°C, δ ref to 0.5 M $Al(OH)_6^{3+}$), 112 br (FWHM 1360 Hz, {^{1}H} 1120 Hz).

Reaction of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6) with Et_2OBF_3. Compound **6** was prepared from 0.77 g (1.04 mmol) of **1** according to the above procedure. A solution of **6** in about 15 mL of toluene was treated with 3 equiv (0.45 mL, 3.12 mmol) of Et_2OBF_3, and after 2 days stirring at room temperature, a white precipitate formed and the color changed from green to red. Ten milliliters of hexanes was added and the mixture allowed to sit for about 3 h. Filtration through a medium frit gave a red solution and a white residual, which was discarded. The solvent was vacuum stripped and the solid dried under vacuum. The yield of red-orange $CpCo(\eta^5\text{-}C_4Ph_4BF)$ (**5**) was 0.35 g (67%). MS, EI, p^+ = 512, one boron. ^{11}B NMR (toluene, 22 °C, δ) 19.3 br (fwhm = 250 Hz). ^{1}H NMR (C_6D_6, 22 °C) δ 7.22–6.86 m (Ph), 4.40 s (Cp). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C, δ) 139.4 (C_3), 135.9 (C_4), 134–125 (Ph, 129–127 obscured by solvent), 99.0 (C_2), 84.5 (Cp).

A 0.15-g (0.3 mmol) sample of **5** was dissolved in 3 mL of THF and cooled to −78 °C and 0.3 mL of 1 M $NaHBEt_3$ was added. After it was stirred for 1 h, the solution was allowed to warm to room temperature, the solvent was stripped off, and the ^{1}H NMR spectrum was recorded in C_6D_6. The major product produced was compound **3** along with some compound **7**.

Reaction of $CpCoC_4Ph_4AlH{\cdot}NEt_3$ (6) with Propene. A solution containing a known amount of **6** ranging between 0.08 and 0.1 mmol in 5 mL of C_6D_6 in a 200-mL Schlenk tube was connected to a mercury manometer and a 1-L reservoir. The tube was cooled to −78 °C and the whole system (total volume 1.25 L) evacuated before returning the tube to the reaction temperature. Then propene was introduced and the pressure recorded (usually around 150 torr of propene was added). The consumption of propene was followed for up to ca. 5000 min with a total pressure change of 3–8 torr, depending on temperature. The reaction temperatures used were −20 °C and room temperature. After terminating the reaction, ^{1}H and ^{13}C NMR analysis of the now red solution showed the presence of **7**, free NEt_3, and propene. A white insoluble product was formed during the reaction and it was isolated by removal of the solvent under vacuum. The analyses of the solid from the two runs gave C, 17.46 (RT) and 23.81, 24.03 (−20 °C); H, 4.61 (RT) and 5.28, 5.56 (−20 °C); and N, 0.02 (RT) (calculated for propene: C, 85.63; H, 14.37).

An independent experiment was carried out under conditions such that the reaction could be monitored by ^{1}H NMR. A sample of **6** in C_6D_6 was placed in an NMR tube with propene at 1 atm pressure. Spectra were then obtained as a function of time with the propene atmosphere being replenished once after the reaction rate approached zero.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged as is the aid of Dr. A. K. Bandyopadhyay and Mr. D. Schifferl with the ^{27}Al NMR experiments. We also thank a referee for correcting our understanding of the ^{27}Al NMR literature.

(η^1-Acyl)titanium Complexes Prepared by the Carbonylation of 1-Oxa-5-titanacyclopentanes

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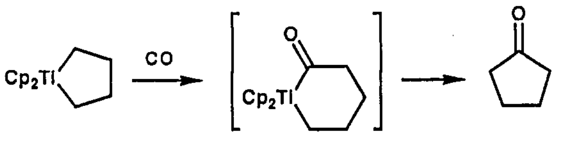
Carbonylation of 1-oxa-5-titanacyclopentanes $Cp^*_2\overline{TiOCH(R)CH_2C}H_2$ (**3**: **a**, R = CH_3; **b**, R = CH_2CH_3; **c**, R = $CHMe_2$; Cp* = pentamethylcyclopentadienyl) in toluene at room temperature under atmospheric pressure of CO afforded $Cp^*_2\overline{TiOCH(R)CH_2CH_2C}O$ (**4**: **a**, R = CH_3 (81%); **b**, R = CH_2CH_3 (77%); **c**, R = $CHMe_2$ (81%)) whose structures have been characterized by spectral data and X-ray analysis. X-ray structure determination of **4c** revealed that it has a novel η^1-acyltitanium structure [space group $P2_1/n$ with cell constants a = 17.874 (4) Å, b = 16.170 (4) Å, c = 8.580 (1) Å, and β = 92.69 (1)°, V = 2482.4 (9) Å^3 (2544 reflections, R = 0.060)]. Reaction of **3** with isocyanide gave the iminoacyl complexes $Cp^*_2\overline{TiOCH(R)CH_2CH_2C}(NCMe_3)$ (**6**: **a**, R = CH_3; **b**, R = CH_2CH_3, **c**, R = $CHMe_2$). The molecular structure of **3c** [space group $P2_1/a$ with cell constants a = 18.529 (3) Å, b = 16.308 (2) Å, c = 8.547 (1) Å, and β = 111.24 (1)°, V = 2407.3 (6) Å^3 (1949 reflections, R = 0.051)] has also been determined by X-ray crystallography.

Introduction

Carbonylation of five-membered metallacycles giving cyclopentanone derivatives has attracted much attention as a promising way for building up five-membered carbocycles.[1-3] Titanacyclohexanone **2** has been postulated as



(1)

1 2

an important intermediate in the carbonylation of titanacyclopentane **1**. Experimental evidence on the mechanism of carbonylation, however, has been limited due to the thermal and/or kinetic lability of the intermediate such

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[†] Kyoto University.

[‡] Kumamoto University.

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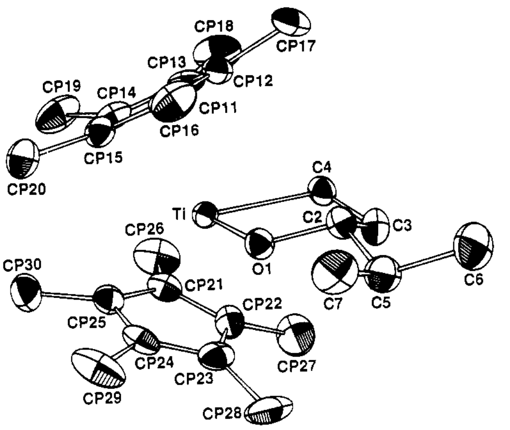
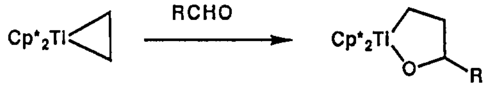


Figure 1. ORTEP drawing of complex **3c** with numbering scheme. All hydrogen atoms are omitted for simplicity.

as **2**.[2a] We found that introduction of an electronegative atom like oxygen into titanacyclopentane rings allowed us, for the first time, to isolate 1-oxa-5-oxo-6-titanacyclohexanes, $\mathrm{Cp^*_2\overline{TiOCH(R)CH_2CH_2C}O}$ (**4**), whose (η^1-acyl)titanium structures have been established based on spectral data and a single-crystal X-ray study.

