prepared by Floriani.[9c] A closely related ketene complex of permethylzirconocene has been structurally characterized as the pyridine adduct.[9a] All three crystal structures exhibit similar η^2 bonding of the ketene fragment. The vinylketene moiety adopts an s-cis conformation, to reduce the steric interaction between the trimethylsilyl group and the cyclopentadienyl ligands. The terminal double bond and the phenyl rings were expected to be coplanar to maximize electronic overlap; however, the substituents are twisted relative to the ketene plane by 38.5 (8) and 42.7 (7)°, respectively. The absence of a planar vinylketene has been observed for an arene-coordinated Cr–vinylketene complex and is attributed to the steric repulsions prevailing over the electronic effects.[7] The PMe$_3$ ligand is slightly (0.42 Å) out of the plane

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(11) For other transition-metal–vinylketene complexes see: (a) Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765–68. (b) Newton, M. G.; Panteleo, N. S.; King, R. B.; Chu, C.-K. *J. Chem. Soc., Chem. Commun.* **1979**, 10–12. (c) Binger, P.; Cetinkaya, B.; Krüger, C. *J. Organomet. Chem.* **1978**, *159*, 63–72. (d) Mitsudo, T.; Sasaki, T.; Watanabe, Y.; Takegami, Y.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Chem. Commun.* **1978**, 252–3. (e) Klines, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (f) Templeton, J. L.; Herrick, R. S.; Rusilo, C. A.; McKenna, C. E.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 1383–8. (e) Hill, A. E.; Hoffmann, H. M. R. *J. Chem. Soc., Chem. Commun.* **1972**, 574–5.

defined by Ti, O, and C(1). The ketene complex **2b** retains the relative connectivity of the phenyl ring, trimethylsilyl group, and the methylene group found in the starting titanacyclobutene **2a**.[8b]

Ketene complexes **2c**, **2d**, and **2e** exist in two isomeric forms. On the basis of NMR nuclear Overhauser experiments, the isomerization occurs about the carbon–carbon double bond of the ketene (eq 2). Addition of trimethylphosphine to a suspension
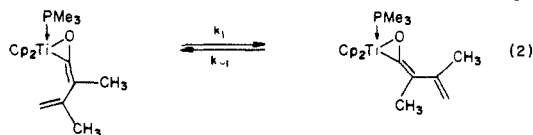
of the oligomeric ketene complex (vide supra) initially yields one isomer of the complex (^{1}H NMR), but over several hours at room temperature an equilibrium between isomers is established. Monitoring the isomerization by NMR yielded a forward rate k_1 of 6.8 ± 1.0 × 10^{-3} min^{-1} and a reverse rate k_{-1} of 4.1 ± 0.6 × 10^{-3} min^{-1} at 303 K. The rate of isomerization and the equilibrium ratio are not influenced by excess trimethylphosphine. The mechanism for isomerization may involve a π-bound ketene intermediate.[12,13] The ketene complexes **2a** and **2b** have bulkier substituents on the ketene skeleton which apparently prevent the isomerization.

During the carbonylation of **1d**, a transient green color is observed. By use of low-temperature ^{1}H and ^{13}C NMR, ^{13}CO labeling, and IR studies, the intermediate is identified as the titanocene–acyl complex **3** (Scheme I). The intermediate is unstable in solution above −30 °C but is moderately stable in the solid state at room temperature. The IR shows an intense absorption at 1615 cm^{-1}, indicative of an acyl with little η^2 character.[14,15] In order to establish into which side of the metallacyclic ring the CO inserted, the acyl intermediate was synthesized with ^{13}CO and the ^{13}C–^{13}C coupling constants were determined from the ^{13}C{^{1}H} NMR. The ^{13}C–^{13}C coupling constant from the acyl carbon to the methylene carbon was 11.9 ± 0.9 Hz, but neither of the ^{13}C couplings to the olefinic carbons were larger than 5.5 ± 0.9 Hz. The 11.9-Hz coupling is small for a one-bond ^{13}C–^{13}C coupling,[16] but it is consistent with other titanocene acyls.[17]

Although the isolation and characterization of the acyl complex **3** are interesting, it does not provide sufficient evidence to distinguish among other possible mechanisms leading to vinylketene formation. the metallacyclobutenes have two different Ti–C bonds, and carbonylation of either bond could lead to the observed product (Scheme I). Of primary importance is to determine if the isolated acyl complex **3** leads directly to ketene product (Scheme I, path a) or if it is simply the kinetic product of carbonylation into the more sterically accessible titanium–carbon bond which, in a subsequent step, decarbonylates, and the reaction occurs via carbonylation of the titanium–vinyl bond (Scheme I, path b). The methyl group at the α position of the metallacycle could hinder the insertion of CO into the titanium–vinyl bond. To test for the possibility of a reversible carbonylation of the metallacycle, a toluene solution of the acyl **3** was prepared with ^{13}CO (90% ^{13}C) and immediately cooled to −78 °C, the ^{13}CO atmosphere was replaced with natural abundance ^{12}CO at 100 psi, and the solution was allowed to warm to −30 °C to effect the rearrangement. Analysis by NMR of the ketene complex thus formed revealed complete loss of the ^{13}C label. The high pressure of CO is necessary to obtain 1 equiv of CO in solution, due to the low solubility of CO in toluene.[18] The loss of the ^{13}C label was observed

regardless of solvent (toluene, diethyl ether, THF) or the addition of trimethylphosphine. The loss of the label proves the acyl intermediate **3** carbonylates reversibly; however, it does not distinguish between paths a or b.

