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Article

Terminal Titanium-Ligand Multiple Bonds. Cleavages of C=O and C=S Double Bonds with Ti Imido Complexes

Shih-Hsien Hsu,[†] Jr-Chiuan Chang,[†] Chun-Liang Lai,[†] Ching-Han Hu,[†] Hon Man Lee,[†] Gene-Hsiang Lee,[‡] Shie-Ming Peng,[‡] and Jui-Hsien Huang*,[†]

Department of Chemistry, National Changhua University of Education, Changhua, Taiwan 500, and Department of Chemistry, National Taiwan University, Taipei, Taiwan 106

Treatment of $^{t-}BuN=TiCl_2Py_3$ with 2 equiv lithium ketiminate compound, Li[OCMeCHCMeN(Ar)] (where Ar = 2,6-diisopropylphenyl), in toluene at room temperature gave $^{t-}BuN=Ti[OCMeCHCMeN(Ar)]_2$ (**1**) in high yield. The reaction of **1** with phenyl isocyanate at room-temperature resulted in imido ligand exchange producing PhN=Ti[OCMeCHCMeN(Ar)]$_2$ (**2**). Compound **1** decomposed at 90 °C to form a terminal titanium oxo compound O=Ti[OCMeCHCMeN(Ar)]$_2$ (**3**) and $^{t-}BuNHCMeCHCMeNAr$ (**4**). Also, the compound **3** could be obtained by reacting **1** with CO_2 under mild condition. Similarly, while **1** reacts with an excess of carbon disulfide, a novel terminal titanium sulfido compound S=Ti[OCMeCHCMeN(Ar)]$_2$ (**5**) was formed via a C=S bond breaking reaction. A novel titanium isocyanate compound Ti[OCMeCHCMeN(Ar)]$_2$(NCO)(OEt) (**6**) was formed on heating **1** with 1 equiv of urethane, $H_2NCOOEt$. Compounds **1**–**6** have been characterized by ^1H and ^{13}C NMR spectroscopies. The molecular structures of **1**, **3**, **5**, and **6** were determined by single-crystal X-ray diffraction. A theoretical calculation predicted that the cleavage of the C–S double bonds for carbon disulfide with the Ti=N bond of compound **1** was estimated at ca. 21.8 kcal·mol^{-1} exothermic.

Introduction

Metal–ligand multiple bonds are of inherent, fundamental interest, as well as of practical importance, due to their versatile reactivity.[1] Metal oxo, imido, and sulfido complexes have been shown to undergo reactions with a variety of unsaturated organic molecules.[2–4] Among these, titanium imido, oxo, and sulfido complexes have been extensively studied by many groups.[5–7] Metal sulfido compounds are also interesting due to their role as intermediates of hydro-desulfurization organo-sulfur compounds in fossil fuels.[7c] Moreover, the reactivity of metal sulfido compounds toward other small organic molecules is of considerable importance in understanding the mechanism of hydro-desulfurization. Terminal metal sulfido compounds have been found in many organometallic compounds,[1] but there are few examples of terminal early transition metal sulfido compounds that have

* Author to whom correspondence should be addressed. E-mail: juihuang@cc.ncue.edu.tw.
† National Changhua University of Education.
‡ National Taiwan University.

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Scheme 1
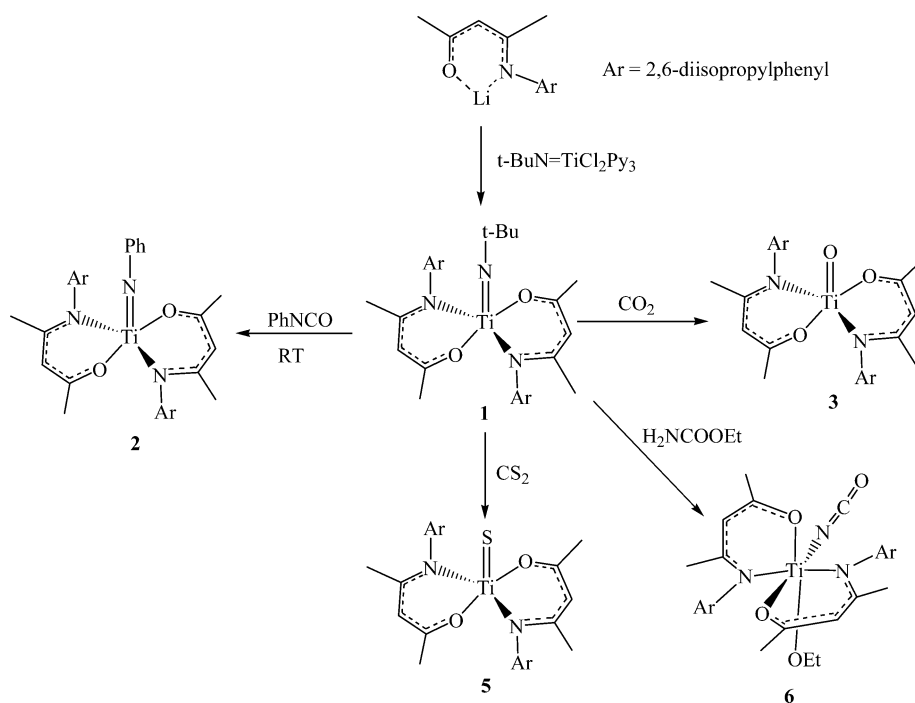
been characterized by X-ray crystallography.[2a,4a,8,9] Exceptions are the terminal titanium sulfido compounds, Cp*$_2$PyTi-(S),[7] [CpTi(μ-S)(S)]$_2{}^{2-}$,[10] [PhC(NSiMe$_3$)$_2$]$_2$Ti(S),[11] and other systems[12] that have been thoroughly studied by several groups.

We have been interested in using ketiminates as ancillary ligands for the synthesis of organometallic compounds.[13] A number of related N,O-donor complexes with Ti=E bonds have also been reported.[14] In this paper, we describe the synthesis of substituted ketiminate titanium imido compounds and the corresponding terminal titanium oxo, sulfido, and isocyanate compounds, which are formed through metathesis reaction of the Ti=N−R moiety with the C=X (X = O, S) double bond.