Results and Discussion

Preparation and Characterization of 1-Oxa-5-titanacyclopentanes (3). 1-Oxa-5-titanacyclopentane **3a** was originally prepared by the reaction of $\mathrm{Cp^*_2Ti(C_2H_4)}$ and acetaldehyde by Cohen and Bercaw.[3] Similar treatment of $\mathrm{Cp^*_2Ti(C_2H_4)}$ with an excess amount of propanal or 2-methylpropanal in toluene at room temperature for 12 h afforded an orange solution. Complexes **3b** and **3c** were isolated as orange crystals in 64% and 83% yields, respectively. NMR and mass spectral data supported the assigned structures. In order to elucidate the structural details of **3**, the crystal structure of **3c** was determined by an X-ray diffraction study. Figure 1 shows the ORTEP drawing of **3c**. Selected bond distances and bond angles are listed in Table I. All the structural parameters connected with the $\mathrm{Cp^*_2Ti}$ moiety are normal. The Ti–C4 bond distance, 2.208 (6) Å, is also normal as a single Ti–C bond. The Ti–O (1.866 (3) Å) bond length is shorter than that of the Ti–O single bond (2.00 Å) estimated by the covalent radii,[4] which shows that the former has double-bond character. A similar short Ti–O bond length has been observed for a number of bent metallocene complexes of titanium(IV) and titanium(III) complexes such as $\mathrm{Cp_2Ti(OCH{=}CH_2)_2}$ (1.903 (2) Å),[5] $\mathrm{Cp_2(Cl)TiOEt}$ (1.855 (2) Å),[6] and $\mathrm{Cp_2TiO(2,6\text{-}(CH_3)_2C_6H_3)}$ (1.892 (2) Å).[7] The Ti–O bond length of **3c** is slightly outside the range of 1.750 (2)–1.777 (1) Å found for $\mathrm{[CpTiCl_2]_2(OCMe_2)_2}$[6] and $\mathrm{[CpTiCl_2]_2(\mu\text{-}O)}$,[8] having typical Ti–O double bonds. These facts suggest that the π-donation from the in-plane $p\pi$ orbital of the oxygen atom to the laterally directed acceptor $1a_1$ orbital of titanocene is significant.[9]



(2)

3

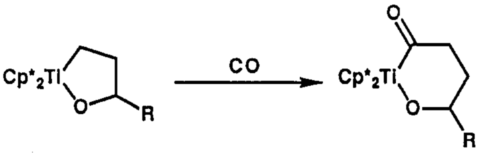
a; R = $\mathrm{CH_3}$
b; R = $\mathrm{CH_2CH_3}$
c; R = $\mathrm{CH(CH_3)_2}$

Table I. Selected Bond Distances (Å) and Angles (deg) with ESD's of Complex 3c

Ti–O	1.866 (3)	Ti–C4	2.208 (6)
Ti–CCp1[a]	2.162	Ti–CCp2[a]	2.153
O–C2	1.420 (7)	C2–C3	1.525 (9)
C2–C5	1.529 (8)	C3–C4	1.519 (7)
C5–C6	1.524 (10)	C5–C7	1.514 (11)
O–Ti–C4	80.9 (2)	CCp1[a]–Ti–CCp2[a]	137.3
Ti–O–C3	121.9 (3)	O–C2–C3	106.1 (4)
O–C2–C5	111.3 (5)	C3–C2–C5	117.3 (5)
C2–C3–C4	110.4 (5)	Ti–C4–C3	104.7 (4)
C2–C5–C6	110.6 (6)	C2–C5–C7	111.7 (5)
C6–C5–C7	111.4 (5)		

[a] CCp1 and CCp2 are the centroids of pentamethylcyclopentadienyl rings of (Cp11–Cp15) and (Cp21–Cp25), respectively.

Carbonylation of Complexes 3. When an orange solution of complex **3c** in toluene was exposed to atmospheric pressure of carbon monoxide at room temperature for 5 h, CO insertion into the Ti–C bond occurred to give **4c** in 81% yield as purple crystals after recrystallization from hexane at −80 °C. No products arising from insertion into the Ti–O bond have been isolated. Similarly, carbonylation of complexes **3a** and **3b** gave **4a** and **4b** in 81% and 77% yields, respectively. IR absorptions in the range 1611–1594 cm^{-1} for complexes **4** are characteristic of the acylmetal complexes. ^{13}C NMR spectra of **4** exhibited resonances at δ 296–297 due to the acyl group bound to titanium. The mass spectral data are consistent with the monomeric structures of these complexes **4**. The η^1-mode of acyltitanium moiety of **4** was determined by X-ray analysis (vide infra). A smooth insertion of CO into the Ti–C bond of **3** is of interest in relation to the fact that no evidence for CO insertion has been observed for an acyclic zirconium(IV) alkoxyalkylmetallocene, $\mathrm{Cp_2Zr(CH_3)OCH_2CH_3}$, having electronegative oxygen π-donor ligand. By contrast, CO inserts into the Zr–C bond of $\mathrm{Cp^*_2\overline{ZrOC({=}CH_2)Si(Me_2)CH_2}}$.[9] Although the interaction between the $1a_1$ orbital (LUMO) and the $p\pi$ orbital of the π-donor ligand should diminish the capability for the metallocene to bind an additional CO ligand,[10,11] the above experimental findings show that CO insertion still occurs for 1-oxa-5-titana- and 1-oxa-5-zirconacyclopentanes. Activation energy of carbonylation of **3c** over



(3)

3 — a; R = $\mathrm{CH_3}$ — b; R = $\mathrm{CH_2CH_3}$ — c; R = $\mathrm{CH(CH_3)_2}$

4 — a; R = $\mathrm{CH_3}$ — b; R = $\mathrm{CH_2CH_3}$ — c; R = $\mathrm{CH(CH_3)_2}$

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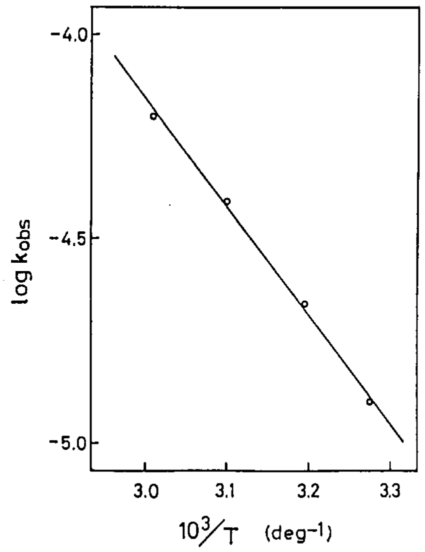
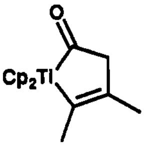


Figure 2. Arrhenius plot for the carbonylation of **3c**.

the range 32.3–50.0 °C has been determined to be 25 ± 2 kcal·mol^{-1} at 39.8 °C based on ^{1}H NMR spectroscopy (Figure 2).[12]

The ^{13}C–^{13}C coupling constant from the acyl carbon ^{13}C5 to the methylene carbon ^{13}C4 in **4a**, as determined by using ^{13}C-enriched CO, is 4.9 Hz, which is significantly smaller than the value of 11.9 ± 0.9 Hz observed for $\mathrm{Cp_2\overline{TiCOCH_2C(CH_3){=}C}CH_3}$ (**5**) for which an η^1-acyl structure has been proposed.[13] Such small coupling constants, 9.2 and 7.3 Hz, have also been found for $\mathrm{Cp^*{}_2\overline{TiCOCH_2CH_2C[{=}Re_2(CO)_9]O}}$ and $\mathrm{Cp^*{}_2\overline{TiCOCH_2CH_2C[{=}W(CO)_5]O}}$, respectively.[14]



5

Although complex **4c** sublimes at 210 °C (0.05 mmHg), slow decomposition of the complex occurs at this temperature to liberate ethylene and carbon monoxide. The structure of residual material containing the titanocene moiety was not determined. The reductive elimination product such as γ-lactone was not detected.

