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Addition and Cycloaddition Reactions of the Nucleophilic Oxo and Sulfido Complexes [tmtaa]Ti=X (X = O, S; tmtaa = Dianion of 7,16-Dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine)[§]

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The complexes [tmtaa]Ti=O (**1**) and [tmtaa]Ti=S (**2**) have highly reactive Ti=O and Ti=S linkages and are demonstrated to undergo a number of new addition and cycloaddition reactions, and complex **1** has been found to be involved in a series of acid–base equilibria. Treatment of **1** or **2** with excess RO_3SCF_3 (R = H, Me, $SiMe_3$) yields the bis(triflate) complex $[tmtaa]Ti(O_3SCF_3)_2$. This species in turn slowly reacts with water to displace the triflate ions and form the bis(aqua) complex $[(tmtaa)Ti(OH_2)_2]^{2+}$ (**5**). Complex **1** reacts with 1 equiv of HO_3SCF_3 to form the oxo-bridged complex $[(tmtaa)Ti\text{–}O\text{–}Ti(tmtaa)]^{2+}$ (**8**), and treatment of either **5** or **8** with $[NH_4]OH$ or wet Et_3N regenerates **1**. Deoxygenation of **1** occurs when it is treated with excess acetyl chloride to form $[tmtaa]TiCl_2$ via a spectroscopically observed [tmtaa]Ti(Cl)(OC{O}Me) intermediate. Complex **1** also reacts with hexafluoroacetic, maleic, and phthalic anhydrides to form bis(carboxylate) complexes, and hexafluoropropylene oxide reacts with **1** to give a metallacycle formed by a net [3 + 2] cycloaddition reaction. Complex **1** undergoes [2 + 2] cycloaddition of the Ti=O bond across the C=O bond of electron deficient ketones to form the dioxatitanacyclobutanes $[tmtaa]Ti(\eta^2[O_2]\text{-}O_2CRR')$ (R = R′ = CF_3; R = CH_3, R′ = CF_3 (**16**); R = CF_3, R′ = Ph). Complex **2** undergoes an analogous [2 + 2] cycloaddition of its Ti=S bond across the C=O bond of $O{=}C(CF_3)_2$ and $O{=}C(CF_3)CH_3$ to form similar metallacycles. The Ti=O bond of **1** also undergoes [2 + 2] cycloaddition across a $C\equiv O$ bond of $[Cp^*Re(CO)_2(NO)]^+$ (**20**) to form the cationic heterobimetallic complex $[(tmtaa)Ti(\mu_2,\eta^3\text{-}O_2C)Re(CO)(NO)Cp^*]^+$ (**21**), and both **20** and **21** were observed to react with $Ph_3P{=}NPh$ to form $[Cp^*Re(C{\equiv}NPh)_2(NO)]^+$. Complex **1** also undergoes [2 + 2] cycloaddition reactions with SO_2 and SO_3 to form $\eta^2[O_2]$-sulfito (**23**) and $\eta^2[O_2]$-sulfato complexes, respectively. These same complexes result when the sulfido complex **2** is allowed to react with SO_2 and SO_3. Complex **1** reacts with COS to form the sulfido complex [tmtaa]Ti=S and CO_2 by successive cycloaddition and retro-cycloaddition reactions. The corresponding reaction of **1** with CS_2 gives a $\eta^2[S_2]\text{-}CS_3$ complex via the intermediate formation of [tmtaa]Ti=S which was independently shown to give this product upon treatment with CS_2. Complex **1** also reacts with Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide, to form the 4-membered non-carbon metallacycle $[tmtaa]Ti(\eta^2[O,S]\text{-}OSP({=}S)(C_6H_4OMe))$ (**34**). The reactions of **1** and [omtaa]Ti=O (omtaa = dianion of 7,16-dihydro-2,3,6,8,11,12,15,17-octamethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine) with CO_2 to form $\eta^2[O_2]$-carbonate complexes have also been studied. The oxo group of complex **1** also displaces the labile acetonitrile and acetone ligands in $Os_3(CO)_{11}(CH_3CN)$, *cis*-$[PtCl(PEt_3)(acetone)]^+$, and *trans*-$[Ir(CO)(PPh_3)(CH_3CN)]^+$ to form new μ_2-oxo heterobimetallic complexes that possess dative $Ti{=}O{\rightarrow}Os$, $Ti{=}O{\rightarrow}Pt$, and $Ti{=}O{\rightarrow}Ir$ bonds, respectively. Complex **1** also reacts with $Cp^*W(O)_2Cl$ to form the oxo-bridged heterobimetallic complex $Cp^*O_2W(\mu\text{-}O)Ti(Cl)(tmtaa)$ which can also be produced by adding $[Cp^*WO_3]^-$ to $(tmtaa)TiCl_2$. Complexes **5**, **8**, **16**, **21**, **23**, **34**, and the complex, **11**, formed between **1** and phthalic anhydride have been crystallographically characterized.

Introduction

Metal–oxo complexes are important species in catalytic and stoichiometric oxidation processes, but until recently it was assumed that the M=O unit was relatively inert and that the oxo group often served only as an important spectator ligand.[1] However, detailed fundamental reactivity studies of the M=O unit have recently begun to appear, and it is now recognized that the metal–oxo linkage has a rich and diverse chemistry of its own.[2-7] Particularly important in defining the chemistry of the M=O group have been Herrmann's studies of R–Re(O)$_3$ (R = Cp*, alkyl, aryl) and its derivatives,[2] Bercaw's work with $Cp^*_2W{=}O$,[3] our examination of the related compounds $Cp_2Mo{=}O$ and $Cp_2W{=}O$,[4] Bergman's studies of the transient complex $Cp^*_2Zr{=}O$,[5] and our recent studies of $[Cp^*MO_3]^-$ (M = Mo, W).[6]

Similarly, despite the importance of metal sulfides as catalysts for a number of industrial processes[8] and the role of metal–sulfur

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[§] Throughout this paper, boldface arabic numerals used to denote complexes may refer to both ions and their salts.

(1) For recent reviews, see: (a) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (c) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1987. (d) Nugent, W. A.; Mayer, W. A. *Metal Ligand Multiple Bonds*; John Wiley: New York, 1988.

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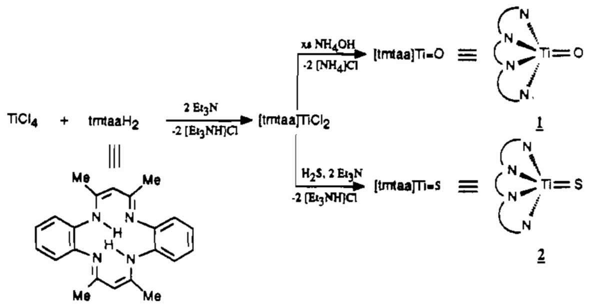
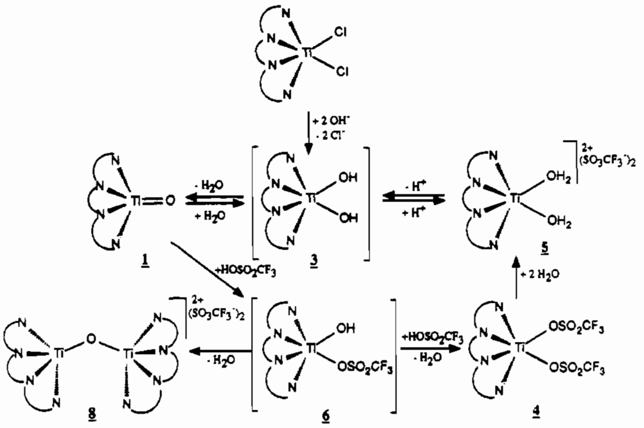
Scheme I [13]



complexes in many biological reactions,[9] the chemistry of the metal–sulfur double bond in terminal metal–sulfido complexes, L_nM=S, has not been extensively developed.[10] This is in part due to the strong preference of sulfur ligands to bridge metal atoms and form polynuclear complexes rather than to exist as mononuclear M=S complexes and is also due to the limited solubility of many sulfido complexes in organic solvents.[11] Bergman's recent demonstration that the transient species Cp^*_2-Zr=S undergoes cycloaddition of nitriles and alkynes across the Zr=S bond to give new types of metallacycles[5c,12] indicates that the M=S double bond is reactive toward organic substrates and hence such M=S complexes are worthy target molecules for synthesis and further investigation.

Compounds that appeared to be particularly suitable for further defining the chemistry of the metal–oxo and metal–sulfido linkages are [tmtaa]Ti=O (**1**) and [tmtaa]Ti=S (**2**) (tmtaa = dianion of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecine) that were first prepared by Goedken and Ladd by the reactions shown in Scheme I.[13] The oxo complex **1** was structurally characterized,[13b] but only a few aspects of the reactivity of these complexes were reported.[13] Complexes **1** and **2** appeared particularly interesting to study further because they are isoelectronic with Cp^*_2Zr=O and Cp^*_2Zr=S, which Bergman showed to be highly reactive species.[5,12] Furthermore, the relatively low Ti=O stretching frequency of **1** (931 cm^{-1}, 40–50 cm^{-1} lower than those for the corresponding titanium–oxo porphyrins[14]) indicates a relatively weak and potentially reactive Ti=O bond, and the crystal structure of **1** showed the titanium atom to stand 0.751 Å above the plane defined by the four tmtaa nitrogen atoms,[13b] thereby allowing the Ti=O unit to be sterically accessible for substrate reactivity. Complexes **1** and **2** are indeed highly reactive species, and herein we describe their addition and cycloaddition reactions with a variety of organic, inorganic, and organometallic substrates. Part of this work has been previously communicated.[15]

Scheme II



Results

Acid–Base Equilibria Involving [tmtaa]Ti=O. Complex **1** can be obtained in good yield by the reactions of Scheme I,[13] and as a solid it can be conveniently handled in air. The ^{17}O NMR spectrum of [tmtaa]Ti=O shows a sharp singlet at δ 965 which is in the δ 700–1100 range typical for terminal oxo ligands,[1d,16] indicating that the complex retains its monomeric character in solution. However, we have found that the complex is involved in a series of acid-base, ligand substitution, and condensation equilibria, as illustrated by the transformations given in Scheme II. The synthesis of [tmtaa]Ti=O from $[tmtaa]TiCl_2$ and $[NH_4]$-OH likely proceeds via the initial formation of the bis(hydroxide) complex **3** which would yield **1** upon elimination of water. We have no direct evidence for the intermediacy of **3**, but its formation is consistent with the other reactions illustrated in Scheme II. When complex **1** was treated with anhydrous $HOSO_2CF_3$, loss of water occurred and the bis(triflate) complex **4** was produced, but in the presence of water reaction of **1** with $HOSO_2CF_3$ gave the bis(aqua) complex **5**, reactions which likely proceed via the intermediacy of compounds **3** and **6**. Complex **4** was isolated as a spectroscopically characterized microcrystalline solid and is similar to the complex $[tmtaa]Ti(OSiMe_3)_2$ reported by Goedken et al.[13b] ^1H NMR experiments indicated that deoxygenation of **1** to form **4** also occurred when **1** was treated with 2 equiv of $Me_3SiO_3SCF_3$ or MeO_3SCF_3. Complex **4** was further shown to react with water to give complex **5**, which was fully defined by a crystallographic study (see below). The solubility of the salt **5** is dramatically lower than that of neutral complex **4**, and the former slowly precipitates upon exposure of solutions of **4** to moist air. It was also observed that treatment of **5** with Et_3N led to the reformation of **1**, apparently via deprotonation of the coordinated water molecules to form **3** and from that **1**.