Attempts to identify the acyl species by decomposition of the intermediate **3** with either trifluoroacetic acid or HCl were unsuccessful due to the apparent rapid decarbonylation of the acyl in the absence of excess carbon monoxide. However, if a solution of the acyl species in diethyl ether under 100 psi of CO is treated with excess anhydrous HCl at −78 °C, the corresponding titanocene–acyl chloride **4** may be obtained (eq 3). ^{1}H NMR
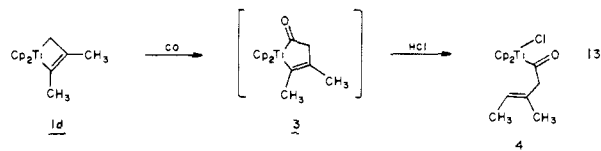
confirms the predicted structure of the acyl chloride derived from Ti–C vinyl bond cleavage by 1 equiv of HCl. If the reaction mixture is allowed to warm to ~−20 °C, the products are titanocene dichloride and 3-methyl-3-pentenal. The aldehyde was very difficult to isolate so it was transformed to the (2,4-dinitrophenyl)hydrazone derivative; however, NMR analysis shows that the β,γ double bond had migrated into conjugation with the hydrazone. It is interesting to note the differentiation of the cleavage of the metallacycle acyl species even in the presence of a large excess of HCl. These observations firmly establish that CO inserts into the Ti–C(sp^3) bond in the initial carbonylation step. It remains to be established if **3** is on the direct reaction path to product.

An experiment which could distinguish between paths a and b would be to allow **3** to undergo rearrangement in the presence of a reactant which would trap any free metallacyclobutene formed from decarbonylation. Both the metallacyclobutene **1d** and the vinylketene complex react with *tert*-butyl isocyanide to give observable products.[19] Treatment of metallacyclobutene **1d** with 1 equiv of *tert*-butyl isocyanide yields quantatively the imino–acyl complex **5** (eq 4). Unfortunately, treatment of the ketene complex
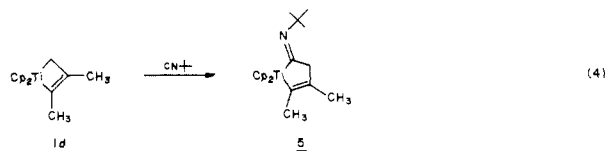
with *tert*-butyl isocyanide gives a mixture of products; however, the ratio of the products is reproducible. To determine the relative rates of the insertion of *tert*-butyl isocyanide vs. CO into the metallacyclobutene, a solution with equimolar concentrations of *tert*-butyl isocyanide and CO was reacted with the metallacycle. Within the detection limits of the NMR, only formation of **5** was observed. This result demonstrates that if any **1d** were found during the rearrangement of **3** to **2d**, it should be rapidly trapped by the *tert*-butyl isocyanide. The imino–acyl complex **5** does not react with CO under the experimental conditions. Treatment of **3** in the absence of CO at −78 °C with 4 equiv of *tert*-butyl isocyanide followed by warming to room temperature results in a ratio of vinylketene products to **5** of 15:1. These results demonstrate that it is not necessary for the acyl complex to decarbonylate during the reaction because if any of the metallacycle were formed it would be trapped as **5**.

Attempts to accurately determine the kinetic parameters of the carbonylation were thwarted by several factors. The observed rate of rearrangement of acyl **3** to product is dependent on the concentration of PMe$_3$ and the partial pressure of CO. An increased concentration of PMe$_3$ slows the rearrangement, and an increase of CO presence accelerates the rate of reaction. However, neither trimethylphosphine nor excess CO is necessary for conversion of the metallacycle to ketene complex. Given the ex-

(12) The thermal decomposition or exhaustive carbonylation of the vinylketene complexes affords some free vinylketene.

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(14) Fachinetti, g.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans* **1977**, 1946–50.

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(16) Marshall, J. L. *Carbon–Carbon and Carbon–Proton NMR Couplings*; Verlag Chemie International: Deerfield Beach, FL, 1983.

(17) The $^1J_{^{13}C-^{13}C}$ for Cp$_2$Ti^{13}COCH$_3$(Cl) is 19 Hz. Meinhart, J. D.; Grubbs, R. H., unpublished results.

(18) Linke, W. F. *Solubilities of Inorganic and Metal-Organic Compounds*, 4th ed.; American Chemical Society: Washington, DC, 1958; Vol. 1.

(19) Meinhart, J. D.; Grubbs, R. H., unpublished results.

Carbonylation of Titanocene Cyclobutenes

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perimental data, we favor path a as the most likely mechanism. Cyclobutenones have been isolated from the reaction of Fischer-carbene complexes with alkynes.[25] The intramolecular attack of a coordinated, cyclic acyl to form a ketone complex in a Zr system has been postulated previously.[15] The lack of η^2-acyl character in **3** and the formation of a Ti–O bond in the ketene provide a driving force for the reaction.

In an effort to demonstrate the cyclobutenone complex as a viable intermediate, a sample of 1,3-diphenylcyclobut-2-en-1-one was prepared[21] and treated with either titanocene–dicarbonyl or titanocene–carbonyl–triethylphosphine complex.[22] However, in neither case was a titanocene–ketene product observed. In retrospect, it is not suprising that a ketene complex was not formed due to the difficulty of displacing the ligands already on the titanium and the propensity of low-valent titanocene derivatives to reduce ketones.[23]

An alternative mechanism involves the ring opening of the titanocene cyclobutene to a titanocene–vinylalkylidene complex[24] followed by direct carbonylation of the alkylidene to the ketene complex (Scheme I, path c). We do not favor this mechanism for several reasons: the observation and isolation of the acyl intermediate **3**, the isocyanide trapping experiments, and the lack of alkylidene transfer reactions of the titanocene cyclobutenes with ketones. In contrast to the reactivity of titanocene cyclobutanes, which is dominated by titanocene–methylene chemistry,[20] the titanocene cyclobutenes exhibit reactivity similar to that observed for titanocene–alkyl complexes.[19]