Results and Discussion

Syntheses and Characterization. The reactions of the titanium imido complex **1** with various substrates are summarized in Scheme 1. Addition of 2 equiv of Li[OCMeCH-CMeN(Ar)],[13] where Ar = 2,6-diisopropylphenyl, to a

toluene solution of $^{t-}$BuN=TiCl$_2$Py$_3{}^{5c}$ at room temperature for 16 h afforded a new titanium imido compound, $^{t-}$BuN=Ti[OCMeCHCMeN(Ar)]$_2$ (**1**) in 85% yield as a brown red solid. The ^{1}H NMR spectrum of **1** shows only one set of ketiminate ligand signals and the methine proton of the ketiminate backbone appears at δ 5.21. Four doublets for the methyl protons of the isopropyl groups were observed at δ 0.89−1.45 and two septets for the methine proton of the isopropyl groups appeared at δ 2.15 and 3.93.

Imido ligand exchanges have been reported in the literature[5b,5c] that involve the reactions of metal imido compounds with different amine ligands. We have found that the imido ligand exchange also takes place if phenyl isocyanate is added to titanium imido compounds. Reaction of **1** with 1 equiv of phenyl isocyanate produced a new titanium phenylimido complex PhN=Ti[OCMeCHCMeN-(Ar)]$_2$ (**2**), a small amount of O=Ti[OCMeCHCMeN(Ar)]$_2$ (**3**), and several unidentified products. The ^{1}H NMR spectrum of **2** shows only one resonance for the methine proton of the ketiminate backbone at δ 5.28.

Compound **1** eliminated the imido group on heating in heptane at 95 °C for 12 h to afford **3** and $^{t-}$BuNHCMe-CHCMeNAr (**4**) with yields of 11% and 10%, respectively. A proposed mechanism for the conversion of Ti=N to Ti=O has been shown in Scheme 2. The low conversion yield has been attributed to the side reactions of final stages of protonations and ligand redistribution. Similar rearrangements were reported elsewhere.[15] The organic compound **4** was characterized by ^{1}H and ^{13}C NMR spectra and single-crystal structure determination. Similarly, monitoring the decomposition of compound **2** in C$_6$D$_6$ also resulted in the generation of compound **3**.

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Scheme 2
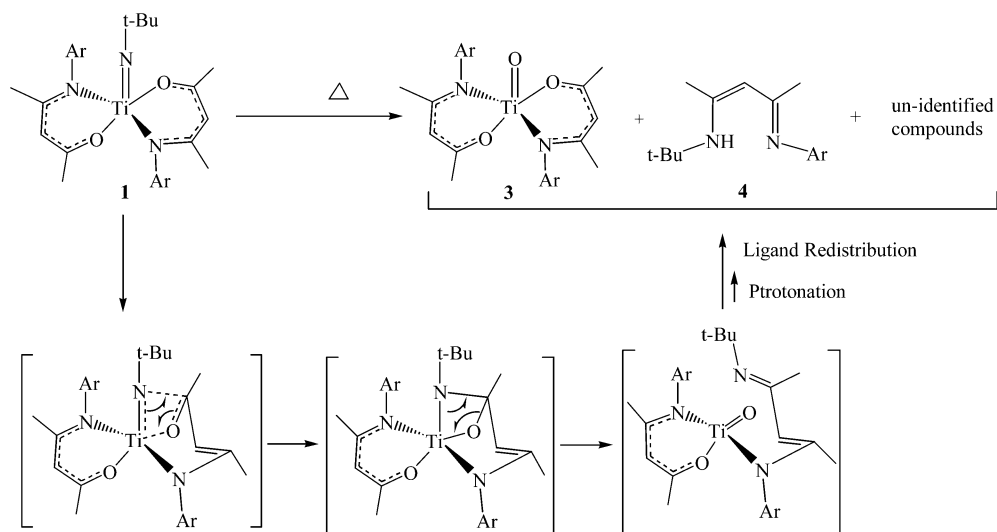
Scheme 3
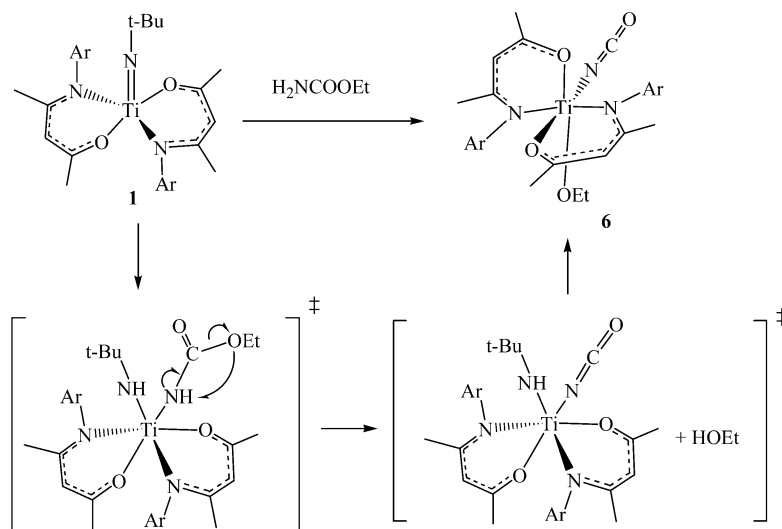
Moreover, compound **3** can also be obtained in 36% and 76% yield, respectively, by reacting **1** with 1 equiv of PhNCO in heptane at 95 °C for 12 h or with an excess of CO_2 in a toluene solution for 12 h. Compound **3** was characterized by ^1H, $^{13}C\{^1H\}$, DEPT, ^{13}C Gated, and ^1H-^{13}C HSQC NMR spectroscopy and a single-crystal X-ray structure determination (vide infra). The ^1H NMR spectrum of **3** exhibited only one resonance for the methine proton of the ketiminate backbone at δ 5.35, indicating a symmetrical geometry of the titanium oxo compound. The methyl groups of isopropyl (CH*Me*$_2$) and ketiminate backbone (OC*Me*CH-C*Me*N) fragments were clearly distinguished by the ^{13}C DEPT and ^1H-^{13}C HSQC NMR spectra.