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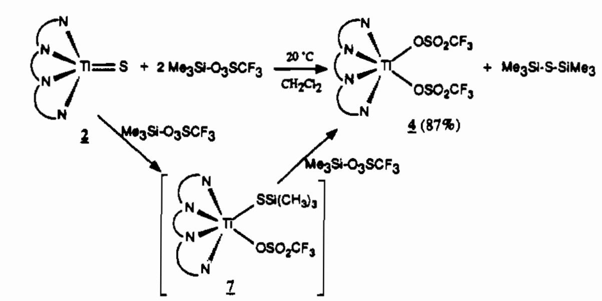
Scheme III



The sulfido complex **2** was also observed to react instantly with $Me_3SiO_3SCF_3$ to form the bis(triflate) complex **4**, Scheme III, a reaction that likely proceeds via silylation of the sulfur atom of **2** to form intermediate **7** which then undergoes further alkylation at the sulfur atom to yield **4** by elimination of $Me_3SiSSiMe_3$.

When only 1 equiv of $HOSO_2CF_3$ was used in the reaction with [tmtaa]Ti=O, the μ-oxo complex **8** was produced. This complex was previously reported by Goedken to form upon treatment of **1** with weak acids,[13a] and we have isolated the complex as the bis(triflate) salt and characterized it by an X-ray diffraction study (see below). ^1H NMR analysis indicated that another compound was formed in about a 1:1 ratio with **8**, but this species was neither isolated nor identified. Its ^1H NMR spectrum showed a typical tmtaa resonance pattern, but the complex was clearly not **1**, **4**, **5**, nor **8**. It is possible that this compound is the proposed intermediate **6**.

It was also observed that compound **1** could be re-formed from **8** by treatment of the latter with $[NH_4]OH$, a reaction that may proceed via hydroxide-induced cleavage of the dimer to form **3**. Similarly, treatment of **8** with an excess of $HOSO_2CF_3$ formed the bis(triflate) complex **4**. Finally, we note that [tmtaa]Ti=O slowly reacts in wet solvents or when solutions are exposed to moist air to form yet another new species which by ^1H NMR is not **1**, **4**, **5**, **8**, or the other unidentified compound described above. This species also shows a typical tmtaa resonance pattern except that the methyl resonances of the tmtaa ligand (δ 2.39) are further upfield than those of any of the other compounds described in this study. This compound may be the bis(hydroxide) complex **3** which would form by water addition to **1**, but our limited data does not allow a definitive assignment of its structure.

Satisfactory C,H analyses were obtained for the new compounds **4** and **5**, as well as for **8**, but only the neutral compound **4** proved volatile enough to give a satisfactory mass spectrum. For this species, a parent ion was observed in its FAB mass spectrum at $m/z = 688$ as well as a prominent peak at $m/z = 539$ assigned to the $(M - O_3SCF_3)^+$ ion. Each of the compounds **1**, **4**, **5**, and **8**, as well as the remainder of the compounds described herein, showed a typical tmtaa ^1H NMR resonance pattern, although each compound gave characteristic and distinct signals (see Experimental Section). Each compound showed a singlet for the tmtaa methyl substituents in the δ 2.3–2.8 region (see Scheme I for a drawing of the tmtaaH_2 molecule), a singlet for the methyne CH hydrogens in the δ 5.3–6.2 region, and aromatic resonances in the δ 7.3–7.9 region. Complex **5** additionally showed a broad resonance centered at δ 2.05 for the coordinated water molecules, and the ^{13}C NMR spectrum of complex **4** showed a characteristic CF_3 quartet at δ 123.3 ($^1J_{CF} = 312$ Hz). In the IR (KBr), the μ_2-oxo complex **8** showed a characteristic $\nu_{Ti-O-Ti}$ vibration at 820 cm^{-1}, as earlier noted by Goedken.[13a,b]

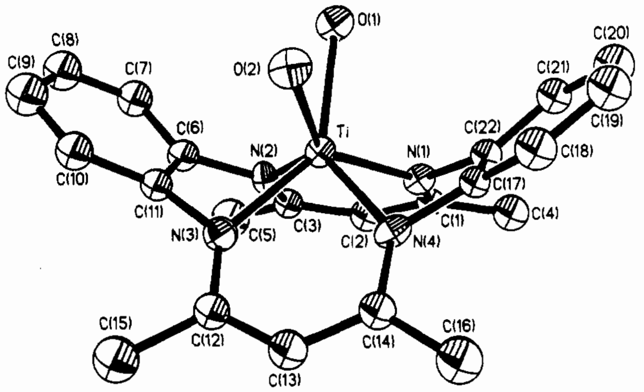


Figure 1. ORTEP drawing for $[(tmtaa)Ti(OH_2)_2][CF_3SO_3]_2$ (**5**). Thermal ellipsoids are drawn at 35% probability.

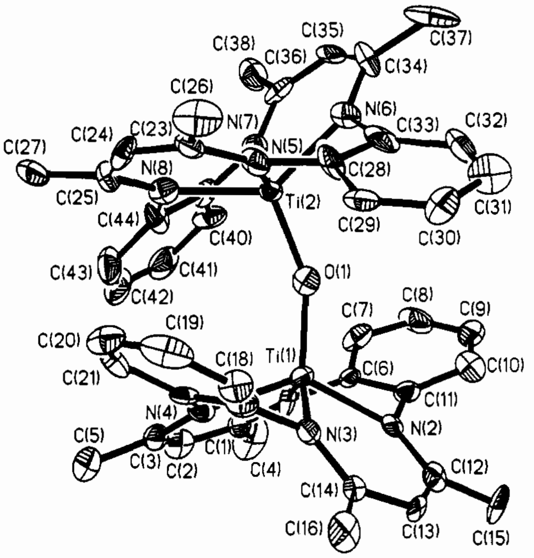


Figure 2. ORTEP drawing for $[(tmtaa)Ti-O-Ti(tmtaa)][CF_3SO_3]_2$ (**8**). Thermal ellipsoids are drawn at 35% probability.

Compounds **5** and **8** were crystallographically characterized as their bis(triflate) salts. ORTEP drawings are shown in Figures 1 and 2, and important crystallographic data are given in Tables I–III. As in the previously determined structure of [tmtaa]Ti=O,[13b] and the five other molecules whose crystal structures are described herein, the titanium atom sits above the plane defined by the four nitrogen atoms (**5**, 0.86 (2) Å; **8**, 0.74 (2), 0.752 (9) Å). In **5**, the titanium atom has a trigonal prismatic arrangement of the six ligands with Ti–O distances of 2.093 (7) and 2.112 (7) Å, which compare well to the 2.066-Å average Ti–O distance found in other Ti–OH_2 complexes.[17] In complex **8**, the titanium atoms have a square pyramidal geometry with a slightly bent Ti–O–Ti linkage (155.0 (8)°). The Ti–O distances of 1.806 (11) and 1.830 (11) Å fall within the 1.794–1.841-Å range observed for other Ti–O–Ti complexes.[17]

Reaction of 1 with Acetyl Chloride. Complex **1** instantly reacts with 2 equiv of acetyl chloride to form $[tmtaa]TiCl_2$ and acetic anhydride (^1H NMR: δ 2.18) (eq 1). This reaction likely proceeds via the intermediate **9**, and spectroscopic evidence was obtained for this species when only 1 equiv of acetyl chloride was used in

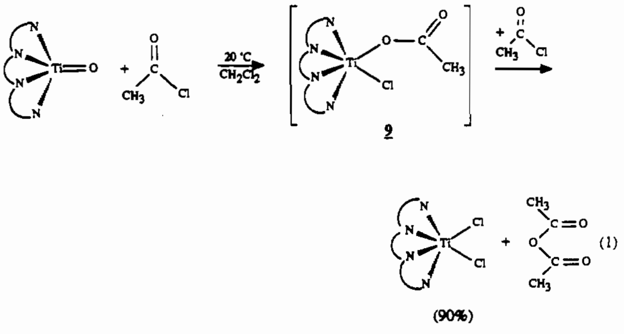


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Table I. Crystal Data for [(tmtaa)]Ti–O–Ti(tmtaa)][O_3SCF_3]$_2$ (**8**), [(tmtaa)Ti(OH_2)$_2$][O_3SCF_3]$_2$ (**5**), [tmtaa]Ti$O_4C_8H_4$ (**11**), and [tmtaa]Ti(η^2[O_2]-$O_2C(CF_3)(CH_3)$) (**16**), [Cp*Re(CO)(NO)(μ_2,η^3-CO_2)Ti(tmtaa)][BF_4] (**21**), [tmtaa]Ti{η^2[O_2]-SO_3} (**23**), and [tmtaa]Ti(η^2[*O,S*]-OSP(=S)(C_6H_4OMe)) (**34**)

