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Novel Titanium−Cobalt Complexes Formed by Reductive Cleavage of a Co−Co Bond in $Co_2(CO)_8$ by Titanocene *tert*-Butoxides: Synthesis, Characterization, and Mechanistic Aspects for Metal−Metal Bond Recombination

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Reactions of titanium(III) complexes (η^5-C_5R_5)$_2$TiO^{t}Bu (R = H (**1**), Me (**4**)) with $Co_2(CO)_8$ are found to be efficient methods to synthesize Ti−Co heterobimetallic complexes. A Ti−Co_3 complex, (η^5-C_5H_5)$_2$Ti(O^{t}Bu)(μ_4-OC)Co(CO)$_9$ (**3**), was formed from **1** and $Co_2(CO)_8$, whereas a Ti−Co bimetallic complex, (η^5-C_5Me_5)$_2$Ti(O^{t}Bu)(μ-OC)Co(CO)$_3$ (**5**), was obtained by the reaction of **4** with $Co_2(CO)_8$. In both cases, the reaction was complete within 5 min. The products were completely characterized by NMR, IR, and X-ray crystallography. Complex **3** contains a quadruply bridging CO group, the oxygen terminus of which is connected to the Ti moiety, whereas the carbon terminus is bound to three Co atoms in the $Co_3(CO)_9$ moiety. In contrast, complex **5** is dinuclear, and its Ti atom is connected to the $Co(CO)_3$ group by an isocarbonyl bridge. A η^5-C_5H_5 analogue of **5**, [(η^5-C_5H_5)$_2$Ti(O^{t}Bu)(μ-OC)Co(CO)$_3$] (**6**), was formed at the initial stage of the reaction of **1** with $Co_2(CO)_8$ in toluene. This dinuclear complex **6** was isolated from a reaction medium of a 5:1 mixture of **1** and $Co_2(CO)_8$, being characterized by spectroscopy. As further evidence for the formation of the Ti−Co heterobimetallic complex, reaction of **6** with THF gave the Ti−Co complex [(η^5-C_5H_5)$_2$Ti(O^{t}Bu)(η-THF)]$^+$[Co(CO)$_4$]$^-$ (**7**), which was completely characterized by spectroscopy, crystallography, and elemental analysis. Thermal decomposition of **6** produced a mixture of **3** and **1**, whereas treatment of **6** with $Co_2(CO)_8$ gave **3**; this is good evidence for the intermediacy of **6** in the formation of **3** from **1** with $Co_2(CO)_8$.

Introduction

Early−late heterobimetallic (ELHB) complexes have received considerable attention from chemists who work with transition-metal clusters, since the Lewis acidic and Lewis basic metal centers in the complexes may cooperatively work with organic substrates to result in their catalytic activation.[1] Earlier examples have been reviewed by Stephan, Casey, and others,[2] in which a series of heterobimetallic complexes, potentially capable of heterolytic cleavage of molecular hydrogen and activation of polar substrates such as CO and CO_2, were synthesized and characterized. The basic concept of activation of polar organic molecules by ELHB has recently been applied to efficient catalytic reactions such as hydroformylation,[3a−d] carbonylation,[3e] hydrogenation/isomerization,[3f] asymmetric synthesis,[3g−j] olefin metathesis,[3k] enol ester formation,[3l] and olefin polymer

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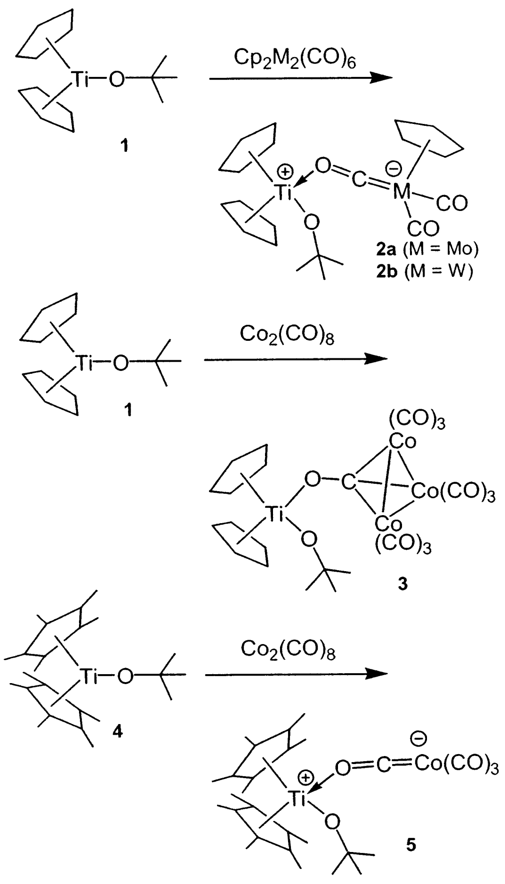
Scheme 1



ization.[3m] Thus, exploration of efficient synthetic routes to ELHB complexes and their fundamental reaction chemistry leading to catalysis have become increasingly valuable. In particular, recent papers reporting that certain Ti–Co heterobimetallic complexes behave as catalytic intermediates for carbonylation of epoxides and aziridines[3e] strongly suggest the importance of developing simple methods to access the Ti–Co heterobimetallic complexes.