Terminal titanium sulfido compounds are commonly prepared by dehydrogenation of hydrosulfide[10] or from elemental sulfur.[7b] The reactions of titanium imido compounds with carbon disulfide to yield terminal titanium sulfido compounds have not been reported. Reaction of **1** with an excess of carbon disulfide formed a novel terminal titanium sulfido compound S=Ti[OCMeCHCMeN(Ar)]$_2$ (**5**) with a 27% isolated yield via a C=S bond breaking reaction.

The ^1H NMR spectrum of **5** is similar to that of **3** where the methine proton of ketiminate backbone appeared at δ 5.57.

Metal isocyanate derivatives are common for the late transition metals;[16] however, there are fewer examples of structurally characterized early transition metals isocyanate compounds.[17] Refluxing of **1** with 1 equiv of urethane, $H_2NCOOEt$, in heptane for 6 h resulted in the elimination of ethanol, which subsequently reacted with the titanium center to remove a *tert*-butylamine. Upon removal of the volatile materials a red solid was isolated which gave titanium isocyanate compound, Ti[OCMeCHCMeN(Ar)]$_2$-(NCO)(OEt) (**6**), in 29% yield after recrystallization from acetonitrile. A suggested reaction mechanism is shown in Scheme 3. The low yield of **6** is attributed to the further reaction of **6** with the resulting ethanol that yielded ketimine ligands and other unknown products. The ^1H NMR spectrum

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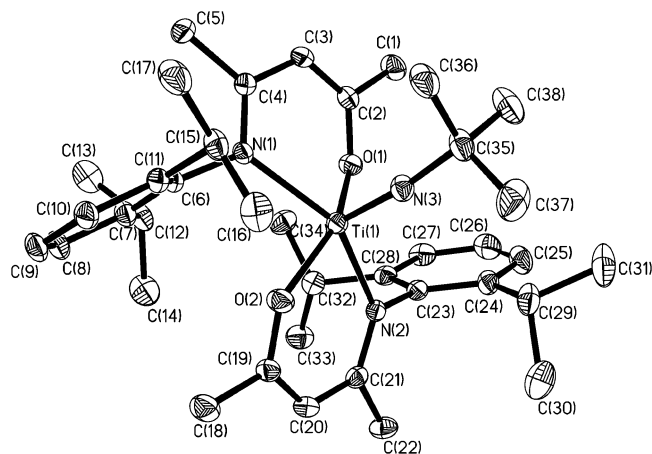
Figure 1. Molecular structure of compound **1** with thermal ellipsoids at 30% probability level. Hydrogen atoms were omitted for clarity.

Figure 2. Molecular structure of compound **3** with thermal ellipsoids at 30% probability level. Hydrogen atoms were omitted for clarity.

Figure 3. Molecular structure of compound **5** with thermal ellipsoids at 30% probability level. Hydrogen atoms were omitted for clarity.
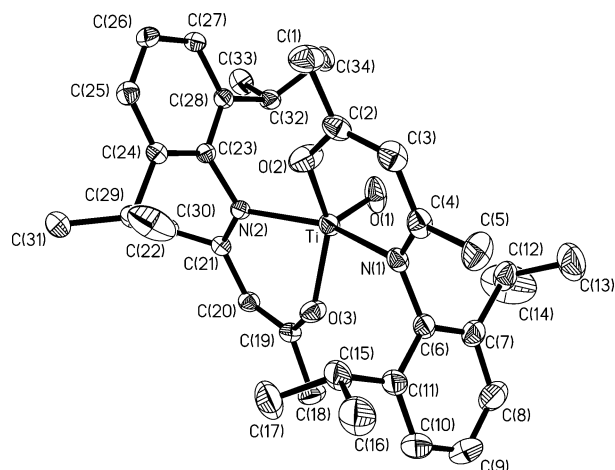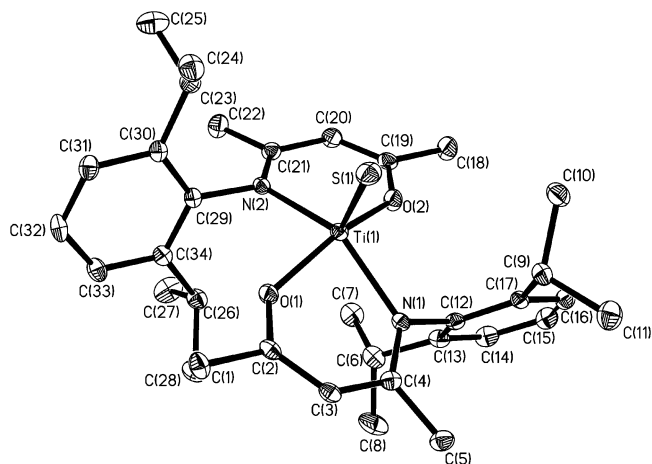

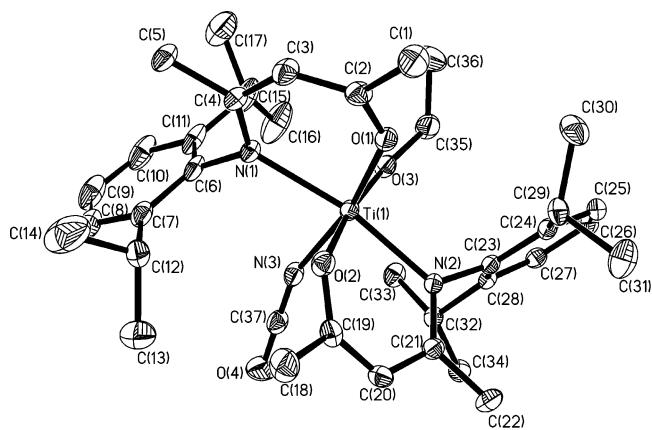**Figure 4.** Molecular structure of compound **6** with thermal ellipsoids at 30% probability level. Hydrogen atoms were omitted for clarity.