	8	**5**	**11**	**16**	**21**	**23**	**34**
formula	$C_{46}H_{44}F_6N_8O_7S_2Ti_2$	$C_{24}H_{26}F_6N_4O_8S_2Ti\cdot CH_2Cl_2$	$C_{30}H_{26}N_4O_4Ti\cdot C_8H_6O_4\cdot CH_2Cl_2$	$C_{25}H_{22}F_3N_4O_2Ti\cdot CH_2Cl_2$	$C_{34}H_{37}BF_4N_5O_4ReTi$	$C_{22}H_{22}N_4O_3STi\cdot CHCl_3$	$C_{29}H_{29}N_4O_2Ti\cdot CH_2Cl_2$
fw	1094.78	809.42	554.44	600.28	900.58	555.25	693.48
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	14.179 (6)	9.930 (3)	15.519 (9)	10.410 (6)	8.7772 (11)	11.233 (6)	11.865 (13)
b, Å	16.623 (4)	19.368 (9)	12.529 (6)	10.487 (6)	12.1983 (17)	12.963 (7)	20.505 (21)
c, Å	21.429 (8)	17.704 (4)	22.110 (11)	13.993 (7)	16.8154 (23)	17.444 (7)	13.382 (11)
α, deg				67.19 (4)	90.122 (11)		
β, deg	104.29 (3)	90.370 (23)	104.25 (4)	85.28 (4)	93.357 (11)	106.40 (11)	98.53 (8)
γ, deg				73.83 (4)	91.902 (11)		
V, Å^3	4895 (3)	3404.8 (19)	4167.4 (5)	1352.0 (13)	1796.2 (4)	2436.6 (22)	3220 (5)
Z	4	4	4	2	2	4	4
D(calc), g cm^{-3}	1.453	1.579	1.416	1.474	1.665	1.513	1.430
μ(Mo Kα), cm^{-1}	4.99	6.13	5.21	5.68	38.50	6.91	6.46
temp, K	297	297	297	297	297	297	297
radiation	Mo Kα (λ = 0.710 73 Å)						
R(*F*), %	11.50	8.23	8.68	10.08	4.54	6.22	7.02
R_w(*F*), %	12.48	6.70	9.48	10.91	4.61	6.93	7.68

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$.

Table II. Selected Bond Lengths (Å) and Angles (deg) for [(tmtaa)Ti(OH_2)$_2$][CF_3SO_3]$_2$ (**5**)

Bond Lengths			
Ti–N(1→4) plane	0.86 (2)[a]		
Ti–O(1)	2.093 (7)	Ti–O(2)	2.112 (7)
Ti–N(1)	2.008 (8)	Ti–N(3)	2.034 (8)
Ti–N(2)	1.994 (8)	Ti–N(4)	2.004 (8)
Bond Angles			
O(1)–Ti–O(6)	76.5 (3)	N(1)–Ti–N(2)	79.5 (3)
N(1)–Ti–N(3)	128.4 (3)	N(1)–Ti–N(4)	79.0 (3)
N(2)–Ti–N(3)	78.3 (3)	N(2)–Ti–N(4)	130.0 (3)
N(3)–Ti–N(4)	80.9 (3)	O(2)–Ti–N(1)	138.0 (3)
O(1)–Ti–N(1)	86.4 (3)	O(2)–Ti–N(2)	137.0 (3)
O(1)–Ti–N(2)	89.1 (3)	O(2)–Ti–N(3)	86.3 (3)
O(1)–Ti–N(3)	138.6 (3)	O(2)–Ti–N(4)	85.6 (3)
O(1)–Ti–N(4)	133.4 (3)		

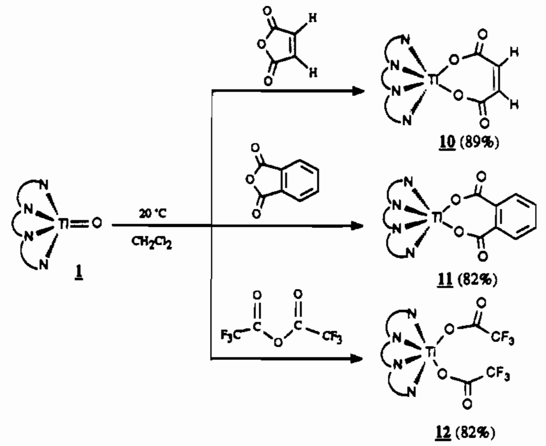
[a] Distance from Ti to the least-squares plane defined by the four nitrogen atoms.

Table III. Selected Bond Lengths (Å) and Angles (deg) for [(tmtaa)Ti–O–Ti(tmtaa)][CF_3SO_3]$_2$ (**8**)

Bond Lengths			
Ti(1)–N(1→4) plane	0.74 (2)[a]	Ti(2)–N(5→8) plane	0.752 (9)[a]
Ti(1)–N(1)	2.002 (12)	Ti(2)–N(5)	1.980 (12)
Ti(1)–N(2)	2.003 (14)	Ti(2)–N(6)	1.991 (15)
Ti(1)–N(3)	1.988 (13)	Ti(2)–N(7)	2.023 (13)
Ti(1)–N(4)	2.007 (15)	Ti(2)–N(8)	2.006 (16)
Ti(1)–O(1)	1.806 (11)	Ti(2)–O(1)	1.830 (11)
Bond Angles			
Ti(1)–O(1)–Ti(2)	155.0 (8)	O(1)–Ti(1)–N(1)	109.7 (5)
N(5)–Ti(2)–N(8)	82.8 (6)	O(1)–Ti(2)–N(5)	112.0 (5)
O(1)–Ti(1)–N(2)	115.6 (6)	O(1)–Ti(2)–N(6)	113.2 (6)
O(1)–Ti(1)–N(3)	112.6 (5)	O(1)–Ti(2)–N(7)	111.6 (5)
O(1)–Ti(1)–N(4)	110.0 (6)	O(1)–Ti(2)–N(8)	111.6 (6)
N(6)–Ti(2)–N(8)	135.2 (6)	N(1)–Ti(1)–N(2)	80.2 (5)
N(3)–Ti(1)–N(4)	79.6 (6)	N(1)–Ti(1)–N(3)	137.6 (6)
N(1)–Ti(1)–N(4)	83.9 (6)	N(2)–Ti(1)–N(3)	84.0 (6)
N(2)–Ti(1)–N(4)	134.4 (5)	N(5)–Ti(2)–N(6)	81.3 (6)
N(5)–Ti(2)–N(7)	136.4 (6)	N(6)–Ti(2)–N(7)	82.9 (5)
N(7)–Ti(2)–N(8)	80.5 (6)		

[a] Distance from Ti to the least-squares plane defined by the four nitrogen atoms.

Scheme IV



the reaction. NMR monitoring of the latter reaction showed the formation of a new species with an acetate ^{1}H NMR methyl resonance at δ 1.75 and a ^{13}C NMR methyl resonance at δ 21.0, in addition to typical tmtaa resonances (see Experimental Section). A FAB mass spectrum of the solid obtained upon evaporation of solvent from the reaction of **1** with 1 equiv of MeC(O)Cl showed the highest mass ion at m/z = 485, corresponding to the addition of a proton to the acetate complex **9**, and a strong peak at m/z = 425 due to the ion [tmtaa]TiCl$^+$.

Reaction of [tmtaa]Ti=O with Anhydrides. Complex **1** rapidly reacts with maleic, phthalic, and hexafluoroacetic anhydride to form the complexes **10–12** shown in Scheme IV. These complexes were isolated in good yields as air stable spectroscopically characterized solids. Each complex gave a satisfactory C,H analysis, showed a parent ion in its mass spectrum, and exhibited ^{1}H and ^{13}C NMR spectra consistent with its formulation (see Experimental Section). Complex **11** has also been crystallographically characterized, and an ORTEP drawing is shown in Figure 3 and relevant data are set out in Tables I and IV. Like **5**, complex **11** has a trigonal prismatic geometry about the titanium atom. The Ti–O(1) and Ti–O(3) bond lengths of 1.995 (7) and 1.990 (7) Å compare well to the 1.967–2.015-Å range found in other titanium carboxylate complexes.[17] The seven-membered metallacycle is puckered with a dihedral angle of 22.9° between the [O(1)–Ti–O(3)] and the [O(3)–C(30)–C(23)–O(1)] least-squares planes, and the phthalic phenyl group stacks 3.623 (9) Å above the proximal tmtaa aromatic ring.

The reactions of Scheme IV likely proceed by addition of the nucleophilic oxygen atom of [tmtaa]Ti=O to one of the carbonyl carbons of the anhydride followed by ring opening and then addition of the free carboxylate to the titanium center. It should be noted that *N*-methylmaleimide and dimethylmaleic anhydride

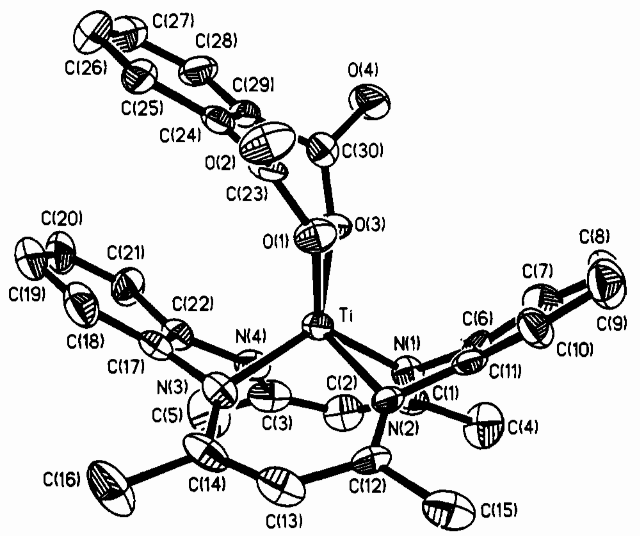


Figure 3. ORTEP drawing for [tmtaa]Ti($O_4C_8H_4$) (**11**). Thermal ellipsoids are drawn at 35% probability.