Crystal Structure of Complex 4c. The molecular structure of the metallacyclic compound **4** has been established by the single-crystal X-ray analysis of **4c**. An ORTEP view of **4c** is shown in Figure 3. Selected bond distances and bond angles are shown in Table II. The Ti–C5 bond distance, 2.179 (4) Å, is normal as a single covalent bond. The Ti–O2 interatomic distance of 3.039 (3) Å is in sharp contrast with the fact that the metal–oxygen bond distances in acyclic η^2-acyl complexes of Ti,[15] Zr,[16] Mo,[17-19] W,[19] Fe,[20] and Ru[21] are in the range of 1.99–2.47 Å. This is rather comparable to the values of η^1-acyl complexes such as $\mathrm{NiCl(\eta^1\text{-}COCH_2SiMe_3)(PMe_3)_2}$ (3.121 Å).[22] The Ti–C5–O2 angle (125.0 (4)°) in the acyl group is also characteristic of η^1-acyl complexes. The corresponding angles in Mo,[17] Fe,[20] Ni,[22,23] and Pt[24-26] complexes fall in the range of 122.9–129.6°. By contrast, those of η^2-acyl complexes of Ti,[15] Zr,[16] Mo,[17-19] W,[19] Fe,[20] and Ru[21] are between 76.4 and 87.5°. Generally, acyl groups bound to early transition metals have η^2-coordination mode as have been found for $\mathrm{Cp_2Ti(COMe)Cl}$[15] and $\mathrm{Cp_2Zr(COMe)Me}$.[16] The structure of **4c** presents, to our knowledge, the first example of an η^1-acyltitanium complex determined by X-ray crystallography. The cyclic structure may put the η^2-coordination mode at a disadvantage from steric reason such as constraints of the ring, as has been suggested by Grubbs.[13] The short Ti–O1 bond length (1.844 (3) Å) of **4c** suggests that there is overlapping between pπ of O1 and dπ of Ti to some extent as has been

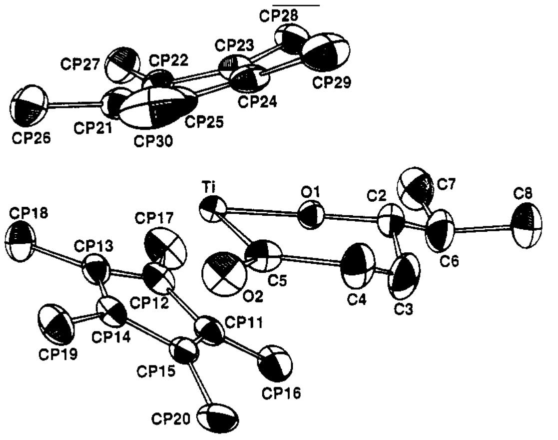


Figure 3. ORTEP drawing of **4c** with numbering scheme. All hydrogen atoms are omitted for simplicity.

Table II. Selected Bond Distances (Å) and Angles (deg) with ESD's of Complex 4c

Ti–O1	1.844 (3)	Ti–C5	2.179 (4)
Ti–CCp1[a]	2.147	Ti–CCp2[a]	2.157
O1–C2	1.398 (5)	O2–C5	1.207 (5)
C2–C3	1.493 (7)	C2–C6	1.493 (7)
C3–C4	1.470 (8)	C4–C5	1.539 (7)
C6–C7	1.498 (8)	C6–C8	1.517 (7)
O1–Ti–C5	88.3 (2)	Ti–O1–C2	141.9 (3)
CCp1[a]–Ti–CCp2[a]	137.5		
O1–C2–C3	110.1 (4)	O1–C2–C6	114.2 (4)
C3–C2–C6	116.7 (4)	C2–C3–C4	119.9 (5)
C3–C4–C5	121.6 (4)	Ti–C5–O2	125.2 (3)
Ti–C5–C4	119.0 (3)	O2–C5–C4	115.8 (4)
C2–C6–C7	115.8 (5)	C2–C6–C8	114.2 (5)
C7–C6–C8	112.8 (5)		

[a] CCp1 and CCp2 are the centroids of pentamethylcyclopentadienyl rings of Cp11–Cp15 and Cp21–Cp25, respectively.

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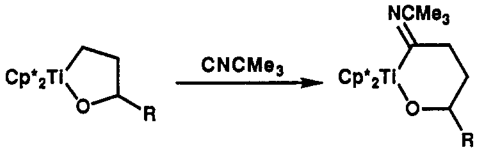
observed for complex **3c**, which may contribute to stabilize the η^1-acyl structure **4**. The η^2-acyl interaction would expand the angle Ti–C5–C4, resulting in a significant reduction of Ti–O1–C2 angle, which in turn would disfavor such O(pπ)–Ti(dπ) interaction.

Reaction of Complexes 3 and *tert*-Butyl Isocyanide. Reaction of 1-oxa-5-titanacyclopentanes **3** with *tert*-butyl isocyanide has been investigated.[11b] Treatment of an orange solution of complex **3c** and *tert*-butyl isocyanide in toluene at room temperature for 15 h gave a dark violet solution, from which complex **6c** was isolated in 96% yield as purple crystals after recrystallization from hexane at −80 °C. Similarly, **6a** and **6b** have been isolated in 91% and 87% yields, respectively, by the reaction of **3a** and **3b** with *tert*-butyl isocyanide. The structures of **6a–c** have been determined by comparison of the spectral data with those of **4**. Although the IR absorption for the iminoacyl group of **6** appears within the range of 1560–1564 cm^{-1}, its position is relatively insensitive to the mode (η^1 vs η^2) of coordination.[11b]



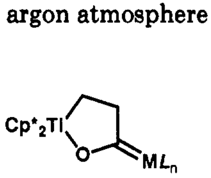
(4)

3
a; R = CH_3
b; R = CH_2CH_3
c; R = $CH(CH_3)_2$

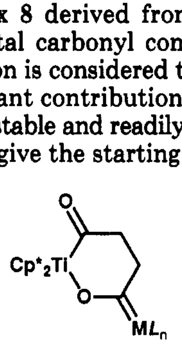
6
a; R = CH_3
b; R = CH_2CH_3
c; R = $CH(CH_3)_2$

