Thermally or Photochemically Induced Reductive Cleavage of Metal−Metal Bonds of Metal Carbonyl Dimers by a Titanocene(III) *tert*-Butoxide: Novel Reversible Access to Heterobimetallic Complexes

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Novel synthetic methods for Ti−Mo, Ti−W, and Ti−Ru heterobimetallic complexes are established by the reaction of a certain titanium(III) alkoxide and the corresponding metal carbonyl dimer, $[CpM(CO)_n]_2$ [M = Mo, W ($n = 3$); M = Ru ($n = 2$)]. Thus, a novel monomeric titanium complex, $Cp_2Ti(OtBu)$ (**1**), which is synthesized from Cp_2TiCl and KO*t*Bu and characterized by spectroscopy and crystallography, smoothly reacts with $[CpM(CO)_3]_2$ (M = Mo (**2a**), W (**2b**)) to give heterobimetallic complexes, $Cp_2Ti(OtBu)(\mu\text{-}OC)M(CO)_2Cp$ (M = Mo (**3a**) and W (**3b**)), of which two metallic moieties are linked by the isocarbonyl bridge. Similar reaction of **1** with $[CpRu(CO)_2]_2$ (**4**) does not occur thermally, but is accomplished under photoirradiation to afford $Cp_2(OtBu)Ti{-}Ru(CO)_2Cp$ (**5**), of which two metallic moieties are linked by a direct metal−metal bond. Use of **1** is particularly important for these reactions; other titanium alkoxides such as $[Cp_2Ti(OMe)]_2$ and $Cp_2Ti[O(2,6\text{-}tBu_2\text{-}4\text{-}Me)C_6H_2]$ do not react with the metal carbonyl dimers. An interesting feature of these new heterobimetallic complexes, **3a**, **3b**, and **5**, is the existence of the thermal fragmentation process to regenerate the starting materials: **3a** or **3b** is actually in equilibrium with a mixture of **1** and **2a** or **1** and **2b**, respectively [$\Delta G^0_{298K} = -4.1 \pm 0.2$ kcal mol^{-1} (**3a**), -4.3 ± 0.2 kcal mol^{-1} (**3b**)]. The Ti−Ru compound **5** thermally undergoes fragmentation to regenerate **1** and **4**. The formation of these heterobimetallic complexes is formally considered as the metal−metal bond cleavage of metal carbonyl dimers by a Ti(III) reducing reagent; possible mechanisms are discussed.

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Introduction

Heterobimetallic complexes have attracted much attention from organometallic chemists in relation to model studies on the surface reaction of heterogeneous catalysts and potential cooperative reactivity of both metal centers leading to discovery of new catalytic reactions.[1] Among them, complexes containing a group IV metallocene moiety and a $CpM(CO)_n$ fragment (M = Fe, Ru, Mo, and W) are one of the most in-depth investigated classes of compounds.[2,3] Two types of these compounds are known: one is a complex having a direct metal−metal bond such as $Cp_2(OtBu)Zr{-}Ru(CO)_2Cp$,[3a] whereas in the other two metal fragments are linked by an isocarbonyl bridge, e.g., $Cp_2Zr(Me)(\mu\text{-}\eta^1{:}\eta^1\text{-}OC)\text{-}Mo(CO)_2Cp$.[3e] Access to these heterodinuclear complexes is typically accomplished by reaction of M−X (X = halogen atoms and other leaving groups) with anionic metal species, e.g., $Cp_2(OtBu)Zr{-}Ru(CO)_2Cp$ from $Cp_2(OtBu)ZrCl$ and $[Ru(CO)_2Cp]^-K^+$,[3a] or condensation reaction, e.g., $Cp_2Zr(Me)(\mu\text{-}\eta^1{:}\eta^1\text{-}OC)Mo(CO)_2Cp$ from Cp_2ZrMe_2 and $HMo(CO)_3Cp$.[3d] Since it is well known that alkali metal reduction of $[CpM(CO)_n]_2$ gives the corresponding alkali metal salt of the $CpM(CO)_n$ anion,[4] reduction of $[CpM(CO)_n]_2$ by an appropriate transition metal reducing reagent ($M'L_n$) may lead to the formation of $CpM(CO)_n{-}M'L_n$. However, examples of such reactions, in which the products were well-characterized, are

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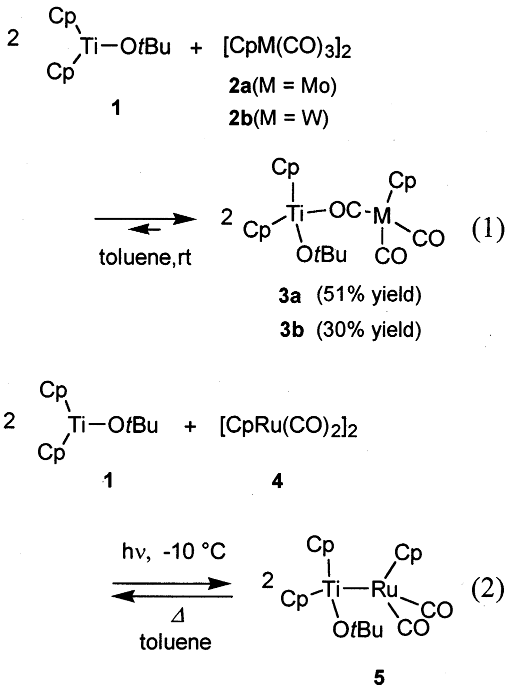
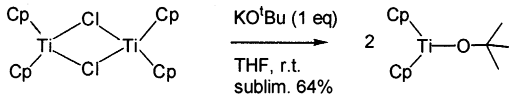
Scheme 1



rare except a series of work on Ti(or Zr)−Mo complexes obtained by the reaction between [Cp_2Ti^{III}(or Zr^{III})PR_2]$_2$ with [CpMo(CO)$_3$]$_2$ reported by Stephan and co-workers.[5−8]