We have demonstrated that carbonylations of titanocene cyclobutenes yield titanocene–vinylketene complexes. The mechanism appears to involve several steps, and one of the intermediates has been isolated. This reaction may provide insight into the mechanism of Fischer-carbene annulation reactions of carbon monoxide and alkynes as well as the carbonylation of metal–alkyl complexes. In particular, the observed products could be derived from the opening of the metallacyclobutene to a vinylalkylidene, though we have shown this is not a viable mechanism in our system. Our findings shed some doubt on the use of a metallacyclobutene opening to a vinylalkylidene in mechanisms of related reactions[24] and suggest that such reactions may also occur by direct insertion in the metal–carbon single bonds of intermediates. We are continuing to investigate the chemistry of titanocene cyclobutenes with organic substrates as well as the reactivity of the titanocene–vinylketene complexes.

Experimental Section

General Experimental Considerations. All manipulations were performed with the use of standard Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert atmosphere drybox under nitrogen. Argon was purified by passage through columns of BASF RF-11 (Chemalog) and Linde 4-Å molecular sieves. Carbonylations were performed in Lab-Glass pressure bottles (60 or 100 mL) fitted with two inlet valves and a pressure gauge.

Toluene, benzene, THF, and diethyl ether were vacuum transferred from sodium benzophenone ketyl and stored in Teflon-valve sealed vessels under argon. Pentane and hexane were stirred over concentrated H_2SO_4, dried, vacuum transferred from sodium benzophenone ketyl, and stored in Teflon-valve sealed vessels under argon. Methylene chloride was vacuum transferred from P_2O_5 or CaH_2 and stored under argon. Benzene-d_6, toluene-d_8, and THF-d_8 were vacuum transferred from sodium

benzophenone ketyl. Carbon monoxide (CP) was obtained from Matheson.

^{13}C-enriched carbon monoxide (90% ^{13}C) was obtained from Monsanto-Mound Laboratories. Trimethylphosphine was obtained from Strem Chemicals. Acetylenes were obtained from Aldrich, Farchan Laboratory, or Wiley Organics and dried or distilled before use.

Infrared spectra were recorded on a Beckman 4240 IR spectrometer. ^{1}H NMR spectra were recorded on a Varian EM-390, JEOL FX-90Q, Varian XL-200, JEOL GX-400, or Bruker WM-500 and referenced to residual solvent (C_6D_6, δ 7.15; C_7D_8, δ 2.09; THF-d_8, δ 3.58 or 1.73).

^{31}P{^{1}H} NMR spectra were recorded on a JEOL FX-90Q and referenced to external 85% H_3PO_4 (positive δ, lower field). ^{13}C{^{1}H} NMR were recorded on a JEOL FX-90Q, Varian XL-200, or JEOL GX-400.

Difference NOE spectra were recorded on the Bruker WM-500 at the Southern California Regional NMR Facility located at the California Institute of Technology. Low-temperature NMR and kinetics were performed on the JEOL-FX-90Q. Elemental analysis were performed by Dornis and Kolbe, Mulheim, West Germany, and the analytical facility of the California Institute of Technology.

η^2-(C,O)-(α-Phenylvinyl)phenylketene–Titanocene–Trimethylphosphine (2a). A solution of 1,1-bis(cyclopentadienyl)-2,3-diphenyltitanacyclobutene (150 mg, 0.405 mmol) and trimethylphosphine (45 μL, 0.444 mmol) in 2 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stir bar and pressure gauge. The transfer cannula and Schlenk flask were rinsed twice with 0.5-mL portions of toluene. The pressure bottle was partially evacuated, and CO (20 psi) was introduced with stirring. After 10 min the color had changed from dark red to clear yellow, and the CO was vented. The solution was transferred into a Schlenk flash, and the pressure bottle was rinsed twice with 0.5-mL portions of toluene. The volatiles were removed in vacuo to yield a yellow solid which was washed twice with 2-mL portions of pentane and dried in vacuo to yield the product as a yellow powder (158 mg, 0.333 mmol, 82%): ^{1}H NMR (200 MHz, C_6D_6) δ 8.20 (d, J = 8.0 Hz, 2 H), 7.84 (d, J = 7.0 Hz, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.2–7.0 (m, 4 H), 5.89 (d, J = 2.7 Hz, 1 H), 5.72 (d, J = 2.7 Hz, 1 H), 5.10 (s, 10 H), 0.73 (d, J = 6.3 Hz, 9 H); ^{31}P{^{1}H} NMR (36.3 MHz, THF-d_8, –20 sC) δ 5.72 (s); ^{13}C{^{1}H} NMR (22.5 HMz, THF-d_8, –20 °C) δ 193.6 (d, J_{C-P} = 11.0 Hz), 152.7, 145.4, 143.4, 128.6, 128.2, 127.6, 127.2, 126.6, 121.1, 112.4, 104.8, 102.8 (d, J_{c-p} = 3.7 Hz), 14.2 (d, J_{c-p} = 14.6 Hz); IR (Nujol, KBr) 1590 (m), 1565 (m), 1540 (s), 1487 (s), 1425 (m), 1305 (m), 1282 (m), 1265 (m), 1155 (m), 1072 (m), 1045 (m), 1028 (m), 1018 (m), 952 (s), 918 (w), 895 (w), 805 (s) cm^{-1}. The band at 1540 cm^{-1} shifts to 1512 cm^{-1} upon the use of ^{13}CO. Anal. Calcd for $C_{29}H_{31}OPTi$: C, 73.42; H, 6.59. Found: C 73.21; H, 6.68.