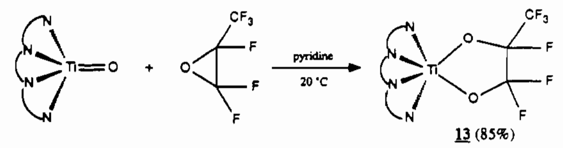
Table IV. Selected Bond Lengths (Å) and Angles (deg) of [tmtaa]Ti($O_4C_8H_4$) (**11**)

	Bond Lengths		
Ti–N(1→4) plane	0.882 (4)[a]	C(24→29)plane–C(17→22) plane	3.623 (9)[b]
Ti–N(1)	2.031 (7)	Ti–O(1)	1.995 (7)
Ti–O(3)	1.990 (7)	C(29)–C(30)	1.495 (13)
C(23)–O(2)	1.232 (13)	C(30)–O(4)	1.239 (13)
C(23)–C(24)	1.473 (15)	C(30)–O(3)	1.289 (11)
C(24)–C(29)	1.405 (15)	C(23)–O(1)	1.290 (10)
Ti–N(2)	2.030 (8)	Ti–O(3)	1.990 (7)
Ti–N(3)	2.019 (8)	Ti–N(4)	2.015 (9)
	Bond Angles		
O(1)–Ti–O(3)	81.2 (3)	O(1)–Ti–N(1)	133.1 (3)
N(1)–Ti–N(2)	77.0 (3)	O(1)–Ti–N(2)	84.3 (3)
N(2)–Ti–N(3)	80.1 (3)	O(1)–Ti–N(3)	88.7 (3)
N(2)–Ti–N(4)	128.1 (3)	O(1)–Ti–N(4)	140.7 (3)
N(1)–Ti–N(3)	128.6 (3)	O(3)–Ti–N(1)	84.9 (3)
N(1)–Ti–N(4)	81.3 (3)	O(3)–Ti–N(2)	138.2 (3)
N(3)–Ti–N(4)	77.8 (3)	O(3)–Ti–N(3)	138.1 (3)
Ti–O(1)–C(23)	142.1 (7)	O(3)–Ti–N(4)	84.8 (3)
Ti–O(3)–C(30)	136.5 (7)	O(3)–C(30)–C(29)	20.3 (9)
O(1)–C(23)–C(24)	120.4 (9)	C(24)–C(29)–C(30)	122.8 (9)
O(4)–C(30)–C(29)	116.8 (8)	C(23)–C(24)–C(29)	123.6 (8)
O(4)–C(30)–O(3)	122.6 (9)	O(2)–C(30)–O(3)	122.6 (9)
O(2)–C(23)–O(1)	120.1 (9)	O(2)–C(23)–C(24)	120.4 (9)

[a] Distance from Ti to the least-squares plane defined by the four nitrogen atoms. [b] Distance from the plane defined by the phthalic phenyl ring to the plane defined by the proximal tmtaa aromatic ring.

did not react with **1**, apparently because they are more electron rich and their carbonyl carbons are not sufficiently electrophilic to add **1**.

[2 + 3] Cycloaddition of Hexafluoropropylene Oxide across the Ti=O Bond of 1. Although complex **1** does not react with ethylene oxide nor with propylene oxide, it does react with the electron deficient hexafluoropropylene oxide to form complex **13** which results from [2 + 3] cycloaddition of the epoxide across the Ti=O bond (eq 2). Complex **13** was isolated as an air-stable



13 (85%)

(2)

microcrystalline solid and was spectroscopically characterized. Its ^1H NMR spectrum showed a typical tmtaa ligand pattern, and it showed a protonated parent ion at $m/z = 573$ $(M + 1)^+$ in its FAB mass spectrum. Also observed was a peak at $m/z =$ 503 corresponding to the loss of a CF_3 group, a characteristic mass spectroscopic feature of trifluoromethylated complexes,[18] and a peak at $m/z = 407$ which corresponds to protonated [tmtaa]-Ti=O that could result from a *retro*-[3 + 2] cycloaddition. Unfortunately, the very low solubility of **13** precluded characterization by ^{13}C NMR, which would have more convincingly identified the structure of the compound. The high thermal and hydrolytic stability of the product is more consistent with the proposed structure **13** than with the alternate peroxy metallacycle **14**.

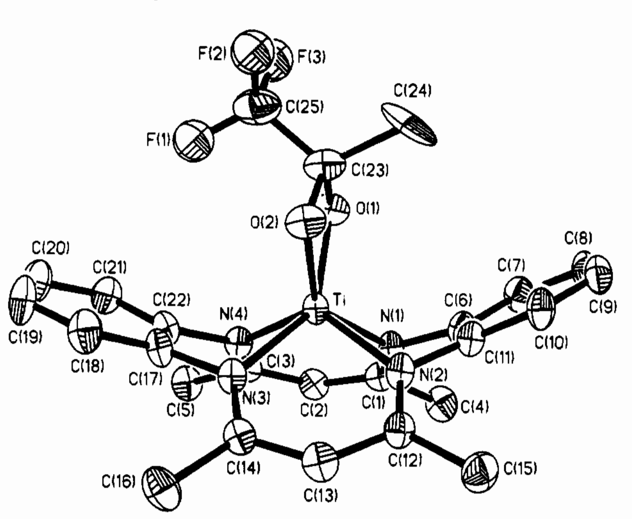
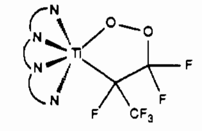
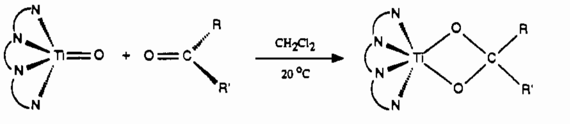


Figure 4. ORTEP drawing for [tmtaa]Ti(η^2[O_2]-$O_2C(CH_3)(CF_3)$), (**16**). Thermal ellipsoids are drawn at 35% probability.



14

[2 + 2] Cycloaddition Reactions of [tmtaa]Ti=O with Ketones. Complex **1** was found to undergo net [2 + 2] cycloaddition of the Ti=O bond across the C=O bond of electron deficient ketones to give the metallacycles shown in eq 3. These reactions occur



(3)

15: R = R' = CF_3 (96%)
16: R = CH_3, R' = CF_3 (98%)
17: R = Ph, R' = CF_3 (85%)

instantly upon addition of the ketone to CH_2Cl_2 solutions of [tmtaa]Ti=O, as indicated by the yellow to red color change, and the resultant metallacycles have been isolated in high yields as air-stable microcrystalline solids. Complex **16** has been crystallographically characterized. An ORTEP drawing is shown in Figure 4 and relevant crystallographic data are set out in Tables I and V. The structure has a 25% disorder between the CH_3 and the CF_3 substituents of the metallacycle, but a satisfactory refinement was achieved. The titanium atom is ligated in a trigonal prismatic coordination environment by the four tmtaa nitrogen atoms and the oxygen atoms of the metallacycle. The Ti–O and C–O bond distances of 1.949 (6) and 1.381 (9) Å are typical single bond distances.[17,19] The metallacycle is slightly bent with a dihedral angle of 4.5° between the O–Ti–O and

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(18) *Eight Peak Index of Mass Spectra*, 2nd ed.; Gresham: Surrey, England, 1974.

(19) Allen, F. A.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Table V. Selected Bond Lengths (Å) and Angles (deg) for [tmtaa]Ti($\eta^2[O_2]$-$O_2C(CH_3)(CF_3)$) (**16**)

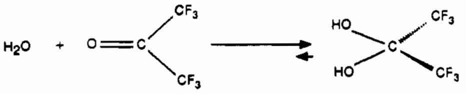
	Bond Lengths		
Ti–N1→4 plane	0.861 (40)[a]	C(24)–ctr of C(6→11) ring	3.726 (6)[b]
Ti–N(1)	2.068 (4)	O(1)–C(23)	1.381 (9)
Ti–O(1)	1.949 (6)	O(2)–C(23)	1.415 (9)
Ti–O(2)	1.937 (5)	Ti···C(23)	2.460 (9)
C(23)–C(24)	1.603 (25)	C(23)–C(25)	1.515 (12)
Ti–N(2)	2.058 (5)	Ti–N(3)	2.088 (5)
Ti–N(4)	2.036 (6)		
	Bond Angles		
Ti–O(1,2)–C(23) (dihedral angle for metallacycle)			4.5
O(1)–Ti–O(2)	69.0 (2)	O(1)–Ti–N(1)	85.8 (2)
N(1)–Ti–N(2)	75.5 (2)	O(1)–Ti–N(2)	125.3 (2)
N(2)–Ti–N(3)	83.4 (2)	O(1)–Ti–N(3)	142.2 (2)
N(2)–Ti–N(4)	132.6 (2)	O(1)–Ti–N(4)	94.6 (2)
N(1)–Ti–N(3)	128.7 (2)	O(2)–Ti–N(1)	138.9 (2)
N(1)–Ti–N(4)	84.3 (2)	O(2)–Ti–N(2)	92.7 (2)
N(3)–Ti–N(4)	76.6 (2)	O(2)–Ti–N(3)	87.5 (2)
C(23)–Ti–N(1)	113.0 (2)	O(2)–Ti–N(4)	128.1 (2)
C(23)–Ti–N(2)	118.2 (2)	Ti–O(1)–C(23)	93.7 (4)
C(23)–Ti–N(3)	111.2 (3)	Ti–O(2)–C(23)	93.1 (4)
C(23)–Ti–N(4)	116.1 (2)	Ti–C(23)–O(1)	52.2 (4)
C(23)–Ti–O(1)	34.1 (2)	Ti–C(23)–O(2)	51.8 (4)
C(23)–Ti–O(2)	35.0 (2)	Ti–C(23)–C(24)	118.8 (6)
C(25)–C(23)–C(24)	115.2 (9)	Ti–C(23)–C(25)	126.0 (7)
C(24)–C(23)–O(2)	107.7 (6)	C(24)–C(23)–O(1)	110.1 (6)
C(25)–C(23)–O(2)	110.1 (6)	C(25)–C(23)–O(1)	109.3 (6)

[a] Distance from Ti to the least-squares plane defined by the four nitrogen atoms. [b] Distance of C(24) to the center of the proximal tmtaa aromatic ring.

O–C–O planes. The O–Ti–O angle of 69.0 (2)° compares well to those observed in the other three compounds described below that have 4-membered metallacycles (**21**, 63.3°; **23**, 70.1°; **34**, 75.1°).

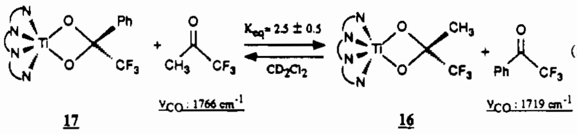
The spectroscopic data for **15–17** are summarized in the Experimental Section and are consistent with their proposed and, for **16**, determined structures. An interesting feature of the ^{1}H NMR spectrum of complex **16** is the resonance of the methyl group of the metallacycle, which appears upfield at δ 0.11. This deshielding effect is likely due to the positioning of this methyl group 3.726 (6) Å from the center of one of the tmtaa aromatic rings (see Figure 4).