In this paper, we wish to report a novel synthetic route to Ti−Mo, Ti−W, and Ti−Ru heterobimetallic complexes by the reductive cleavage of the metal−metal bond in [CpMo(CO)$_3$]$_2$ (**2a**), [CpW(CO)$_3$]$_2$ (**2b**), and [CpRu(CO)$_2$]$_2$ (**4**) by a particular Ti(III) compound, Cp$_2$TiO*t*Bu (**1**). Thus, the reaction of **1** with **2a** or **2b** takes place instantly to form heterobimetallic complexes, in which two metal moieties are linked by the isocarbonyl bridge, Cp$_2$Ti(O*t*Bu)(μ-OC)M(CO)$_2$Cp [M = Mo (**3a**) and W (**3b**)] as shown in Scheme 1, eq 1. In sharp contrast, reaction of the ruthenium dimer **4** with **1** does not occur thermally, but actually produces Cp$_2$(O*t*Bu)Ti−Ru(CO)$_2$Cp (**5**), in which the titanium and ruthenium moieties are linked by a direct Ti−Ru bond, with the aid of photoirradiation (Scheme 1, eq 2). As described above, these types of synthetic routes to heterobimetallic complexes containing titanium and other metals are rare in thermal reaction, whereas there is no example of photoassisted reactions. Furthermore, the reactions have the following interesting features. First, in both of the reactions shown in Scheme 1, eqs 1 and 2, Cp$_2$Ti(O*t*Bu) is a special reagent to realize the formation of the heterobimetallic complexes; other Ti(III) compounds such as [Cp$_2$TiCl]$_2$ and other titanocene(III) alkoxides did not react with the metal carbonyl dimers. Second, the formed heterobimetallic complexes are thermally labile, and the reactions from **3a** or **3b** to a mixture of **1** and **2a** or **1** and **2b**, respectively, are in equilibrium with the heterobimetallic complex formation. In the case of the Ti−Ru complex **5**, photochemically generated **5** undergoes fragmentation to regenerate **1** and **4** when the solution stands in the dark for a while. To our knowledge, neither heterobimetallic complexes with thermal reversibility nor those formed by thermally reversible photochemical reactions have been reported in the literature.

Scheme 2



Results and Discussion

Preparation of Cp$_2$TiO*t*Bu (1). As briefly noted in the Introduction, our new synthetic route to heterobimetallic complexes is accomplished by a particular titanocene(III) compound, Cp$_2$TiO*t*Bu (**1**). Titanocene(III) alkoxides are reportedly prepared by reactions of [Cp$_2$TiCl]$_2$ with alkali metal alkoxides,[9] by amine elimination from [Cp$_2$TiNMe$_2$]$_2$ from alcohols,[9] and by treatment of Cp$_2$TiMe$_2$ with Si(OR)$_3$H (R = Me and Et).[10] X-ray crystallography of the titanocene methoxide and ethoxide reveals their dinuclear structures including two bridging alkoxides,[10] whereas [Cp$_2$TiOAr] (Ar = 2,6-*t*Bu-4-MePh) having a bulky phenoxy group is proved to have a monomeric form.[11] However, the preparative method and the structure of titanocene(III) *tert*-butoxide, Cp$_2$TiO*t*Bu (**1**), are unknown to our best knowledge.

Compound **1** was successfully prepared by the reaction of [Cp$_2$TiCl]$_2$ with KO*t*Bu in THF (Scheme 2), and purification of **1** was facilely achieved by sublimation of the product to afford dark green crystals in 65% yield. Although the other titanocene(III) alkoxides, [Cp$_2$TiOR]$_2$ (R = Me, Et), have reportedly dimeric structures as described above,[10] crystallography and the ESR spectrum (in toluene) unequivocally showed this particular compound **1** to be a monomeric form. Similar to its Cp* homologue, **1** is a paramagnetic compound showing an ESR signal at $g = 1.977$ and a broad ^{1}H resonance due to the *t*Bu group at δ −0.04.[12] The molecular structure of **1** is shown in Figure 1. Representative bond distances and angles are listed in Table 1. The interatomic Ti(1)−O(1) bond length of **1** is 1.810(3) Å, which is similar to those of analogous monomeric compounds

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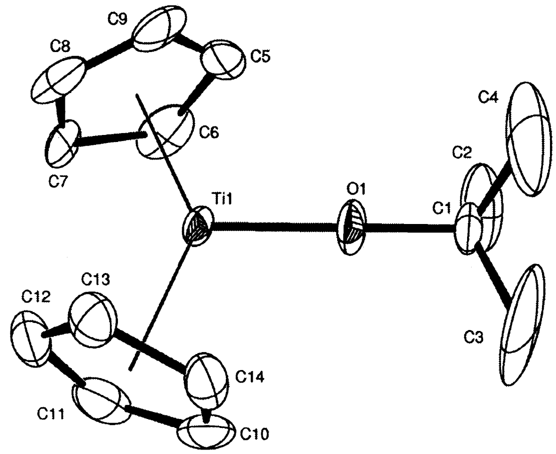

Figure 1. Molecular structure of **1**. Anisotropic displacement parameters are drawn at 50% probability. All hydrogen atoms were omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1

Ti(1)−O(1)	1.810(3)	Ti(1)−C(9)	2.361(12)
O(1)−C(1)	1.411(5)	Ti(1)−C(10)	2.412(13)
Ti(1)−C(5)	2.376(4)	Ti(1)−C(11)	2.373(16)
Ti(1)−C(6)	2.389(12)	Ti(1)−C(12)	2.405(4)
Ti(1)−C(7)	2.400(10)	Ti(1)−C(13)	2.384(13)
Ti(1)−C(8)	2.398(11)	Ti(1)−C(14)	2.377(13)
Ti(1)−O(1)−C(1)	175.4(11)	O(1)−C(1)−C(3)	107.7(5)
O(1)−C(1)−C(2)	108.0(9)	O(1)−C(1)−C(4)	109.4(12)