η^2-(C,O)-(α-(Trimethylsilyl)vinyl)phenylketene–Titanocene–Trimethylphosphine (2b). A solution of 1,1-bis(cyclopentadienyl)-2-phenyl-3-(trimethylsilyl)titanacyclobutene (500 mg, 1.36 mmol) and trimethylphosphine (150 μL, 1.48 mmol) in 8 mL of THF was transferred into a Lab-Glass pressure bottle fitted with a stir bar and pressure gauge. The transfer cannula and Schlenk flask were rinsed twice with 1-mL portions of THF. The pressure bottle was charged with 60 psi of CO. The solution was stirred at room temperature for 3 h during which the color changed from purple to yellow. The CO was vented, and the solution was transferred to a Schlenk flask. The volatiles were removed in vacuo to yield a yellow solid which was washed twice with 2 mL of pentane and dried in vacuo to yield the product (590 mg, 1.25 mmol, 92%). The material can be recrystallized from diethyl ether at –50 °C (10 mg/mL): ^{1}H NMR (90 MHz, C_6D_6) δ 7.80 (m, 2 H), 7.37 (m, 3 H), 6.33 (d, 1 H, J = 3.7 Hz), 5.82 (d, 1 H, J = 3.7 Hz), 5.16 (s, 10 H), 0.69 (d, 9 H, J = 6.6 Hz), 0.33 (s, 9 H); ^{1}H NMR (90 MHz, THF-d_8) δ 7.33 (m, 2 H), 7.04 (m, 2 H), 6.81 (m, 1 H), 6.04 (d, 1 H, J = 3.9 Hz), 5.51 (d, 1 H, J = 3.9 Hz), 5.42 (s, 10 H), 1.38 (d, 9 H, J = 7.1 Hz), 0.01 (s, 9 H); ^{31}P{^{1}H} NMR (36.3 MHz, THF-d_8, –20 °C) δ 5.25 (36.3 MHz, toluene-d_8, –20 °C) δ 3.06; ^{13}C{^{1}H} NMR (22.5 MHz, THF-d_8, –20 °C) δ 190.3 (d, J_{C-P} = 12.2 Hz), 155.7, 145.1, 128.0, 127.6, 122.4, 121.4, 104.8, 14.0 (d, J_{C-P} = 14.6 Hz), 1.3; IR (Nujol, KBr) 1585 (w), 1520 (m) 1300 (m)8 1280 (m), 1258 (m), 1235 (m), 1062 (w), 1030 (w), 1015 (m), 975 (m), 960 (m), 910 (w), 870 (m), 855 (m), 838 (m), 825 (m), 805 (s) cm^{-1}. The absorption at 1520 cm^{-1} shifts to 1492 cm^{-1} upon the use of ^{13}CO. Anal. Calcd for $C_{26}H_{35}OPSiTi$: C, 66.37; H, 7.50. Found: C, 66.03; H, 7.29.

η^2-(C,O)-(α-Methylvinyl)phenylketene–Titanocene–Trimethylphosphine (2c). A solution of 1,1-bis(cyclopentadienyl)-2-phenyl-3-methyltitanacyclobutene (200 mg, 0.649 mmol) and trimethylphosphine (70 μL, 0.69 mmol) in 2 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The transfer cannula and Schlenk flask were rinsed twice with 0.5-mL portions of toluene. The pressure bottle was charged with 15 psi CO. The solution was stirred for 10 min during which time the color changed from dark red to yellow. The CO was vented. The solution was transferred to a

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Schlenk flask, and the volatiles wre removed in vacuo. The yellow solid was washed twice with 2-mL portions of pentane then dried in vacuo to yield the product (215 mg, 0.521 mmol, 80%). Analysis by ^{1}H NMR revealed two isomers in a 3:1 ratio: ^{1}H NMR (90 MHz, C_6D_6) major isomer δ 7.84 (m, 2 H), 7.39 (m, 3 H), 5.32 (m, 1 H), 5.20 (m, 1 H), 5.17 (s, 10 H), 2.39 (m, 3 H), 0.65 (br d, 9 H); minor isomer δ 5.10 (s, 10 H), 2.42 (br s, 3 H), 0.65 (br d, 9 H), vinyl resonances obscured by other resonances; ^{13}C$\{^1$H$\}$ NMR (22.5 MHz, toluene-d_8, -20 °C) major isomer δ 188.6 (d, J_{c-p} = 11.0 Hz), 146.8 144.9, 138.3, 136.3, 129.3, 122.9, 106.2, 105.1 (d, J_{C-P} = 3.7 Hz), 103.9, 24.9 (s), 13.3 (d, J_{C-P} = 14.6 Hz); minor isomer δ 102.8; ^{31}P$\{^1$H$\}$ (36.3 MHz, toluene-d_8, -20 °C) major isomer δ 3.84, minor isomer δ 4.78; IR (Nujol, KBr) 1608 (w), 1575 (m), 1560 (m), 1525 (s), 1300 (w), 1278 (m), 1260 (w), 1062 (w), 1010 (s), 945 (s), 895 (m), 850 (m), 838 (m), 800 (s) cm^{-1}. The absorption at 1525 cm^{-1} shifts to 1498 cm^{-1} upon the use of ^{13}CO. Anal. Calcd for $C_{24}H_{29}OPTi$: C, 69.91; H, 7.09. Found: C, 69.58; H, 7.00.