Conclusion

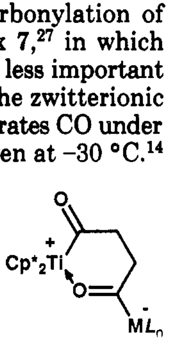
The intermediate **2** is too unstable to be detected by spectroscopic methods. By contrast, it was revealed in this work that the presence of a strong Ti–O bond in the ring stabilizes η^1-acyl complexes **4**, which made it possible to determine their molecular structures by spectroscopic and single-crystal X-ray analysis. *tert*-Butyl isocyanide, which is isoelectronic with CO, also reacted with **3** smoothly to give the corresponding insertion products **6** in high yields. It was suggested that π-donation from the pπ-orbital of the O1 to the acceptor 1a$_1$ orbital of titanocene is responsible for remarkable stability of **4**. Interestingly, the acyltitanium complex **8** derived from carbonylation of (titanoxycarbene)metal carbonyl complex **7**,[27] in which such orbital interaction is considered to be less important because of an important contribution of the zwitterionic structure **9**, is very unstable and readily liberates CO under argon atmosphere to give the starting **7** even at −30 °C.[14]



7



8



9

Experimental Section

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk technique under argon atmosphere purified through a column packed with BASF catalyst R3-11. All solvents were purified by distillation under argon after being dried over calcium hydride or sodium benzophenone ketyl. ^{1}H NMR spectra were recorded on a Varian EM390 (90-MHz) spectrometer or a JEOL GX400 (400-MHz) spectrometer. ^{13}C NMR spectra were measured on a JEOL GX400 (100 MHz). Other spectra were recorded by the use of the following instruments: IR, Hitachi 295; low-resolution mass and high-resolution mass spectra, JEOL D300 (70 eV). Gas chromatographic analyses were conducted on a Hitachi 263-30 equipped with a flame ionization detector. Elemental analyses were performed by the Wako Pure Chemical Industries Ltd. All melting points were measured in sealed tubes and uncorrected. $Cp^*_2Ti(C_2H_4)$ was prepared according to the published procedure.[28] Carbon monoxide was obtained from Takachiho Chemical Industries Co. ^{13}CO (99.3 atom %) was used as obtained from MDS Isotopes.

Preparation of 3a. The title complex was prepared by the literature method. The NMR spectrum was superimposable with that of an authentic sample.[3]

Preparation of 3b. To a solution of complex **2** (0.64 g, 1.85 mmol) in toluene (25 mL) was added propanal (20 μL, 0.30 mmol) via syringe. The mixture was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure. The residue was dissolved in hexane (5 mL), and the solution was kept at −80 °C overnight to afford **3b** as orange crystals: 0.48 g, 64% yield; mp 97–103 °C dec; ^{1}H NMR (benzene-d_6) δ 0.31–0.36 (m, H_{4a}), 0.91 (t, CH_2CH_3, J = 7.33 Hz), 1.21–1.38 (m, CH_2CH_3), 1.87 (s, C_5Me_5), 1.91 (s, C_5Me_5), 2.24–2.32 (m, H_{4b}), 2.55–2.60 (m, H_{3a}), 2.67–2.78 (m, H_{3b}), 4.45–4.52 (m, H_2); ^{13}C NMR (benzene-d_6) δ 11.76 (CH_2CH_3,J_{C-H} = 125 Hz), 12.06 (C_5Me_5, 125 Hz), 12.12 (C_5Me_5, 125 Hz), 33.31 (CH_2CH_3, 124 Hz), 52.19 (C_4, 127 Hz), 53.92 (C_3, 122 Hz), 81.72 (C_2, 134 Hz), 120.93 (C_5Me_5), 121.26 (C_5Me_5); IR (KBr) 2965 (s), 2902 (s), 2967 (s), 2845 (sh), 2817 (s), 1442 (m), 1375 (m), 1328 (w), 1115 (m), 1092 (s), 1045 (m), 1020 (m), 961 (s), 843 (m), 805 (m), 781 (m), 667 (m), 631 (m), 615 (m), 591 (s), 521 (w), 480 (w), 409 (s) cm^{-1}; mass spectrum (^{48}Ti) m/z 404 (M^+), 389 ($M^+ - CH_3$), 318 (Cp^*_2Ti, base peak), 239 ($M^+ - Cp^* - 2\ CH_3$), 199 (Cp^*TiO); exact mass spectrum m/z calcd for $C_{25}H_{40}O^{48}Ti$ 404.2559, found 404.2558. Anal. Calcd for $C_{25}H_{40}OTi$: C, 74.23; H, 9.97. Found: C, 73.94; H, 10.15.

Preparation of 3c. To a solution of titanocene–ethylene complex (0.83 g, 2.40 mmol) in toluene (30 mL) was added 2-methylpropanal (314 μL, 3.46 mmol) at room temperature. After being stirred for a period of 12 h, the resulting deep red solution was concentrated and then the solid was dried in vacuo. Recrystallization from hexane (5 mL) at −80 °C afforded complex **3c** (0.83 g, 83% yield) as orange crystals: mp 140–143 °C dec; ^{1}H NMR (benzene-d_6) δ 0.31 (ddd, H_{4a},$J_{3a,4a}$ = 7.33 Hz, $J_{3b,4a}$ = 4.40 Hz, $J_{4a,4b}$ = 10.99 Hz), 0.81 (d, $CH(CH_3)$, J = 6.60 Hz), 0.95 (d, $CH(CH_3)$, J = 6.60 Hz), 1.44 (dqq, $CH(CH_3)_2$, J = 8.87 Hz), 1.87 (s, C_5Me_5), 1.90 (s, C_5Me_5), 2.24 (ddd, H_{4b}, $J_{3a,4b}$ = 8.70 Hz, $J_{3b,4b}$ = 11.27 Hz), 2.71 (dddd, H_{3a}, $J_{2,3a}$ = 9.44 Hz, $J_{3a,3b}$ = 12.46 Hz), 2.75 (dddd, H_{3b}, $J_{2,3b}$ = 4.68 Hz), 4.15 (ddd, H_2); ^{13}C NMR (benzene-d_6) δ 12.09 (C_5Me_5, J_{C-H} = 126 Hz), 19.65 ($CH(CH_3)$, 125 Hz), 20.92 ($CH(CH_3)$, 125 Hz), 38.28 ($CH(CH_3)_2$, 128 Hz), 51.61 (C_4, 122 Hz), 52.76 (C_3, 122 Hz), 86.81 (C_2, 134 Hz), 120.87 (C_5Me_5), 121.23 (C_5Me_5); IR (KBr) 2968 (s), 2906 (s), 2866 (s), 2826 (s), 1440 (m), 1378 (m), 1261 (m), 1078 (s), 1055 (s), 1013 (s), 987 (s), 871 (w), 803 (m), 643 (vs), 619 (m), 606 (m), 553 (w), 485 (w), 408 (m), 400 (sh), 330 (w) cm^{-1}; mass spectrum (^{48}Ti) m/z 418 (M^+), 403 ($M^+ - CH_3$), 318 (Cp^*_2Ti, base peak), 253 ($M^+ - Cp^* - 2\ CH_3$), 199 (Cp^*TiO); exact mass spectrum m/z calcd for $C_{26}H_{42}O^{48}Ti$ 418.2715, found 418.2713. Anal. Calcd for $C_{26}H_{42}OTi$: C, 74.62; H, 10.12. Found: C, 73.56; H, 10.15.