As reported in our previous paper, we have recently discovered that $(\eta^5\text{-}C_5H_5)_2TiO^tBu$ (**1**) is a special reagent able to promote reductive cleavage of a metal–metal bond in $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W), which results in formation of the corresponding $(\eta^5\text{-}C_5H_5)_2Ti(O^tBu)(\mu\text{-}OC)M(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Mo (**2a**); M = W (**2b**)), as shown in eq 1 of Scheme 1.[4] The reaction is atom economically efficient, and the heterobimetallic products **2a** and **2b** are simply obtained by mixing **1** with the corresponding metal dimer. As an extension of this study, we are interested in the preparation of Ti–Co complexes by treatment of **1** with $Co_2(CO)_8$. Titanium–cobalt complexes are one of the earliest examples of heterometallic complexes and have been synthesized from Ti(IV) complexes and anionic cobalt precursors;[2a–d] the reaction is accompanied by the formation of salts. Interestingly, the products are, in many cases, not the Ti–Co heterobimetallic compounds but Ti–Co_3 heterotetrametallic complexes. For example, Schmid and co-workers reported that the reaction of $Co_2(CO)_8$ with $(\eta^5\text{-}C_5H_5)_2TiCl_2$ gave a cluster containing one titanium and three cobalt atoms, $(\eta^5\text{-}C_5H_5)_2Ti(Cl)(\mu_4\text{-}OC)Co_3(CO)_9$, which was characterized by an X-ray structure determination.[5a] The same compound was later synthesized from the reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $[Co_3(CO)_{10}]^-Li^+$.[5b] In the former reaction, $Co_2(CO)_8$ should behave as $[Co(CO)_4]^+[Co(CO)_4]^-$ and nucleophilic displacement of a chlorine atom of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ by the anionic cobalt species would be involved. However, the expected product of this displacement is $(\eta^5\text{-}C_5H_5)_2Ti(Cl)(\mu\text{-}OC)Co(CO)_3$ or $(\eta^5\text{-}C_5H_5)_2Ti(Cl)Co(CO)_4$, and further explanation is required for the formation of the Ti–Co_3 complex. Similarly, formation of complexes having a Ti^{IV}–$(\mu_4\text{-}OC)Co_3(CO)_9$ moiety was reported in the reaction of $(\eta^5\text{-}C_5H_5)TiCl_3$ with $NaCo(CO)_4$, the expected products of which must have Ti^{IV}–$(\mu\text{-}OC)Co(CO)_3$ or Ti^{IV}–$Co(CO)_4$ moieties.[6,7] How can we account for the formation of the Ti^{IV}–$(\mu_4\text{-}OC)Co_3(CO)_9$ moiety in these reactions? For a mechanism related to the formation of the Ti–Co_3 complexes described above, Moïse and co-workers proposed the reaction of $(\eta^5\text{-}C_5H_5)_2Ti(Cl)(\mu\text{-}OC)Co(CO)_3$ with $Co_2(CO)_8$ to form $(\eta^5\text{-}C_5H_5)_2Ti(Cl)(\mu\text{-}OC)Co_3(CO)_9$; however, only IR evidence was given to support this proposal.[8] Treatment of Lewis acids (LA) such as $AlCl_3$ and $SiCl_4$ with $Co_2(CO)_8$ reportedly produces LA–$(\mu_4\text{-}OC)Co_3(CO)_9$.[9] Although mechanisms through Lewis acid induced recombination of the Co–Co bonds have been proposed,[9] possible reaction pathways are complicated and depend on the Lewis acid used. Thus, the mechanism for Ti–Co_3 formation in the reactions of Ti(IV) precursors and anionic cobalt carbonyls requires further detailed investigation.

In this paper we wish to report the preparation of Ti–Co heterometallic complexes by Ti(III)-induced Co–Co bond cleavage reactions. Two types of Ti–Co heterometallic complexes were obtained by treatment of titanocene(III) *tert*-butoxides with $Co_2(CO)_8$. The first is a Ti–Co_3 complex, $(\eta^5\text{-}C_5H_5)_2Ti(O^tBu)(\mu_4\text{-}OC)Co_3(CO)_9$ (**3**), which was prepared by reaction of $(\eta^5\text{-}C_5H_5)_2TiO^tBu$ with $Co_2(CO)_8$ (eq 2 of Scheme 1). The second is a Ti–Co complex, $(\eta^5\text{-}C_5Me_5)_2Ti(O^tBu)(\mu\text{-}OC)Co(CO)_3$ (**5**), formed by treatment of $(\eta^5\text{-}C_5Me_5)_2TiO^tBu$ with $Co_2(CO)_8$ as shown in eq 3 of Scheme 1. Since $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}OC)Co(CO)_3$, reported by Moïse, was based on only IR evidence,[8] **5** is the first example of a fully characterized Ti–Co bimetallic complex bearing a $(\eta^5\text{-}C_5R_5)_2Ti$–OC–$Co(CO)_3$ moiety. Both of the reactions to form **3** and **5** take place instantly at room temperature, being

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(7) Pályi and co-workers reported formation of $(\eta^5\text{-}C_5H_5)_2Ti[Co(CO)_4]_2$ by the reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $NaCo(CO)_4$ or that of $(\eta^5\text{-}C_5H_5)_2TiR_2$ (R = Ph, CH_2Ph) with $HCo(CO)_4$. However, the products were not fully characterized; more importantly, no crystallographic evidence was included. (a) Bartik, T.; Windisch, H.; Sorkau, A.; Thiele, K.; Kriebel, C.; Herfurth, A.; Tschoerner, C. M.; Zucchi, C.; Pályi, G. *Inorg. Chim. Acta* **1994**, *227*, 201. For related work, see: (b) Bartik, T.; Happ, B.; Sorkau, A.; Thiele, K.-H.; Pályi, G. *Organometallics* **1989**, *8*, 558. (c) Bartik, T.; Happ, B.; Sieker, A.; Stein, S.; Sorkau, A.; Thiele, K.-H.; Kriebel, C.; Pályi, G. *Z. Anorg. Allg. Chem.* **1992**, *608*, 173.

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Table 1. ^{1}H and ^{13}C NMR and IR Data for 3, 5, 6, and 7

	3	5	6	7
^{1}H NMR (δ)[a]	1.05 (s, ^{t}Bu) 5.93 (s, Cp)	1.48 (s, ^{t}Bu) 1.65 (s, Cp*)	1.03 (s, ^{t}Bu) 5.71 (s, Cp)	1.48 (s, ^{t}Bu) 1.77 (THF) 3.62 (THF) 6.62 (s, Cp)
^{13}C NMR (δ)[a]	31.47 (^{t}Bu) 88.52 (^{t}Bu) 115.50 (Cp) 203.30 (CO)	12.80 (Cp*) 34.17 (^{t}Bu) 89.37 (^{t}Bu) 128.44 (Cp*) 201.20 (CO)	31.49 (^{t}Bu) 115.22 (Cp)	32.06 (^{t}Bu) 91.84 (^{t}Bu) 119.19 (Cp)
IR (cm^{-1}) (ν_{CO}, KBr)	2077 w, 2028 sh, 2015 s, 2001 s, 1989 sh, 1972 m, 1472 s	2019 s, 1921 s, 1766 s	2083 w, 2049 w, 2023 s, 1983 m, 1955 sh, 1938 s, 1886 s, 1847 sh, 1734 s	1880 s
IR (cm^{-1}) ($\nu_{CO,}$ solvent[c])	2084 m, 2026 s, 2016 s, 1994 s, 1444 s	2025 m, 1937 s, 1741 s	2035 m, 2029 m, 1949 s, 1716 s	2024 w, 1941 sh, 1916 sh, 1898 sh, 1887 s

[a] All measurements were performed at room temperature in the following solvents: **3**, toluene-d_8; **5**, benzene-d_8; **6**, toluene-d_8; **7**. THF-d_8. [b] Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5. [c] All measurements were performed at room temperature in the following solvents: **3**, *n*-hexane; **5**, toluene; **6**, toluene; **7**, THF.

valuable as an additional example that a Ti(III) compound, (η^5-C_5H_5)$_2$TiO^{t}Bu, effectively cleaves a metal−metal bond in metal carbonyl dimers to form early−late heterometallic complexes containing Ti(IV) species. Furthermore, formation of the Ti−Co product shown in eq 3 of Scheme 1 offered an intriguing entry to investigate mechanisms of the Ti−Co$_3$ formation shown in eq 2 of Scheme 1. After a detailed investigation, experimental evidence was obtained to suggest the involvement of a Ti−Co intermediate in the formation of the Ti−Co$_3$ complex, from which mechanisms of the Co−Co bond cleavage by the Ti(III) moiety and the cobalt atom recombination are discussed.