η^2-(C,O)-(α-Methylvinyl)methylketene–Titanocene–Trimethylphosphine (2d). A solution of 1,1-bis(cyclopentadienyl)-2,3-dimethyltitanacyclobutene (200 mg, 0.812 mmol) and trimethylphosphine (100 μL, 0.986 mmol) in 2 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The Schlenk flask and cannula were rinsed twice with 0.5-mL portions of toluene. The pressure bottle was charged with 15 psi of CO. The solution was stirred for 10 min during which time the color changed from red to yellow. The CO was vented, the solution was transferred to a Schlenk flask, and the volatiles wre removed in vacuo. The yellow solid was washed twice with 2-mL portions of pentane and dried in vacuo to yield the product (220 mg, 0.628 mmol, 77%). Analysis by ^{1}H NMR revealed two isomers in approximately 2:1 ratio: ^{1}H NMR (90 MHz, C_6D_6) major isomer δ 5.15 (s, 10 H), 4.95 (m, 2 H), 2.61 (s, 3 H), 2.45 (br s, 3 H), 0.72 (d, 9 H, J = 6.5 Hz); minor isomer δ 5.05 (s, 10 H), 4.78 (m, 2 H), 2.61 (s, 3 H), 2.31 (s, 3 H), 0.72 (d, 9 H, J = 6.5 Hz); ^{1}H NMR (500.13 MHz, toluene-d_8) major isomer δ 5.126 (s, 10 H), 4.885 (d, 1 H, J = 2.1 Hz), 4.815 (br s, 1 H), 2.411 (s, 3 H), 2.355 (br s, 3 H), 0.798 (br s, 9 H) (irradiation of the signal at δ 2.355 results in the collapse of the signal at δ 4.815 to a doublet, J = 2.1 Hz); minor isomer δ 5.041 (s, 10 H), 4.738 (d, 1 H, J = 1.7 Hz), 4.575 (br s, 1 H), 2.455 (br s, 3 H), 2.208 (s, 3 H), 0.798 (br s, 9 H) (irradiation of the signal at δ 2.455 results in the collapse of the signal at δ 4.575 to a doublet, J = 1.7 Hz); ^{1}H NMR (500.13 MHz, C_6D_6) major isomer δ 5.154 (s, 10 H), 5.074 (d, 1 H, J = 2.5 Hz), 4.987 (br s, 1 H), 2.603 (s, 3 H), 2.450 (br s, 3 H), 0.71 (br s, 9 H); minor isomer δ 5.058 (s, 10 H), 4.937 (d, 1 H, J = 2.4 Hz), 4.772 (br s, 1 H), 2.613 (br s, 3 H), 2313 (s, 3 H), 0.71 (br s, 9 H); ^{1}H NMR (500.13 MHz, THF-d_8) major isomer δ 5.382 (s, 10 H, 4.290 (d, 1 H, J = 2.7 Hz), 4.245 (br s, 1 H), 2.124 (s, 3 H), 1.862 (s, 3 H), 0.90 (v br, 9 H) (irradiation of the signal at δ 2.124 results in the collapse of the signal at δ 4.245 to a doublt, J = 2.7 Hz); minor isomer δ 5.316 (s, 10 H, 4.116 (d, 1 H, J = 2.7 Hz), 3.968 (br s, 1 H), 2.012 (s, 3 H), 1.912 (s, 3 H), 0.90 (v br, 9 H) (irradiation of the signal at δ 2.012 results in the collapse of the signal at δ 3.968 to a doublet, J = 2.7 Hz); ^{1}H NMR of product from ^{13}CO (500.13 MHz, toluene-d_8) major isomer δ 5.126 (s, 10 H), 4.885 (d, 1 H, J = 2.1 Hz), 4.815 (br s, 1 H), 2.411 (d, 3 H, J_{C-H} = 4.4 Hz), 2.355 (s, 3 H), 0.798 (br s, 9 H); minor isomer δ 5.041 (s, 10 H), 4.738 (d, 1 H, J = 1.7 Hz), 4.575 (br s, 1 H), 2.455 (s, 3 H), 2.208 (d, 3 H, J_{C-H} = 5.9 Hz), 0.798 (br s, 9 H); ^{1}H NMR of product from ^{13}CO (500.13 MHz, THF-d_8) major isomer δ 5.381 (s, 10 H), 4.293 (d, 1 H, J = 2.4 Hz), 4.247 (br s, 1 H, 2.124 (s, 3 H), 1.862 (d, 3 H, J_{C-H} = 4.3 Hz), 0.90 (v br, 9 H); minor isomer δ 5.315 (s, 10 H), 4.118 (d, 1 H, J = 2.3 Hz), 3.968 (br s, 1 H), 2.013 (s, 3 H), 1.912 (d, 3 H, J_{C-H} = 5.89 Hz), 0.90 (v br, 9 H); ^{31}P$\{^1$H$\}$ NMR (36.3 MHz, toluene-d_8, -20 °C) δ 4.55 minor isomer, 3.53 major isomer; ^{13}C$\{^1$H$\}$ NMR (22.5 MHz, toluene-d_8, -20 °C) major isomer δ 185.47 (d, J_{C-P} = 11.0 Hz), 146.84, 103.83, 98.63, 98.36 (d, J_{C-P} = 3.6 Hz), 22.95, 19.53, 13.14 (d, J_{C-P} = 14.6 Hz); minor isomer δ 185.25 (d, J_{C-P} = 9.8 Hz), 146.14, 102.91, 97.82 (d, J_{C-P} = 9.8 Hz), 96.89, 24.84, 18.66, 13.14 (d, J_{C-P}) = 14.6 Hz); IR (Nujol, KBr) 1598 (m), 1558 (s), 1546 (s), 1421 (m), 1317 (m), 1300 (m), 1278 (m), 1205 (m), 1120 (w), 1020 (m), 1010 (m), 948 (s), 830 (m), 795 (s) cm^{-1}. The use of ^{13}CO results in a shift of the absorption at 1546 cm^{-1} to 1523 cm^{-1}. Anal. Calcd for $C_{19}H_{27}OPTi$: C, 65.15; H, 7.77. Found: C, 65.20; H, 7.55.