$Cp_2Ti(O\text{-}2,6\text{-}tBu\text{-}4\text{-}MePh)$ (1.892(2) Å)[11] and $(C_5Me_4H)_2TiOtBu$ (1.8425(14) Å).[13] In contrast, the Ti−O bond distance of the dimeric $[Cp_2Ti(OMe)]_2$ or $[Cp_2Ti(OEt)]_2$ (Ti−O distance: 2.065(2) or 2.076(3) Å, respectively) is about 0.25 Å longer than that of **1**.[10] The Ti(1)−O(1)−C(1) bond angle is almost linear (175.4(11)°), and this Ti−O−C bond angle is the highest in linearity among those of the monomeric titanocene alkoxides including $Cp_2Ti(O\text{-}2,6\text{-}tBu_2\text{-}4\text{-}MePh)$ (Ti−O−C = 142.3(2)°)[11] and $(C_5Me_4H)_2TiOtBu$ (Ti−O−C = 162.16(13)°).[13] The short Ti−O bond length and Ti−O−C linearity suggest that the lone pair of an oxygen atom in **1** effectively contributes to stabilizing the titanium center by electron donation.[14]

Preparation of $Cp_2Ti(OtBu)(\mu\text{-}OC)M(CO)_2Cp$ {M = Mo (3a) and W (3b)}. Treatment of **1** with 0.5 equiv of the Mo or W dimer, **2a** or **2b**, in toluene at room temperature resulted in 90% conversion of the starting materials to form the heterobimetallic complex, **3a** or **3b**, respectively (Scheme 1, eq 1). In contrast, the reactions of $[CpM(CO)_3]_2$ (M = Mo and W) with $[Cp_2TiCl]_2$ or titanocene(III) alkoxides, $[Cp_2TiOMe]_2$, $[Cp_2TiOEt]_2$, and $Cp_2Ti(O\text{-}2,6\text{-}tBu_2\text{-}4\text{-}MePh)$, resulted in complete recovery of the starting materials. Although these reactions are reversible as described below, isolation of **3a** (51% isolated yield) or **3b** (40% isolated yield) was successfully achieved by addition of hexane to the reaction mixture.

Table 2. Spectral Data for 3a and 3b

		3a	3b
^1H NMR[a] (^{13}C NMR), δ	CH of Cp_2Ti	5.91 (117.2)	5.94 (117.1)
	CH of CpMo(W)	5.29 (89.4)	5.19 (87.8)
	CH_3 of O*t*Bu	1.07 (31.2)	1.07 (31.1)
	CO	(226.9, 248.1)	(214.3, 242.5)
IR (KBr), cm^{-1}	ν_{CO}	1920 s, 1833 s, 1648 m, 1612 m	1909 s, 1813 s, 1601 s

[a] In toluene-d_8.

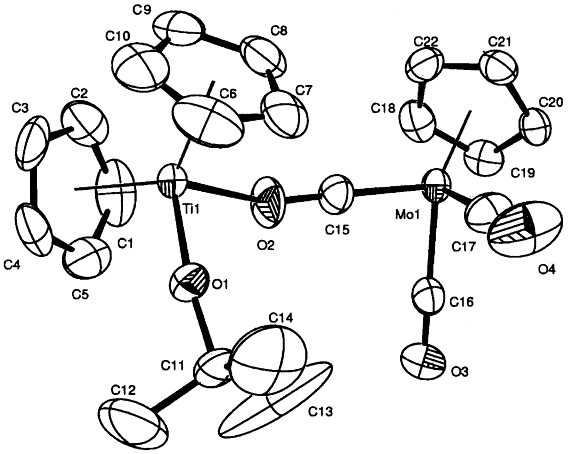

Figure 2. Molecular structure of **3a**. Anisotropic displacement parameters are drawn at 50% probability. All hydrogen atoms were omitted for clarity.

NMR spectra demonstrate that **3a** and **3b** are diamagnetic. Their ^1H and ^{13}C resonances are listed in Table 2. In the ^1H NMR, three singlets due to the Cp_2Ti, CpMo, and Me of *t*Bu in **3a** appeared at δ 5.91, 5.29, and 1.07, whereas those due to the Cp_2Ti, CpW, and Me of *t*Bu in **3b** were observed at δ 5.94, 5.19, and 1.07. The ^{13}C resonances due to the Cp_2Ti, CpMo, and Me of *t*Bu of **3a** at δ 117.2, 89.4, and 31.2 were also consistent with those of **3b** at δ 117.1, 87.8, and 31.1. The ^{13}C signal assigned as the μ_2-carbonyl ligand was observed at δ 248.1 (**3a**) or 242.5 (**3b**), and the IR absorptions appeared at 1648 and 1612 (**3a**) or 1601 cm^{-1} (**3b**) (Table 2). All of the spectral data of **3a** or **3b** in Table 2 seem to be consistent with the structure in which two metal moieties are linked by the bridging carbonyl ligands as shown in Scheme 1, eq 1. However, it was pointed out by Norton and co-workers that identification of the isocarbonyl bridge from other possible μ_2-carbonyl ligands was difficult based on the spectroscopic evidence.[3i,6] To obtain unequivocal evidence, we next carried out an X-ray structure determination of **3a**.