X-ray Structure Determination of 3c and 4c. Orange crystals of **3c** were grown from saturated hexane solution kept at −20 °C overnight. Several crystals were placed in thin-walled glass capillaries under argon atmosphere, and the tubes were flame-sealed. The cell parameters were obtained from a least-squares refinement of 2θ values of 50 independent reflections in the range of 20° < 2θ < 30°. The detailed procedures of data collection are given in Table III. The 1949 unique raw intensity data with $|F_o| > 3\ \sigma\ (F_o)$ were converted to the values of the structure factor corrections for absorption, Lorentz, and polarization effects. During the data collection, 3 standard reflections measured after every 50 reflections showed no systematic variation in intensity of reflections.

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[27] Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145.

[28] Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

Table III. Crystal Data and Data Collection Parameters for Complexes 3c and 4c

complex	**3c**	**4c**
formula	$C_{26}H_{42}OTi$	$C_{27}H_{42}O_2Ti$
mol wt	418.27	446.27
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
a, Å	18.529 (3)	17.874 (4)
b, Å	16.308 (2)	16.170 (4)
c, Å	8.547 (1)	8.580 (1)
β, deg	111.24 (1)	92.69 (1)
V, Å^3	2407.3 (6)	2482.4 (9)
Z	4	4
D_{calcd}	1.154	1.194
cryst size, mm	0.38 × 0.28 × 0.15	0.40 × 0.30 × 0.25
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ(Mo Kα), cm^{-1}	3.833	3.777
diffractometer	Rigaku AFC-5	Rigaku AFC-5
temp, °C	25	25
scan type	θ–2θ	θ–2θ
scan range, deg	$1.2 + 0.5 \tan \theta$	$1.3 + 0.5 \tan \theta$
bkgd, s	8	8
scan speed, deg/min	3	3
data collected	$\pm h,k,l$	$\pm h,k,l$
$2\theta_{max}$, deg	60	60
no. of reflns collected	2425	3071
no. of rflns used in refinement	1949	2544
no. of variables	422	440
R	0.051	0.057
R_w	0.052	0.052
GOF	2.723	2.313

Table IV. Atomic Parameters of Complex 3c[a]

	x	y	z	B_{eq}, Å
Ti	1479 (1)	2046 (1)	7024 (1)	2.8
O	2142 (2)	1434 (2)	8814 (4)	3.4
C2	2930 (3)	1301 (3)	9032 (7)	4.2
C3	2951 (3)	1218 (4)	7272 (8)	5.1
C4	2442 (3)	1864 (3)	6114 (6)	3.8
C5	3280 (3)	603 (4)	10268 (8)	5.5
C6	4138 (4)	505 (4)	10571 (9)	6.9
C7	3148 (4)	724 (4)	11900 (8)	6.5
Cp11	1892 (3)	3133 (3)	9180 (6)	3.6
Cp12	2265 (3)	3336 (3)	8072 (7)	3.8
Cp13	1694 (3)	3503 (3)	6486 (6)	3.9
Cp14	965 (3)	3454 (3)	6655 (6)	3.9
Cp15	1089 (3)	3191 (3)	8325 (7)	3.8
Cp16	2281 (4)	2934 (4)	11020 (7)	5.6
Cp17	3123 (3)	3474 (4)	8549 (8)	6.0
Cp18	1829 (4)	3821 (4)	4965 (8)	6.7
Cp19	241 (4)	3826 (4)	5452 (8)	6.8
Cp20	516 (4)	3163 (4)	9186 (8)	5.9
Cp21	403 (3)	1644 (3)	4464 (6)	3.9
Cp22	935 (3)	988 (4)	4840 (7)	4.5
Cp23	955 (3)	640 (3)	6337 (7)	4.6
Cp24	468 (3)	1092 (4)	6914 (6)	4.2
Cp25	87 (3)	1690 (3)	5708 (7)	3.9
Cp26	140 (4)	2100 (4)	2807 (7)	6.9
Cp27	1282 (4)	616 (5)	3654 (9)	8.0
Cp28	1370 (4)	−124 (4)	7144 (10)	7.8
Cp29	323 (4)	909 (5)	8505 (8)	7.6
Cp30	−655 (3)	2115 (4)	5578 (8)	6.3

[a] Positional parameters are multiplied by 10^4.

Table V. Atomic Parameters of Complex 4c[a]

	x	y	z	B_{eq}, Å
Ti	1453 (1)	2045 (1)	9520 (1)	2.6
O1	2273 (2)	1474 (2)	8862 (3)	3.2
O2	1686 (2)	2291 (2)	13020 (4)	5.4
C2	3016 (3)	1278 (3)	9307 (6)	4.3
C3	3084 (3)	1110 (4)	11025 (7)	6.8
C4	2784 (3)	1707 (4)	12123 (6)	5.5
C5	1973 (3)	2034 (3)	11873 (5)	3.8
C6	3371 (3)	673 (4)	8252 (7)	6.0
C7	3170 (3)	762 (4)	6553 (7)	6.5
C8	4206 (3)	558 (4)	8591 (8)	7.0
Cp11	1008 (3)	602 (3)	9459 (5)	3.6
Cp12	587 (3)	1058 (3)	8346 (5)	3.8
Cp13	126 (3)	1618 (3)	9153 (5)	3.7
Cp14	313 (3)	1543 (3)	10750 (5)	3.6
Cp15	863 (3)	906 (3)	10922 (5)	3.5
Cp16	1475 (3)	−133 (3)	9094 (7)	5.6
Cp17	566 (3)	899 (4)	6616 (6)	6.1
Cp18	−574 (3)	2004 (4)	8458 (7)	6.0
Cp19	−58 (3)	1967 (4)	12065 (6)	5.4
Cp20	1109 (3)	497 (4)	12445 (7)	5.8
Cp21	903 (3)	3442 (3)	9155 (6)	4.4
Cp22	1177 (3)	3166 (3)	7741 (5)	3.6
Cp23	1960 (3)	3136 (3)	7905 (5)	3.6
Cp24	2172 (3)	3363 (3)	9440 (6)	4.2
Cp25	1506 (3)	3551 (3)	10221 (6)	4.8
Cp26	123 (4)	3768 (4)	9416 (8)	7.3
Cp27	749 (3)	3113 (4)	6182 (6)	5.4
Cp28	2470 (3)	2947 (4)	6612 (6)	4.8
Cp29	2955 (4)	3565 (4)	10043 (8)	7.1
Cp30	1462 (5)	3955 (4)	11786 (7)	8.8

[a] Positional parameters are multiplied by 10^4.

Crystals of complex **4c** were obtained from a saturated hexane solution kept at −20 °C overnight. Dark violet crystals were placed in thin-walled glass capillaries, and the tubes were flame-sealed under argon. The details of data collection and the cell dimensions are listed in Table III. The 2544 unique reflections with $|F_o| > 3\sigma(F_o)$ were corrected for effects of absorption, Lorentz, and polarization. Three standard reflections measured after every 50 reflections showed no decay in the intensities of the standard reflections measured during data collection.