Results and Discussion

Reaction of (η^5-C_5H_5)$_2$TiO^{t}Bu (1) with $Co_2(CO)_8$ Leading to Formation of (η^5-C_5H_5)$_2$Ti(O^{t}Bu)(μ_4-OC)$Co_3(CO)_9$ (3). As reported earlier, (η^5-C_5H_5)$_2$TiO^{t}Bu (**1**) is a versatile reagent for cleaving a metal−metal bond in several metal carbonyl dimers.[4] When **1** was treated with 0.5 molar equiv of $Co_2(CO)_8$ in toluene-d_8 at room temperature, the diamagnetic product **3**, showing two singlets at δ 5.93 and 1.05 ppm in ^{1}H NMR spectroscopy, was observed (Table 1). The singlet at δ 5.93 ppm is due to a (η^5-C_5H_5)Ti^{IV} moiety, whereas that at δ 1.05 ppm is assigned to the ^{t}*Bu*O−Ti^{IV} group. Of importance is the stoichiometry of the reaction; a broad singlet due to a ^{t}*Bu*O−Ti^{III} moiety still remained unconsumed. This suggests that the product is not (η^5-C_5H_5)$_2$Ti(O^{t}Bu)(μ-OC)Co(CO)$_3$, which would be the expected product from analogy to the reactions of **1** with (η^5-C_5H_5)$_2$M$_2$(CO)$_6$ to form (η^5-C_5H_5)Ti(O^{t}Bu)(μ-OC)M(CO)$_2$(η^5-C_5H_5) (M = Mo (**2a**), W (**2b**)).[4] In contrast to the fact that **2a** and **2b** showed IR bands due to the bridging CO ligand around 1600 cm^{-1}, the characteristic feature of the Ti−Co product **3** is a ν_{CO} band at 1472 cm^{-1}. The stoichiometry of the reaction and the IR absorption described above indicate that **3** may have a multiply bridging CO ligand to dual cobalt atoms; this is actually proved by the X-ray structure determination of a single crystal of **3**.

As shown in Figure 1, the molecular structure of **3** revealed that **3** has a tricobalt core in which three terminal CO ligands are bonded to each cobalt atom. Representative bond distances and angles as well as crystallographic data are summarized in Table 2 and Table 3, respectively. There is a triply bridging CO ligand, the carbon terminus of which is bound to three cobalt atoms, whereas the oxygen atom is connected to the (η^5-C_5H_5)$_2$TiO^{t}Bu moiety. Two η^5-C_5H_5 ligands, one ^{t}BuO group, and the (OC)Co$_3$(CO)$_9$ group are tetrahedrally arranged around the titanium atom, the oxidation state of which is IV. The Ti−O, O−C, and C−Co(average) bond distances of the Ti−O=C−Co$_3$ moiety are 2.026(5), 1.231(7), and 1.96(2) Å, respectively. The molecular structure of **3** is very similar to that of (η^5-C_5H_5)$_2$Ti(Cl)(μ_4-OC)Co$_3$(CO)$_9$ reported by Schmid;[5a] the only notable difference is the Ti−O distance in the Ti−O=C−Co$_3$ moiety (1.938(8) Å), which is approximately 0.1 Å shorter than that of **3**. The electron negativity of the chlorine atom of (η^5-C_5H_5)$_2$Ti(Cl)(μ_4-OC)Co$_3$(CO)$_9$ causes the enhancement of the Lewis acidity of the titanium center, which results in shortening of the Ti−O bond. Spectroscopic data (^{1}H and ^{13}C NMR and IR) are consistent with the structure of **3**, as shown in Table 1.

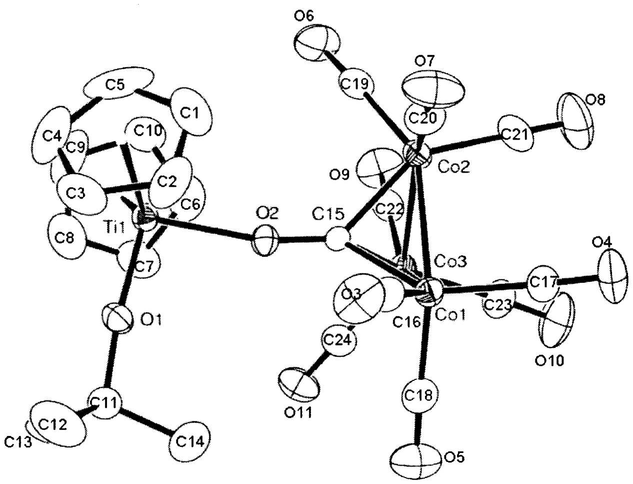

Figure 1. ORTEP drawing of **3** (50% probability of the thermal ellipsoids; hydrogen atoms are omitted for clarity).

The chemical equation shows that the formation of **3** requires treatment of 1.5 equiv of $Co_2(CO)_8$ based on **1**. Reaction of a 1:1.5 mixture of **1** and $Co_2(CO)_8$ in pentane at room temperature for 5 min gave **3** in quantitative yield, on the basis of ^{1}H and ^{13}C NMR analysis of the reaction mixture. Because of the good solubility of **3** in

Table 2. Crystallographic Data for 3, 5, and 7

	3	5	7
empirical formula	$C_{24}H_{19}O_{11}TiCo_3$	$C_{28}H_{39}O_5TiCo$	$C_{22}H_{27}O_6TiCo$
formula wt	708.08	562.45	403.94
temp, K	293(2)	123(2)	123(2)
radiation		Mo Kα (0.710 69 Å)	
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P1$
a, Å	8.8500(5)	9.026(5)	7.628(2)
b, Å	27.7320(17)	21.59(1)	9.686(3)
c, Å	11.8344(6)	30.62(1)	10.081(3)
α, deg	90	109.38(4)	58.36(2)
β, deg	108.8790(10)	94.40(4)	72.66(2)
γ, deg	90	93.22(5)	64.84(2)
V, Å^3	2748.2(3)	5589(4)	571.2(4)
Z	4	8	1
D_{calcd}, mg/m^3	1.711	1.337	1.437
abs coeff, mm^{-1}	2.116	0.913	1.109
F(000)	1416	2368	256
cryst size, mm	0.25 × 0.25 × 0.05	0.70 × 0.30 × 0.15	0.35 × 0.35 × 0.05
θ range, deg	2.34−27.48	4.01−27.48	3.01−27.34
no. of indep rflns	5820 (R(int) = 0.0000)	24 516 (R(int) = 0.0000)	4188 (R(int) = 0.0000)
no. of obsd rflns	3223 ($>2\sigma$)	16 227 ($>2\sigma$)	3985 ($>2\sigma$)
refinement method		full-matrix least squares on F^2	
no. of data/restraints/params	5820/0/352	24516/0/1417	4188/0/271
GOF[a] on F^2	1.006	1.056	1.055
final R indices ($I > 2\sigma(I)$)[b]	R1 = 0.0683[b] wR2 = 0.1281[c]	R1 = 0.0583[b] wR2 = 0.1023[c]	R1 = 0.0597[b] wR2 = 0.1568[c]
R indices (all data)[c]	R1 = 0.1410[b] wR2 = 0.1517[c]	R1 = 0.1061[b] wR2 = 0.1178[c]	R1 = 0.0616[b] wR2 = 0.1589[c]
largest diff peak and hole, e Å^{-3}	0.729 and-0.593	0.500 and −0.598	0.494 and −0.824