Assignment of geometry by difference NOE experiment: major isomer (Cp δ 5.382), irradiation of the signal at δ 1.862 results in enhancement of the signal at δ 4.290. Irradiation of the signal at δ 2.124 results in enhancement of the signals at δ 4.245 and 5.382. the J_{C-H} of δ 1.862 with ^{13}CO is 4.3 Hz. Minor isomer (Cp δ 5.316), irradiation of the signal at δ 1.912 results in enhancement of the signal at δ 4.116. Irradiation of the signal at δ 2.012 results in enhancement of the signal at δ 3.968. The J_{C-H} of δ 1.912 with ^{13}CO is 5.8 Hz.

η^2-(C,O)-(α-Ethylvinyl)ethylketene–Titanocene–Trimethylphosphine (2e). A solution of 1,1-bis(cyclopentadienyl)-2,3-diethyltitanacyclo-

butene (150 mg, 0.547 mmol) and trimethylphospine (60 μL, 0.590 mmol) in 1 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The cannula and Schlenk flask were rinsed twice with 0.5-mL portions of toluene. The pressure bottle was charged with 20 psi of CO. The solution was stirred at room temperature for 10 min during which time the color changed from red to yellow. The excess CO was vented, the solution was transferred to a Schlenk flask, and the volatiles were removed in vacuo. The yellow solid was washed twice with 1-mL portions of pentane and dried in vacuo to yield the product (145 mg, 0.383 mmol, 70%). Analysis by ^{1}H NMR revealed two isomers in approximately a 3:1 ratio: ^{1}H NMR (500.13 MHz, C_6D_6 major isomer δ 5.175 (s, 10 H), 5.158 (d, J = 1.93 Hz, 1 H), 4.952 (br s, 1 H), 2.988 (q, J = 7.29 Hz, 2 H), 2.731 (q, J = 7.45 Hz, 2 H), 1.516 (t, J = 7.45 Hz, 3 H), 1.396 (t, J = 7.29 Hz, 3 H), 0.711 (d, J_{P-H} = 6.89 Hz, 9 H); minor isomer δ 5.102 (s, 10 H), 4.914 (d, J = 2.27 Hz, 1 H), 4.876 (br s, 1 H), 3.010 (q, J = 7.27 Hz, 2 H), 2.787 (q, J = 7.29 Hz, 2 H), 1.662 (t, J = 7.27 Hz, 3 H), 1.284 (t, J = 7.19 Hz, 3 H), 0.711 (d, J_{P-H} = 6.89 Hz, 9 H); ^{1}H NMR (90 MHz, THF-d_8) major isomer δ 5.39 (s, 10 H), 4.49 (d, J = 2.2 Hz, 1 H), 4.31 (br s, 1 H), 2.44 (br q, J = 7.6 Hz, 2 H), 2.35 (q, J = 7.3 Hz, 2 H), 1.34 (d, J_{P-H} = 6.8 Hz, 9 H), 1.21 (t, J = 7.6 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H); ^{1}H NMR of product from ^{13}CO (90 MHz, C_6D_6) major isomer δ 5.17 (s, 10 H), 5.13 (sh, 1 H), 4.93 (br s, 1 H), 2.97 (d of q, J = 7.3 Hz, 4.4 Hz, 2 H), 2.72 (q, J = 7.3 Hz, 2 H), 1.51 (t, J = 7.3 Hz, 3 H), 1.39 (t, J = 7.3 Hz, 3 H), 0.71 (d, J = 6.6 Hz, 9 H); ^{13}C$\{^1$H$\}$ (22.5 Mhz, THF-d_8), -20 °C) δ 185.9 (d, J_{C-P} = 11.0 Hz), 152.2, 109.9, 104.6, 94.3, 27.2 (partially obscured by solvent), 15.8, 14.6, 13.7 (d, J_{C-P} = 14.6 Hz). ^{31}P$\{^1$H$\}$ (36.3 MHz, THF-d_8, -20 °C) major isomer δ 5.55, minor isomer δ 6.06; IR (KBr, cm^{-1}) 3110 (w), 3085 (w), 3070 (w), 2965 (m), 2860 (m), 1590 (w), 1570 (m), 1538 (s), 1443 (m), 1420 (w), 1370 (w), 1355 (w), 1305 (w), 1286 (m), 1280 (m), 1264 (m), 1245 (w), 1195 (m), 1130 (m), 1058 (w), 1015 (m), 948 (s), 845 (w), 808 (s). The use of ^{13}CO results in a shift of the absorption at 1538 cm^{-1} to 1508 cm^{-1}. Anal. Calcd for $C_{21}H_{31}OPTi$: C, 66.67; H, 8.26. Found: C, 66.92; H, 8.01.