The structures of **3c** and **4c** were solved by the Patterson method. A series of standard block-diagonal least-squares refinement and Fourier synthesis revealed all non-hydrogen atoms and some hydrogen atoms. Remaining hydrogen atoms were located at calculated positions. Non-hydrogen atoms as anisotropic temperature factors and hydrogen atoms as isotropic temperature factors were refined to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.051$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.052$ for **3c** and $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.057$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.052$ for **4c**. A weighting scheme, $1/w = \sigma_c^2 + (0.015|F_o|)^2$, was employed. A final difference Fourier map indicated no significant residual peaks remained. Selected bond lengths and angles of **3c** and **4c** are listed in Tables I and II, respectively. Atomic positional parameters for complex **3c** and **4c** are presented in Tables IV and V, respectively.

Reaction of 3a with CO and ^{13}CO. To a solution of **3a** (0.37 g, 0.95 mmol) in toluene (5 mL) was introduced atmospheric pressure of carbon monoxide. The solution was stirred at room temperature for a period of 5 h. Orange color of the solution turned to deep wine red. All volatiles were removed under reduced pressure. Recrystallization of the resulting residue from hexane at −20 °C afforded **4a** as dark violet solids: 0.32 g, 81% yield; mp 106–112 °C dec; ^{1}H NMR (benzene-d_6) δ 1.30 (d, CH_3, J = 5.87 Hz), 1.47 (dddd, H_{3a}, $J_{3a,3b}$ = 13.55 Hz, $J_{3a,4a}$ = 2.2 Hz, $J_{3a,4b}$ = 4.76 Hz, $J_{2,3a}$ = 10.62 Hz), 1.55 (dddd, H_{3b}, $J_{3b,4a}$ = 5.86 Hz, $J_{3b,4b}$ = 2.20 Hz, $J_{2,3b}$ = 1.84 Hz), 1.76–1.85 (m, H_{4a}), 1.81 (s, C_5Me_5), 1.82 (s, C_5Me_5), 2.24 (ddd, H_{4b}, $J_{4a,4b}$ = 17.22 Hz), 4.59 (ddq, H_2); ^{13}C NMR (benzene-d_6) δ 12.37 ($C_5\mathit{Me}_5$, J_{C-H} = 127 Hz), 12.56 ($C_5\mathit{Me}_5$, 127 Hz), 27.83 (CH_3, 125 Hz), 36.83 (C_3, 124 Hz), 47.55 (C_4, 123 Hz), 80.42 (C_2, 132 Hz), 121.53 (C_5Me_5), 296.68 (C_5); IR (KBr) 2965 (s), 2900 (s), 2849 (s), 2720 (w), 1600 (vs), 1436 (s), 1367 (s), 1326 (s), 1221 (s), 1120 (s), 1083 (s), 1052 (s), 1040 (s), 961 (vs), 906 (m), 821 (m), 805 (m), 766 (m), 630 (w), 597 (s), 572 (s), 552 (sh), 512 (w), 455 (m), 390 (m), 373 (m) cm^{-1}; mass specturm (^{48}Ti) m/z 418 (M^+), 390 (M^+ – CO), 375 (M^+ – CO – CH_3), 318 (Cp^*_2Ti, base peak), 255 (M^+ – Cp* – CO), 199 (Cp*TiO); exact mass spectum m/z calcd for $C_{25}H_{38}O_2{}^{48}Ti$ 418.2351, found 418.2334. Anal. Calcd for $C_{25}H_{38}O_2Ti$: C, 71.75; H, 9.15. Found: C, 71.17; H, 9.44.

The reaction of **3a** and ^{13}CO in toluene-d_8 was carried out in a sealed NMR tube, and the ^{13}C NMR spectrum was measured at room temperature. The value of J_{C3-C4} is 4.9 Hz.

Reaction of 3b with CO. A solution of **3b** (100 mg, 0.25 mmol) in toluene (10 mL) was placed in a Schlenk tube, and then atmospheric pressure of carbon monoxide was introduced. The solution was stirred at room temperature for a period of 12 h. All volatiles were removed under reduced pressure to afford a violet residue. Recrystallization from hexane gave **4b** as violet crystals: 82 mg, 77% yield; mp 75–80 °C dec; ^{1}H NMR (benzene-d_6) δ 0.99 (t, $\mathrm{CH_2C}\mathit{H}_3$, J = 7.51 Hz), 1.34 (dddd, $\mathrm{H_{3a}}$, $J_{2,3a}$ = 10.65 Hz, $J_{3a,3b}$ = 13.74 Hz, $J_{3a,4a}$ = 13.74 Hz, $J_{3a,4b}$ = 4.40 Hz), 1.48 (ddq, $\mathrm{C}\mathit{H}\mathrm{HCH_3}$, $J_{a,b}$ = 13.37 Hz, $J_{2,\mathrm{CH}}$ = 5.52 Hz), 1.61 (dddd, $\mathrm{H_{3b}}$, $J_{2,3b}$ = 1.95 Hz, $J_{3b,4a}$ = 5.50, $J_{3b,4b}$ = 2.38 Hz), 1.64 (ddq, $\mathrm{CH}\mathit{H}\mathrm{CH3}$, $J_{2,\mathrm{CH}}$ = 7.42 Hz), 1.80 (ddd, $\mathrm{H_{4a}}$, $J_{4a,4b}$ = 17.04 Hz), 1.81 (s, 2 $\mathrm{C_5Me_5}$), 2.29 (ddd, $\mathrm{H_{4b}}$), 4.37 (dddd, $\mathrm{H_2}$); ^{13}C NMR (benzene-d_6) δ 11.46 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$, $J_{\mathrm{C-H}}$ = 127 Hz), 12.27 ($\mathrm{C_5}\mathit{Me}_5$, 126 Hz), 12.34 ($\mathrm{C_5}\mathit{Me}_5$, 126 Hz), 34.22 ($\mathrm{C_3}$, 124 Hz), 34.58 ($\mathit{C}\mathrm{H_2CH_3}$, 127 Hz), 48.00 ($\mathrm{C_4}$, 124 Hz), 85.93 ($\mathrm{C_2}$, 137 Hz), 121.29 ($\mathit{C}_5\mathrm{Me_5}$), 296.35 ($\mathrm{C_5}$); IR (KBr) 2956 (s), 2896 (s), 2845 (sh), 2807 (sh), 1594 (s), 1434 (m), 1380 (m), 1344 (w), 1330 (w), 1260 (s), 1220 (m), 1096 (s), 1063 (s), 1019 (s), 1001 (sh), 986 (s), 964 (s), 799 (s), 583 (w), 566 (s), 440 (w), 385 (m), 363 (m) cm^{-1}; mass spectrum (^{48}Ti) m/z 432 ($\mathrm{M^+}$), 404 ($\mathrm{M^+ - CO}$), 389 ($\mathrm{M^+ - CO - CH_3}$), 318 ($\mathrm{Cp^*{}_2Ti}$, base peak), 269 ($\mathrm{M^+ - Cp^* - CO}$), 199 (Cp*TiO); exact mass spectrum m/z calcd for $\mathrm{C_{25}H_{40}O_2{}^{48}Ti}$ 432.2508, found 432.2517.