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$. [b] R1($F$) = $\sum||F_o| - |F_c||/\sum|F_o|$. [c] wR2($F^2$) = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3, 5, and 7

3		5		7	
Ti(1)−O(1)	1.782(5)	Ti(1)−O(1)	1.818(2)	Ti(1)−O(1)	1.806(4)
O(1)−C(11)	1.417(9)	O(1)−C(21)	1.437(5)	O(1)−C(11)	1.444(6)
Ti(1)−O(2)	2.026(5)	Ti(1)−O(2)	2.130(3)	Ti(1)−O(6)	2.133(4)
O(2)−C(15)	1.231(7)	O(2)−C(25)	1.186(5)	Co(1)−C[b]	1.77(2)
C(15)−Co[a]	1.96(2)	C(25)−Co(1)	1.715(4)	C−O[b]	1.15(1)
Co(1)−C[b]	1.81(4)	Co(1)−C[b]	1.77(1)		
C−O[b]	1.13(3)	C−O[a]	1.14(1)		
Ti(1)−O(1)−C(11)	172.1(5)	Ti(1)−O(1)−C(21)	166.5(3)	Ti(1)−O(1)−C(11)	166.9(3)
Ti(1)−O(2)−C(15)	166.6(4)	Ti(1)−O(2)−C(25)	151.3(3)	O(1)−Ti(1)−O(6)	92.2(15)
O(1)−Ti(1)−O(2)	93.5(2)	O(1)−Ti(1)−O(2)	90.7(1)		
		O(2)−C(25)−Co(1)	178.1(4)		

[a] Average. [b] Average of terminal CO ligand.

pentane, the isolated yield was ~60%. The closest analogy of this reaction is given in a report by Moïse, who treated $(\eta^5\text{-}C_5H_5)_2TiCl$ with $Co_2(CO)_8$ (1.5 equiv) in toluene to give the Schmid complex, $(\eta^5\text{-}C_5H_5)_2Ti(Cl)(\mu_4\text{-}OC)Co_3(CO)_9$. We reexamined Moïse's result and found that the reaction (in toluene-d_8, at room temperature) is much slower than the reaction of **1** with $Co_2(CO)_8$ (incomplete at 72 h). This clearly shows that **1** is an excellent reagent for the effective reductive cleavage of a Co−Co bond in $Co_2(CO)_8$ leading to the Ti−Co heterometallic compound.

As reported earlier, the reaction of **1** with $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W) to give **2a** or **2b** is reversible.[4] The regeneration of $Co_2(CO)_8$ and $(\eta^5\text{-}C_5H_5)_2TiO^tBu$ was not observed by variable-temperature NMR spectra of **3**. However, only a single ^{13}C resonance due to the CO ligands in **3** was observed in toluene-d_8 in the temperature range from −80 °C to room temperature; this suggests that rapid exchange of the coordinated CO groups of the Co_3 core occurs on the NMR time scale during cleavage and reconnection of a Ti−O═C bond in **3**.

Reaction of $(\eta^5\text{-}C_5Me_5)_2TiO^tBu$ (4) with $Co_2(CO)_8$ Leading to Formation of $(\eta^5\text{-}C_5Me_5)_2Ti(O^tBu)(\mu\text{-}OC)Co(CO)_3$ (5). The reaction of **1** with $Co_2(CO)_8$ gave the Ti−Co$_3$ product **3** as described above. When the Ti(III) precursor is switched from **1** to the sterically more bulky $(\eta^5\text{-}C_5Me_5)_2TiO^tBu$ (**4**), a different type of product was obtained which contained only one Ti and one Co atom in the molecule. Treatment of **4** with 0.5 molar equiv of $Co_2(CO)_8$ in toluene-d_8 at room temperature gave the diamagnetic product **5**, showing two singlets at δ 1.65 and 1.48 ppm in ^1H NMR spectroscopy. The singlet at δ 1.65 ppm is due to a $(\eta^5\text{-}C_5Me_5)_2Ti^{IV}$ moiety, whereas that at 1.48 ppm is assigned as a ^{t}BuO−Ti^{IV} group. A large-scale reaction of a 2:1 mixture of **4** and $Co_2(CO)_8$ in pentane at room temperature for 5 min gave **5** quantitatively on the basis of NMR analysis of the reaction mixture. The Ti−Co complex **5** was isolated by recrystallization from THF/pentane (in 67% yield).

As described above, the Ti atom in all of the reported Ti−Co$_3$ complexes is linked to the Co$_3$ moiety by an isocarbonyl bridge. In contrast, it is known that there

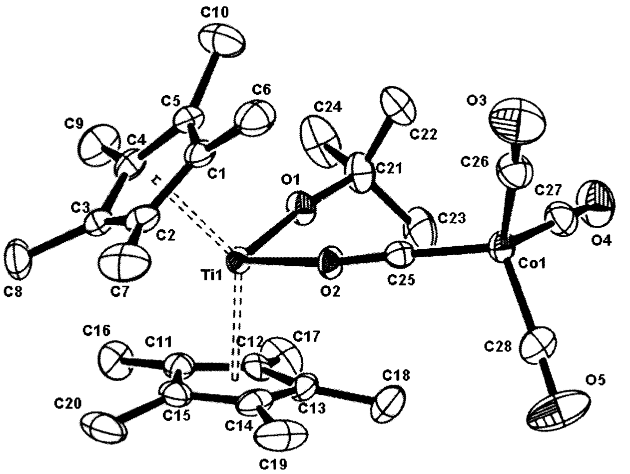

Figure 2. ORTEP drawing of **5** (50% probability of the thermal ellipsoids; hydrogen atoms are omitted for clarity).

are two types of Ti−Co heterobimetallic complexes: one is the type that has a Ti−O=C−Co isocarbonyl bridge,[5,6,8,10] whereas the other is the type that bears a Ti−Co direct bond.[11] As shown in Figure 2, the molecular structure of **5** revealed that **5** is a heterobimetallic complex whose two metals are linked by an isocarbonyl bridge, Ti−O=C−Co. Representative bond distances and angles as well as crystallographic data are summarized in Tables 2 and 3. The tetrahedral arrangement of the ligands, two η^5-C_5Me_5 ligands, one ^tBuO group, and the (OC)Co(CO)$_3$ group, around the titanium center in **5** is similar to that of **3**. The oxidation state is IV. The Ti−O, O−C, and C−Co bond distances of the Ti−O=C−Co moiety are 2.130(3), 1.186(5), and 1.715(4) Å, respectively. The longer Ti−O and shorter C=O bond distances compared with those of **3** result from the effect of electron-donating η^5-C_5Me_5 ligands. Spectroscopic data (^1H and ^{13}C NMR and IR) are consistent with the structure of **5**, as shown in Table 1. Appearance of only a single ^{13}C resonance due to the CO ligands in **5** at a temperature range from −80 °C to room temperature suggests the rapid exchange of the coordinated CO groups of the Co core on the NMR time scale during cleavage and reconnection of a Ti−O=C bond in **5**.

