Synthesis and Reactions of Titanoxycarbene-Metal Carbonyl Complexes

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A family of titanoxycarbene-metal carbonyl complexes of formula $\overline{Cp^*_2TiOC(=ML_n)CH_2CH_2}$ (**3**), where $Cp^*=\eta^5\text{-}C_5Me_5$ and $ML_n=Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $Mn_2(CO)_9$, and $Re_2(CO)_9$, has been prepared by the treatment of titanocene–ethylene complex **1** with metal carbonyls of group 6 and 7. Complex **3b** crystallizes in space group $P2/a$ ($Z=8$) with cell constants $a=30.401(1)$, $b=9.251(1)$, $c=27.561(5)$ Å, $\beta=105.73(1)$°, and $V=7460(2)$ Å^3 (data taken at −40 °C, 6715 reflections, $R=0.069$). Two independent molecules of **3b** in crystal make an enantiomorphic pair. A notable feature of the structure is the long distance of Ti–O bond coupled with the short distance of C(2)–O bond, which is characterized by a large contribution of zwitterionic canonical form **7**. Thermal decomposition of **3** affords ethylene and the corresponding metal carbonyls, indicating that the C(carbenic)–C(3) bond fission occurred selectively, which is rather unusual for conventional Fischer-type carbene complexes. Complexes **3** react rapidly with atmospheric pressure of carbon monoxide below −30 °C to produce cyclic acyltitanium complexes **12**. The reverse reactions occur even below −30 °C upon replacement of carbon monoxide by argon. Complex **3b** also reacts with *t*-butyl isocyanide with a cleavage of the Ti–O bond to give 1:2 adduct **17**, whose molecular structure has been elucidated by X-ray crystallography [$P2_1/n$ with cell constants $a=14.964(2)$, $b=26.207(4)$, $c=14.719(3)$ Å, $\beta=100.30(1)$°, and $V=5679(2)$ Å^3 (measured at −120 °C, 5311 reflections, $R=0.068$)], revealing that it has a novel zwitterionic structure possessing (η^2-imidoyl)titanium cation and anionic acyldirhenium carbonyl moieties linked by an ethylene bridge. The controlled experiments show that complex **16** in which acyl ligand is trans to the Re–Re bond is the precursor of complex **17**. Complex **18**, a tungsten analogue of **17**, has also been prepared. Reactions of **3b** and **3e** with acetylenes are also described.

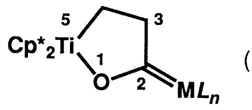
Activation of carbon monoxide by coordination to transition metals has been actively investigated.[1] Fischer and his co-workers in their pioneering works accomplished synthesis of so-called Fischer-type carbene–metal complexes by the reaction of carbon monoxide coordinated to transition metals of group 6 and 7 with nucleophiles followed by alkylation.[2,3] Recently a new entry to a synthesis of Fischer-type carbene complexes has been developed, which is based on the reaction of early transition metal or actinoid metal complexes such as (1,3-diene)zirconocene, (η^2-aryne)zirconocene, (dinitrogen)zirconocene, and so on with a variety of metal carbonyls to form carbene–metal complexes.[4,5] We have found that titanocene–ethylene complex **1** reacts readily with metal carbonyl complexes of group 6 and 7 to afford new cyclic titanoxycarbene–metal carbonyl complexes and revealed their characteristic features in molecular structures and chemical properties.[6]

Results and Discussion

Preparation of Cyclic Titanoxycarbene–Metal Carbonyl Complexes 3. The reaction of titanocene–ethylene complex **1** with decacarbonyldirhenium (**2b**) in toluene-d_8 was monitored by ^{1}H NMR measurement. Above −30 °C, resonances due to complex **1** disappeared slowly and a new set of two triplets assignable to complex **3b** appeared reaching to 84% yield. Above −10 °C, however, amount of **3b** decreased gradually and ethylene was formed, which indicates that the product **3b** starts to decompose even at −10 °C. Therefore, a mixture of complexes **1** and **2b** in toluene was stirred at −20 °C for 48 h and then the reaction mixture was diluted with hexane to afford after cooling to −80 °C titanoxycarbene–dirhenium carbonyl complex **3b** as orange red prisms in 57% yield (Eq. 1). The isolated **3b** is relatively stable and decomposes at 95—99 °C. Similar reaction of **1** with decacarbonyldimanganese (**2a**) gave complex **3a** in 30% isolation yield. This approach can also be applied to the reaction of **1** with metal carbonyls of group 6 transition metals. Thus, complexes **3c** and **3e** were isolated as orange solids in 26% and 34% yields, respectively. The molybdenum derivative **3d** was also formed

$$\underset{\mathbf{1}}{Cp^*_2Ti(C_2H_4)} \quad + \quad O{\equiv}C{-}ML_n \quad \xrightarrow{-20\ ^\circ C}$$

2a, $ML_n = Mn_2(CO)_9$
2b, $ML_n = Re_2(CO)_9$
2c, $ML_n = Cr(CO)_5$
2d, $ML_n = Mo(CO)_5$
2e, $ML_n = W(CO)_5$



(1)

3a, $ML_n = Mn_2(CO)_9$
3b, $ML_n = Re_2(CO)_9$
3c, $ML_n = Cr(CO)_5$
3d, $ML_n = Mo(CO)_5$
3e, $ML_n = W(CO)_5$

Table 1. ^{1}H and ^{13}C NMR Spectral Data of Complexes 3[a]

Complex		Chemical shift[b]/ppm				
		C (3)	C (4)	C (carbene)	Cp*	CO
3a	^{1}H	4.20	1.53 (6.8)		1.74	
	^{13}C	80.34 (124)	65.99 (130)	333.97	11.93 (127)	226.45 225.60 218.58
3b	^{1}H	4.02	1.60 (7.1)		1.78	
	^{13}C	85.02 (124)	66.35 (128)	289.76	11.96 (127)	200.95 199.04
3c	^{1}H	4.35	1.62 (6.9)		1.78	
	^{13}C	81.01 (124)	67.44 (129)	349.79	11.99 (127)	220.19 225.2 (broad)
3d	^{1}H	4.20	1.65 (7.0)		1.78	
	^{13}C	82.10 (122)	67.87 (129)	344.94	12.09 (128)	209.30
3e	^{1}H	4.10	1.60 (7.1)		1.78	
	^{13}C	83.59 (124)	67.56 (127)	328.36	12.02 (127)	201.07[c] 205.2 (broad)

a) All spectra were recorded in toluene-d_8 at $-30\,^\circ$C using solvent absorptions at $\delta=2.31$ (^{1}H) and $\delta=137.70$ (^{13}C) as internal standards. b) Coupling constants are given in parentheses (Hz). c) $J_{\text{C-W}}=125$ Hz.

from **1** and Mo(CO)$_6$, but it was too unstable to be isolated in pure form and characterized based solely on NMR spectra. Similar tendency in stability has been observed for the carbene complexes of the type (CO)$_5$-M=C(OCH$_3$)R (M=Cr, Mo, W; R=CH$_3$ and C$_6$H$_5$).[3)]

The structures of titanoxycarbene–metal carbonyl complexes **3a**—**e** were assigned based mainly on the elemental analyses and spectroscopic data. The NMR spectral data of complexes **3** are summarized in Table 1. The absorptions due to C(3) methylene protons (δ= 4.02—4.35) appear at a little lower field than those due to methylene protons α to the carbenic carbon of Fischer-type carbene complexes [e.g. δ=3.22 for (CO)$_5$W=C(OCH$_3$)CH_2CH$_3$].[7)] ^{13}C{^{1}H} NMR spectra exhibited absorptions due to carbenic carbons in the range of 290—350 ppm which are comparable with the chemical shift values of carbenic carbons reported for Fischer-type carbene complexes.[8)] The chemical shift values of C(4) methylene protons and ^{13}C resonances due to C(4) are also comparable with those of titanacyclopentanes.[9–11)]

The trans structure of dinuclear metal carbonyl moieties in **3a** and **3b** were determined based on ^{13}C{^{1}H} NMR spectra, which exhibited three absorptions for **3a** and two for **3b** due to coordinated carbon monoxide. In the ordinary syntheses of Fischer-type carbene complexes of dinuclear group 7 metal carbonyls, nucleophiles are known to attack initially equatorial CO which has lower electron density than axial ones, while, in the present reaction, electrophilic titanium atom reacts with axial CO having a higher electron density. Moreover, in the trans complexes **3a** and **3b**, the steric interaction between CO on rhenium atom and Cp* ligands on titanium is minimized.