of **6** displayed two singlets for the methine protons of the two ketiminate backbones at δ 5.32 and 5.25, indicating an unsymmetrical arrangement of the two ketiminate fragments. The $^{13}C\{^1H\}$ NMR spectrum of **6** exhibited four distinct signals for the C−N and C−O bonds of the two ketiminate fragments in the range of δ 169−180; however, the carbon signal of NCO fragment could not be located on a 300 MHz NMR spectrometer presumably due to the overlapping with the resonances of phenyl groups at ca. δ 120. Therefore, a spectrum of compound **6** was recorded again using a 600 MHz NMR spectrometer and the NCO ^{13}C resonance was located as a singlet at δ 124.0. Again, the methyl groups of isopropyl (CH*Me*$_2$) and ketiminate backbone (OC*Me*CHC-*Me*N) fragments were clearly identified by the ^{13}C DEPT and ^1H-^{13}C HSQC NMR spectra. The IR spectrum of **6** contains a strong stretching frequency at 2205 cm^{-1} consistent with the existence of NCO fragment.[17]

Solid-State Structures of Compounds 1, 3, 5, and 6. The X-ray single-crystal structures of **1**, **3**, **5**, and **6** were

determined and the molecular structures are shown in Figures 1−4. The summary of data collections and selected bond distances and angles are shown in Tables 1 and 2, respectively. The molecule of titanium imido compound **1** possesses a distorted square pyramidal geometry where the two ketiminate ligands occupy the base and the imido nitrogen atom takes the apical position. The two ketiminate ligands chelate the central titanium atom with acute bite angles of 83.25(6)° and 83.70(6)°, respectively. The bond angle Ti(1)−N(3)−C(35) of 169.75(16)° and bond distance Ti(1)−N(3) of 1.7041(16) Å are within the normal range for titanium imido compounds.[18]

The structures of **3** and **5** are similar to that of **1**, where the terminal oxo and sulfido ligands lie in the apical position of the square pyramidal. It is interesting to compare deviation of the titanium atom from the square planar base, formed by the nitrogen and oxygen atoms of two ketiminate fragments, of compounds **1**, **3**, and **5** as shown in Scheme 4. The distances (r) of the titanium atom, above base plane, are 0.6055 Å for E = N^{t}Bu, 0.5535 Å for E = O, and 0.6242

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Table 1. Summary of Data Collections for Compounds **1**, **3**, **4**, **5**, and **6**

	1	3	5	6
formula	$C_{38}H_{57}N_3O_2Ti$	$C_{34}H_{48}N_2O_3Ti$	$C_{34}H_{48}N_2O_2TiS$	$C_{38}H_{54.5}N_{3.5}O_4Ti$
fw	635.77	580.64	596.70	672.25
temp, K	150(2)	150(2)	150(2)	150(2)
cryst syst	monoclinic	rhombohedral	triclinic	triclinic
space group	$P2_1/n$	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.7696(5)	36.3893(5)	10.2706(6)	13.2331(2)
b, Å	21.4932(14)	36.3893(5)	12.5962(8)	14.9156(2)
c, Å	20.3254(13)	13.0575(2)	14.3469(9)	18.9913(3)
α, deg	90	90	71.125(1)	88.9675(7)
β, deg	99.190(1)	90	88.106(1)	80.9697(7)
γ, deg	90	120	71.686(1)	86.5625(7)
V (Å^3)/Z	3781.9(4)/4	14974.0(4)/18	1662.43(18)/2	3695.23(9)/4
D_{calcd} (Mg/m^3)	1.117	1.159	1.192	1.208
abs coeff (mm^{-1})	0.260	0.291	0.351	0.274
cryst size (mm)	0.34 × 0.25 × 0.22	0.30 × 0.20 × 0.20	0.32 × 0.28 × 0.25	0.30 × 0.20 × 0.20
no. of ind reflns	8595 (R_{int} = 0.0314)	7632 (R_{int} = 0.0494)	7340 (R_{int} = 0.0252)	16961 (R_{int} = 0.0526)
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0479	R_1 = 0.0601	R_1 = 0.0413	R_1 = 0.0534
	wR_2 = 0.1391	wR_2 = 0.1685	wR_2 = 0.1099	wR_2 = 0.1364

Table 2. Selected Bond Lengths and Angles for Compounds **1**, **3**, **4**, **5**, and **6**

1

Ti(1)−N(1)	2.1702(16)	Ti(1)−N(2)	2.2102(15)
Ti(1)−O(1)	1.9558(13)	Ti(1)−O(2)	1.9580(14)
Ti(1)−N(3)	1.7041(16)		
O(1)−Ti(1)−O(2)	149.50(6)	N(1)−Ti(1)−N(2)	142.92(6)
O(1)−Ti(1)−N(1)	83.25(6)	O(2)−Ti(1)−N(2)	83.70(6)

3

Ti(1)−N(1)	2.1882(19)	Ti(1)−N(2)	2.1660(18)
Ti(1)−O(1)	1.620(2)	Ti(1)−O(2)	1.927(2)
Ti(1)−O(3)	1.9157(17)		
O(2)−Ti(1)−O(3)	140.02(10)	N(1)−Ti(1)−N(2)	156.12(7)
O(2)−Ti(1)−N(1)	83.84(8)	O(3)−Ti(1)−N(2)	83.61(7)

5

Ti(1)−N(1)	2.1366(17)	Ti(1)−N(2)	2.1758(17)
Ti(1)−O(1)	1.9024(14)	Ti(1)−O(2)	1.9069(14)
Ti(1)−S(1)	2.1189(7)		
O(1)−Ti(1)−O(2)	149.36(7)	N(1)−Ti(1)−N(2)	139.53(7)
O(1)−Ti(1)−N(1)	83.60(6)	O(2)−Ti(1)−N(2)	82.98(6)