Similar yellow to red color changes occurred when complex **1** was allowed to react with 1,1-dichloroacetone and chloroacetone, but the presumed metallacyclic products were not isolated. No reaction was detected when **1** was treated with acetone, 3-pentanone, and methyl styryl ketone. It should be noted that those ketones which react with **1** all have $\nu_{CO} \geq 1719$ cm^{-1} whereas those which do not have $\nu_{CO} \leq 1712$ cm^{-1}. This reactivity pattern parallels the well-known tendency of ketone hydration equilibria (e.g., eq 4) to lie far to the right for ketones with strong electron-withdrawing substituents but far to the left for ketones lacking those substituents.[20]



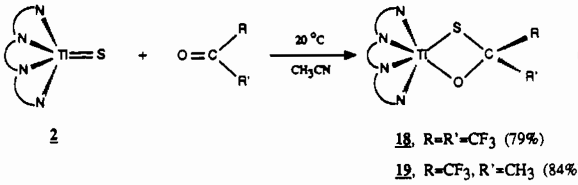
(4)

It was also observed that complexes **16** and **17** readily undergo ketone exchange (eq 5). Thus, complex **16** was readily converted into complex **17** and released 1 equiv of $(CF_3)(CH_3)C{=}O$ upon addition of excess $(CF_3)(Ph)C{=}O$. Similarly, complex **17** was transformed into complex **16** in the presence of excess $(CF_3)(CH_3)C{=}O$ with the release of $(CF_3)(Ph)C{=}O$. ^{1}H NMR analysis indicated that the equilibrium constant for reaction 5 is ~2.5. The mechanism of this exchange reaction has not been explored, but it is significant that the exchange reactions require several hours to reach completion in CD_3CN solvent whereas they are nearly instantaneous in CD_2Cl_2. This suggests that the acetonitrile solvent may weakly coordinate to the titanium center and that it must be displaced before the exchange occurs, suggesting an associative process rather than a dissociative mechanism to form **1** and free ketone.



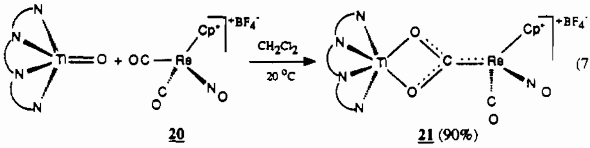
(5)

Cycloaddition Reactions of [tmtaa]Ti=S with Ketones. The sulfido complex **2** has also been found to react slowly with α,α,α-trifluoroacetone and rapidly with hexafluoroacetone in acetonitrile to give the metallacycles **18** and **19** which form via net [2 + 2] cycloaddition of the Ti=S bond across the C=O bond of the ketones (eq 6). Less electron deficient ketones such as acetone and acetophenone failed to react with **2**. Complexes **18** and **19** were characterized spectroscopically and by their C,H analyses. Parent ions were observed in their FAB mass spectra, and the EI mass spectrum of complex **18** showed ions due to [tmtaa]Ti=O and $S{=}C(CF_3)_2$, fragments which result from a *retro*-[2 + 2] cycloaddition by cleavage of Ti—S and C—O bonds. Similarly, the EI mass spectrum of **19** showed ions due to [tmtaa]Ti=O and $S{=}C(CF_3)(CH_3)$. Typical tmtaa resonance patterns were observed in the ^{1}H NMR spectra of **18** and **19** (see Experimental Section), except that the methyl groups of the tmtaa ligand of **19** appeared as two separate peaks due to the low symmetry of the complex induced by the chiral center in the metallacycle. The ^{1}H NMR resonance of the methyl substituents on the metallacycle of **19** appeared at δ 0.40 (q, $^4J_{HF}$ = 1.22 Hz), with this upfield position attributed to a ring current effect due to the proximity of this group to one of the tmtaa aromatic rings, as noted above for **16**. The ^{13}C NMR spectrum of **19** showed a characteristic tmtaa resonance pattern and quartets for the O–*C*–S carbon of the metallacycle (δ 85.3, $^2J_{CF}$ = 31 Hz) and the *C*F$_3$ carbon (δ 123.5, $^1J_{CF}$ = 285 Hz). In **18**, the CF$_3$ ^{13}C NMR resonance appeared as a quartet at δ 123.6 ($^1J_{CF}$ = 288 Hz), but the metallacyclic O–*C*–S resonance was not observed due to the low solubility of the compound and the broadening of this resonance due to its coupling with the six fluorine atoms.



(6)

Cycloaddition of [tmtaa]Ti=O with [Cp*Re(CO)$_2$(NO)]BF$_4$. Complex **1** also undergoes net [2 + 2] cycloaddition of the Ti=O bond across the C=O bond of a carbonyl ligand in the electrophilic complex [Cp*Re(CO)$_2$(NO)]$^+$ (**20**) to form the bimetallic complex **21**, which possesses a μ_2,η^3-CO_2 ligand (eq 7). Cationic carbonyl complexes like **20** are well-known to be highly susceptible to attack by a variety of nucleophiles,[21] implying that reaction 7 likely proceeds via initial addition of the nucleophilic oxygen of [tmtaa]Ti=O to a carbonyl carbon of **20** followed by ring closure to give the metallacycle **21**. The oxo complex $Cp_2W{=}O$



(7)

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(20) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley: New York, 1985.

(21) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

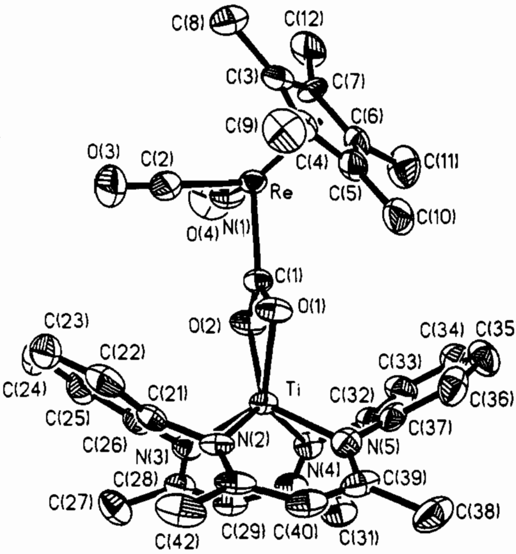


Figure 5. ORTEP drawing for $[(tmtaa)Ti(\mu_2,\eta^3\text{-}O_2C)Re(CO)(NO)Cp^*][BF_4]$ (**21**). Thermal ellipsoids are drawn at 35% probability.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[tmtaa]Ti(\mu_2,\eta^3\text{-}O_2C)Re(CO)(NO)Cp^*][BF_4]$ (**21**)

	Bond Lengths		
Ti–N(2→5) plane	0.840 (2)[a]		
Re–C(1)	2.081 (9)	N(1)–O(4)	1.179 (13)
Ti···C(1)	2.465 (9)	Ti–O(1)	2.066 (6)
Ti–O(2)	2.023 (7)	C(2)–O(3)	1.141 (14)
O(1)–C(1)	1.281 (11)	Re–C(2)	1.923 (11)
O(2)–C(1)	1.309 (11)	Re–N(1)	1.775 (9)
Re–Cp*(ctr)	1.958 (9)	Ti–N(3)	2.011 (8)
Ti–N(2)	2.014 (8)	Ti–N(5)	2.026 (8)
Ti–N(4)	2.017 (7)		
	Bond Angles		
Ti–O(1,2)–C(1) (dihedral angle for metallacycle)	2.4		
O(1)–Ti–O(2)	63.3 (3)	O(1)–Ti–N(2)	90.6 (3)
N(2)–Ti–N(3)	78.3 (3)	O(1)–Ti–N(3)	132.0 (3)
N(2)–Ti–N(4)	130.9 (3)	O(1)–Ti–N(4)	134.2 (3)
N(2)–Ti–N(5)	81.3 (3)	O(1)–Ti–N(5)	92.2 (3)
N(3)–Ti–N(4)	81.9 (3)	O(2)–Ti–N(2)	133.4 (3)
N(3)–Ti–N(5)	130.7 (3)	O(2)–Ti–N(3)	91.2 (3)
N(4)–Ti–N(5)	78.6 (3)	O(2)–Ti–N(4)	91.1 (3)
N(1)–Re–C(1)	92.5 (4)	O(2)–Ti–N(5)	133.7 (3)
N(1)–Re–C(2)	94.1 (4)	C(1)–Re–C(2)	85.9 (4)
Re–C(1)–Ti	177.7 (5)	Ti–O(1)–C(1)	91.8 (5)
Re–C(1)–O(1)	125.5 (7)	Re–C(1)–O(2)	122.6 (7)
O(1)–O(2)–C(2)	111.9 (8)	C(1)–O(2)–Ti	92.9 (5)

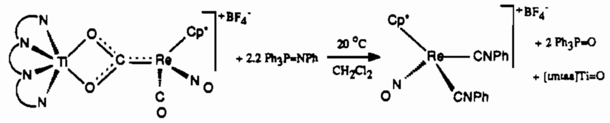
[a] Distance from Ti to the least-squares plane defined by the four nitrogen atoms.

was earlier shown to add similarly to **20** to give an analogous W—Re complex,[4] and similar $\mu_2,\eta^3\text{-}CO_2$ complexes have been prepared by other means.[22]

Complex **21** was isolated as a microcrystalline solid and has been crystallographically characterized. An ORTEP drawing is shown in Figure 5, and relevant crystallographic data are given in Tables I and VI. The tmtaa and Cp(CO)(NO)Re parts of the molecule are typical, and we focus here only on the bonding of the $\mu_2,\eta^3\text{-}CO_2$ ligand. This unit is bound to the titanium atom via the oxygen atoms, and the Ti–O(1) [2.066 (6) Å] and Ti–O(2) [2.023 (7) Å] distances compare well to the Ti–O single bond distances found in the other compounds described herein. The C–O distances average 1.295 Å, a value intermediate between typical (sp²)C—O single bond [1.368 (15) Å] and (sp²)C=O double bond [1.210 (8) Å] values.[19] The Re–C(1) distance of 2.081 (9) Å compares to the corresponding distance of 2.04 (4) Å in $Cp^*(CO)(NO)Re(\mu_2,\eta^3\text{-}CO_2)WCp_2$[4b] but is slightly longer than Re=C double bond distances in typical carbene complexes $\{[Cp(NO)(PPh_3)Re({=}CHPh)]^+$, 1.949 (6) Å;[23a] $Cp(CO)_2Re({=}CHSiPh_3)$, 1.92 (2) Å[23b]$\}$. The TiO_2CRe unit is essentially planar, with a dihedral angle of 2.4° between the O–Ti–O and O–C–O planes.