When NMR spectra of complexes **3a**—**c** and **3e** were monitored over a temperature range of 0—30 °C, quantitative formations of ethylene and the corresponding metal carbonyls were observed. The fate of titanocene moiety has not been revealed. Clear first-order disappearance of these complexes was observed. Plots of these observed first-order rate constants were made as shown in Fig. 1 for complex **3a**, which gave activated parameters summarized in Table 2. The results show that the complexes **3a** and **3b** derived from **1** and group 7 metal carbonyls are more stable than those obtained from group 6 transition metal carbonyls. The C(2)–C(3) bond of 1-oxa-5-titanacyclopentane moiety in complex **3** was selectively cleaved during the thermolysis. This corresponds to the reverse reaction of the formation of **3** [Eq. 1], where a concerted pericyclic [2$_s$+2$_s$]-type

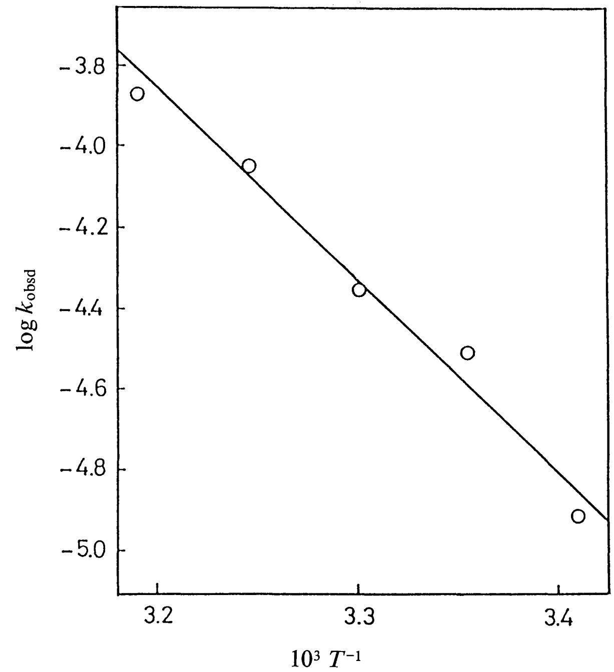
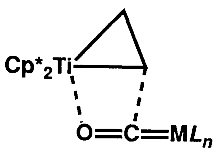


Fig. 1. An Arrhenius plot for the thermal decomposition of **3a**.

Table 2. Activation Parameters (at 303 K) of Thermolysis of Complexes **3**

Complex	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$t_{1/2}$
	kcal	kcal	cal K^{-1} mol^{-1}	min
3a	23.8	20.8	−5.0	116 (30°C)
3b	24.2	11.6	−21.1	223 (30°C)
3c	21.2	16.8	−8.2	73 (0°C)
3e	23.4	18.5	−8.2	64 (30°C)

reaction via a transition state **4** is proposed.[12] Such fission of C(carbenic)-C bond is rarely observed for conventional Fischer-type carbene complexes,[13] while this fission is rather common in the thermolysis of 5-membered titanacycles such as titanacyclopentane **5**[9-12] and 1-oxa-5-titanacyclopentane complexes **6**.[14] This shows that the complexes **3** have thermal behaviors characteristic of five-membered metallacycles, rather than those of Fischer-type carbene complexes.



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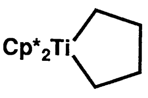

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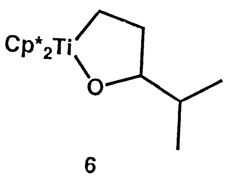

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Crystal Structure of Titanoxycarbene-Dirhenium Complex 3b. For further elucidation of the molecular structure of **3**, a single crystal X-ray diffraction study has been done for the most stable complex **3b**. Selected data on the molecular geometry are listed in Table 3. The molecular structure of **3b** with numbering scheme is shown in Fig. 2. Two molecules of **3b–I** and **3b–II** with different conformations of the metallacyclic five-membered ring are crystallographically independent and make an enantiomorphic pair. A stereoview of crystal packing of **3b–I** and **3b–II** is shown in Fig. 3.

Table 3. Selected Bond Distances (Å) and Angles (Degree) of Complex **3b–I** and **3b–II**[a]

	3b–I	**3b–II**
	Bond distances	
Re1–Re2	3.057 (2)	3.054 (2)
Re1–C2	2.12 (3)	2.12 (2)
Ti–O	2.02 (2)	2.04 (2)
Ti–C4	2.25 (2)	2.26 (2)
O–C2	1.26 (3)	1.28 (3)
C2–C3	1.57 (4)	1.56 (4)
C3–C4	1.52 (4)	1.60 (3)
	Angles	
Re2–Re1–C2	176.7 (7)	176.5 (7)
O–Ti–C4	79.1 (9)	79.5 (8)
Ti–O–C2	121.6 (18)	120.4 (17)
Re1–C2–O	125.2 (22)	124.1 (21)
O–C2–C3	116.6 (22)	119.1 (21)
Re1–C2–C3	118.2 (16)	116.7 (16)
C2–C3–C4	110.1 (21)	107.4 (20)
Ti–C4–C3	106.0 (18)	105.9 (16)

a) Two molecules **3b–I** and **3b–II** are crystallographically independent and make an enantiomorphic pair.

The Ti–C(4) bond distances, 2.25(2) Å for molecule **I** and 2.26(2) Å for molecule **II**, are normal as a single covalent Ti–C bond. The C(2)–O bond distances of 1.26(3) Å for molecule **I** and 1.28(3) Å for molecule **II** are considerably shorter than that of usual covalent C–O bond (1.43 Å), while Ti–O bond distances of 2.02(3) Å for **I** and 2.04(2) Å for **II** are much longer than those of

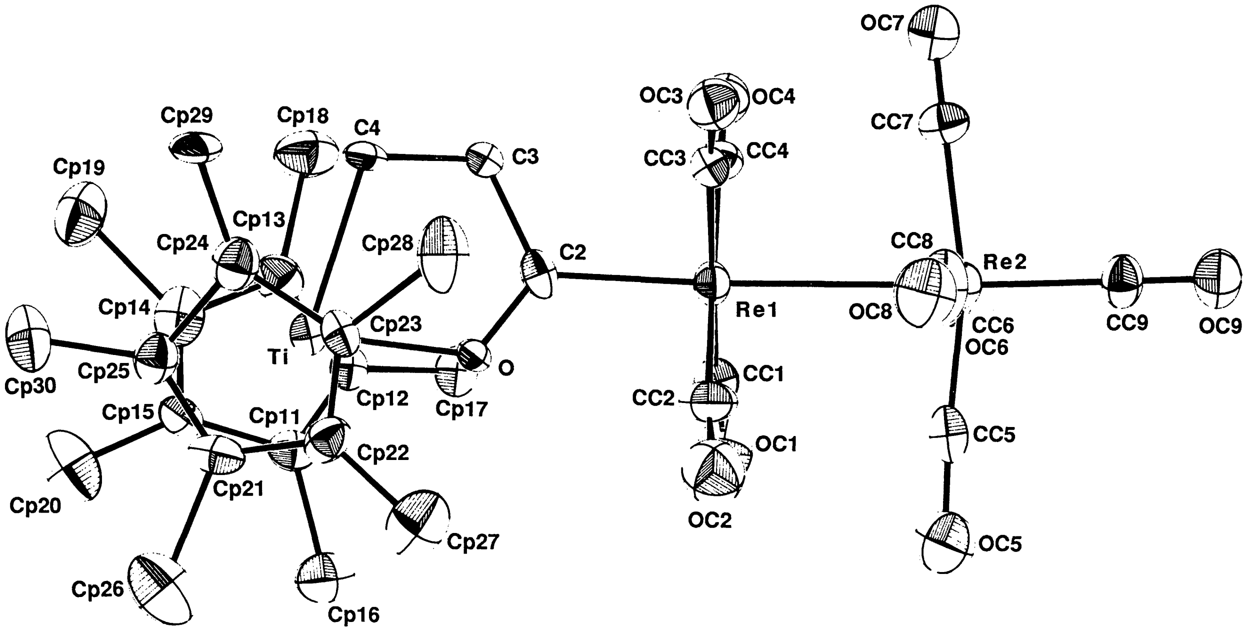


Fig. 2. ORTEP drawing of a molecule of complex **3b–I** showing the atom-labeling scheme. Ellipsoids represent 30% probability. Hydrogen atoms are omitted.