6

Ti(1)−N(1)	2.2200(16)	Ti(1)−N(2)	2.1556(16)
Ti(1)−N(3)	2.0096(19)	Ti(1)−O(1)	1.9218(15)
Ti(1)−O(2)	1.9701(16)	Ti(1)−O(3)	1.7868(16)
N(3)−C(37)	1.183(3)	C(37)−O(4)	1.188(3)
Ti(2)−N(5)	2.2324(16)	Ti(2)−N(4)	2.1409(16)
Ti(2)−N(6)	1.9865(19)	Ti(2)−O(5)	1.9903(14)
Ti(2)−O(6)	1.9314(15)	Ti(2)−O(7)	1.7785(14)
N(7)−C(75)	1.143(4)	C(74)−O(8)	1.178(3)
O(2)−Ti(1)−O(3)	169.87(7)	N(1)−Ti(1)−N(2)	168.48(7)
O(1)−Ti(1)−N(3)	166.83(7)	O(2)−Ti(1)−N(2)	82.81(6)
O(1)−Ti(1)−N(1)	83.58(6)	Ti(1)−N(3)−C(37)	160.50(17)
N(3)−C(37)−O(4)	179.0(3)	Ti(1)−O(3)−C(35)	158.91(17)
O(7)−Ti(2)−O(5)	168.50(7)	N(4)−Ti(2)−N(5)	169.13(6)
O(6)−Ti(2)−N(6)	167.44(6)	O(5)−Ti(2)−N(4)	82.26(6)
O(6)−Ti(2)−N(5)	83.49(6)	Ti(2)−N(6)−C(74)	166.49(18)
N(6)−C(74)−O(8)	178.5(3)	Ti(2)−O(7)−C(72)	156.55(15)

Å for E = S. The sulfur atom of **5** and N^{t}Bu of **1** have the same effects on the molecular geometries and give rise to a larger deviation from the basal plane in comparison to that of **3**.

The Ti−O bond distance (1.620(2) Å) of **3** is within the normal range of titanium oxo compounds.[5] The Ti−S bond distance (2.1189(7) Å) of **5** is similar to that in [NEt$_4$]$_2$-[TiSCl$_4$]; however, it is on the short end when compared with those observed in Cp*$_2$PyTi(S),[7a] [CpTi(μ-S)(S)]$_2$$^{2-}$,[10] and [PhC(NSiMe$_3$)$_2$]$_2$Ti(S).[12a] The comparisons of bond lengths of structurally characterized Ti=S compounds have been collected in Table 3.

Table 3. Comparisons of Bond Lengths of Structural Characterized Ti=S Compounds

compound	bond length (Ti=S)	reference
S=Ti[OCMeCHCMeN(Ar)]$_2$	2.1189(7)	this work
Cp*$_2$Ti(S)Py	2.217(1)	7a
[CpTi(μ-S)(S)]$_2$$^{2-}$	2.187(1)/2.202(1)	10
[PhC(NSiMe$_3$)$_2$]$_2$Ti(S)Py	2.139(1)	11
TiCl$_2$(S)(μ-S)$_2$Pd$_2$(PEt$_3$)$_4$	2.117(1)	19
[NEt$_4$]$_2$[TiSCl$_4$]	2.111(2)	12

Scheme 4
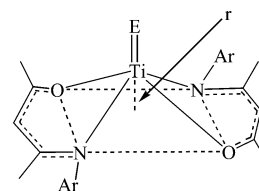
1, E = N^{t}Bu

3, E = O

5, E = S

r = distance of titanium above the base plane

The crystals of **6** were obtained from a concentrated acetonitrile solution. Two independent molecules of **6** and one acetonitrile solvent molecule are observed in one unit cell. However, the two molecules of **6** have similar bond distances and angles; therefore, only one of these is discussed here. The geometry about titanium center of **6** (Figure 4) is pseudo-octahedral and is composed of two ketimine fragments, a NCO, and an OEt group. The nitrogen atoms of the two ketimine ligands are arranged in trans positions (N(1)−Ti(1)−N(2) = 168.48(7)°) and the two oxygen atoms of the two ketimine ligands are trans to NCO and OEt fragments, respectively, with the bond angles O(1)−Ti(1)−N(3) of 166.83(7)° and O(2)−Ti(1)−O(3) of 169.87(7)°.

DFT Calculation for the Reaction of 1 with CS$_2$. The formation of titanium oxo and sulfido compounds and the intriguing reactivity of compound **1** toward CS$_2$ were studied carefully by means of density functional theory, which includes Becke's three-parameter nonlocal exchange potential and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP)[20] with the 6-31G* basis sets. The computed bond energies of Ti=N bond in **1**, C=S bond in CS$_2$, Ti=S

Table 4. Comparisons of Theoretical and Experimental Data for Compound **5**

	theoretical	experimental
Ti(1)−N(1)	2.2176	2.1702(16)
Ti(1)−N(2)	2.2815	2.2102(15)
Ti(1)−N(3)	1.6857	1.7041(16)
Ti(1)−O(1)	1.9689	1.9558(13)
Ti(1)−O(2)	1.9697	1.9580(14)
C(1)−C(2)	1.5082	1.500(3)
C(2)−O(1)	1.2980	1.299(2)
C(2)−C(3)	1.3841	1.375(3)
C(6)−N(1)	1.4452	1.451(2)
C(23)−N(2)	1.4480	1.452(2)
N(1)−Ti(1)−N(2)	142.12	142.92(6)
N(3)−Ti(1)−N(1)	104.17	103.46(7)
N(3)−Ti(1)−N(2)	116.21	113.58(7)
N(3)−Ti(1)−O(1)	101.96	102.10(7)
N(3)−Ti(1)−O(2)	106.44	108.22(7)
O(1)−Ti(1)−N(1)	83.16	83.25(6)
O(1)−Ti(1)−N(2)	86.84	87.33(5)
O(1)−Ti(1)−O(2)	148.04	149.50(6)
O(2)−Ti(1)− N(1)	87.70	86.53(6)
O(2)−Ti(1)− N(2)	83.20	83.70(6)

bond in **5**, and N=C bond in t-BuNCS are 115.8, 186.1, 123.4, and 196.2 kcal·mol^{-1}, respectively. Therefore, the reaction of **1** + CS$_2$ → **5** + t-BuNCS is the result of the preference of forming of Ti=S bond in **5** (−7.6 kcal·mol^{-1}) and N=C bond in t-BuNCS (−10.1 kcal·mol^{-1}). The predicted geometrical parameters at the B3LYP/6-31G* level agree reasonably well with those obtained from X-ray data as shown in Table 4 The computations were performed using the Gaussian98 series of programs.[21]

Conclusions

In summary, we demonstrated C=O and C=S double bonds cleavage by terminal titanium imido compounds, which results in the formation of terminal titanium oxo and titanium sulfido compounds, respectively. In addition, the titanium oxo compound **3** can also be obtained from the reactions of **1** with PhNCO or by decomposition at 95 °C for 12 h through an unusual Ti−O/Ti=N bond exchange. The unusual Ti−NCO compound **6** was obtained from the reaction of **1** with urethane through protonation and amine elimination. Investigations with respect to the reactivity of ketiminate titanium **1**, **3**, **5**, and **6** are currently under way.