As shown in eq 1 of Scheme 1, the Ti^{III}−O^{t}Bu group actually induces metal−metal bond cleavage in $(\eta^5$-$C_5H_5)_2Mo_2(CO)_6$ and $(\eta^5$-$C_5H_5)_2W_2(CO)_6$, affording the corresponding heterobimetallic complexes which contain one Ti and one Mo or W atom.[4] In the case of $Co_2(CO)_8$, a Ti−Co heterobimetallic complex is formed only when the titanium moiety contains sterically crowded η^5-C_5Me_5 ligands. To look at the molecular structures of **3** and **5** more closely, the Co_3 core in **3** is relatively bulky, and the η^5-C_5H_5 rings of the titanium center are proximate to CO ligands (C(19)=O(6), C(16)=O(3), and C(24)=O(11)) in this core (Figure 1). When the molecular structure of a η^5-C_5Me_5 homologue of **3** is considered, there should be steric hindrance between some CO ligands in the Co_3 core and methyl groups of the η^5-C_5Me_5 ligands. In other words, steric bulkiness of the η^5-C_5Me_5 ligand is likely to prevent the formation of the Co_3 core, even when **5** is allowed to contact excess $Co_2(CO)_8$.

Mechanistic Consideration of Cobalt Atom Recombination. The above results suggest that nuclearity of the Ti−Co heterometallic product by the reaction of Ti(III) *tert*-butoxide and $Co_2(CO)_8$ is dependent on the steric bulkiness around the metal center of the Ti(III) precursor; a tetrametallic product containing a 1:3 ratio of Ti and Co atoms is formed when there is no steric constraint between the Ti and Co_3 moieties. This suggests that there may be a reaction pathway involving the reaction from **1** and $Co_2(CO)_8$ to a heterobimetallic intermediate,[12] $(\eta^5$-$C_5H_5)_2Ti(O^tBu)(\mu$-$OC)Co(CO)_3$ (**6**), i.e., a η^5-C_5H_5 homologue of **5**, which is thought to produce the Ti−Co_3 product **3** by the reaction of **6** with excess $Co_2(CO)_8$. As a closely related hypothesis, Merola and co-workers reported the reaction of either $(\eta^5$-$C_5H_5)_2Ti(CO)_2$ or $(\eta^5$-$C_5Me_5)_2Ti(CO)_2$ with $Co_2(CO)_8$; the former reaction gave a Ti−Co_3 compound, $(\eta^5$-$C_5H_5)_2Ti[(\mu_4$-$OC)Co_3(CO)_9]_2$, whereas the latter produced $[(\eta^5$-$C_5Me_5)_2Ti(\mu$-$OC)Co(CO)_3]_2$, the Ti:Co ratio of which is 1:1.[10] They proposed a mechanism of formation of $(\eta^5$-$C_5H_5)_2Ti[(\mu_4$-$OC)Co_3(CO)_9]_2$ through $[(\eta^5$-$C_5H_5)_2Ti(\mu$-$OC)Co(CO)_3]_2$ on the basis of these findings.

We examined the intermediacy of the Ti−Co compound **6** by the following experiments. In a NMR tube, **1** was treated with $Co_2(CO)_8$ (0.5 equiv with respect to **1**) in toluene-d_8 at −78 °C, and ^1H and ^{13}C NMR measurements were then undertaken at this temperature. The spectra showed two singlets due to the $(\eta^5$-$C_5H_5)_2Ti$ moiety in a ratio of 3:7; the major product was assigned as **6** as described below, whereas the minor product was the Ti−Co_3 species **3**. The product ratio remained unchanged even when the reaction mixture was warmed to room temperature. When a solution of $Co_2(CO)_8$ (0.2 equiv of **1**) was slowly added to a solution of **1** at room temperature, **6** was formed as almost a single heterometallic product. Removal of excess amounts of **1** by washing the reaction mixture with pentane at −30 °C gave **6** containing a small amount of **3**. Characterization of **6** was carried out as follows. First, the characteristic IR absorption of **6** at 1734 cm^{-1} due to the isocarbonyl bridge is similar to that of **5**. ^1H and ^{13}C resonances due to the $(\eta^5$-$C_5H_5)_2TiO^tBu$ group appeared at δ_H 1.03, 5.71 and δ_C 31.49, 115.22 ppm at room temperature.[13] No CO peak was seen in low-temperature ^{13}C NMR spectra due to the rapid CO exchange. Second, treatment of **6** with THF gave the Ti−Co compound $[(\eta^5$-$C_5H_5)_2Ti(O^tBu)(\eta$-$THF)]^+[Co(CO)_4]^-$ (**7**) in quantitative yield on the basis of the IR spectrum. This product was alternatively produced by treatment of **1** with $Co_2(CO)_8$ (0.5 equiv with respect to **1**) in THF, which was unequivocally characterized by crystallography and spectroscopy.[14]

As shown in Figure 3, the molecular structure of **7** revealed that **7** is a cationic titanium complex with the

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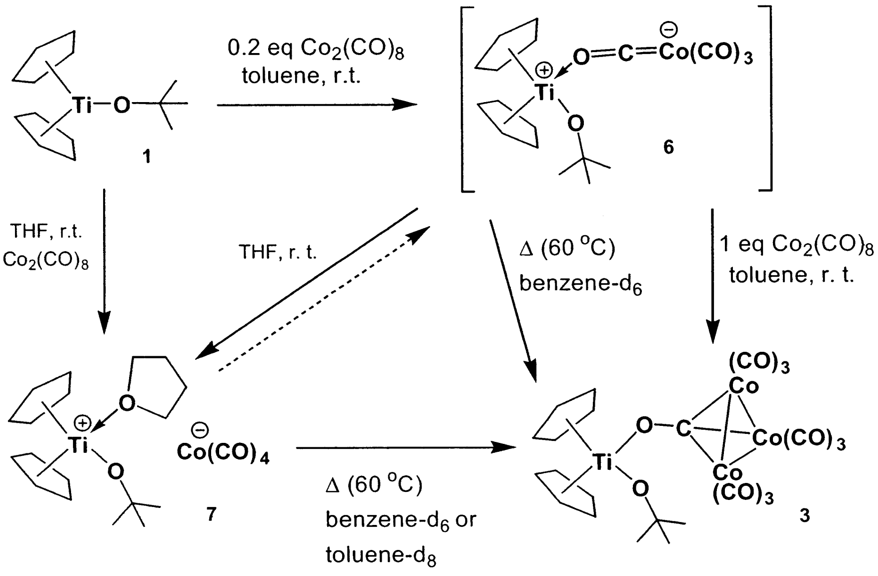
[10] Merola, J. S.; Campo, K. S.; Gentile, R. A. *Inorg. Chem.* **1989**, *28*, 2950.