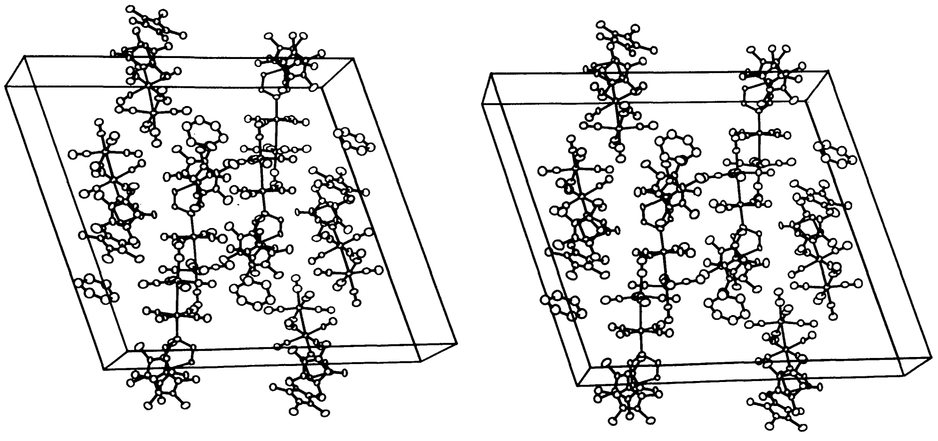
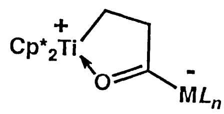


Fig. 3. Stereoview of crystal packing of complex **3b**. Two molecules are crystallographically independent and make an enantiomorphic pair. Methyl carbon of crystalline solvent toluene was not located.

$Cp_2TiCl(OC_2H_5)$ [1.855(2) Å][15) and complex **6** [1.866 (3) Å].[14a) These results contrast with the fact that Ti–O bond of titanacyclopentanes such as **6** has a double bond character due to the considerable degree of donation from the pπ orbital of oxygen to the laterally-directed dπ acceptor orbital of titanocene. The C(2)–C(3) bond distances, 1.57(4) Å for **I** and 1.56(4) Å for **II**, are almost comparable with 1.493(11) Å reported for *cis*-$Mn(CO)_5$-$Re(CO)_4$=$C(OCH_3)CH_3$.[16) Thus, complex **3b** has a characteristic Fischer-type carbene structure[17) and there is an important contribution of a dipolar resonance structure **7**. Such contribution of dipolar resonance structures has been already pointed out for many zirconoxycarbene complexes.[5)

Titanium atom in complex **3b** has a monomeric pseudo tetrahedral configuration defined by two η^5-C_5Me_5, methylene carbon, and an oxygen ligands. The angles C(4)–Ti–O, 79.1(9)° for molecule **I** and 79.5(8)° for molecule **II**, are comparable with that of **6** [80.9(2)°].[14a)

Angles of C(2)–Re(1)–Re(2) for **I** and **II** are 176.7(7)° and 176.5(7)°, respectively. The carbenic ligand is *trans* to Re–Re bond which contrasts with the complexes derived from $Re_2(CO)_{10}$ by conventional Fischer method where the carbene is *cis* to the Re–Re bond as is seen in complex **8**.[18) The Re(1)–C(2) bond distances of 2.12(3) and 2.12(2) Å for molecules **I** and **II**, respectively, are comparable with the reported values of 2.094(7) Å for *cis*-$Mn(CO)_5Re(CO)_4$=$C(OCH_3)CH_3$[16) and 2.09(2) Å for **8**,[18b) but longer than that of *trans* C(carbenic)–Re bond of 1.85(3) Å.[18b) Carbonyl groups on one rhenium atom occupy the staggered position relative to those on the another rhenium metal. Similar staggered geometry is commonly observed for the complexes such as $Re_2(CO)_{10}$[19) and $Re_2(CO)_9(CNCMe_3)$.[20) The Re–Re bond distances of 3.057(2) Å for **I** and 3.054(2) Å for **II** are comparable with those of carbene complexes such as **8**



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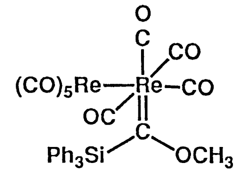

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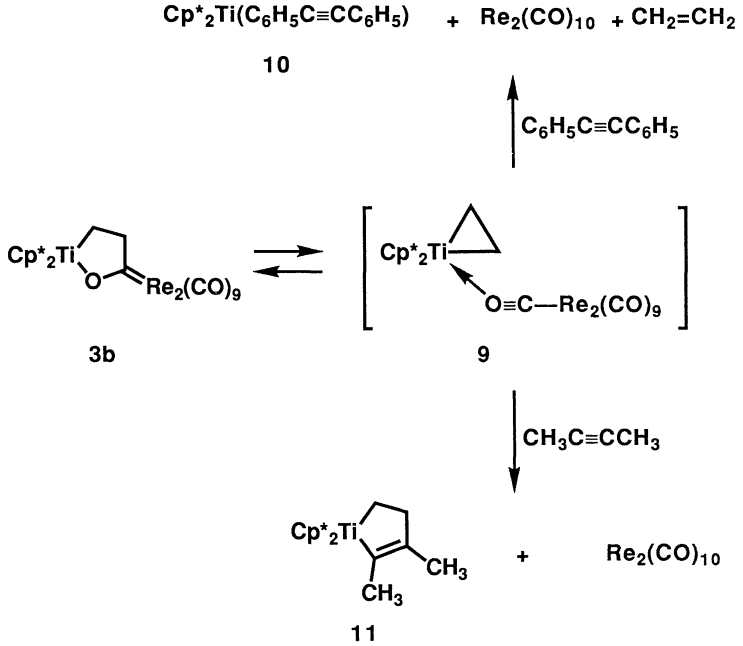
[3.052(1) Å] and *cis*-$Re(CO)_5Re(CO)_4$=$C(SiPh_3)(OEt)$ [3.050(3) Å],[18b) but are longer by 0.013—0.016 Å than that of $Re_2(CO)_{10}$ [3.041(1) Å].[19)