The spectroscopic data for **21** given in the Experimental Section are consistent with its determined structure. Particularly noteworthy is the presence of a ^{13}C NMR resonance at δ 226.2 assigned to the bridging CO_2 carbon which compares well to the corresponding δ 247.4 resonance reported earlier for the related complex $[Cp^*(CO)(NO)Re(\mu_2,\eta^3\text{-}CO_2)WCp_2]^+$.[4b] A curious feature of the room-temperature ^1H NMR spectrum of complex **21** is the observation of a single resonance at δ 2.73 for the four tmtaa methyl groups although the crystal structure indicates that the methyl groups are inequivalent (Figure 5). This implies that rotation about the Re=C bond occurs, as often found in metal carbene complexes.[24] When the sample is cooled to −23 °C, the δ 2.73 resonance splits into two separate resonances at δ 2.78 and δ 2.68 assigned to the two pairs of equivalent methyl groups as predicted by the crystal structure. Line shape analysis gave an activation energy of 6.5 kcal/mol for this exchange process. This value compares well to the activation energy of 7.8 kcal/mol observed for carbene rotation in the complex $[Cp(CO)(PPh_3)Fe{=}CHCH_3]^+$.[24b] However, it is substantially lower than the corresponding 19–22 kcal/mol barriers found in rhenium carbene complexes of the type $[Cp(NO)(PPh_3)Re{=}CRR']^+$.[24c–f]

Reactivity of Complexes 20 and 21 with Phosphine Imides. In an effort to define the reactivity of the $\mu_2,\eta^3\text{-}CO_2$ functionality in complex **21**, we discovered an interesting transformation with phosphine imides. In the presence of 2 equiv of $Ph_3P{=}NPh$, complex **21** reacted to displace free [tmtaa]Ti=O and form the new bis(isocyanide) complex **22** along with 2 equiv of $Ph_3P{=}O$ (eq 8). Complex **22** was also obtained in 82% yield by directly treating $[Cp^*Re(CO)_2(NO)][BF_4]$ (**20**) with $Ph_3P{=}NPh$. Although simple in composition, complex **22** is a new complex. It was isolated as a microcrystalline solid and has been spectroscopically characterized. It showed a parent ion in its mass spectrum at m/z = 557 and two isonitrile ν(CN) IR bands at 2159 and 2120 cm⁻¹ along with a nitrosyl stretch at 1730 cm⁻¹. The conversion of a carbonyl ligand into an isocyanide ligand by the use of phosphine imides has precedent in other systems, and this class of reactions is believed to proceed via initial addition of the nucleophilic nitrogen atom of the phosphine imide to the carbon atom of the electrophilic metal carbonyl.[25] The reaction of $Ph_3P{=}NPh$ with **20** likely proceeds by a similar mechanism, Scheme V. The reaction of $Ph_3P{=}NPh$ with the bimetallic



21 **22** (8)

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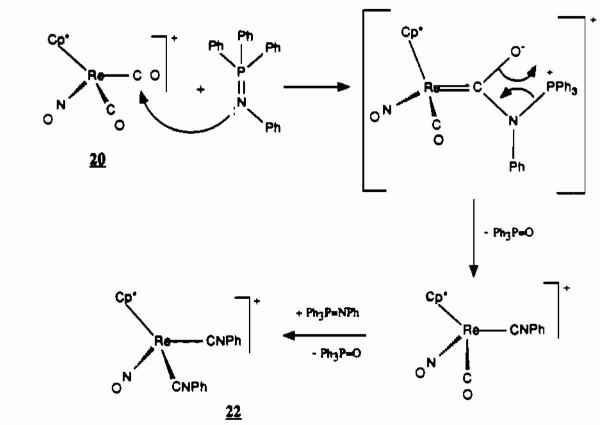
Scheme V



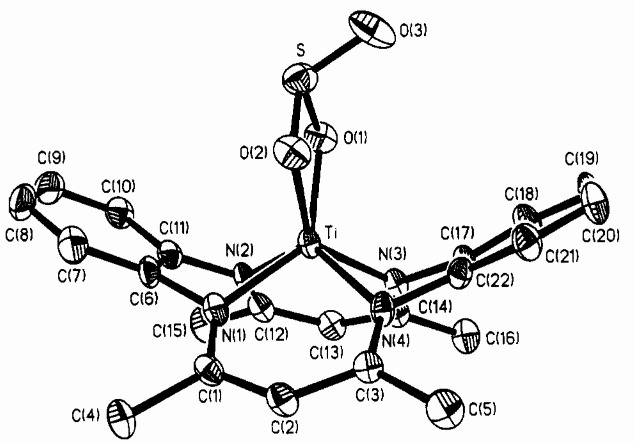
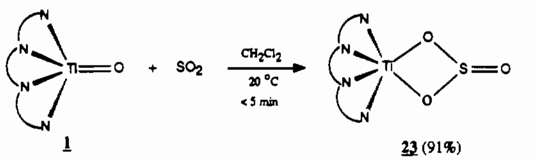


Figure 6. ORTEP drawing for [tmtaa]Ti(η^2[O_2]-SO_3) (**23**). Thermal ellipsoids are drawn at 35% probability.

complex **21** could proceed via addition of the nucleophilic nitrogen atom of the phosphine imide to the electrophilic carbonyl carbon of **21** to induce a *retro*-[2 + 2] cycloaddition of the metallacycle and elimination of the [tmtaa]Ti=O unit. Alternatively, complex **21** could be in equilibrium with a small amount of complex **20** and **1**, and the product **22** could form by direct reaction of $Ph_3P{=}NPh$ with the equilibrium amount of **20**. Although we see no NMR evidence for the reversibility of eq 7, this possibility cannot be ruled out.

Cycloaddition Reactions of [tmtaa]Ti=O and [tmtaa]Ti=S with Sulfur Oxides. Complex **1** rapidly undergoes cycloaddition of the Ti=O bond across the S=O bond of SO_2 to form the η^2-[O_2]-sulfito complex **23** (eq 9). This complex was isolated in excellent yield and has been crystallographically characterized. An ORTEP drawing is shown in Figure 6, and relevant crystallographic data are given in Tables I and VII. The titanium atom has the trigonal prismatic geometry seen in the other complexes described herein and has typical Ti—O and S—O single bonds.[17,19] The exocyclic S—O distance is shorter [1.434 (6) Å] and consistent with a S=O double bond.[19] Although many η^2[O_2]-sulfito complexes are known,[26] to the best of our knowledge complex **23** is the first reported η^2[O_2]-sulfito complex of titanium.



(9)

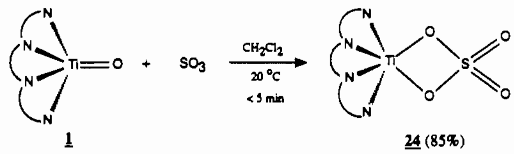
Table VII. Selected Bond Lengths (Å) and Angles (deg) for [tmtaa]Ti(η^2[O_2]-SO_3) (**23**)

Bond Lengths			
Ti–N(1→4) plane	0.853 (30)[a]		
S–O(3)	1.434 (6)	Ti–O(1)	1.992 (4)
Ti–O(2)	2.049 (5)	Ti···S	2.708 (2)
S–O(1)	1.581 (4)	S–O(2)	1.565 (4)
Ti–N(1)	2.030 (5)	Ti–N(2)	2.049 (5)
Ti–N(3)	2.027 (4)	Ti–N(4)	2.035 (4)

Bond Angles			
Ti–O(1,2)–S (dihedral angle for metallacycle)	5.3°		
O(1)–Ti–O(2)	70.1 (2)	O(1)–Ti–N(1)	135.8 (2)
N(1)–Ti–N(2)	76.8 (2)	O(1)–Ti–N(2)	89.3 (2)
N(2)–Ti–N(3)	82.2 (2)	O(1)–Ti–N(3)	89.4 (2)
N(2)–Ti–N(4)	132.3 (2)	O(1)–Ti–N(4)	132.6 (2)
N(1)–Ti–N(3)	128.5 (2)	O(2)–Ti–N(1)	88.4 (2)
N(1)–Ti–N(4)	83.0 (2)	O(2)–Ti–N(2)	131.8 (2)
N(3)–Ti–N(4)	77.7 (2)	O(2)–Ti–N(3)	137.9 (2)
Ti–O(1)–S	97.9 (2)	O(2)–Ti–N(4)	89.5 (2)
Ti–O(2)–S	98.5 (2)	O(1)–S–O(2)	93.3 (2)
S–Ti–O(1)	35.3 (1)	O(1)–S–O(3)	108.1 (3)
S–Ti–O(2)	34.9 (1)	O(2)–S–O(3)	109.3 (3)

[a] Distance from Ti to the least-squares plane defined by the four nitrogen atoms.

Complex **1** also undergoes cycloaddition of the Ti=O bond across the S=O bond of SO_3 to generate the η^2[O_2]-sulfato complex **24** shown in eq 10. Complex **24** was isolated in good yield and has been spectroscopically characterized. Its ^1H and ^{13}C NMR spectra showed the usual tmtaa resonance patterns. The η^2[O_2]-SO_4 coordination of the sulfato ligand is indicated by its IR spectrum which shows bands at ν_{SO} = 1276, 1172, 922, 912, 712, 671, 558 cm^{-1} which are similar to those found in other η^2[O_2]-SO_4 sulfato complexes (e.g., IrI(PPh_3)$_2$(CO)(η^2[O_2]-SO_4), ν_{SO} = 1296, 1172, 880, 856, 662, 610, 549 cm^{-1}).[29] The reaction of ^{18}O-labeled **1** with excess SO_2 and SO_3 gave complexes in which the ^{18}O label could not be detected, implying that reactions 9 and 10 are reversible and that repeated cycloaddition and retrocycloaddition reactions washed out the labeled oxygen into the excess SO_2 and SO_3.



(10)

Both complexes **23** and **24** have been found to react rapidly with NH_4OH to regenerate complex **1** in nearly quantitative yield and respectively release $[NH_4]_2SO_3$ and $[NH_4]_2SO_4$ (Scheme VI). The ammonium salts were isolated and characterized by comparing their IR data to data for authentic samples. Complex **23** was also observed to undergo oxidation with PhIO and with O_2 under sunlight to form **24** (Scheme VII). Similar oxidation also occurs with H_2O_2, although this reaction is less clean and does not give pure product.