[11] (a) Selent, D.; Beckhaus, R.; Pickardt, J. *Organometallics* **1993**, *12*, 2857. (b) Jansen, G.; Schubart, M.; Findeis, B.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *J. Am. Chem. Soc.* **1998**, *120*, 7239.

[12] The reaction may involve coupling of a cobalt carbonyl radical with **1**. For a related review, see: Pályi, G.; Ungvary, F.; Galamb, V.; Marko, L. *Coord. Chem. Rev.* **1984**, *53*, 37.

[13] There is an unsolved problem in variable-temperature NMR experiments of **6**. A singlet due to the $(\eta^5$-$C_5H_5)_2Ti$ moiety of **6** broadened at 15 °C, and two separate singlets were observed below 0 °C. A reverse change in the spectra was observed by rewarming the solution to room temperature. This suggests that **6** has two structural isomers which interconvert on the NMR time scale. Further experiments to identify these isomeric structures are underway.

Scheme 2



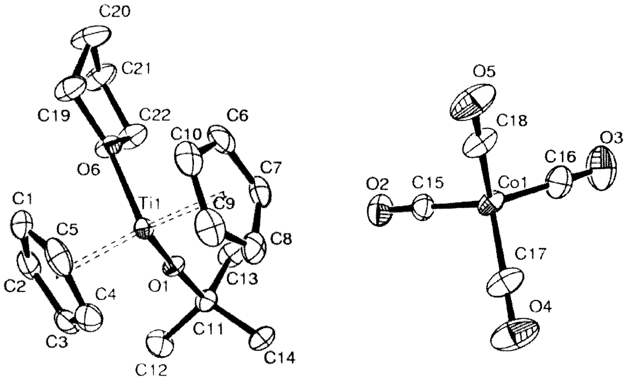


Figure 3. ORTEP drawing of **7** (50% probability of the thermal ellipsoids; hydrogen atoms are omitted for clarity).

oxygen atom of THF bound to the Ti center, which has $Co(CO)_4^-$ species as a counteranion. Representative bond distances and angles as well as crystallographic data are summarized in Tables 2 and 3. The tetrahedral arrangement of the ligands, two η^5-C_5H_5 ligands, one ^tBuO group, and the THF group, around the titanium center in **7** is similar to those in **3** and **5**. The Ti−O(THF) and Ti−O(O^{t}Bu) bond distances are 2.133(4) and 1.806(4) Å, respectively. Spectroscopic data (^1H and ^{13}C NMR and IR) are consistent with the structure of **7** as shown in Table 1. No ^{13}C resonance due to the CO ligands was observed, presumably due to rapid site exchange of CO ligands of the $Co(CO)_4$ moiety in **7** at a temperature range from −60 °C to room temperature.

All of these results suggest the formation of **6** in the reaction of **1** with $Co_2(CO)_8$. The following experiments provided a further clue to understanding whether **6** was an intermediate of the formation of **3** from **1** and $Co_2(CO)_8$. (1) Heating a benzene-d_6 solution of **6** at 60 °C for 12 h gave a mixture of **1** and **3** (**6** → **1** + **3**). (2) Treatment of **6** with $Co_2(CO)_8$ (1 equiv with respect to **6**) at room temperature for 5 min gave **3** as a single product (**6** + $Co_2(CO)_8$ → **3**). (3) When the THF adduct **7** was heated in benzene-d_6, **6** and uncoordinated THF appeared first, and then a mixture of **1**, **3**, and uncoordinated THF was formed (**7** → **6** + THF, and then **6** → **1** + **3**). Thus, there apparently exist two reaction pathways, one from a mixture of **1** and $Co_2(CO)_8$ to give **6**, and the other being through **6** to give **3**.

Mechanistic Considerations. The results presented in this paper demonstrate the special reactivity of (η^5-C_5H_5)$_2$TiO^{t}Bu (**1**) and its η^5-C_5Me_5 homologue **4** in the reductive cleavage of a Co−Co bond in $Co_2(CO)_8$ leading to formation of heterometallic products. The Ti(III) complex **1** is also a good precursor for a Ti−Mo or Ti−W heterobimetallic complex in reacting with (η^5-C_5H_5)$_2$$Mo_2(CO)_6$ or (η^5-C_5H_5)$_2$$W_2(CO)_6$, as shown in eq 1 of Scheme 1. A series of reactions of **1** with various metal carbonyl dimers reveals that the heterobimetallic product formation proceeds when the electrochemical potentials for the reduction of the M−M bond are lower than 1.6 V;[4] the reduction potential of $Co_2(CO)_8$ actually measured by cyclic voltammetry was 0.9 V.[15] The mechanism of the reaction of **4** with $Co_2(CO)_8$ to form the heterobimetallic product is similar to that of **1** with (η^5-C_5H_5)$_2$$Mo_2(CO)_6$ or (η^5-C_5H_5)$_2$$W_2(CO)_6$. However, additional explanation is necessary for the formation of the Ti−Co_3 product in the reaction of **1** with $Co_2(CO)_8$. The experiments to capture the heterobimetallic intermediate **6** described above account for the two-step reaction pathway **1** + $Co_2(CO)_8$ → **6** and **6** + $Co_2(CO)_8$ → **3** (Scheme 2). A possible mechanism is illustrated in Scheme 3. As pointed out in the literature, Lewis acid promoted (Ti(IV)) recombination of $Co_2(CO)_8$ gave the Lewis acid adduct of (μ_4-OC)$Co_3(CO)_9$.[9] Lewis acid activation of a CO ligand in the $Co(CO)_4$ moiety in **3** or **6** makes the mononuclear cobalt species unstable, leading to clustering of the cobalt atoms to form the Co_3 core. The reaction of the Ti−Co product with $Co_2(CO)_8$