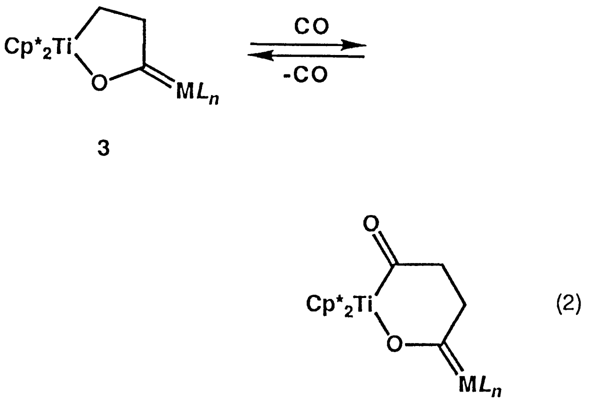
Reactions of 3b and 3e with Alkynes. Reaction of complex **3b** with diphenylacetylene was monitored by NMR spectroscopy. The addition of diphenylacetylene to a solution of **3b** in toluene-d_8 at room temperature induced rapid change in color from orange to deep red. ^1H and ^{13}C {^1H} NMR spectra indicated the formation of ethylene, $Re_2(CO)_{10}$ (**2b**), and titanocene–diphenylacetylene complex **10**[9b) (Scheme 1). Reaction of **3e** with diphenylacetylene afforded the same complex **10**, ethylene, and $W(CO)_6$. On the other hand, reaction of **3b** with 2-butyne afforded $Re_2(CO)_{10}$ and titanacyclopentene complex **11**.[9b) By contrast, reaction of **3e** with 2-butyne afforded no metallacyclic compounds, but ethylene, $W(CO)_6$, and unidentified titanocene species as detected by NMR. The complex **9** in which carbon monoxide of metal carbonyl coordinates to titanium may be an intermediate. In fact, similar complexes, $Cp^*_2Ti(CH_3)OCW(CO)_2Cp$,[21a) $Cp_2Ti(THF)OCMo(CO)_2Cp$,[21b) $Cp_2Zr(\eta^2\text{-}COCH_3)OCMo(CO)_2Cp$,[21c,21d) and $Cp^*_2Yb(THF)OCCo(CO)_3$[21e) have been prepared and characterized. No products arising from the reaction of carbene moiety and alkynes have been detected.

Reaction of 3 with Carbon Monoxide. Complex **3b**



Scheme 1.

was allowed to react with atmospheric pressure of CO in a sealed NMR tube, and the reaction was monitored by ^{1}H NMR spectroscopy, showing that the carbonylation reaction was completed in a few minutes at −30 °C. Absorptions due to **3b** were rapidly replaced by those due to acyltitanium complex **12b**, which indicates that the yield is quantitative. On allowing the solution to warm up to room temperature, however, complex **12b** decomposed gradually to give ethylene, $Re_2(CO)_{10}$, and unidentified titanocene species, the same product obtained by the thermal reaction of **3b**. Interestingly when the CO was replaced by argon, complex **12b** liberated CO to give **3b**. Similar decarbonylation has been found in the reaction of dialkyl derivatives of zirconocene and hafnocene, but not reported for titanium analogues.[22] The carbonylations of other titanoxycarbene complexes **3a**, **3c**, and **3e** afforded the corresponding acyltitanium complexes **12a**, **12c**, and **12e** in quantitative yields, though they are too unstable to be isolated. These results contrast with the reported fact that 1-oxa-5-oxo-6-titanacyclohexanes, structurally related complexes to **12**, are thermally stable.[14a)] For stabilization of cyclic η^1-acyltitanium(IV) complexes, π-donation from the p_π orbital of O(1) to the acceptor $1a_1$ orbital of titanocene is considered to be important. As can be easily deduced from the molecular structure of carbene complex **3** determined by X-ray analysis, such π-donation from O(1) will not be significant for complex **12** due to the presence of electron-accepting carbene moiety adjacent to the O(1) atom.



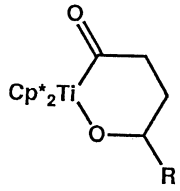
12a, $ML_n = Mn_2(CO)_9$
12b, $ML_n = Re_2(CO)_9$
12c, $ML_n = Cr(CO)_5$
12e, $ML_n = W(CO)_5$

The structures of **12a**—**e** were determined on the basis of spectral data. The ^{13}C NMR resonances due to acyl carbons were observed around 294 ppm (Table 4) which are comparable with those of η^1-acyltitanium complexes $Cp^*{}_2\overline{TiOCH(R)CH_2CH_2C}O$ (**13**).[14a)] The IR spectrum of **12b** exhibited an absorption at 1600 cm^{-1} which is consistent with acyltitanium structure. When ^{13}C enriched CO was allowed to react with complexes **3b** and **3e**, the products exhibited signals with ^{13}C–^{13}C coupling constants of 9.2 and 7.3 Hz for $J_{CO\text{-}C(4)}$, respectively. These values contrast with those of acyl complexes such as **14** and **15** which showed coupling constants of 19 Hz[23)] and 28 Hz,[24)] respectively, and comparable with the values 4.9 Hz and 11.9 Hz for **13**[14a)] and titanacyclopentanone, $Cp_2\overline{TiCMe{=}CMeCH_2C}({=}O)$,[25)] respectively.

Table 4. NMR Spectral Data of Carbonylated Complexes

Complex	Nucleus	Chemical shift[a,b)]/ppm					
		C (4)	C (3)	C (2)	Cp*	Ti-acyl	M (CO)
12a	^{1}H	1.57	3.22 (6.2)		1.73		
	^{13}C	44.07 (127)	58.55 (129)	329.66	12.30 (127)	293.70	225.96 225.4 (broad)
12b	^{1}H	1.61	3.07 (6.4)		1.74		
	^{13}C	44.23 (127)	64.04 (128)	283.32	12.36 (127)	293.91	201.29 198.3 (broad)
12c	^{1}H	1.47	3.32 (6.4)		1.75		
	^{13}C	42.59 (128)	58.25 (127)	343.41	12.33 (127)	294.19	224.02 219.34
12e	^{1}H	1.44	3.14 (6.4)		1.74		
	^{13}C	42.37 (126)	61.19 (127)	320.32	12.39 (128)	294.37	204.38 200.68[c)]

a) Measured in toluene-d_8 at −30 °C under CO atmosphere. b) Coupling constants are given in parentheses (Hz). c) $J_{\text{C-W}}$=129 Hz.



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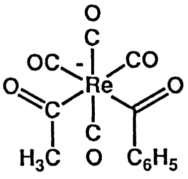

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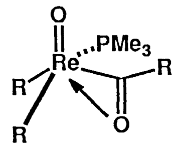
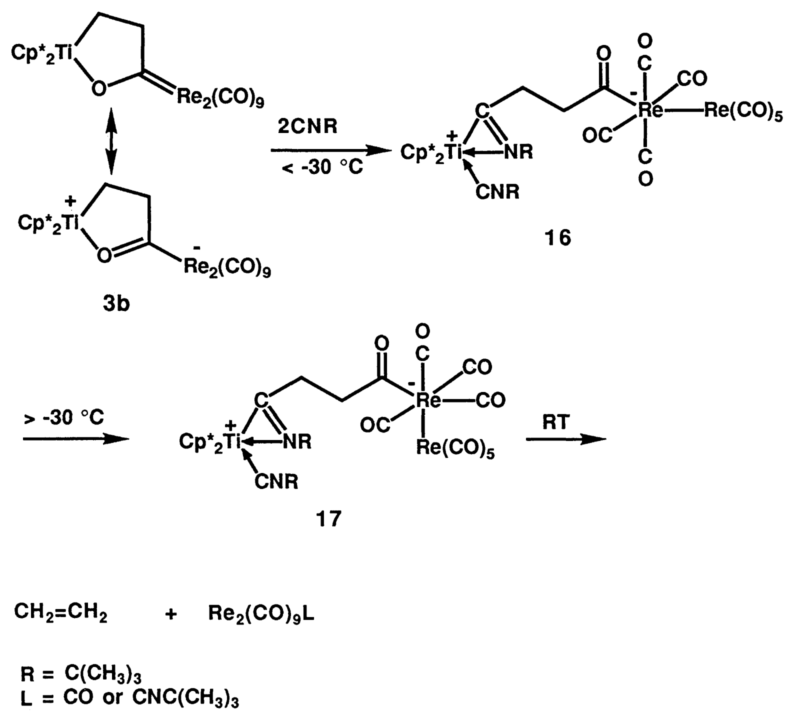


15 R = CH$_2$Si(CH$_3$)$_3$

Reaction of 3b and 3e with *t*-Butyl Isocyanide. Reaction of titanoxycarbene–dirhenium carbonyl complex **3b** with excess *t*-butyl isocyanide completed in 1 h at −15 °C in toluene to give a 1:1 mixture of **16** and **17** in 81% yield. Complex **17** crystallized as yellow plates at −20 °C. When the solution of **17** in toluene-d_8 was allowed to warm to 20 °C, the complex gradually decomposed and formations of ethylene, free *t*-butyl isocyanide, and unidentified species with titanocene moiety were detected by NMR spectroscopy. The first order disappearance of **17** was observed by ^{1}H NMR spectroscopy to give $\Delta G^{\neq}$ value at 30 °C of 25 kcal mol^{-1}.