The molecular structure of **3a** is illustrated in Figure 2. The titanium atom is bonded to the oxygen atom of the one of the CO ligands, whereas the molybdenum atom is bound to its carbon terminus. As shown in Table 3, the Ti(1)−O(2), O(2)−C(15), and C(15)−Mo(1) bond lengths of the bridging isocarbonyl ligand are 2.073(3), 1.206(5), and 1.880(4) Å, respectively. The bond angles Ti(1)−O(2)−C(15) and Mo(1)−C(15)−O(2) are 150.4(3)° and 176.4(4)°, respectively. These bond distances and angles around the isocarbonyl bridge are similar to those in $[Cp^*_2Ti(CH_3)(\mu,\eta^1:\eta^1\text{-}OC)MoCp(CO)_2]$[3h] (*A*) and $[Cp_2Ti(thf)(\mu,\eta^1:\eta^2\text{-}OC)MoCp(CO)_2]$[5c] (*B*); the Ti−O, O−C, and C−Mo distances are 2.057(3), 1.212(5), and 1.875(4) Å in *A*, whereas they are 2.128(3), 1.205(5), and 1.876(4) Å in *B*. The Ti−O−C and Mo−C−O bond angles are 144.3(3)° and 178.8(4)° in *A*, while they are 145.0(3)° and 178.0(4)° in *B*. In these complexes, the bonding

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Table 3. Selected Bond Distances (Å) and Angles (deg) for 3a

Ti(1)−O(1)	1.769(3)	O(1)−C(11)	1.416(5)
Ti(1)−O(2)	2.073(3)	O(2)−C(15)	1.206(5)
Mo(1)−C(15)	1.880(4)	O(3)−C(16)	1.158(6)
Mo(1)−C(16)	1.950(5)	O(4)−C(17)	1.156(7)
Mo(1)−C(17)	1.935(5)		

C(11)−O(1)−Ti(1)	171.2(3)	O(4)−C(17)−Mo(1)	178.4(6)
C(15)−O(2)−Ti(1)	150.4(3)	C(15)−Mo(1)−C(17)	89.5(2)
O(1)−Ti(1)−O(2)	91.73(15)	C(15)−Mo(1)−C(16)	85.69(19)
O(2)−C(15)−Mo(1)	176.4(4)	C(17)−Mo(1)−C(16)	86.9(2)
O(3)−C(16)−Mo(1)	179.7(5)		

mode of the Ti−O−C−Mo moiety is considered to be "$Ti^{+}\leftarrow O{=}C{=}Mo^{-}$" rather than its resonance structure, "Ti−O−C=Mo". We consider from the structural similarity between **3a** and *A* or *B* that **3a** also has the "$Ti^{+}\leftarrow O{=}C{=}Mo^{-}$" bonding mode. The molecular structure of the W homologue **3b** was also determined by crystallography, which is almost identical to that of **3a**.[15]

When the crystals of **3a** or **3b** were dissolved in toluene-d_8, some portions of the starting carbonyl dimer, **2a** or **2b**, were regenerated. This result suggests that formation of the heterobimetallic complexes shown in Scheme 1, eq 1, is thermally reversible. In fact, the ratios of **3a** to **2a** or **3b** to **2b** at 22, 40, and 60 °C were determined by NMR to be 80:20, 72:28, and 63:37 or 81:19, 77:23, and 68:32, respectively: the calculated $\Delta G^{0}{}_{298K}$ of generation of **3a** was -4.1 ± 0.2 kcal mol^{-1}, whereas that of **3b** was -4.3 ± 0.2 kcal mol^{-1}. Such reversibility of **3a** and **3b** had not been reported in other heterobimetallic complexes.

These results reveal that the reaction of **1** with **2a** or **2b** leads to the bond formation between the titanium atom in **1** with the oxygen atom in a CO ligand in **2a** or **2b**, which is accompanied by oxidation of Ti(III) to Ti(IV). Cleavage of the metal−metal bond in **2a** or **2b** furnishes the formation of the Ti−Mo or Ti−W compounds bearing the isocarbonyl bridge, **3a** or **3b**. The closest examples of these reactions including unequivocal determination of the heterobimetallic products are reported by Stephan and co-workers; reaction of titanium (III) phosphide complexes, $Cp_2Ti(\mu\text{-}PR_2)_2TiCp_2$, with **2a** gave $Cp_2Ti(\mu\text{-}PR_2)(\mu\text{-}CO)Mo(CO)Cp$ in benzene, whereas it resulted in formation of $Cp_2Ti(\eta\text{-thf})(\mu\text{-}CO)Mo(CO)_2Cp$ in THF.[5c] Both of the reactions involve the cleavage of the Mo−Mo bond in **2a**, and in the former case, the reaction is accompanied by the oxidation of Ti(III) to Ti(IV). It is complicated that the former reaction involves dissociation of a CO ligand, whereas the μ-phosphide ligand is eliminated in the latter reaction. A striking feature of the reaction of **1** with **2a** or **2b** different from Stephan's results is that the reaction does not involve any elimination reaction, being essentially in equilibrium with **1** + **2a** or **2b**. In other words, the present report discloses the first example of thermally reversible heterobimetallic formation by way of reductive cleavage of the metal−metal bond in **2a** or **2b** by a Ti(III) species.

Table 4. Spectral Data for 5 and $Cp_2Zr(OtBu)Ru(CO)_2Cp$[a]

		5	$Cp_2Zr(OtBu)Ru(CO)_2Cp$
^{1}H NMR (^{13}C NMR), δ	CH of Cp_2Ti	5.81 (109.8)[b]	5.92 (111.5)[c]
	CH of CpRu	4.50 (86.6)[b]	4.61 (86.8)[c]
	CH_3 of O*t*Bu	1.14 (31.9)[b]	1.16 (32.1)[c]
	CO	(207.9)[b]	(207.9)[c]
IR (KBr), cm^{-1}	ν_{CO}	2028 m, 1956 s	1958 s, 1884 s

[a] Ref 3a. [b] In toluene-d_8, at room temperature. [c] In benzene-d_6, at room temperature.

Photochemical Formation of $Cp_2Ti(OtBu)Ru(CO)_2Cp$ (5). We examined thermal reaction of **1** with other metal carbonyl dimers, but many of them did not give the corresponding heterobimetallic compounds (vide infra). Although attempted thermal reaction of **1** with $[CpRu(CO)_2]_2$ (**4**) did not result in the formation of Ti−Ru compounds, to our surprise, the desired reaction was accomplished photochemically (Scheme 1, eq 2). A toluene-d_8 solution of a 1:2 mixture of **4** and **1** was irradiated with a 500 W Xe lamp for 4 h at −10 °C, during which no thermal reverse reaction (vide infra) occurred. Studies on the wavelength dependency of this photochemical reaction using UV cutoff filters revealed that irradiation through the $\lambda > 420$ nm or $\lambda > 500$ nm filter resulted in complete consumption of **1** and **4** after 4 h, whereas no reaction took place with light of $\lambda > 600$ nm. The reaction with light through a UV interference filter of 450 ± 10 nm was more efficient than that with light of 360 ± 10 nm; the conversion of **4** reached 97% after 3 h in the former reaction, whereas it was only 36% in the latter after 20 h.