Complexes **23** and **24** were also observed to form when the sulfido complex **2** was allowed to react with SO_2 and SO_3,

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(28) Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1982**, 799. dppe = 1,2-bis(diphenylphosphino)ethane.

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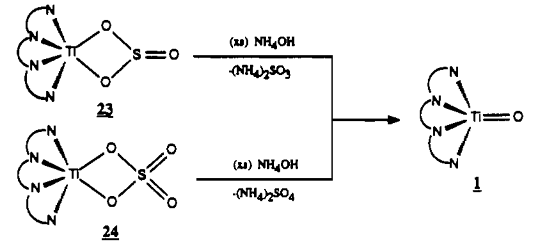
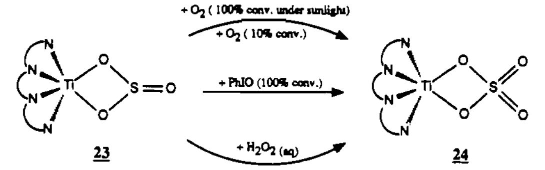
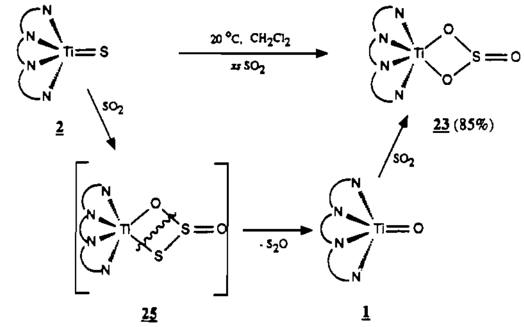
Scheme VI



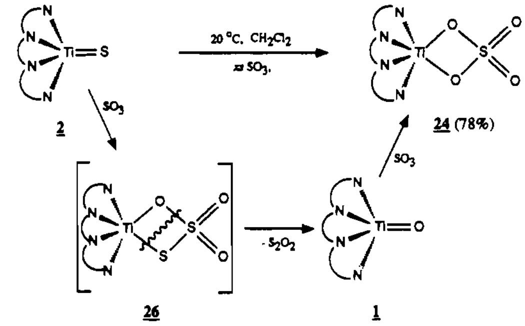
Scheme VII



Scheme VIII

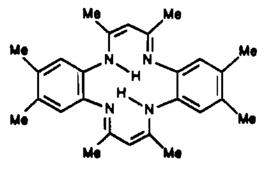


Scheme IX

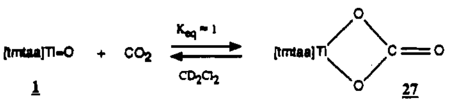


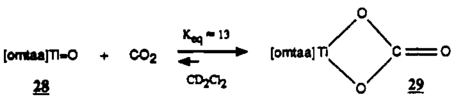
apparently by the mechanisms shown in Schemes VIII and IX. These reactions likely proceed via the initial formation of the intermediate metallacycles **25** and **26**, but no direct evidence was obtained for either species. Elimination of S_2O from **25** and S_2O_2 from **26** would form [tmtaa]Ti═O which would then react with the excess SO_2 and SO_3 present in the separate reactions to form complexes **23** and **24**.

Cycloaddition Reactions of [tmtaa]Ti═O and [omtaa]Ti═O with CO_2. Goedken has presented evidence that [tmtaa]Ti═O reacts with CO_2 at 2 atm and below 0 °C to give the $\eta^2[O_2]$-carbonate complex [tmtaa]Ti($\eta^2[O_2]$-CO_3) (**27**).[13a] We have observed by ^1H NMR that, at 20 °C and 1 atm pressure, complex **1** and CO_2 are in equilibrium with **27** (eq 11, $K_{eq} \approx 1$). It was reasoned that this equilibrium could be shifted to the right by preparing the more electron rich oxo complex [omtaa]Ti═O (**28**), which has four additional methyl groups on the aryl rings. Indeed, ^1H NMR data indicated that **28** reacts with CO_2 at 20 °C and 1 atm pressure to form the corresponding carbonate complex **29** with an equilibrium constant of ~13 (eq 12). The carbonate complexes **27** and **29** could not be isolated due to their facile loss of CO_2, although complex **29** was characterized in situ by ^1H and ^{13}C NMR. In particular, its ^{13}C NMR spectrum showed



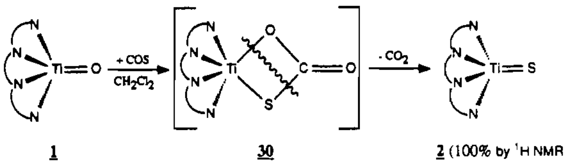
[omtaa]H₂

 (11)

 (12)

a carbonate resonance at δ 163.2. An IR spectrum recorded in a CO_2-saturated IR cell showed a band at 1618 cm^{-1} assigned to the carbonate ligand. In contrast to these results, no reaction was observed when the sulfido complex [tmtaa]Ti═S was stirred with CO_2 under similar reaction conditions.

Cycloaddition Reactions of [tmtaa]Ti═O with COS and CS_2. Complex **1** also reacts with COS to form the sulfido complex **2** (eq 13). This reaction likely proceeds via cycloaddition of **1** with

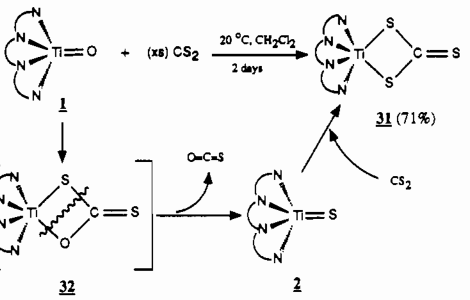
 (13)

COS to form the metallacycle **30** which then undergoes a *retro*-[2 + 2] cycloaddition to eliminate CO_2 and form **2**. ^{13}C NMR analysis of the reaction of **1** with COS in a flame-sealed NMR tube showed a resonance at δ 125.9 assigned to the released CO_2. Consistent with these results, it was observed that separate treatment of **2** with COS led to no reaction.

In contrast to the rapid reaction between **1** and COS, carbon disulfide reacts slowly with **1** and requires ~2 days for complete reaction. The product formed after this time is the $\eta^2[S_2]$-CS_3 complex **31**, Scheme X, which we have also shown to result in 62% yield from the direct reaction of [tmtaa]Ti═S with CS_2. Thus complex **31** apparently forms by the route illustrated in Scheme X involving initial cycloaddition of CS_2 with **1** to form **32**, which eliminates COS to form the sulfido complex **2**. Cycloaddition of CS_2 with **2** would then give **31**. The intermediate formation of [tmtaa]Ti═S was indicated by ^1H NMR monitoring of the reaction which showed the slow disappearance of [tmtaa]-Ti═O and the concomitant appearance of [tmtaa]Ti═S, with no other species detected. After 2 days, the resonances of both **1** and **2** had disappeared as the very insoluble **31** precipitated out of solution. Complex **31** was isolated as a gray-brown powder but proved to be insoluble in all solvents examined. It has thus only been characterized by C,H analysis and by its IR spectrum which showed ν_{CS} vibrations at 1025, 1014, and 861 cm^{-1}. These compare well to those reported for other trithiocarbonate complexes[27,28] (e.g., Ni(dppe)($\eta^2[S_2]$-CS_3),[28] ν_{CS} = 1055, 1045, 870 cm^{-1}).

Cycloaddition of [tmtaa]Ti═O with Lawesson's Reagent. Lawesson's reagent, 2,4-bis-(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (**33**) has been shown to be an extremely useful compound for converting carbonyl groups to their corresponding thiocarbonyl groups by sulfur for oxygen

Scheme X



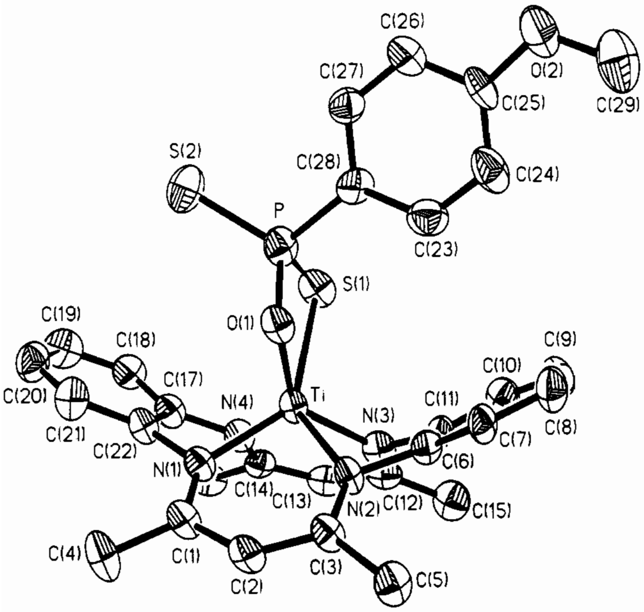


Figure 7. ORTEP drawing for [tmtaa]Ti(η^2[*O,S*]-OSP(=S)(C_6H_4-OCH_3)) (**34**). Thermal ellipsoids are drawn at 35% probability.

exchange.[30] In an attempt to use this reagent to transform [tmtaa]-Ti=O into [tmtaa]Ti=S, we observed the formation of the stable metallacycle **34** (eq 14). This complex has been crystallographically characterized (see Figure 7 and Tables I and VIII) and shown to possess an unusual ring system having four different non-carbon atoms in its metallacycle. Its spectroscopic data given in the Experimental Section are consistent with the determined structure. Particularly important is the observed ^{31}P NMR resonance at δ 87.7 which compares well to the corresponding resonance at δ 80.45 reported for the similar compound **35**.[31] The crystal structure of **34** shows the titanium atom to have the usual trigonal prismatic coordination of the four nitrogen atoms of the tmtaa ligand and the oxygen and sulfur atoms of the metallacycle. The 4-membered metallacycle is slightly puckered with a dihedral angle of 11.5° between the S–Ti–O and O–P–S planes. The Ti–O, Ti–S, O–P, and S–P bond distances within the metallacycle are all single bond values.[17,19]

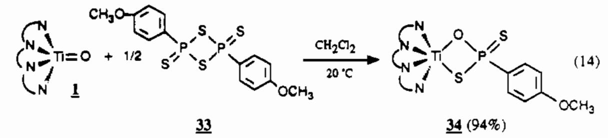


Table VIII. Selected Bond Lengths (Å) and Angles (deg) for [tmtaa]Ti(η^2[*O,S*]-OSP(=S)($C_6H_4OCH_3$)) (**34**)