The spectroscopic data of **17** are consistent with the structure assigned. ^{1}H NMR spectrum of **17** consists of two singlets at δ=1.50 and 1.80, indicating the presence of

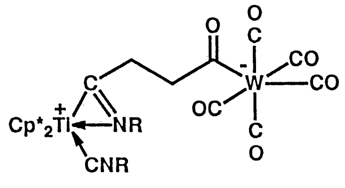


Scheme 2.

two magnetically nonequivalent *t*-butyl groups. Four kinds of carbon monoxide coordinated to rhenium were displayed by ^{13}C{^{1}H} NMR spectrum which supported the *cis* geometry between acyl group and dirhenium moiety. The low $\nu_{C=N}$ of 1586 cm^{-1} suggested the presence of iminoacyl moiety and the other $\nu_{C\equiv N}$ of 2162 cm^{-1} is due to an isocyanide coordinated to titanium. A weak absorption at 1650 cm^{-1} was tentatively assigned to acyl-rhenium moiety. The molecular geometry of **17** has been determined by a single-crystal X-ray analysis (vide infra).

When the above reaction was carried out at −55 °C for 4 h and then the liquid phase was decanted below −30 °C, another 1:2 complex **16** could be obtained as yellow crystals in 77% yield. ^{1}H NMR spectrum of the complex resembles with that of **17** which indicates that the complex is stereoisomer of **17**. ^{13}C{^{1}H} NMR spectrum is consistent with the structure **16** in which acyl ligand is trans to the Re–Re bond.

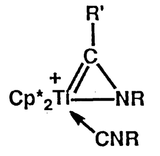
The compound **16** in THF-d_8 gradually isomerized to **17** even at −10 °C, as monitored by ^{1}H NMR spectroscopy. The half life of **17** in THF at 0 °C is 41 min. This indicates that the formation of *cis*-product **17** proceeds sequentially by way of the *trans*-isomer **16**. Although the driving force of the isomerization from **16** to **17** is not clear at present, *cis* structures are common to anionic acyl-M(CO)$_4$M(CO)$_5$ species (M=Mn and Re).[16)]



18 R = C(CH$_3$)$_3$

Reaction of **3e** with *t*-butyl isocyanide gave the analogous tungsten derivative **18**, whose structural determination is based on spectroscopic data. Therefore, these reactions can be regarded as general for the cyclic titanoxycarbene–metal carbonyl complexes of type **3**. In spite of the strong oxophilic nature of the central titanium atom, dissociation of oxygen ligand from titanium occurred. This may be attributed to the important contribution from the dipolar resonance structure **7** in the starting complex **3**.

Molecular Structure of Zwitterionic Complex 17. In order to get more insights into the molecular structure of **17**, an X-ray crystal structure determination was performed. Figure 4 shows an ORTEP drawing of the molecule with the atom numbering scheme. Selected bond distances and angles are listed in Table 5. No unusually short intermolecular contacts are observed. The Ti–C(6) and Ti–N(2) bond distances are 2.14(3) and 2.17(2) Å, respectively. The bond distances 2.17(2) Å for Ti–C(1) and 1.14(3) Å for C(1)–N(1) in complex **17** are comparable with those of η^2-iminoacyl complexes of Y,[26)] U,[27)] Ti,[28–30)] Zr,[30,31)] and Mo.[32)] Contribution from the carbene resonance form **19** can be considered to



19 R = C(CH$_3$)$_3$

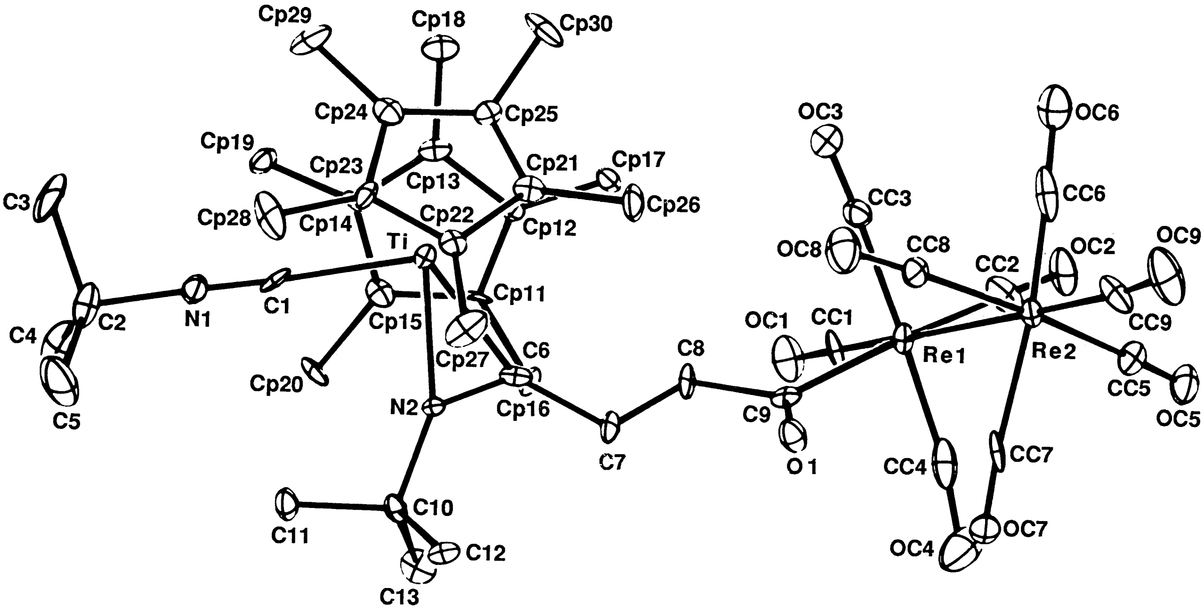


Fig. 4. ORTEP drawing of a molecule of complex **17** with the numbering scheme. Ellipsoids represent 30% probability. Hydrogen atoms are omitted.

Table 5. Selected Bond Distances (Å) and Angles (Degree) of Complex **17**

	Bond distances		
Re1-Re2	3.060 (2)	Re1-C9	2.27 (2)
Ti-N2	2.17 (2)	Ti-C1	2.17 (2)
Ti-C6	2.14 (3)		
O1-C9	1.20 (3)		
N1-C1	1.16 (3)	N1-C2	1.51 (3)
N2-C6	1.26 (3)	N2-C10	1.56 (3)
C2-C3	1.55 (5)	C2-C4	1.56 (5)
C2-C5	1.43 (5)	C6-C7	1.51 (3)
C7-C8	1.52 (3)	C8-C9	1.57 (3)
C10-C11	1.54 (3)	C10-C12	1.51 (4)
C10-C13	1.49 (4)		
	Angles		
Re2-Re1-C9	91.7 (6)	N2-Ti-C1	83.6 (9)
N2-Ti-C6	33.9 (7)	C1-Ti-C6	117.4 (9)
C1-N1-C2	177.0 (26)	Ti-N2-C6	72.1 (14)
Ti-N2-C10	157.4 (14)	C6-N2-C10	130.5 (20)
Ti-C1-N1	176.8 (23)	N1-C2-C3	102.3 (24)
N1-C2-C4	106.0 (22)	N1-C2-C5	109.9 (26)
C3-C2-C4	108.1 (26)	C3-C2-C5	118.2 (30)
C4-C2-C5	111.4 (31)	Ti-C6-N2	74.1 (15)
Ti-C6-C7	155.0 (16)	N2-C6-C7	130.8 (22)
C6-C7-C8	116.0 (21)	C7-C8-C9	113.2 (21)
Re1-C9-O1	127.4 (17)	Re1-C9-C8	113.3 (16)
O1-C9-C8	119.4 (20)	N2-C10-C11	107.1 (20)
N2-C10-C12	111.2 (19)	N2-C10-C13	107.8 (19)
C11-C10-C12	111.0 (20)	C11-C10-C13	109.1 (22)
C12-C10-C13	110.5 (24)		

be little, if any. Titanium atom has only three anionic ligands, but the coordination of an isocyanide on titanium brings about a closed 18-electron valence shell, and this might be the reason for the observed stability of **17**. Thus, intramolecular charge separation occurred upon reaction with isocyanides to afford a zwitterionic complex, where positive charge is on the titanium moiety, while negative charge is on the rhenium carbonyl residue. Such charge separation within a molecule has been reported recently.[13)]