Experimental Section

General Procedures. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a

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glovebox. Toluene and diethyl ether were dried by refluxing over sodium benzophenone ketyl. CH$_2$Cl$_2$ was dried over P$_2$O$_5$. All solvents were distilled and stored in solvent reservoirs which contained 4-Å molecular sieves and were purged with nitrogen. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker AC 200 or Avance 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were recorded in ppm relative to the residual proton and ^{13}C of CDCl$_3$ (δ 7.24, 77.0), C$_6$D$_6$ (δ 7.15, 128.0), or CD$_2$Cl$_2$ (δ 5.24, 54.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. [OCMeCHCMeNH(Ar)] was prepared according to a previously reported procedure.[13] TiCl$_4$ was used as received.

Synthesis of ^{t}−BuN=Ti[OCMeCHCMeN(Ar)]$_2$ (1). A Schlenk flask charged with Li[OCMeCHCMeN(Ar)] (5.112 g, 19.3 mmol) and [t-BuN=TiCl$_2$Py$_3$] (4.06 g, 9.6 mmol) was cooled to 0 °C, and 30 mL of toluene was added. The mixture was stirred at room temperature for 16 h and was filtered through Celite. The filtrate was dried under vacuum and the product was recrystallized from toluene resulting in 5.2 g (85% yield) of brown red solid. ^{1}H NMR-(CDCl$_3$): 7.20−7.08 (m, 6H, phenyl C*H*), 5.21 (s, 2H, CMeC*H*-CMe), 3.93 (m, 2H, C*H*Me$_2$), 2.15 (m, 2H, C*H*Me$_2$), 1.68 (s, 6H, C*Me*), 1.49 (s, 6H, C*Me*), 1.45 (d, 6H, CH*Me$_2$*), 1.12 (d, 6H, CH*Me$_2$*), 0.97 (d, 6H, CH*Me$_2$*), 0.89 (d, 6H, CH*Me$_2$*), 0.82 (s, 9H, C*Me$_3$*). ^{13}C NMR (CDCl$_3$): 179.0 (s, *C*O), 171.8 (s, *C*N), 147.9 (s, phenyl *C*$_{ipso}$), 141.8 (s, phenyl *C*$_{ipso}$), 141.1 (s, phenyl *C*$_{ipso}$), 125.0 (d, J_{CH} = 159 Hz, phenyl C*H*), 123.3 (d, J_{CH} = 159 Hz, phenyl C*H*), 123.2 (d, J_{CH} = 159 Hz, phenyl C*H*), 101.2 (d, J_{CH} = 161 Hz, CMe*C*HCMe), 70.6 (s, *C*Me$_3$), 31.4 (q, J_{CH} = 129 Hz, C*Me$_3$*), 27.7 (d, J_{CH} = 124 Hz, *C*HMe$_2$), 27.6 (d, J_{CH} = 124 Hz, *C*HMe$_2$), 24.7 (q, J_{CH} = 126 Hz, CH*Me$_2$*), 24.6 (q, J_{CH} = 126 Hz, CH*Me$_2$*), 24.1 (q, J_{CH} = 129 Hz, CH*Me$_2$*), 24.0 (q, J_{CH} = 129 Hz, CH*Me$_2$*). Anal. Calcd for C$_{38}$H$_{57}$N$_3$O$_2$Ti (635.77): C, 71.79; H, 9.04; N, 6.61. Found: C, 71.28; H, 8.98; N, 7.00.

Synthesis of PhN=Ti[OCMeCHCMeN(Ar)]$_2$ (2). Method A. A solution of **1** and PhNCO in CDCl$_3$ was transferred to a J. Young NMR tube and ^{1}H NMR spectra were acquired. The methine proton for **1** (δ 5.21) disappeared with 3 days and a new methine proton resonance of **2** (δ 5.28) was observed. **Method B.** A solution of PhNCO (0.17 mL, 0.78 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of **1** (0.5 g, 0.78 mmol) in toluene (20 mL). The resulting solution was stirred for 72 h. The volatile materials were removed under vacuum and the resulting mixture was recrystallized from a toluene solution to generate 0.046 g of colorless solids in very low yield (9%). ^{1}H NMR(CDCl$_3$): 7.26−6.80 (m, 11H, phenyl C*H*), 5.28 (s, 2H, CMeC*H*CMe), 3.35 (m, 2H, C*H*Me$_2$), 2.13 (m, 2H, C*H*Me$_2$), 1.66 (s, 6H, C*Me*), 1.37 (s, 6H, C*Me*), 1.19 (d, 6H, CH*Me$_2$*), 0.97 (d, 6H, CH*Me$_2$*), 0.87 (d, 6H, CH*Me$_2$*), 0.80 (d, 6H, CH*Me$_2$*). ^{13}C NMR (CDCl$_3$): 178.2 (s, *C*O), 173.4 (s, *C*N), 145.8 (s, phenyl *C*$_{ipso}$), 142.4 (s, phenyl *C*$_{ipso}$), 140.7 (s, phenyl *C*$_{ipso}$), 139.5 (s, phenyl *C*$_{ipso}$), 128.7 (d, J_{CH} = 161 Hz, phenyl C*H*), 125.9 (d, J_{CH} = 151 Hz, phenyl C*H*), 123.9 (d, J_{CH} = 161 Hz, phenyl C*H*), 123.2 (d, J_{CH} = 150 Hz, phenyl C*H*), 119.0 (d, J_{CH} = 160 Hz, phenyl C*H*), 102.3 (d, J_{CH} = 160 Hz, CMe*C*HCMe), 28.3 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 27.9 (d, J_{CH} = 130 Hz, *C*HMe$_2$), 25.1 (q, J_{CH} = 121 Hz, C*Me*), 24.3 (q, J_{CH} = 126 Hz, C*Me*), 24.1 (q, J_{CH} = 128 Hz, CH*Me$_2$*), 23.4 (q, J_{CH} = 127 Hz, CH*Me$_2$*), 23.3 (q, J_{CH} = 127 Hz, CH*Me$_2$*).