1,1-Bis(cyclopentadienyl)-2,3-dimethyltitanacyclopent-2-en-5-one (3). A solution of the 1,1-bis(cyclopentadienyl)-2,3-dimethyltitanacyclobutene (112 mg, 0.455 mmol) and trimethylphosphine (50 μL, 0493 mmol) in 1 mL of toluene was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The Schlenk flask and cannula were rinsed twice with 1-mL portions of toluene. The pressure bottle was briefly evacuated, cooled to -50 °C, and 10 psi of CO added. The solution was warmed slowly from -50 °C with stirring. When the temperature had reached approximately -20 to -10 °C a color change from red → brown → green was observed. The solution was immediately cooled to -78 °C, excess CO was vented, and the solution was placed under Ar atmosphere. The solution was rapidly transferred by cannula into a precooled Schlenk flask with no apparent change of color. The solution was layered with 4 mL of pentane and allowed to stand at -78 °C for several hours as a green precipitate was deposited on the walls of the flask. The mother liquor was removed via cannula, and the green solid was washed twice with 2-mL portions of -78 °C pentane and dried in vacuo to yield 72 mg of green powder. The product was stored at -40 °C in the drybox. NMR data are reported from sealed tube reactions and formation of the intermediate in situ [^{1}H NMR (90 MHz, THF-d_8, -25 °C) δ 6.20 (s, 10 H), 2.42 (br s, 2 H), 1.32 (s, 3 H), 0.80 (br s, 3 H)]. When ^{13}CO is used the signal at δ 2.42 becomes a broad doublet J_{C-H} = 4.6 Hz: ^{1}H NMR (90 MHz, toluene-d_8, -30 °C) δ 5.81 (s, 10 H), 2.67 (br s, 2 H), 1.46 (s, 3 H), 0.70 (s, 3 H); ^{13}C$\{^1$H$\}$ NMR (22.5 MHz, THF-d_8, THF-d_8, -25 °C) δ 294.0, 186.4, 121.6, 115.5, 61.3, 17.5, 16.5; ^{13}C$\{^1$H$\}$ NMR (22.5 MHz, toluene-d_8, -30 °C) δ 293.6, 185.6, 121.6, 114.8, 61.3, 17.7, 16.7; ^{13}C$\{^1$H$\}$ NMR (22.5 MHz, THF-d_8, -25 °C, with ^{13}CO) δ 294.0 (s), 185.2 (s), 121.6 (d, J_{C-C} = 7 ± 1.8 Hz), 115.3 (s), 61.3 (d, J_{C-C} = 13 ± 1.8 Hz), 17.5 (d, J_{C-C} = 6 ± 1.8 Hz), 16.5 (s); ^{13}C$\{^1$H$\}$ NMR (22.5 MHz, toluene-d_8, -30 °C, with ^{13}CO) δ 293.4 (s), 185.3 (s), 121.2 (d, J_{C-C} = 5.5 ± 0.9 Hz), 114.5 ns), 61.0 (d, J_{C-C} = 11.9 ± 0.9 Hz), 17.5 (d, J_{C-C} = 5.5 ± 0.9 Hz), 16.3 (s). The resonance at δ 185 may be obscured by the ketene complex; the use of pyridine instead of trimethyl phosphine shifts the resonance of the ketene product to lower field. IR (KBr) 3090 (m), 2960 (m), 2890 (m), 2845 (s), 2820 (s), 2745 (m), 1615 (s), 1435 (m), 1365 (m), 1280 (w), 1168 (w), 1148 (w), 1128 (w), 1070 (m), 1050 (m), 1013 (s), 972 (w), 950 (m), 820 (s), 805 (s) cm^{-1}.

1,1-Bis(cyclopentadienyl)-2-(tert-butylimino)-4,5-dimethyltitanacyclopentene. A stirred solution of 1,1-bis(cyclopentadienyl)-2,3-dimethyltitanacyclobutene (166 mg, 0.67 mmol) in 1 mL of THF was treated with tert-butyl isocyanide (68 μL, 0.74 mmol) at room temperature. An immediate color change from red to orange was observed; the mixture was stirred at room temperature for 15 min, and then the volatiles were removed in vacuo. The solid was extracted with 4 mL of hexane, and the solution was filtered and cooled to -50 °C. The orange crystals were isolated, washed twice with 0.5-mL portions of cold pentane,

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and dried in vacuo to yield the 112 mg of the product (0.34, 51%); ^{1}H NMR (C_6D_6) δ 5.24 (s, 10 H), 3.55 (br s, 2 H), 2.14 (br s, 3 H), 1.98 (br, s, 3 H), 0.93 (s, 9 H); ^{13}C{^{1}H} NMR (C_6D_6) δ 224.81, 181.75, 134.70, 105.36, 59.68, 52.93, 29.88, 26.55, 1602; IR (Nujol, cm^{-1}) 1770. Anal. Calcd for $C_{20}H_{27}NTi$: C, 72.94; H, 8.26; N, 4.25. Found: C, 72.88; H, 8.06; N, 4.23.

Ti-(3-Methyl-trans-3-pentenoyl)titanocene Chloride (4). A solution of 1,1-bis(cyclopentadienyl)-2,3-dimethyltitanacyclobutene (**1d**) (210 mg, 0.853 mmol) in 10 mL of Et_2O was transferred into a 100-mL Lab-Glass pressure bottle fitted with a pressure gauge and stirbar. The solution was cooled to −78 °C and 100 psi of CO added. The solution was warmed with stirring until the color began to change to a brown/green and then immediately cooled to −78 °C to obtain a green solution with some green precipitate. To this mixture was added 25 psi of anhydrous HCl gas (Matheson) to bring the total pressure to 125 psi. Over 15 min at −78 °C with stirring all of the green color disappeared and a yellow/orange precipitate was formed. The pressure was vented, and the reaction vessel was evacuated at −78 °C for several hours. To speed the removal of solvent the Et_2O mixture was splashed onto the warmer sides of the vessel where the solvent immediately evaporated. After the solvent had been removed, the solid was dried overnight in vacuo to yield 175 mg of a red/orange powder. NMR analysis ($CDCl_3$) indicated approximately 66% of the material was Cp_2TiCl_2 and 34% was the acyl chloride chloride 4 (0.192 mmol, 22%) [^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.77 (s, 10 H, 5.57 (d of q, J = 6.8, 1.2 Hz, 1 H), 3.95 (br s, 2 H), 1.81 (d, J = 1.2, 3 H), 1.69 (d of t, J = 6.8, 1.2 Hz, 3 H); IR (KBr, cm^{-1}) 1610]. The acyl chloride may be cleaved to the aldehyde and Cp_2TiCl_2 by treatment with HCl at >−20 °C. The aldehyde was characterized by ^{1}H NMR (C_6D_6, 90 MHz) δ 9.48 (t, J = 2.3 Hz, 1 H), 5.03 (br q, 1 H), 2.17 (br t, J = 2.3 Hz, 2 H); CH_3 groups were obscured by residual diethyl ether. The aldehyde was immediately converted to the 2,4-DNP derivative, mp 135 °C.