The acyl ligand in **17** is *cis* to Re–Re bond, which contrasts with the fact that in the starting complex **3b** the carbenic carbon is *trans* to Re–Re bond. The Re(1)–C(9)–O(1) bond angle of 127(2)° shows that the acyl ligand has η^1 coordination mode. To our knowledge, the present study provides the first structural data for anionic acyldirhenium carbonyl complex determined by a single-crystal X-ray analysis.

Conclusion

A direct synthesis of new Fischer-type carbene complexes has been developed by the reaction of titanocene–ethylene complex with various group 6 and 7 metal carbonyls and their molecular structures have been determined by spectroscopic techniques and X-ray crystallography. The structural characteristics of cyclic titanoxycarbene–metal carbonyl complexes **3** thus obtained have been shown to be reflected in their chemical properties. The modes of thermal reaction of **3** and of the reactions of **3** with CO are closely related to those of 1-oxa-5-titanacyclopentanes, though the carbonylation products **12** are much less stable than those derived from the latter complexes. Reactions of **3** with *t*-butyl isocyanide give rise to novel zwitterionic 1:2 adducts. These characteristic features of **3** could be attributed to an important contribution from the dipolar resonance structure **7**.

Experimental

General: All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of standard Schlenk techniques under argon atmosphere purified by passing through a hot column packed with BASF-Catalyst R3-11. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl. All NMR spectra were recorded in toluene-d_8 at −30 °C using a Varian EM-390 (90 MHz) spectrometer or a JEOL GX400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer. Chemical shifts were determined using solvent absorption at δ=2.31 (^{1}H) and δ=137.70 (^{13}C) as internal standards. Other spectra were recorded by the use of the following instruments: IR, Hitachi 295; low and high resolution mass spectra, JEOL D300 (70 eV). Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 equipped with a flame ionization detector. Elemental analyses were performed by the Wako Pure Chemical Ind. Ltd. All melting points were measured in sealed tubes and uncorrected. $Cp^*_2Ti(C_2H_4)$ was prepared according to the published procedure.[9a)] The metal carbonyls **2a**—**e** were obtained from Strem Chem. Inc. *t*-Butyl isocyanide was obtained from Aldrich Chem. Co. 2-Butyne and diphenylacetylene were obtained from Tokyo Kasei Kogyo Co., Ltd. Carbon monoxide was obtained from Takachiho Chem. Ind. Co. ^{13}CO (99.3 atom %) was used as obtained from MDS Isotopes.

Titanoxycarbene–Dimanganese Complex 3a. To decacarbonyldimanganese (**2a**) (0.31 g, 0.80 mmol) and titanocene–ethylene complex **1** (0.28 g, 0.81 mmol) placed in a Schlenk tube at −50 °C was added toluene (25 mL) via a syringe. The mixture was stirred at −20 °C for a period of 120 h and the deep red solution was obtained. The liquid phase was separated from the residual manganese carbonyl, concentrated to 10 mL under reduced pressure at −30 °C, and to this hexane (15 mL) was layered. The solution was kept at −80 °C overnight to afford **3a** as orange red crystalline solid (0.18 g, 30% yield), mp 115—118 °C (decomp). ^{1}H and ^{13}C NMR data are listed in Table 1. IR (KBr) 2085 (vw), 2001 (sh), 1950 (vs), 1923 (vs) cm^{-1}. Mass spectrum (^{100}Mn^{48}Ti) *m*/*z* 391 (M^+−345, base peak), 337 (M^+ −399), 318 (Cp^*_2Ti), 251 [$Mn_2(CO)_5$], 223 [$Mn_2(CO)_4$], 196 (M^+−540), 167 [$Mn(CO)_4$]. Anal.Found: C, 52.06; H, 4.89%. Calcd for $C_{32}H_{34}O_{10}Mn_2Ti$: C, 52.20; H, 4.65%.

Titanoxycarbene–Dirhenium Complex 3b. To a solution of dirhenium decacarbonyl (**2b**) (0.52 g, 1.5 mmol) in toluene (10 mL) at −40 °C was added a solution of **1** (0.25 g, 0.38 mmol) in toluene (5 mL) via a syringe. The solution was stirred for 48 h at −20 °C until the color became deep red. The residual **2b** was separated by decantation, the solution was concentrated to 5 mL under reduced pressure in the temperature range of −30—−20 °C, and then hexane (15 mL) was layered. After

12 h at −80 °C, orange red crystals were isolated (0.41 g, 57% yield), mp 95—99 °C (decomp). IR (KBr) 2089 (w), 2011 (s), 1969 (vs), 1951 (vs), 1914 (vs) cm^{-1}. IR (toluene) 2091 (w), 2016 (m), 1985 (vs), 1951 (m), 1919 (m) cm^{-1}. Mass spectrum ($^{187}\mathrm{Re}^{48}\mathrm{Ti}$) *m*/*z* 654 $[\mathrm{Re_2(CO)_{10}}]$, 626 ($\mathrm{M^+}$ −374), 596 $[\mathrm{Re_2(CO)_8}]$, 570 $[\mathrm{Re_2(CO)_7}$, base peak], 542 $[\mathrm{Re_2(CO)_6}]$, 514 $[\mathrm{Re_2(CO)_5}]$, 337 ($\mathrm{M^+}$ −663), 318 ($\mathrm{Cp^*_2Ti}$), 299 $[\mathrm{Re(CO)_4}]$. Anal. Found: C, 40.39; H, 3.74%. Calcd for $\mathrm{C_{32}H_{34}O_{10}Re_2Ti\cdot 1/2(C_7H_8)}$: C, 40.80; H, 3.67%.

Titanoxycarbene–Chromium Complex 3c. To a solution of chromium hexacarbonyl (**2c**) (0.14 g, 0.64 mmol) in toluene (8 mL) cooled at −50 °C was added a solution of **1** (0.21 g, 0.61 mmol) in toluene (8 mL) via a syringe. After the mixture was stirred at −20 °C for a period of 120 h, the deep red solution was separated from the white solid of unreacted **2c**. Hexane (8 mL) was layered on the solution and the mixture was kept at −80 °C overnight to afford **3c** as deep red crystalline solid (0.09 g, 26% yield), mp 98—103 °C (decomp). IR (KBr) 2041 (vw), 1966 (sh), 1876 (vs) cm^{-1}. Mass spectrum ($^{52}\mathrm{Cr}^{48}\mathrm{Ti}$) *m*/*z* 337 ($\mathrm{M^+}$−229), 318 ($\mathrm{Cp^*_2Ti}$), 220 $[\mathrm{Cr(CO)_6}$, base peak]. Anal. Found: C, 59.76; H, 6.25%. Calcd for $\mathrm{C_{28}H_{34}O_3CrTi}$: C, 59.37; H, 6.05%.

Titanoxycarbene–Molybdenum Complex 3d. To molybdenum hexacarbonyl (**2d**) (6.9 mg, 2.6×10^{-5} mol) and **1** (6.6 mg, 1.9×10^{-5} mol) placed in NMR tube (5ϕ) was added toluene-d_8 (0.5 mL) by trap-to-trap distillation and then the tube was sealed. ^{1}H and ^{13}C NMR data are summarized in Table 1, which showed the formation of titanoxycarbene–molybdenum complex **3d**. Attempted isolation of **3d** failed due to the thermal instability of the product even below −20 °C.