Synthesis of O=Ti[OCMeCHCMeN(Ar)]$_2$ (3). Method A. A solution of **1** (1.0 g, 1.56 mmol) in heptane (30 mL) was heated at 95 °C for 12 h. A small amount of crystals was obtained while the solution was cooled to room temperature. These were isolated and recrystallized from methanol to yield 0.05 g of **4** (10% yield). The remaining solution was reducing to 5 mL and cooled at −20 °C to

generate 0.10 g of **3** (11% yield). **Method B.** PhNCO (0.190 g, 1.573 mmol) was added to a heptane (20 mL) solution of **1** (1.0 g, 1.573 mmol) at room temperature. The resulting solution was heated at 95 °C for 12 h and volatiles were removed under vacuum to yield off-white solids. The solid was recrystallized from a toluene and heptane mixing solvent to yield bright-yellow crystals (0.333 g, 36% yield). Yield loses occurred during isolation. **Method C.** A solution of **1** (0.5 g, 0.78 mmol) in toluene (30 mL) was transferred to a Fisher−Porter glass reactor. The reactor was pressurized with CO_2 gas at 14 psi for 12 h. The volatiles were removed under vacuum to generate 0.343 g of **3** in 76% yield. For compound **3**, ^1H NMR(CDCl$_3$): 7.21−7.07 (m, 6H, phenyl CH), 5.35 (s, 2H, CMeCHCMe), 3.50 (m, 2H, CHMe$_2$), 2.23 (m, 2H, CHMe$_2$), 1.77 (s, 6H, CMe), 1.47 (s, 6H, CMe), 1.33 (d, 6H, CHMe_2), 1.19 (d, 6H, CHMe_2), 0.97 (d, 6H, CHMe_2), 0.91 (d, 6H, CHMe_2). ^{13}C NMR (CDCl$_3$): 178.1 (s, CO), 173.2 (s, CN), 145.9 (s, phenyl C_{ipso}), 142.4 (s, phenyl C_{ipso}), 140.6 (s, phenyl C_{ipso}), 125.7 (d, $J_{CH} = 159$ Hz, phenyl CH), 123.8 (d, $J_{CH} = 155$ Hz, phenyl CH), 123.1(d, $J_{CH} = 153$ Hz, phenyl CH), 102.3 (d, $J_{CH} = 161$ Hz, CMeCHCMe), 28.3 (d, $J_{CH} = 127$ Hz, CHMe$_2$), 27.7 (d, $J_{CH} = 127$ Hz, CHMe$_2$), 25.2 (q, $J_{CH} = 127$ Hz, CHMe_2), 24.4 (q, $J_{CH} = 131$ Hz, CHMe_2), 24.1 (q, $J_{CH} = 128$ Hz, CMe), 24.0 (q, $J_{CH} = 128$ Hz, CHMe_2), 23.4 (q, $J_{CH} = 127$ Hz, CMe), 23.0 (q, $J_{CH} = 127$ Hz, CHMe_2). Anal. Calcd for C$_{34}$H$_{48}$N$_2$O$_3$Ti: C, 70.33; H, 8.33; N, 4.82. Found: C, 69.79; H, 7.92; N, 4.21. For compound **4**, ^1H NMR(CDCl$_3$): 11.19 (s, 1H, NH), 7.11−6.99 (m, 3H, phenyl CH), 4.57 (s, 1H, CMeCHCMe), 2.86 (m, 2H, CHMe$_2$), 2.12 (s, 3H, CMe), 1.58 (s, 3H, CMe), 1.31 (s, 9H, CMe_3), 1.18 (d, 6H, CHMe_2), 1.11 (d, 6H, CHMe_2). ^{13}C NMR (CDCl$_3$): 165.7 (s, CN), 155.6 (s, CN), 147.1 (s, phenyl C_{ipso}), 138.0 (s, phenyl C_{ipso}), 122.5 (d, $J_{CH} = 159$ Hz, phenyl-CH), 122.3 (d, $J_{CH} = 159$ Hz, phenyl-CH), 94.4 (d, $J_{CH} = 163$ Hz, CMeCHCMe), 51.5 (s, CMe$_3$), 31.3 (q, $J_{CH} = 130$ Hz, CMe_3), 28.1 (d, $J_{CH} = 132$ Hz, CHMe$_2$), 23.9 (q, $J_{CH} = 131$ Hz, CMe), 22.5 (q, $J_{CH} = 130$ Hz, CMe), 21.6 (q, $J_{CH} = 126$ Hz, CHMe_2), 21.4 (q, $J_{CH} = 126$ Hz, CHMe_2). MS (M$^+$): 314.