^{1}H and ^{13}C{^{1}H} NMR spectra of the irradiated solution revealed formation of a diamagnetic product with complete consumption of the starting materials. Unfortunately, extremely high air and moisture sensitivity of the product and the existence of a thermally reversible pathway as described below have thwarted our efforts to obtain single crystals suitable for X-ray crystallography to be successful. However, the fact that the spectroscopic features are nearly identical to those of crystallographically identified $Cp_2Zr(OtBu)Ru(CO)_2Cp$[3a] as shown in Table 4 strongly suggests that the product can be assigned as $Cp_2Ti(OtBu)Ru(CO)_2Cp$ (**5**), in which the titanium and ruthenium moieties are linked by a Ti−Ru bond. The ^{1}H and ^{13}C resonances due to Cp_2Ti, CpRu, and Me of O*t*Bu of **5** (δ_H 5.81, 4.50, and 1.14, and δ_C 109.8, 86.6, and 31.9) are quite similar to those due to Cp_2Zr, CpRu, and Me of O*t*Bu of $Cp_2Zr(OtBu)Ru(CO)_2Cp$ (δ_H 5.92, 4.61, and 1.16, and δ_C 111.5, 86.8, and 32.1).[3a] Only a single ^{13}C resonance due to the CO ligand (−15 °C) was visible at δ 207.9, which is similar in its chemical shift as that of the Zr−Ru complex. This suggests that the product contains only terminal CO ligands as the Zr−Ru complex does,[3a] and this is supported by its IR spectrum of **5** ($\nu = 2028$ and 1956 cm^{-1}). The Ti−Ru complex formed by the reaction of **1** with **4** has a direct Ti−Ru bond; this is in sharp contrast to the fact that the two-metal unit is linked by an isocarbonyl bridge in the Ti−Mo and Ti−W complexes described above. Similar differences in the bonding mode between the two-metal units are also seen in other heterobimetallic complexes; Ti(or Zr)−Ru complexes have a direct metal−metal bond, whereas Ti(or Zr)−Mo or Ti(or Zr)−W compounds have an isocarbonyl bridge or a μ_2,η^2-CO ligand.[3]

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[15] Two chemically equivalent but crystallographically independent structures are included in a unit cell. The bond lengths and angles in the crystal structure of **3b** are similar to those of **3a** except that the Ti−O−C angles in the $Ti^{+}\leftarrow O{=}C{=}W^{-}$ unit [137.9(7)° and 139.7(7)°] are smaller than that of **3a**. Details are described in the Supporting Information.

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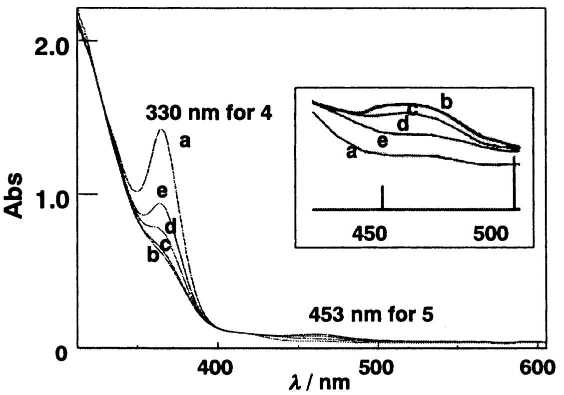


Figure 3. UV–visible spectra of thermally reversible photochemical reaction: (a and b) before and just after the irradiation (6 min, 450 W high-pressure Hg lamp, rt) of **1** + **4** (1:1, 1×10^{-4} M in cyclohexane); (c–e) conversion of **5** to **1** + **4** in the dark (c 1 h, d 5 h, e 28 h).

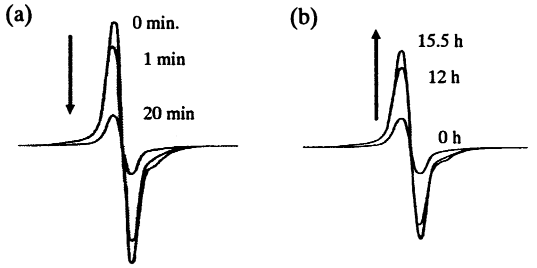
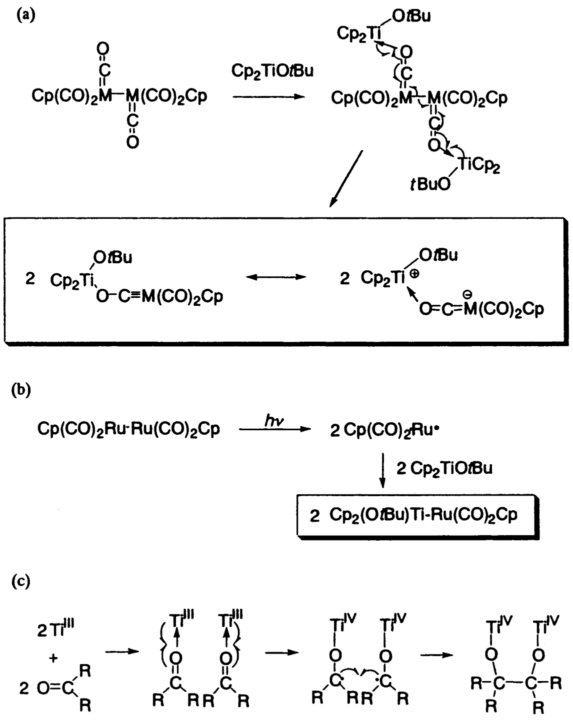


Figure 4. ESR spectra of thermally reversible photochemical reaction (1×10^{-3} M in toluene, rt): (a) irradiation of **1** + **4** to **5** (500 W Xe lamp, through 440 nm UV cutoff filter, −5 °C); (b) thermal reaction (rt) of **5** to **1** + **4**.