Titanoxycarbene–Tungsten Complex 3e. To a mixture of tungsten hexacarbonyl (**2e**) (0.31 g, 0.64 mmol) and complex **1** (0.22 g, 0.88 mmol) placed in a Schlenk tube was added toluene (15 mL) at −50 °C. The mixture was stirred at −20 °C for 90 h. To the deep red solution separated from the remaining white solid of tungsten hexacarbonyl was layered hexane (10 mL). The mixture was kept at −80 °C overnight and the product **3e** was obtained as deep orange crystalline solid (0.15 g, 34% yield), mp 106—110 °C (decomp). IR (KBr) 2051 (w), 1974 (m), 1904 (vs), 1887 (vs) cm^{-1}. IR (toluene) 2051 (vw), 1984 (vs), 1919 (s) cm^{-1}. Mass spectrum ($^{184}\mathrm{W}^{48}\mathrm{Ti}$) *m*/*z* 352 $[\mathrm{W(CO)_6}]$, 318 ($\mathrm{Cp^*_2Ti}$), 296 $[\mathrm{W(CO)_4}]$, 268 $[\mathrm{W(CO)_3}$, base peak], 240 $[\mathrm{W(CO)_2}]$, 212 $[\mathrm{W(CO)}]$. Anal. Found: C, 47.84; H, 5.09%. Calcd for $\mathrm{C_{28}H_{34}O_6TiW}$: C, 48.16; H, 4.91%.

Thermal Decomposition of Titanoxycarbene–Metal Complexes 3a—e. A solution of complex **3b** (10 mg) in toluene-d_8 (0.5 mL) was sealed in an NMR tube under argon. The disappearance of complex **3b** was measured at specified constant temperatures. The half lives (min) of **3a**, **3b**, **3c**, and **6e** in toluene-d_8 are 116 (30 °C), 223 (30 °C), 73 (0 °C), and 64 (30 °C), respectively. The thermodynamic parameters thus obtained are listed in Table 2.

Reaction of 3b or 3e with Diphenylacetylene. A solution of complex **3b** (15 mg, 1.5×10^{-2} mmol) and diphenylacetylene (2 equiv) in toluene-d_8 (0.5 mL) was placed in an NMR tube at room temperature. Color of the solution darkened. The formation of **10** was confirmed by the comparison of ^{1}H and ^{13}C NMR spectral data with those reported.[9b)] Reaction of **3e** with diphenylacetylene in a similar manner gave the same complex **10** in quantitative yield.

Reaction of 3b or 3e with 2-Butyne. A solution of complex **3b** (10 mg, 1.0×10^{-5} mol) and 2-butyne (excess) in toluene-d_8 (0.5 mL) was placed in an NMR tube. Color of the solution gradually darkened. The formation of **11** was confirmed by the comparison of ^{1}H and ^{13}C NMR spectral data with the reported ones.[9b)] Similar treatment of **3e** with excess 2-butyne did not give **11**, but afforded ethylene, tungsten hexacarbonyl (**2e**), and unidentified species containing titanocene residue.

Reaction of 3a—e with Carbon Monoxide. To complex **3b** (0.06 g, 0.06 mmol) placed in an NMR tube (10ϕ) was added toluene-d_8 (2.5 mL) by the trap-to-trap distillation technique. Atmospheric pressure of carbon monoxide was introduced into the tube and the tube was sealed. A yellow-green solution was obtained after a few min at −50 °C. ^{1}H and ^{13}C NMR data were taken which are listed in Table 4.

Reactions of **3a**, **3c**, and **3e** with carbon monoxide were carried out in similar manners as described above and the ^{1}H and ^{13}C NMR spectral data obtained are summarized in Table 4.

Reaction of 3b with *t*-Butyl Isocyanide. To a solution of **3b** (47 mg, 0.047 mmol) in toluene (12 mL) at −35 °C was added *t*-butyl isocyanide (0.05 μL, 0.44 mmol). The reaction mixture was slowly warmed up to −15 °C and then stirred at this temperature for 1 h in which pale yellow crystalline solid (43 mg, 81% yield) deposited. The product is a 1:1 mixture of **16** and **17**, from which **17** was separated by recrystallization of the product from toluene at −20 °C, mp 119—122 °C (decomp). ^{1}H NMR (22 °C, THF-d_8) δ=1.50 (s, $\mathrm{CMe_3}$), 1.80 (s, $\mathrm{CMe_3}$), 1.87 (s, $\mathrm{2C_5Me_5}$), 3.29—3.33 (m) and 3.44—3.48 (m) [$\mathrm{C(7)H_2}$ and $\mathrm{C(8)H_2}$]. ^{13}C NMR (−30 °C, THF-d_8) δ=13.34 ($J_{\mathrm{C-H}}$ 125 Hz, $\mathrm{C_5}\mathit{Me}_5$), 30.42 (129 Hz, $\mathrm{C}\mathit{Me}_3$), 31.15 [127 Hz, C(7) or C(8)], 31.97 (127 Hz, $\mathrm{C}\mathit{Me}_3$), 60.29 ($\mathit{C}\mathrm{Me_3}$), 63.84 ($\mathit{C}\mathrm{Me_3}$), 118.36 ($\mathit{C}_5\mathrm{Me_5}$), 189.81, 195.76, 197.49, 200.22 (rel intensities 1.0:2.4:2.7:4.9, CO), 205.45 ($\mathit{C}\mathrm{NCMe_3}$), 226.91 ($\mathit{C}$=N), 250.70 (C=O). When ^{13}C NMR was measured in $\mathrm{CD_2Cl_2}$ (the absorption at δ=53.60 due to the solvent was used as internal standard), signals due to C(7) and C(8) were observed at δ=29.59 ($J_{\mathrm{C-H}}$ 127 Hz) and 66.16 (127 Hz). IR (KBr) 2162 (m, CN), 2084 (m), 2008 (s), 1973 (vs), 1955 (sh), 1932 (s), 1918 (s), 1876 (s) (CO), 1650 (m, acyl), 1586 (m, C=N) cm^{-1}. Anal. Found: C, 43.41; H, 4.78; N, 2.50%. Calcd for $\mathrm{C_{42}H_{52}N_2O_{10}Re_2Ti}$: C, 43.29; H, 4.50; N, 2.40%.

Reaction of 3b with *t*-Butyl Isocyanide at Low Temperature. To a solution of **3b** (40 mg, 0.040 mmol) in toluene (8 mL) at −55 °C was added *t*-butyl isocyanide (0.05 μL, 0.44 mmol). The reaction mixture was stirred at this temperature for a period of 4 h. The pale yellow crystalline solid was isolated by decantation to give complex **16** (36 mg, 77% yield), mp 124—126 °C (decomp). NMR measurement at −50 °C showed that **16** was the only product. ^{1}H NMR (−50 °C, THF-d_8) δ=1.54 (s, $\mathrm{CMe_3}$), 1.81 (s, $\mathrm{CMe_3}$), 1.89 (s, $\mathrm{2C_5Me_5}$), 3.45—3.49 (m) and 3.58—3.60 (m) [$\mathrm{C(7)H_2}$ and $\mathrm{C(8)H_2}$]. ^{13}C NMR (−50 °C, THF-d_8) δ=13.34 ($J_{\mathrm{C-H}}$ 127 Hz, $\mathrm{C_5}\mathit{Me}_5$), 30.34 (129 Hz, $\mathrm{C}\mathit{Me}_3$), 31.84 (129 Hz, $\mathrm{C}\mathit{Me}_3$), 31.24 (127 Hz) and 72.49 (129 Hz) [C(7) and C(8)], 60.30 ($\mathit{C}\mathrm{Me_3}$), 63.80 ($\mathit{C}\mathrm{Me_3}$), 118.29 ($\mathit{C}_5\mathrm{Me_5}$), 191.43, 203.21, 203.65 (rel intensity 1.0:7.8:5.6, CO), 205.52 ($\mathit{C}\mathrm{NCMe_3}$), 226.89 ($\mathit{C}$=N), 235.60 (C=O). IR (KBr) 2162 (w) (CN), 2085 (m), 1960 (vs), 1935 (sh), 1883 (s) (CO), 1648 (w) (tentatively assigned to acyl), 1565 (vw) (C=N) cm^{-1}. Mass spectrum ($^{187}\mathrm{Re}^{48}\mathrm{Ti}$) *m*/*z* 1165 ($\mathrm{M^+}$−1), 1138 ($\mathrm{M^+}$−CO), 895 ($\mathrm{M^+}$−271), 707, 652, 624, 596, 570 (base peak), 135 (Cp*). Anal. Found: C, 43.28; H, 4.52; N, 2.23%. Calcd for $\mathrm{C_{42}H_{52}N_2O_{10}Re_2Ti}$: C, 43.29; H, 4.50; N, 2.40%.