Trapping Experiments of 3 by tert-Butyl Isocyanide. Compound 3 (16 mg, 0.058 mmol) was weighed into an NMR tube in the drybox, and the tube was capped with a septum, removed from the box, and cooled to −78 °C. Toluene-d_8 (400 mL) was added by syringe through the septum at a rate such that the solvent was cooled as it flowed down the side of the tube. The tert-butyl isocyanide (22 L, 0.23) was then added by syringe to the sample. The tube was shaken to dissolve the solid, and the sample was quickly warmed to room temperature. An immediate color change for green to red was observed, and the ^{1}H NMR was recorded at room temperature. The major products had resonances at δ 6.05 and 5.47. The Cp ^{1}H NMR resonances of the imino acyl insertion product **5** were well-separated at δ 5.20. The resonances at δ 6.05 and 5.47 were confirmed to be derived from reaction of the ketene complex oligomer **2d** with tert-butyl isocyanide by independent reactions. Integration of the Cp resonances yielded a ratio of ketene products to metallacyclobutene products of 15:1.

Kinetics Study of the Isomerization of 2d. Two NMR tubes were charged with 14 mg (0.051 mmol) of the phosphine-free ketene oligomer of **2d**. To each tube was added 400 μL of benzene-d_6, and then each was capped with a septum. The tubes were removed from the drybox and frozen in an ice bath. To one tube was added 6 μL (0.059 mmol) of trimethylphosphine via syringe. To the second tube was added 18 μL (0.177 mmol) of trimethyl phosphine. Both samples were thawed simultaneously at room temperature, and the progress of the isomerization was followed by ^{1}H NMR integration of the CH_3 resonances. The initial NMR spectrum showed a >30:1 ratio of isomers. Over 18 h the reaction was monitored periodically until an equilibrium ratio of 0.60 ± 0.1 (δ 5.15 isomer to δ 5.05 isomer). The forward and reverse rate constants were calculated in the usual manner.

Reaction to Determine [13]CO/[12]CO **Exchange.** A solution of the dimethyltitanacyclobutene (100 mg, 0.406 mmol) in 4 mL diethyl ether was transferred into a Lab-Glass pressure bottle fitted with a stirbar and pressure gauge. The cannula was rinsed twice with 0.5-mL portions of toluene. The pressure bottle was partially evacuated and cooled to −78 °C, and 15 psi of [13]CO (90% [13]C) was introduced. The reaction mixture was allowed to warm slowly to about −10 °C to 0 °C at the time a clear green solution had formed. The reaction was immediately cooled to −78 °C, and CO was vented. The pressure bottle was refilled with 100 psi of [12]CO (natural abundance) and allowed to warm to −30 °C with stirring. The rearrangement as noted by the loss of green color was complete in ~15 min. The ketene complex was isolated as previously described to yield 70 mg (0.255 mmol, 63%) of product. Analysis by ^{1}H NMR (C_6D_6) showed the signal at δ 2.61 to be a singlet, indicative of no incorporation of [13]CO in the product.

X-ray Crystal Structure of 2b. Suitable crystals of **2b** were obtained from an Et_2O solution (~10 mg/mL) cooled to −50 °C. A crystal of dimensions 0.023 × 0.033 × 0.198 mm was mounted in a glass capillary under N_2. Oscillation and Weissenberg photographs indicated monoclinic symmetry and the space group $P2_1/c$ ($0k0$ absent for k odd, $h0l$ absent for l odd); the unit cell parameters (a = 9.625 (2) Å, b = 16.217 (2) Å, c = 16.917 (4) Å, $β$ = 101.28(10)°, V = 2589.5(9) Å^3, Z = 4) were obtained by least-squares refinement of four sets average 2θ-values of 17 reflections. The data were collected at room temperature on a crystal mounted approximately along c in a glass capillary under N_2 with a locally-modified Syntex $P2_1$ diffractometer (graphite monochromator and Mo Kα radiation, λ = 0.7101 Å). The total of 6717 (+h, ±k, ±l) yielded an average of set of 3038 reflections; 2735 had I > 0, 1775 had I > 3σI. The three check reflections indicated no decomposition. No absorption correction was performed, and the data were averaged to F_0^2. The position of the Ti was derived from the Patterson map, and the subsequent Fourier map phased on the Ti revealed the remainder of the structure. Hydrogen atoms H(1) and H(2) were located from the difference map and refined with isotropic U; the remaining H atoms were introduced into the model with fixed coordinates and isotropic Gaussian amplitudes are idealized positions. Least-squares refinement of the non-hydrogen atoms with anisotropic U_{ij}'s minimizing $\sum w(F_0^2 - (F_{c/k})^2)^2$ using all the data (3038 reflections) led to S (goodness-of-fit) = 1.66 (280 parameters), R_f 0.050, and F_f 0.084. The final shift errors were <0.10. Form factors were taken from Table 2.2B (*International Tables for X-ray Crystallography* 1978; those for Ti, Si, and P were corrected for anomalous dispersion. A correction for secondary extinction (Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664–5, eq 3) was included, and the final value of the extinction coefficient was 0.22 (4) × 10^{-6}. All calculations were carried out on a VAX 11/780 computer by using the CRYRM system of programs.

Supplementary Material Available: Summary of crystal data and intensity information (Table X1), atom coordinates (Tables X2 and X5), bond lengths and angles (Table X3), anisotropic Gaussian amplitudes (Table X4), least-squares planes (Table X6), torsion angles (Table X7), and structure factor amplitudes (Table X8) (27 pages). Ordering information is available on any current masthead page.