In contrast to thermal stability of the Zr–Ru homologue, the Ti–Ru complex **5** is labile, and the reverse reaction to a mixture of **1** and **4** occurrs. The thermal fragmentation is also seen in the Ti–Mo and Ti–W complexes as described above. NMR observation revealed that **5** was completely converted to a mixture of **4** and **1** when the solution of **5** was kept at 40 °C in the dark for 30 h. Photochemical conversion from **1** and **4** to **5** and its thermal reaction actually resulted in a significant change of color of the solution (**1** + **4** orange vs **5** dark red). Time-dependent UV–vis spectra are shown in Figure 3. As soon as a cyclohexane solution of **1** + **4** was irradiated, the band at 330 nm, which is assignable to $d\sigma \rightarrow d\sigma^*$ transition of **4**,[16] diminished and the peak at 453 nm appeared. The signal at 330 nm was regenerated when the irradiated solution stood in the dark for 28 h. This reversible reaction of Ti(III) $\rightleftarrows$ Ti(IV) also caused a change in the EPR signal intensity; the EPR signal due to **1** was decreased with the irradiation, whereas it was increased when heated in the dark (Figure 4). These spectral changes were repeatable several times.

This photochemical reaction and the thermal reaction of the molybdenum or tungsten dimer described above resemble each other in the fact that the titanium(III) complex induces the metal–metal bond cleavage in the metal carbonyl dimer, which furnishes the formation of the heterobimetallic complex. The fragmentation of the formed heterobimetallic complex to the starting materials is also a feature in both of the reactions. A striking difference in these two reactions is an essential requirement of photoirradiation in the reaction of the ruthenium dimer and a difference in the structure of the product; the Ti–Ru complex has a direct Ti–Ru bond, whereas two metallic moieties are linked by the isocarbonyl bridge in the Ti–Mo and Ti–W compounds. This type of photochemical reaction has not been reported in the literature. As a related reaction, photochemical synthesis of heterobimetallic compounds, e.g., $[M(CO)_n]_2 + [M'(CO)_m]_2 \rightarrow 2(CO)_nM-M'(CO)_m$, was investigated by Wrighton and co-workers;[17] however, the reaction is essentially in equilibrium to produce a statistical mixture of the starting materials and the product and cannot be applied to synthesis of heterobimetallic complexes containing a titanium atom.

Scheme 3



Mechanistic Consideration. As described above, the Ti(III) compound **1** effectively induces reductive cleavage of the metal–metal bond in Mo_2, W_2, and Ru_2 complexes either thermally or photochemically. The thermal reaction may be analogous to well-known alkali metal or alkali earth metal reduction of metal carbonyl dimers to produce anionic metal carbonyl complexes.[2] For example, reduction of $[CpFe(CO)_2]_2$ by Na/Hg gives the corresponding $Na[CpFe(CO)_2]$, which is characterized by spectroscopy and crystallography.[18] In the reaction of **1** and **2a** or **2b**, the titanium(III) complex may act as a reducing reagent instead of alkali or alkali earth metals. A possible mechanism is illustrated in Scheme 3 (a). Since the titanium(III) is not a powerful reducing reagent ($E_{ox} = -0.9$ V) and has strong oxophilicity, we propose a mechanism containing the

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coordination of the oxygen atom in **2a** or **2b** to the titanium center followed by electron transfer from the titanium to the molybdenum or tungsten species which furnishes the metal−metal cleavage to form the heterobimetallic complexes. The first two steps of this mechanism, namely, coordination of the oxygen atom in a substrate to a Ti(III) species followed by electron transfer from the Ti center to the substrate via the inner sphere mechanism, may be analogous to the well-known mechanism of the pinacol coupling in organic chemistry as shown in Scheme 3 (c).[19] Since reduction of the metal carbonyl dimers leads to metal−metal bond cleavage reactions,[4] their reduction potential might have correlation to their reactivity toward titanocene(III) *tert*-butoxide **1**. Cyclic voltammetric studies of **2** showed that $E_{red} = -1.4$ V (**2a**) and -1.6 V (**2b**).[20] Preliminary CV measurements of several other metal carbonyl dimers suggested that the complex shown in $E_{red} > -1.6$ V underwent thermal cleavage of the metal−metal bond by **1**.[21]

Since E_{red} of the Ru_2 complex **4** is -2.4 V, thermal reaction does not take place. Many examples are reported about the photochemical cleavage of the metal−metal bond in metal carbonyl dimers.[22] As described above, photoirradiation of a mixture of $[M(CO)_n]_2$ and $[M'(CO)_m]_2$ provides $(CO)_nM-M'(CO)_m$ via formation and recombination of $^{\bullet}M(CO)_n$ and $^{\bullet}M'(CO)_m$.[17] It is also known that homolytic cleavage of the metal−metal bond in $[CpRu(CO)_2]_2$ upon irradiation of UV or visible light leads to formation of an unstable radical $Cp(CO)_2Ru^{\bullet}$.[22] Experiments using UV cutoff filters revealed that efficient reaction occurred with light of $\lambda > 500$ nm, where there is absorption of **4** but no peak of **1**. Thus, the photochemical assistance in the reaction of **1** with **4** presumably leads to homolysis of the Ru−Ru bond to produce $Cp(CO)_2Ru^{\bullet}$, which reacts with a paramagnetic **1** to form diamagnetic **5** as shown in Scheme 3 (b). Trapping of the metal radical species by Ti(III) compounds has not been reported to our knowledge.