Reaction of Titanoxycarbene–Tungsten Complex with *t*-

Butyl Isocyanide. To a solution of **3e** (78.5 mg, 0.11 mmol) in toluene (10 mL) at −60 °C was added *t*-butyl isocyanide (0.05 mL, 0.44 mmol). The mixture was stirred at −50 °C for 1.5 h, and to this was added hexane (10 mL). The yellow precipitates formed were separated by filtration to give **18** (66.7 mg, 70% yield), mp 66—70 °C (decomp). ^{1}H NMR (−50 °C, THF-d_8) δ=1.52 (s, CMe$_3$), 1.81 (s, CMe$_3$), 1.87 (s, 2C$_5$Me$_5$), 3.35—3.39 (m) and 3.45—3.48 (m) [C(7)H$_2$ and C(8)H$_2$]. ^{13}C NMR (−50 °C, THF-d_8) δ=12.00 ($J_{\text{C-H}}$=127 Hz, C$_5$*Me*$_5$), 12.05 (J=127 Hz, C$_5$*Me*$_5$), 28.05 [J=126 Hz, C(7) or C(8)], 29.46 (J=129 Hz, C*Me*$_3$), 30.53 (J=126 Hz, C*Me*$_3$), 58.21 (*C*Me$_3$), 62.00 (*C*Me$_3$), 68.41 [J=127 Hz, C(7) or C(8)], 116.30 (2*C*$_5$Me$_5$), 191.34 (CO, $J_{\text{C-W}}$=122 Hz), 202.95 (CO, $J_{\text{C-W}}$= 129 Hz), 207.90 (*C*NCM$_3$), 224.78 (C=N), 274.58 (C(9), $J_{\text{C-W}}$= 88 Hz). IR (KBr) 2162 (m) (NC), 2041 (m), 1986 (w), 1947 (w), 1894 (s), 1874 (sh) (CO), 1642 (w) (tentatively assigned to acyl), 1553 (w) (C=N) cm^{-1}. Anal. Found: C, 51.26; H, 5.69; N, 2.98%. Calcd for $C_{38}H_{52}N_2O_6TiW$: C, 52.79; H, 6.06; N, 3.24%.

X-Ray Structure Determination of 3b. Deep red crystals were grown from a saturated toluene–hexane solution of **3b** at −20 °C overnight. Crystals were placed in thin-walled glass capillaries under argon at −20 °C and then sealed. Preliminary measurements of several crystals yielded rough cell dimensions and peak profiles. A suitable crystal with dimensions 0.21×0.32×0.53 mm was finally mounted on Rigaku AFC-5 diffractometer at −40 °C and centered in the beam. Below this temperature the crystal cracked. Automatic peak search and indexing procedure yielded the primitive cell. The pertinent datails of data collection and the final cell dimensions, which were obtained from a least-squares refinement of 2θ values of 50 independent reflections in the range of $20° < 2\theta < 30°$, are given in Table 6.

The 6715 unique raw intensity data with $|F_o| > 3\sigma(F_o)$ were corrected for absorption, Lorentz and polarization effects. Three standard reflections measured after every 50 reflections showed no systematic variation in intensity. In unit cell, two independent molecules of titanoxycarbene–dirhenium complex are involved and make an enantiomorphic pair. The location of four rhenium and two titanium atoms were determined by the direct method (MULTAN 78 program). A series of standard least-squares refinement and Fourier synthesis revealed the remaining carbon and oxygen atoms as anisotropic temperature factors. Aromatic carbons of the solvated toluene were located also by the following difference Fourier synthesis, but the methyl carbon of toluene was not located, which might be attributed to the disorder. Final difference Fourier synthesis did not locate all hydrogen atoms. Molecular and crystal structures of **3b** are shown in Figs. 2 and 3. Atomic coordinates have been deposited.[6a)]

X-Ray Structure Determination of 17. Pale yellow crystals were grown from the saturated toluene–hexane solution of **17** at 4 °C overnight. Selected crystals were mounted in thin-walled glass capillaries under argon at −40 °C, and a suitable crystal (0.10×0.15×0.45 mm) was selected as for **17**. Data were collected at −120 °C by using Rigaku AFC-5 diffractometer. The data collection procedure and the cell parameters, obtained from a least-squares refinement of 2θ values of 50 independent

Table 6. Crystal Data and Data Collection Parameters of Complexes **3b** and **17**

	3b	**17**
Formula	$C_{32}H_{34}O_{10}Re_2Ti\cdot 1/2(C_7H_8)$	$C_{42}H_{52}O_{10}N_2Re_2Ti\cdot C_7H_8$
FW	1044.98	1257.32
Crystal system	Monoclinic	Monoclinic
Space group	$P2/a$	$P2_1/n$
a/Å	30.401(1)	14.964(2)
b/Å	9.251(1)	26.207(4)
c/Å	27.561(5)	14.719(3)
β/deg	105.73(1)	100.30(1)
V/Å^3	7460(2)	5679(2)
Z	8	4
D_{calcd}/g cm^{-3}	1.86	1.47
Crystal size	0.21×0.32×0.53	0.10×0.15×0.45
μ(Mo $K\alpha$)/cm^{-1}	71.14	46.88
Diffractometer	Rigaku AFC-5	Rigaku AFC-5
Monochrometer	Graphite	Graphite
Temperature/°C	−40	−120
Scan type	ω scan ($2.0 < 2\theta < 20.0°$) θ–2θ scan ($20.0 < 2\theta$)	θ–2θ scan
bkgd/s	8	8
Scan range/deg	$0.9 + 0.5\tan\theta$	$1.1 + 0.5\tan\theta$
Scan speed/deg min^{-1}	3	3
stds	3 every 50 reflections	3 every 50 reflections
Data collected	$\pm h, k, l$	$\pm h, k, l$
$2\theta_{\text{max}}$/deg	50.0	55.0
No. of total reflections	9494	6520
No. of unique reflections	6715	4852
No. of variables	866	578
Weighting scheme	$w = [\sigma_c^2 + (0.015\lvert F_o\rvert)^2]^{-1}$	$w = [\sigma_c^2 + (0.015\lvert F_o\rvert)^2]^{-1}$
R	0.069	0.068
R_w	0.082	0.089
Goodness of fit	5.68	5.69

reflections in the range of $20° < 2\theta < 30°$, are listed in Table 6.

The 4852 intensity data with $|F_o| > 3\sigma(F_o)$ were converted to the structure factor amplitudes by correction for absorption, Lorentz and polarization effects. No correction for systematic variation in intensity is necessary. The structure of **17** was solved by Patterson method to locate two rhenium atoms in unit cell. A series of standard least-squares refinement and Fourier synthesis revealed the remaining titanium, oxygen, nitrogen, and carbon atoms as anisotropic temperature factors. Aromatic carbons of the solvated toluene were also located by the following difference Fourier synthesis. Final difference Fourier synthesis did not locate any hydrogen atoms. Molecular structure of **17** is shown in Fig. 4. Atomic coordinates have been deposited.[6b)]

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