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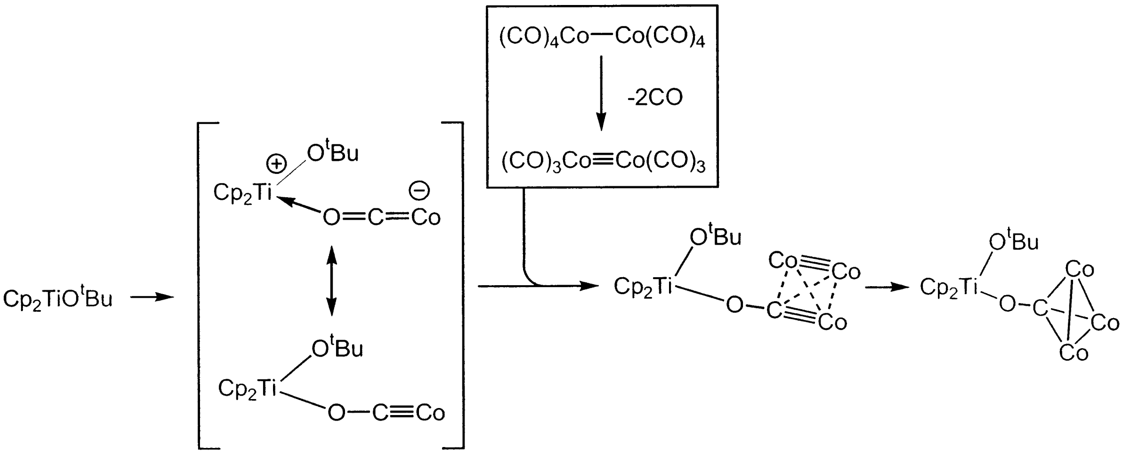
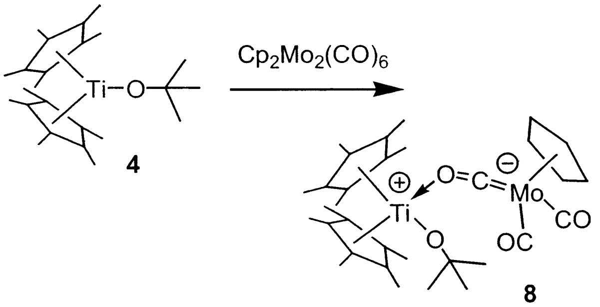
[14] For other ionic Ti−Co complexes, see: (a) Merola, J. S.; Campo, K. S.; Gentile, R. A.; Modrick, M. A. *Inorg. Chim. Acta* **1989**, *165*, 87. (b) Schubart, M.; Mitchell, G.; Gade, L. H.; Kottke, T.; Scowen, I. J.; McPartlin, M. *Chem. Commun.* **1999**, 233.

[15] Cyclic voltammetric studies were carried out using a BAS 50 B/W electrochemical analyzer in a glovebox. A platinum working electrode, a platinum-wire counter electrode, and a silver reference electrode comprised of a silver wire in contact with 0.01 M $AgNO_3$ and 0.2 M ($^nBu)_4N^+PF_6^-$ in acetonitrile were used. The measurement was carried out using a THF solution of the sample (2 × 10^{-4} M) and ($^nBu)_4N^+PF_6^-$ (0.1 M; supporting electrolyte) in the presence of a small amount of ferrocene (internal standard). The scan rate was 0.1 V/s.

Scheme 3



Scheme 4



is not favorable and only occurred when the cobalt center was protected by the bulky ligands on the titanium atom.

An interesting feature of the formation of the Ti−Mo and Ti−W complexes **2a** and **2b** shown in eq 1 of Scheme 1 is that the reaction is essentially reversible, and regeneration of **2a** or **2b** back to the starting materials was confirmed experimentally. In sharp contrast, no reverse pathway has yet been observed from either the (η^5-C_5Me_5)Ti−Co complex (**5**) or the (η^5-C_5H_5)-Ti−Co intermediate (**6**). We believe that the Ti−Co heterobimetallic compound formation is also essentially reversible, but the equilibrium is much more favorable to heterobimetallic product formation. In fact, reversible cleavage of a Ti−O bond in **5** or **6** is suggested from the rapid CO exchange process observed in ^{13}C NMR spectra. There was a recent homologous discovery in our laboratory: treatment of (η^5-C_5Me_5)$_2$Ti(O^{t}Bu) (**4**) with (η^5-C_5H_5)$_2$Mo$_2$(CO)$_6$ afforded the corresponding Ti−Mo product (η^5-C_5Me_5)Ti(O^{t}Bu)(μ-OC)Mo(CO)$_2$(η^5-C_5H_5) (**8**) (Scheme 4), the molecular structure of which is shown in Figure 4. This reaction should be reversible by analogy to the reaction shown in eq 1 of Scheme 1; however, the equilibrium was not observed in ^{1}H NMR spectroscopy at room temperature. Variable-temperature ^{13}C NMR spectra revealed a CO scrambling process, indicating reversible cleavage of the Ti−O bond.

Conclusion

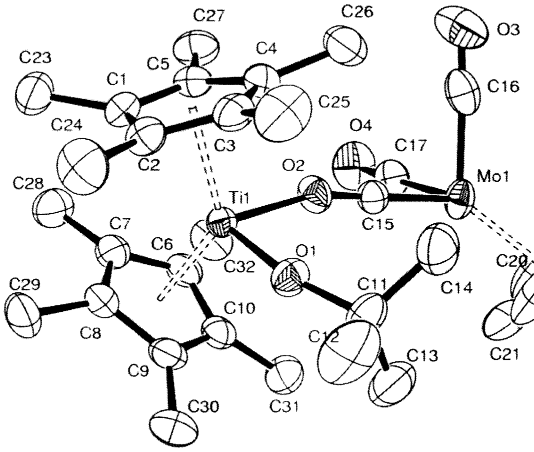


Figure 4. ORTEP drawing of **8** (50% probability of the thermal ellipsoids; hydrogen atoms are omitted for clarity).

In summary, we have proved that the titanocene (III) *tert*-butoxides **1** and **4** are good reagents to cleave a Co−Co bond of $Co_2(CO)_8$ (E_{red} = 0.9 V). By appropriate choice of the η^5-C_5H_5 ligand in the titanocene(III) precursor, both the Ti−Co_3 tetranuclear complex **3** and the Ti−Co dinuclear complex **5** can be synthesized by the reaction between the Ti(III) complex **1** and $Co_2(CO)_8$. These are unequivocally characterized by crystallography and spectroscopy. The η^5-C_5H_5 version of **5**, (η^5-C_5H_5)$_2$Ti(O^t-Bu)(μ-OC)Co(CO)$_3$ (**6**), is also isolable, though it includes a small amount of **3** as an impurity. Thus, the Ti(III)-induced Co−Co bond cleavage reaction is an efficient preparative method for Ti−Co heterometallic compounds which would be valuable for homogeneous catalysis, as described in the Introduction. Application of these new Ti−Co complexes to organic synthesis is already in progress.

Apart from the synthetic merit, the mechanisms to form Ti−Co_3 complexes, which have often been seen in Ti−Co heterobimetallic chemistry, have been confirmed by isolation of **6**; a series of reactions, which contain thermal decomposition of **6**, the reaction of **6** with $Co_2(CO)_8$, and reversible reaction of **6** with THF, revealed the involvement of **6** as an intermediate in the reaction of **1** and $Co_2(CO)_8$ to give the Ti−Co_3 product **3**. These findings have contributed to a better understanding of the chemistry of Ti−Co EHLB complexes.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere using glovebox techniques. THF, benzene, toluene, and pentane were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. THF-d_8, toluene-d_8, benzene-d_6, THF, toluene, benzene, and *n*-pentane were degassed and dried over Na/K alloy (THF-d_8) or benzophenone ketyl (other solvents). Other reagents were used as received. The ^{1}H NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer. Chemical shifts (δ) are recorded in ppm from the solvent signal. IR spectra are recorded in cm^{-1} on a JASCO FT/IR-550 spectrometer. The Ti(III) complexes **1**[4] and **4**[16] were prepared according to the published methods. ^{1}H and ^{13}C NMR and IR data are summarized in Table 1.