Synthesis of S=Ti[OCMeCHCMeN(Ar)]$_2$ (5). To a 50-mL Schenk flask charged with **1** (1.0 g, 1.56 mmol) and 20 mL toluene was added excess carbon disulfide via syringe at room temperature. The solution was stirred at room temperature for 36 h and volatiles were removed under vacuum. The resulting solid was recrystallized from a mixture of diethyl ether and methylene chloride to yield 0.27 g of **5** (27% yield). ^1H NMR(CDCl$_3$): 7.23 (m, 4H, phenyl CH), 7.03 (m, 2H, phenyl CH), 5.57 (s, 2H, CMeCHCMe), 3.70 (m, 2H, CHMe$_2$), 1.82 (s, 6H, CMe), 1.67 (m, 2H, CHMe$_2$), 1.62 (s, 6H, CMe),1.43 (d, 6H, CHMe_2), 1.68 (d, 6H, CHMe_2), 0.85 (d, 6H, CHMe_2), 0.77 (d, 6H, CHMe_2). ^{13}C NMR (CDCl$_3$): 177.9 (s, CO), 172.5 (s, CN), 146.6 (s, phenyl C_{ipso}), 142.4 (s, phenyl C_{ipso}), 140.5 (s, phenyl C_{ipso}), 126.1 (d, $J_{CH} = 159$ Hz, phenyl CH), 124.2 (d, $J_{CH} = 159$ Hz, phenyl CH), 123.1 (d, $J_{CH} = 159$ Hz, phenyl CH), 103.7 (d, $J_{CH} = 161$ Hz, CMeCHCMe), 28.3 (d, $J_{CH} = 127$ Hz, CHMe$_2$), 27.9 (d, $J_{CH} = 127$ Hz, CHMe$_2$), 26.0 (q, $J_{CH} = 121$ Hz, CHMe_2), 24.6 (q, $J_{CH} = 125$ Hz, CHMe_2), 24.4 (q, $J_{CH} = 129$ Hz, CMe), 24.3 (q, $J_{CH} = 125$ Hz, CHMe_2), 23.0 (q, $J_{CH} = 130$ Hz, CMe), 22.9 (q, $J_{CH} = 130$ Hz, CHMe_2). Anal. Calcd for C$_{34}$H$_{48}$N$_2$O$_2$STi (596.70): C, 68.44; H, 8.11; N, 4.70. Found: C, 68.44; H, 8.23; N, 5.09.

Synthesis of Ti[OCMeCHCMeN(Ar)]$_2$(NCO)(OEt) (6). A solution of **1** (0.5 g, 0.78 mmol) and urethane, H$_2$NCOOEt, (0.54 g, 0.78 mmol) in heptane (30 mL) was heated at 95 °C for 6 h. The volatile materials were removed under vacuum and the residual was recrystallized from an acetonitrile solution to yield 0.147 g of red crystals (29% yield). ^1H NMR(CDCl$_3$): 7.24−7.11 (m, 6H, phenyl CH), 5.32 (s, 1H, CMeCHCMe), 5.25 (s, 1H, CMeCHCMe), 3.31−3.08 (m, 6H, CHMe$_2$ and OCH_2CH$_3$), 2.03 (s, 3H, CMe), 2.01 (s, 3H, CMe), 1.98 (s, CH_3CN), 1.64 (s, 3H, CMe), 1.61 (s, 3H, CMe), 1.32 (d, 3H, CHMe_2), 1.28 (d, 3H, CHMe_2), 1.22 (d, 3H, CHMe_2), 1.18 (d, 3H, CHMe_2), 1.09 (d, 3H, CHMe_2), 1.07 (d, 3H, CHMe_2), 0.98 (d, 3H, CHMe_2), 0.97 (d, 3H, CHMe_2), 0.74 (t, 3H, OCH$_2$CH_3). ^{13}C NMR (CDCl$_3$): 180.8 (s, CO), 174.4 (s, CO), 170.3 (s, CN), 170.0 (s, CN), 149.7 (s, phenyl C_{ipso}), 148.9 (s, phenyl C_{ipso}), 142.2 (s, phenyl C_{ipso}), 140.8 (s, phenyl C_{ipso}), 140.7 (s, phenyl C_{ipso}), 140.2 (s, phenyl C_{ipso}), 126.0 (d, $J_{CH} = 159$ Hz, phenyl CH), 125.8 (d, $J_{CH} = 159$ Hz, phenyl CH), 124.8 (d, $J_{CH} = 160$ Hz, phenyl CH), 124.1 (d, $J_{CH} = 156$ Hz, phenyl CH), 123.6 (d, $J_{CH} = 161$ Hz, phenyl CH), 123.5 (s, NCO), 123.3 (d, $J_{CH} = 158$ Hz, phenyl CH), 102.8 (d, $J_{CH} = 161$ Hz, CMeCHCMe), 102.1 (d, $J_{CH} = 160$ Hz, CMeCHCMe), 73.0 (t, $J_{CH} = 144$ Hz, OCH$_2$CH$_3$), 27.5 (d, $J_{CH} = 128$ Hz, CHCMe$_2$), 27.2 (d, $J_{CH} = 128$ Hz, CHCMe$_2$), 25.6 (q, $J_{CH} = 128$ Hz, CMe), 25.5 (q, $J_{CH} = 128$ Hz, CMe), 25.2 (q, $J_{CH} = 126$ Hz, CHMe_2), 24.9 (q, $J_{CH} = 126$ Hz, CHMe_2), 24.8 (q, $J_{CH} = 126$ Hz, CHMe_2), 24.7 (q, $J_{CH} = 125$ Hz, CHMe_2), 24.6 (q, $J_{CH} = 125$ Hz, CHMe_2), 24.5 (q, $J_{CH} = 128$ Hz, CHMe_2), 24.3 (q, $J_{CH} = 128$ Hz, CHMe_2 and CMe), 24.27 (q, $J_{CH} = 128$ Hz, CMe), 17.2 (q, $J_{CH} = 126$ Hz, OCH$_2$$CH_3$), 0.99 (q, $J_{CH} = 126$ Hz, CH$_3$CN). IR (KBr): 2205 cm^{-1}(ν_{NCO}). Anal. Calcd for C$_{37}$H$_{53}$N$_3$O$_4$Ti (651.70): C, 68.19; H, 8.20; N, 6.45. Found: C, 66.98; H, 8.24; N, 5.84.

X-ray Structure Determination for Compounds 1, 3, 4, 5, and 6. All the crystals were mounted on a glass fiber using epoxy resin and transferred to a goniostat. Data collections were preformed at 298 K for compound **4** and 150 K under liquid nitrogen vapor for compounds **1**, **3**, **5**, and **6**. Data were collected on a Bruker SMART CCD or a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation. Structure determinations were perormed using the SHELXTL package of programs. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were added at calculated positions. The crystal data for **1**, **3**, **5**, and **6** are summarized in Table 1.

Supporting Information Available: CIF files for complexes **1**, **3**, **4**, **5**, and **6**, and ^1H−^{13}C HSQC spectra for complexes **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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