Another interesting feature in these reactions is the essential requirement of Cp_2TiO*t*Bu (**1**). Neither the Ti^{III} dimers such as $[Cp_2TiCl]_2$,[23] $[Cp_2TiOMe]_2$,[10] and $[Cp_2TiOEt]_2$[10] nor the monomeric Cp_2TiOAr (Ar = 2,6-bis(*tert*-butyl)-4-methylphenyl),[11] where the OAr group spatially occupies most of the coordination sphere of the Ti atom,[11] promotes the metal−metal bond cleavage of **2a**, **2b**, or **4**. In other words, both the μ-alkoxy bridge of the dimeric Ti^{III} species and the steric hindrance of the OAr group inhibit the contact of the titanium center with the carbonyl oxygen of the metal carbonyl dimers to result in no formation of the heterobimetallic complexes. The appropriate size of the O*t*Bu group allows the reaction with other metallic species.

Conclusion

In summary, novel paramagnetic Ti^{III} complex Cp_2TiO*t*Bu (**1**) was prepared and its monomeric structure was determined by X-ray crystallography. This compound **1** reacts with homodinuclear carbonyl complexes, **2a** and **2b**, thermally to form the corresponding heterobimetallic compounds having the isocarbonyl bridge, **3a** and **3b**, respectively. In contrast, photochemical reaction ($\lambda > 500$ nm) of **1** with **4** gave the Ti−Ru compound, in which the titanium and ruthenium moieties are linked by the direct Ti−Ru bond. In all cases, thermal fragmentation of the resulting heterobimetallic compounds was observed; **3a** (or **3b**) was in equilibrium with a mixture of **1** and **2a** (or **2b**), whereas **5** was completely converted to a mixture of **1** and **4** in the dark. The reactions are governed by two factors; one is the essential importance of monomeric Cp_2TiO*t*Bu, whereas the other is the reduction potential of the metal carbonyl dimers. We propose the mechanism involving the inner sphere electron transfer process shown in Scheme 3 (a) for the thermal process and that through a 17-electron metal radical in the photochemical process. It is of interest that the particular Ti(III) compound efficiently induces the reversible formation of heterobimetallic complexes which involves the oxidation of the Ti(III) species and fission of the metal−metal bond in the metal carbonyl dimers. We consider that this reversible formation of the heterobimetallic complexes is an interesting entry to the organometallic molecules, which thermally or photochemically change the magnetic property due to the Ti(III) species. In this context, exploration aimed at construction of the intramolecular version of this reversible system is under way.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, THF, hexane, and toluene-d_8 were distilled from benzophenone ketyl just before use. KO*t*Bu was sublimed just before use. $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$ were used as purchased. $[CpRu(CO)_2]_2$[24] and $[Cp_2TiCl]_2$[25] were prepared according to the literature. NMR spectra were taken with a JEOL Lambda 400 or 600 spectrometer. Chemical shifts are given in ppm, relative to the solvent (toluene-d_8) signal (^{1}H, δ 2.09; ^{13}C, δ 20.4). IR spectra were recorded in cm^{-1} on a JASCO FT/IR-550 spectrometer. ESR spectra were measured with a JEOL JES-RE2X, and a benzene solution of DPPH (1×10^{-4} M, $g = 2.0036$) was used as an external standard.

Preparation of $Cp_2TiOC(CH_3)_3$ (1). In a Schlenk tube, $[Cp_2TiCl]_2$ (204 mg, 0.479 mmol) and KO*t*Bu (111 mg, 0.982 mmol) were dissolved in toluene (ca. 15 mL) at room temperature, and the reaction mixture was stirred for 5 h. Insoluble products (KCl) were removed by filtration, and the filtrate was

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[20] Cyclic voltammetry: scan rate 100 mV/s, solvent THF, electrolyte 0.1 M $TBAPF_6$, working electrode Pt, reference electrode Ag/Ag^+. The irreversible reduction waves were observed in the cyclic voltammetry of the metal carbonyl dimer, whereas the oxidation wave appeared irreversible in the voltammogram of **1**. A general review of cyclic voltammetry of metal complexes: Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; Wiley-VCH: New York, 1995.

[21] Reaction of cobalt carbonyl dimers, $Co_2(CO)_8$ ($E_{red} = -0.7$ V) and $Co_2(CO)_6(P(OPh)_3)_2$ (-1.4 V) with **1** led to Co−Co bond cleavage; however, the product is not $Cp_2Ti(O$*t*$Bu)(\mu$-$CO)Co(CO)_n(L)_{3-n}$ (L = CO, $P(OPh)_3$). In contrast, no reaction occurred when **1** was treated with $[CpNi(CO)]_2$ (-1.7 V), $Co_2(CO)_6(PEt_3)_2$(-1.8 V), $[CpFe(CO)_2]_2$ (-1.9 V), or $Re_2(CO)_{10}$ (-2.6 V). Niibayashi, S.; Matsubara, K.; Nagashima, H. Manuscript in preparation.

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concentrated in vacuo. The resulting air-sensitive solids were sublimed in vacuo (55 °C, 1 × 10^{-3} Torr) to give dark green crystals of **1** (155 mg, 0.62 mmol, 64%). Mp: 88 °C(dec). ^{1}H NMR (toluene-d_8, 23 °C): δ 0.03 (s(br), 9H, *t*Bu). The ^{1}H signal of the cyclopentadienyl ring was not observed. ESR (toluene, 23 °C): *g* 1.977. HRMS(EI) *m*/*e* calcd for $C_{14}H_{19}OTi$ 251.0915, found 251.0919. Anal. Calcd for $C_{14}H_{19}OTi$: C, 66.93; H, 7.62. Found: C, 67.04; H, 7.81.