Reaction of 3c with CO. To a solution of **3c** (67 mg, 0.16 mmol) in toluene (10 mL) was introduced atmospheric pressure of carbon monoxide at −70 °C. The solution was stirred at room temperature for a period of 10 h. All volatiles were removed under reduced pressure to give a deep reddish violet residue, which was recrystallized from hexane at −20 °C. Reddish violet crystals (58 mg, 81% yield) of **4c** were obtained: mp 145–149 °C dec; ^{1}H NMR (benzene-d_6) δ 0.93 (d, $\mathrm{CH(C}\mathit{H}_3\mathrm{)}$, J = 6.59 Hz), 1.06 (d, $\mathrm{CH(C}\mathit{H}_3\mathrm{)}$, J = 6.96 Hz), 1.24 (ddd, $\mathrm{H_{3a}}$, $J_{2,3a}$ = 10.26 Hz, $J_{3a,3b}$ = 15.02 Hz, $J_{3a,4a}$ = 10.62 Hz), 1.68 (dqq, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$, J = 8.80 Hz), 1.74–1.88 (m, $\mathrm{H_{4a}}$), 1.77–1.85 (m, $\mathrm{H_{3b}}$), 1.81 (s, $\mathrm{C_5Me_5}$), 1.82 (s, $\mathrm{C_5Me_5}$), 2.35 (dd, $\mathrm{H_{4b}}$, $J_{3b,4b}$ = 4.03 Hz, $J_{4a,4b}$ = 14.29 Hz), 4.13 (ddd, $\mathrm{H_2}$, $J_{2,3b}$ = 2.20 Hz); ^{13}C NMR (benzene-d_6) δ 12.37 ($\mathrm{C_5}\mathit{Me}_5$, $J_{\mathrm{C-H}}$ = 126 Hz), 19.95 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)}$, 122 Hz), 20.96 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)}$, 122 Hz), 32.25 ($\mathrm{C_3}$, 125 Hz), 37.95 ($\mathit{C}\mathrm{H(CH_3)_2}$, 131 Hz), 48.85 ($\mathrm{C_4}$, 124 Hz), 90.82 ($\mathrm{C_2}$, 137 Hz), 121.23 ($\mathit{C}_5\mathrm{Me_5}$), 295.50 ($\mathrm{C_5}$); IR (KBr) 2970 (s), 2910 (s), 2858 (s), 2798 (m), 1611 (sh), 1594 (s), 1436 (m), 1379 (m), 1224 (m), 1077 (s), 1043 (m), 1025 (m), 967 (s), 869 (w), 824 (w), 800 (w), 766 (w), 638 (s), 617 (m), 607 (m), 528 (w), 489 (w), 390 (w), 359 (m) cm^{-1}; mass spectrum (^{48}Ti) m/z 446 ($\mathrm{M^+}$), 418 ($\mathrm{M^+ - CO}$), 403 ($\mathrm{M^+ - CO - CH_3}$), 318 ($\mathrm{Cp^*{}_2Ti}$, base peak), 253 ($\mathrm{M^+ - Cp^* - CO - 2\ CH_3}$), 199 (Cp*TiO); exact mass spectum m/z calcd for $\mathrm{C_{27}H_{42}O_2{}^{48}Ti}$ 446.2664, found 446.2672. Anal. Calcd for $\mathrm{C_{27}H_{42}O_2Ti}$: C, 72.63; H, 9.48. Found: C, 72.22; H, 9.65.

Kinetics of the Carbonylation of 3c. To **3c** (83.0 mg, 2.0 × 10^{-4} mol) placed in a Schlenk tube was added benzene-d_6 (5.5 mL). This solution (0.5 mL) was transferred into an NMR tube equipped with 50-mL gas reservoir. Then, the carbonylation of **3c** under atmospheric pressure of carbon monoxide was followed by ^{1}H NMR spectroscopy with integration of the signals due to $\mathrm{H_{4a}}$ (δ 0.31) at variable temperature. An Arrhenius plot for the carbonylation of **3c** is shown in Figure 2.

Thermolysis of 4c. The complex **4c** (20 mg) was placed in a Schlenk tube connected to a cold trap, and the system was evacuated. The tube was rapidly heated up to 210 °C in an oil bath, and the products were condensed into the trap cooled at liquid $\mathrm{N_2}$ temperature. ^{1}H NMR and GC–MS analysis of the condensate and the gaseous products indicated that ethylene and CO were formed.

Reaction of 3a with *tert*-Butyl Isocyanide. To a solution of **3a** (167 mg, 0.43 mmol) in toluene (10 mL) was added *tert*-butyl isocyanide (0.05 mL, 0.44 mmol). The mixture was stirred at room temperature overnight, and then all volatiles were removed under reduced pressure. Recrystallization from hexane at −80 °C gave **6a** (184 mg, 91% yield) as violet crystalline solids: mp 39–44 °C dec; ^{1}H NMR (benzene-d_6) δ 1.30 (d, $\mathrm{CHC}\mathit{H}_3$, J = 6.22 Hz), 1.48–1.54 (m, $\mathrm{H_{4a}}$), 1.51 (s, $\mathrm{C(CH_3)_3}$), 1.76–1.91 (m, $\mathrm{H_{3a}}$ and $\mathrm{H_{4b}}$), 1.86 (s, $\mathrm{C_5Me_5}$), 2.67 (ddd, $\mathrm{H_{3b}}$, $J_{3b,4a}$ = 3.30 Hz, $J_{3b,4b}$ = 3.30 Hz, $J_{3a,3b}$ = 16.12 Hz), 4.38–4.46 (m, $\mathrm{H_2}$); ^{13}C NMR (benzene-d_6) δ 12.52 ($\mathrm{C_5}\mathit{Me}_5$, $J_{\mathrm{C-H}}$ = 126 Hz), 12.79 ($\mathrm{C_5}\mathit{Me}_5$, 126 Hz), 27.70 ($\mathrm{CH_3}$, 124 Hz), 31.70 ($\mathrm{C(CH_3)_3}$, 125 Hz), 34.82 ($\mathrm{C_4}$, 125 Hz), 39.47 ($\mathrm{C_3}$, 121 Hz), 57.71 ($\mathrm{C(CH_3)_3}$), 79.86 ($\mathrm{C_2}$, 137 Hz), 121.02 ($\mathit{C}_5\mathrm{Me_5}$), 121.17 ($\mathit{C}_5\mathrm{Me_5}$), 231.31 ($\mathrm{C_5}$); IR (KBr) 2963 (s), 2898 (s), 2860 (sh), 2712 (vw), 1560 (m), 1440 (m), 1375 (sh), 1358 (m), 1330 (w), 1261 (w), 1235 (w), 1207 (w), 1177 (w), 1165 (sh), 1120 (sh), 1083 (s), 1065 (s), 1018 (s), 978 (s), 951 (s), 915 (sh), 799 (s), 685 (w), 667 (w), 625 (w), 586 (s), 571 (sh), 545 (sh), 470 (w), 436 (w), 395 (w), 350 (w) cm^{-1}; mass spectrum (^{48}Ti) m/z 473 ($\mathrm{M^+}$), 416 ($\mathrm{M^+ - CMe_3}$), 390 ($\mathrm{M^+ - CNCMe_3}$), 375 ($\mathrm{M^+ - CH_3 - CNCMe_3}$), 338 ($\mathrm{M^+ - Cp^*}$), 318 ($\mathrm{Cp^*{}_2Ti}$, base peak), 281 ($\mathrm{M^+ - Cp^* - CMe_3}$), 199 (Cp*TiO); exact mass spectrum m/z calcd for $\mathrm{C_{29}H_{47}NO^{48}Ti}$ 473.3137, found 473.3137.