Preparation of (η^5-C_5H_5)$_2$(^{t}BuO)Ti(μ_4-OC)$Co_3(CO)_9$ (3). (η^5-C_5H_5)$_2$TiO^{t}Bu (**1**; 40 mg, 0.16 mmol) and $Co_2(CO)_8$ (40 mg, 0.12 mmol) were placed in a 20 mL Schlenk tube. Pentane (10 mL) was added, and the resulting homogeneous dark red solution was stirred for 5 min at room temperature. Slow evaporation of the solvent from the reaction mixture gave black crystals of the desired product **3** (20 mg, 40%). Anal. Calcd for $C_{24}H_{19}O_5TiCo_3$: C, 40.80; H, 2.82. Found: C, 40.70; H, 2.70. Mp 130 °C dec.

Preparation of (η^5-C_5Me_5)$_2$(^{t}BuO)Ti(μ-OC)Co(CO)$_3$ (5). (η^5-C_5Me_5)$_2$TiO^{t}Bu (**4**; 40 mg, 0.10 mmol) and $Co_2(CO)_8$ (17 mg, 0.050 mmol) were placed in a 20 mL Schlenk tube. Benzene (4 mL) was added, and the resulting homogeneous dark red solution was stirred for 5 min at room temperature. The solvent was removed in vacuo, and the residue was recrystallized at −30 °C from a mixture of toluene and pentane to give brown crystals of **5** (38 mg, 0.067 mmol, 67%). Anal. Calcd for $C_{28}H_{39}O_5TiCo$: C, 59.79; H, 6.99. Found: C, 59.57; H, 7.03. Mp 125 °C dec.

Preparation of the Ti−Co Bimetallic Intermediate (η^5-C_5H_5)$_2$(^{t}BuO)Ti(μ-OC)Co(CO)$_3$ (6). A toluene solution (2 mL) of $Co_2(CO)_8$ (34 mg, 0.1 mmol) was added to a toluene solution (2 mL) of **1** (91 mg, 0.36 mmol) in a 20 mL Schlenk tube. The resulting brown solution was stirred for 5 min at room temperature, and the solvent was removed in vacuo. The residue was washed with cold *n*-pentane (2 mL) and recrystallized at −30 °C from a mixture of toluene and pentane to give tiny brown crystals of **6** (15 mg, 15% yield). The product **6** contained a small amount of **3** as an impurity; which made it difficult to carry out elemental analysis. Mp 60 °C dec.

Preparation of the Ti−Co Complex [(η^5-C_5H_5)$_2$(^{t}BuO)Ti(η-THF)]$^+$[Co(CO)$_4$]$^-$ (7). In a 20 mL Schlenk tube were placed (η^5-C_5H_5)$_2$TiOC(CH_3)$_3$ (91 mg, 0.36 mmol) and $Co_2(CO)_8$ (34 mg, 0.1 mmol). THF (4 mL) was added, and the resulting brown-red solution was stirred for 5 min at room temperature. The solvent was removed in vacuo, and the residue was recrystallized at −30 °C from a mixture of THF and pentane to give brown crystals of **7** (42 mg, 50% yield). Mp 107 °C dec. Anal. Calcd for $C_{22}H_{27}O_5TiCo$: C, 53.46; H, 5.51. Found: C, 53.22; H, 5.46.

Preparation of the (η^5-C_5Me_5)Ti−Mo Complex (η^5-C_5Me_5)$_2$(^{t}BuO)Ti(μ-OC)Mo(CO)$_3$(η^5-C_5H_5) (8). In a 20 mL Schlenk tube were placed **4** (40 mg, 0.102 mmol) and (η^5-C_5H_5)$_2$$Mo_2(CO)_6$ (24 mg, 0.049 mmol). Then, benzene (4 mL) was added, and the resulting red solution was stirred for 5 min at room temperature. The solvent was removed in vacuo, and the residue was recrystallized at −30 °C from a mixture of THF and pentane to give brown crystals of **8** (45 mg, 0.071 mmol, 70%). Mp 188 °C dec. Anal. Calcd for $C_{32}H_{44}O_4TiMo$: C, 60.38; H, 6.97. Found: C, 60.37; H, 6.91. ^{1}H NMR (600 MHz, C_6D_6, room temperature): δ 1.51 (9H, s, ^{t}Bu), 1.78 (30H, s, Cp*), 5.40 (5H, s, Cp). ^{13}C{^{1}H} NMR (150 MHz, C_6D_6, room temperature): δ 13.00 (Me of ^{t}Bu), 34.50 (Me of Cp*), 89.16 (Cp), 233.50 (terminal CO), 241.34 (bridging CO) (Cp* = η^5-C_5Me_5). IR (KBr): ν(cm^{-1}) 1923 s, 1833 s, 1653 s. Crystallographic data as well as the bond distances and angles are shown in the Supporting Information.

X-ray Data Collection and Reduction. Single crystals of **3**, **5**, **7**, and **8** were grown from pentane (in the case of **3**), THF/pentane (in the case of **5** and **7**), or toluene/pentane (in the case of **8**). X-ray crystallography was performed on an Enraf-Nonius CAD4 four-circle axis diffractometer (for **3**) or a Rigaku RAXIS RAPID imaging plate diffractometer (for **5**, **7**, and **8**) with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å). The data were collected at 293(2) K (**3** and **8**) and 123(2) K (**5** and **7**) using $\omega-2\theta$ scans in the θ range of $2.34 \le \theta \le 27.48°$ (**3**) and using ω scans in the θ range of $4.01 \le \theta \le 27.48°$ (**5**), $3.01 \le \theta \le 27.34°$ (**7**), and $1.82 \le \theta \le 27.48°$ (**8**). Data collection and cell refinement of **3** were done using the program system "CAD4 Express" on a MS VAX computer, whereas those of **5**, **7**, and **8** were done using "MSC/AFC Diffractometer Control" on a Pentium computer. The structures were solved by direct methods (SIR92 (for **3** and **8**)[17a] or SIR2002 (for **5** and **7**)[17b]) and were refined using full-matrix least squares (SHELXL97)[17c] based on F^2 values of all independent reflections measured. All H atoms were located at ideal positions. They were included in the refinement but restricted to riding on the atom to which they were bonded. Isotropic thermal factors of H atoms were held to 1.2−1.5 times (for methyl groups) the U_{eq} values of the riding atoms.

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Supporting Information Available: Molecular structures and X-ray crystallographic data of **3**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0340701

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[16] Pattiasina, J. W.; Heeres, H. J.; van Bolhuis, F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1004.

[17] (a) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435. (b) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna., R. SIR2002; 2003. (c) Sheldrick, G. M. SHELXL-97; 1997.