Preparation of $Cp_2Ti(O\mathit{t}Bu)(\mu\text{-}\eta^1{:}\eta^1\text{-}OC)M(CO)_2Cp$ (3a, M = Mo; 3b, M = W). For example, a mixture of **1** (15 mg, 0.06 mmol) and $[CpMo(CO)_3]_2$ (10 mg, 0.02 mmol) was dissolved in toluene (1 mL). After the solution was stirred for 5 min, *n*-hexane was added to the resulting dark red solution. The mixture was kept at −30 °C. Crystals of **3a** grown from the solution were separated by decantation (10 mg, 0.02 mmol, 51% yield). The compound **3b** was also isolated as crystals from a mixture of **1** (32 mg, 0.13 mmol) and $[CpW(CO)_3]_2$ (28 mg, 0.04 mmol) in THF by adding *n*-pentane; crystals of **3b** are grown from the solution at −30 °C (20 mg, 0.03 mmol, 40% yield). **3a**: Mp: 121 °C (dec). ^{1}H NMR (toluene-d_8): δ 5.91 (s, 10H, CpTi), 5.29 (s, 5H, CpMo), 1.07 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 226.9 (2C, CO), 248.1 (1C, CO), 117.19 (CpTi), 89.35 (CpMo), 31.17 (Me of *t*Bu). IR (KBr, cm^{-1}): ν(CO) 1920 s, 1833 s, 1648 m, 1612 m. Anal. Calcd for $C_{22}H_{24}O_4TiMo$: C, 53.25; H, 4.87. Found: C, 53.30; H, 4.88. **3b**: Mp: 110 °C (dec). ^{1}H NMR (toluene-d_8): δ 5.94 (s, 10H, CpTi), 5.19 (s, 5H, CpW), 1.07 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (toluene-d_8): 214.25 (2C, CO), 242.47 (1C, CO), 117.08 (CpTi), 87.81 (CpW), 31.09 (Me of *t*Bu). IR (KBr, cm^{-1}): ν(CO) 1909 s, 1813 s, 1601 s. Anal. Calcd for $C_{22}H_{24}O_4TiW$: C, 45.23; H, 4.14. Found: C, 44.91; H, 3.82. Crystals of **3b** were used for elemental analysis. The purity was confirmed by ^{1}H NMR of these crystals at −80 °C, and details are described in the Supporting Information.

Reaction of 1 with $[CpRu(CO)_2]_2$. In a Schlenk tube, **1** (15 mg, 0.06 mmol) and **4** (10 mg, 0.02 mmol) were dissolved in toluene (ca. 3 mL) at room temperature, and the mixture was irradiated by a 500 W Xe lamp for 4 h at −10 °C with stirring. The solvent was removed in vacuo to give **5** as red solids. This material contained a small amount of impurity (∼20%) which was formed by the decomposition of **5**. Attempted purification of **5** was unsuccessful due to its high sensitivity. ^{1}H NMR (toluene-d_8, 23 °C): δ 5.81(s, 10H, CpTi), 4.50(s, 5H, CpRu), 1.14(s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (toluene-d_8, −15 °C): δ 109.83 (CpTi), 86.57 (CpRu), 31.90 (Me of *t*Bu), 207.85 (CO). IR (KBr, cm^{-1}): ν(CO) 2028 m, 1956 s.

X-ray Crystallography. Crystal data and measurement data of both **1** and **3a** are summarized in Table 5. Results of crystallographic analysis of **3b** are shown in the Supporting Information. X-ray crystallography was performed on an Enraf-Nonius CAD4 four-cycle axis diffractometer (for **1**) or Rigaku RAXIS RAPID imaging plate diffractometer (for **3a** and **3b**) with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). The diffraction data of **1** were collected at 173(2) K using $\omega-2\theta$ technique in the θ range of 2.68° ≤ θ ≤ 27.46°, whereas those of **3a** and **3b** were collected at 293(2) and 123(2) K in the θ range 1.51° ≤ θ ≤ 27.48° and 3.00° ≤ θ ≤ 27.48°, respectively (44 oscillation exposures). Data collection and cell refinement of **1** were carried out using the program system CAD4 Express on a MS VAX computer, whereas those of **3a** and **3b** were done using MSC/AFC Diffractometer Control on a Pentium computer. These structures were solved by the direct method (SIR-97)[26a] and were refined using full-matrix least squares (SHELXL-97)[26b] based on F^2 of all independent reflections measured. All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located at ideal positions and were included in the refinement, but were restricted to ride 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) U_{eq} of the parent atoms.

Table 5. X-ray Crystallographic Data for 1 and 3a

	1	**3a**
empirical formula	$C_{14}H_{19}OTi$	$C_{22}H_{24}O_4TiMo$
fw	251.19	546.55
cryst syst	orthorhombic	triclinic
space group	$Pna2_1$	$P\bar{1}$
a, Å	8.4742(11)	10.2111(7)
b, Å	16.383(4)	13.5423(11)
c, Å	10.231(3)	8.1300(5)
α, deg	90	92.215(4)
β, deg	90	108.879(2)
γ, deg	90	85.251(4)
V, Å^3	1317.2(5)	1060.02(13)
Z	4	2
D_{calcd}, Mg/m^3	1.267	1.555
abs coeff (μ, mm^{-1})	0.627	0.992
F(000)	532	504
cryst size, mm	1.00 × 0.30 × 0.20	0.50 × 0.40 × 0.04
no. of reflns measd	1591	4508
no. of ind reflns	1591 [R(int) = 0.00]	4508 [R(int) = 0.00]
no. of reflns obsd (>2σ)	1217	3815
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF[a]	1.068	1.092
R_1 (I>2σ(I))[b]	0.0477	0.0437
wR_2 (I>2σ(I))[b]	0.1246	0.1087
R_1 (all data)[c]	0.0751	0.0566
wR_2 (all data)[c]	0.1405	0.1170
$\Delta\rho$ max, e Å^{-3}	0.437 and −0.983	0.606 and −0.882

[a] GOF = $[\sum w(F_o^2 - F_c^2)_2/(N - P)]^{1/2}$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR(F_2) = [\sum w(F_o^2 - F_c^2)_2/\sum w(F_o^2)^2]^{1/2}$.

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Supporting Information Available: Details of crystallographic data of **1**, **3a**, and **3b** and explanation for the purity of **3** including a ^{1}H NMR chart. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020869L

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