Reaction of 3b with *tert*-Butyl Isocyanide. To a solution of **3b** (118 mg, 0.29 mmol) in toluene (10 mL) was added *tert*-butyl isocyanide (0.05 mL, 0.44 mmol). After the mixture was stirred at room temperature for 12 h, all volatiles were removed. Recrystallization from hexane gave **6b** (124 mg, 87% yield) as dark violet crystals: mp 77–83 °C dec; ^{1}H NMR (benzene-d_6) δ 1.01 (t, $\mathrm{CH_2C}\mathit{H}_3$, J = 7.51 Hz), 1.07–1.20 and 1.56–1.75 (m, $\mathrm{H_{3a}}$, $\mathrm{H_{3b}}$, $\mathrm{H_{4a}}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.52 (s, $\mathrm{CMe_3}$), 1.86 (s, 2 $\mathrm{C_5Me_5}$), 2.72 (ddd, $\mathrm{H_{4b}}$, $J_{3a,4b}$ = 3.39 Hz, $J_{3b,4b}$ = 15.76 Hz), 4.16–4.21 (m, $\mathrm{H_2}$); ^{13}C NMR (benzene-d_6) δ 11.55 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$, $J_{\mathrm{C-H}}$ = 127 Hz), 12.61 ($\mathrm{C_5}\mathit{Me}_5$, 126 Hz), 12.76 ($\mathrm{C_5}\mathit{Me}_5$, 125 Hz), 31.79 ($\mathrm{NCMe_3}$, 126 Hz), 34.55 and 37.37 ($\mathrm{C_3}$ and $\mathit{C}\mathrm{H_2CH_3}$, 124 Hz), 35.34 ($\mathrm{C_4}$), 57.65 ($\mathrm{N}\mathit{C}\mathrm{Me_3}$), 85.78 ($\mathrm{C_2}$, 137 Hz), 120.99 ($\mathit{C}_5\mathrm{Me_5}$), 121.17 ($\mathit{C}_5\mathrm{Me_5}$), 121.25 ($\mathit{C}$=N); IR (KBr) 2962 (s), 2922 (sh), 2904 (s), 2862 (sh), 2712 (vw), 1565 (m), 1441 (m), 1376 (m), 1360 (m), 1346 (m), 1259 (vw), 1235 (w), 1210 (w), 1178 (w), 1096 (m), 1064 (s), 1024 (m), 980 (s), 789 (m), 776 (m), 766 (m), 638 (s), 616 (m), 604 (m), 464 (sh), 444 (w), 422 (vw), 396 (w) cm^{-1}; mass spectrum (^{48}Ti) m/z 487 ($\mathrm{M^+}$), 430 ($\mathrm{M^+ - CMe_3}$), 404 ($\mathrm{M^+ - CNCMe_3}$); exact mass spectum m/z calcd for $\mathrm{C_{30}H_{49}NO^{48}Ti}$ 487.3294, found 487.3299. Anal. Calcd for $\mathrm{C_{30}H_{49}NOTi}$: C, 73.90; H, 10.13; N, 2.87. Found: C, 73.17; H, 10.46; N, 2.70.

Reaction of 3c with *tert*-Butyl Isocyanide. To a solution of **3c** (110 mg, 0.26 mmol) in toluene (10 mL) was added *tert*-butyl isocyanide (0.05 mL, 0.44 mmol). The reaction mixture was stirred at room temperature for 12 h to give dark violet solution. All volatiles were removed, and **6c** (127 mg, 96% yield) was crystallized from saturated hexane solution at −80 °C: mp 95–99 °C dec; ^{1}H NMR (benzene-d_6) δ 0.96 (d, $\mathrm{CH}\mathit{Me}$, J = 6.59 Hz), 0.99–1.07 (m, $\mathrm{H_{4a}}$), 1.10 (d, $\mathrm{CH}\mathit{Me}$, J = 6.59 Hz), 1.53 (s, $\mathrm{CMe_3}$), 1.62–1.80 (m, $\mathrm{H_{3b}}$, $\mathrm{H_{4a}}$, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.86 (s, $\mathit{C}_5\mathrm{Me_5}$), 1.87 (s, $\mathrm{C_5Me_5}$), 2.78 (ddd, $\mathrm{H_{4b}}$, $J_{3a,4b}$ = 3.30 Hz, $J_{3b,4b}$ = 3.30 Hz, $J_{4a,4b}$ = 15.76 Hz), 3.92 (t, $\mathrm{H_2}$); ^{13}C NMR (benzene-d_6) δ 12.67 ($\mathrm{C_5}\mathit{Me}_5$, $J_{\mathrm{C-H}}$ = 126 Hz), 12.76 ($\mathrm{C_5}\mathit{Me}_5$, 125 Hz), 20.29 ($\mathrm{CH}\mathit{Me}$, 125 Hz), 20.95 ($\mathrm{CH}\mathit{Me}$, 124 Hz), 31.85 ($\mathrm{N}\mathit{C}\mathrm{Me_3}$, 126 Hz), 35.28 ($\mathrm{C_3}$, 124 Hz), 36.16 ($\mathrm{C_4}$, 124 Hz), 37.74 ($\mathit{C}\mathrm{HMe_2}$, 122 Hz, 57.65 ($\mathrm{N{=}}\mathit{C}\mathrm{Me_3}$), 90.82 ($\mathrm{C_2}$, 128 Hz), 120.93 ($\mathit{C}_5\mathrm{Me_5}$), 121.17 ($\mathit{C}_5\mathrm{Me_5}$), 230.98 ($\mathrm{C_6}$); IR (KBr) 2965 (s), 2895 (s), 2863 (sh), 1564 (m), 1437 (m), 1375 (sh), 1361 (m), 1345 (sh), 1259 (m), 1241 (m), 1208 (vw), 1177 (w), 1097 (sh), 1075 (s), 1046 (s), 1022 (s), 982 (s), 958 (sh), 934 (sh), 864 (w), 799 (vs), 665 (w), 633 (m), 607 (m), 546 (vw), 498 (w), 483 (w), 439 (w), 389 (w) cm^{-1}; mass spectrum (^{48}Ti) m/z 501 ($\mathrm{M^+}$), 444 ($\mathrm{M^+ - Me - CMe_3}$), 418 ($\mathrm{M^+ - CNCMe_3}$); exact mass spectum m/z calcd for $\mathrm{C_{31}H_{51}NO^{48}Ti}$ 501.3450, found 501.3443.

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Supplementary Material Available: Tables of atomic parameters of hydrogen atoms, mean square displacement tensors of atoms, and bond distances and angles for complexes **3c** and **4c**, a table of kinetic data for carbonylation of **3c**, and a time conversion plot for the carbonylation of **3c** (12 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.