Bond Lengths

Ti–N(1→4) plane 0.884 (12)[a]

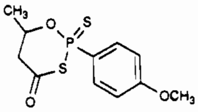
Ti–O(1)	1.994 (7)	P–S(2)	1.956 (4)
Ti–S(1)	2.501 (3)	Ti···P	2.895 (4)
P–S(1)	2.093 (4)	P–C(28)	1.808 (10)
P–O(1)	1.557 (7)	Ti–N(1)	2.054 (7)
Ti–N(2)	2.042 (6)	Ti–N(3)	2.056 (9)
Ti–N(4)	2.039 (7)		

Bond Angles

Ti–[O(1),S(1)]–P (dihedral angle for metallacycle) 11.5°

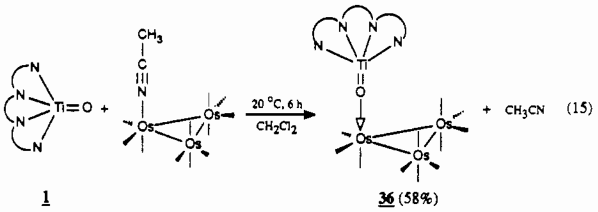
O(1)–Ti–S(1)	75.1 (2)	O(1)–Ti–N(1)	88.6 (3)
N(1)–Ti–N(2)	81.7 (3)	O(1)–Ti–N(2)	89.4 (3)
N(2)–Ti–N(3)	77.0 (3)	O(1)–Ti–N(3)	137.0 (3)
N(2)–Ti–N(4)	129.4 (3)	O(1)–Ti–N(4)	134.2 (3)
N(1)–Ti–N(3)	128.2 (3)	N(1)–Ti–N(4)	76.5 (3)
N(3)–Ti–N(4)	81.8 (3)	O(1)–P–C(28)	107.0 (4)
O(1)–P–S(2)	115.9 (3)	S(1)–Ti–N(1)	136.6 (2)
S(1)–Ti–N(2)	136.5 (2)	S(1)–Ti–N(3)	87.1 (2)
Ti–P–O(1)	40.7 (2)	Ti–O(1)–P	108.6 (3)
P–C(28)–C(27)	122.3 (7)	S(1)–P–C(28)	110.5 (3)
S(1)–P–S(2)	115.6 (2)	S(2)–P–C(28)	109.5 (4)

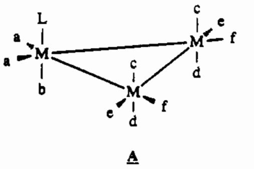
[a] Distance from Ti to the least squares plane defined by the four nitrogen atoms.



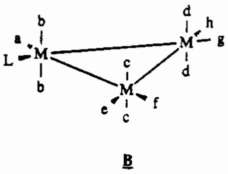
35

Reaction of [tmtaa]Ti=O with $Os_3(CO)_{11}(NCCH_3)$. Goedken earlier showed that [tmtaa]Ti=O can coordinate to electrophilic metals through the electron rich oxo ligand.[13b] As an extension of that work we have found that complex **1** can also serve as a ligand to low-valent metals as illustrated by its ability to displace the acetonitrile ligand from $Os_3(CO)_{11}(NCCH_3)$[32] to form [tmtaa]-Ti=O→$Os_3(CO)_{11}$ (**36**) (eq 15) and by the reactions described below. Complex **36** was isolated in good yield as a spectroscopically characterized microcrystalline solid. It showed a parent ion at m/z = 1286(M)$^+$ in its FAB mass spectrum, a typical tmtaa ^1H NMR pattern, and IR bands consistent with an $Os_3(CO)_{11}L$ cluster (see Experimental Section). ^{13}C NMR data showed that the [tmtaa]Ti=O unit occupies an axial coordination site (A) similar to that found in other $M_3(CO)_{11}L$ complexes in which no branching exists at the ligating atom (such as nitriles and isocyanides)[33] rather than the equatorial site (B) preferred





A



B

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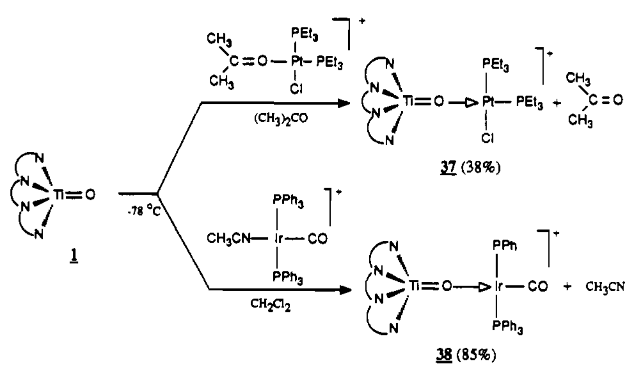
(30) (a) Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061. (b) El-Barbary, A. A.; Lawesson, S.-O. *Tetrahedron* **1981**, *37*, 2647. (c) El-Barbary, A. A.; Lawesson, S.-O. *Tetrahedron* **1981**, *37*, 2641. (d) Pedersen, P. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223. (e) Rasmussen, J. B.; Jorgensen, K. A.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 307. (f) Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 229. (g) Scheibye, S.; Pedersen, B. S.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 299. (h) Pedersen, B. S.; Lawesson, S.-O. *Tetrahedron* **1979**, *35*, 2433.

(31) Shabana, R.; Rasmussen, J. B.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1981**, *90*, 103.

(32) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407. (b) Nicholls, J. N.; Vargas, M. D. *Inorg. Synth.* **1989**, *26*, 289.

Scheme XI

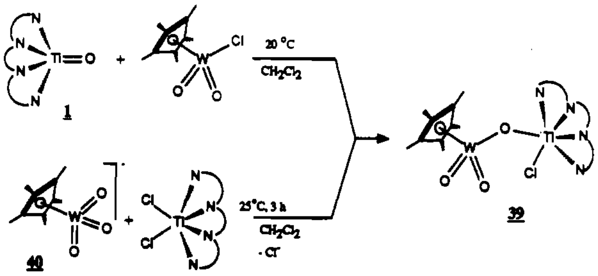


by ligands with branches at the ligating atom (such as phosphines).[34] The −58 °C proton-coupled ^{13}C NMR spectrum of ^{13}CO enriched **36** (17%) showed six resonances in the metal carbonyl region. Two of these (δ 184.8, 187.6) exhibited ^{13}C satellites with coupling constants of ~34.5 Hz each, indicating that the carbonyls are inequivalent and trans to each other. These two resonances integrated to 2 carbons each and are assigned to carbonyl ligands c and d in A. The remaining four resonances integrated 2:2:2:1. The lowest intensity resonance at δ 182.6 is assigned to carbonyl ligand b, the two peaks at δ 179.0 and 177.5 are assigned to carbonyl ligands e and f, and the peak at δ 183.8 is attributed to carbonyl ligands a since the chemical shifts of carbonyls e and f should be more similar to each other than either pair would be with carbonyls a. If the [tmtaa]Ti=O unit were coordinated equatorially as in B, the ^{13}C NMR spectrum at the low-temperature limit should exhibit eight resonances in the carbonyl region in a 2:2:2:1:1:1:1:1 ratio, and most importantly, none of these would show satellites due to trans coupling (~30 Hz) since each axial carbonyl ligand is equivalent to its potential coupling partner.

It is interesting that the $\nu_{\mathrm{Ti=O}}$ vibration of **36** is at 896 cm^{-1}, only 35 cm^{-1} lower than the 931-cm^{-1} $\nu_{\mathrm{Ti=O}}$ stretch of [tmtaa]-Ti=O.[13a,b] A similar lowering of the $\nu_{\mathrm{Ti=O}}$ stretch was observed in the various [tmtaa]Ti–O–ML$_n$ compounds prepared by Goedken.[13b] The relatively small decrease in the $\nu_{\mathrm{Ti=O}}$ vibration implies that the Ti–O–Os linkage is best formulated as a relatively weak Ti=O→Os dative interaction and suggests that the [tmtaa]-Ti=O unit might be easily displaced from **36**. However, the latter is not the case since no reaction was observed when **36** was stirred under 4 atm of CO for 24 h. Also, the oxo linkage is not easily hydrolyzed since the compound was stable even when THF solutions of **36** were exposed to moist air for several hours. Complex **36** is slightly soluble in CH_3CN, in which no displacement of the [tmtaa]Ti=O ligand was observed.

Reaction of [tmtaa]Ti=O with *cis*-[PtCl(PEt$_3$)$_2$(acetone)]$^+$ and *trans*-[Ir(CO)(PPh$_3$)$_2$(CH$_3$CN)]$^+$. Complex **1** also reacts with the title complexes[35,36] to displace the weakly coordinated solvent molecules and form the cationic oxo-bridged heterobimetallic complexes **37** and **38** (Scheme XI). Both of these complexes were isolated as spectroscopically characterized microcrystalline solids. Both complexes showed parent ions in their positive ion FAB mass spectra, and **38** showed a single ν_{CO} band at 1959 cm^{-1}. This band is 47 cm^{-1} lower than the corresponding band of [Ir(CO)(PPh$_3$)$_2$(CH$_3$CN)]$^+$, indicating that [tmtaa]Ti=O is a better electron-donating ligand to the Ir center than is acetonitrile. The IR spectra of **37** and **38** showed $\nu_{\mathrm{Ti=O}}$ vibrations at 894 and 883 cm^{-1}, respectively. The cis coordination of the phosphine ligands in **37** was indicated by its NMR data in which two inequivalent sets of equally integrated ethyl groups were observed in the ^{1}H NMR spectrum and inequivalent phosphorus atoms were apparent in the ^{31}P NMR spectrum at δ 0.35 (d, $J_{\mathrm{P-P}}$ = 20 Hz, $J_{\mathrm{Pt-P}}$ = 3550), and 13.4 (d, $J_{\mathrm{P-P}}$ = 20 Hz; $J_{\mathrm{Pt-P}}$ = 3582 Hz). For **38**, the single ^{31}P NMR resonance at δ 27.2 indicates the phosphine ligands to be in a trans arrangement.

Formation of Cp*(O)$_2$W–O–Ti(Cl)(tmtaa) from the Reaction of [tmtaa]Ti=O with Cp*W(O)$_2$Cl and from the Reaction of [Cp*WO$_3$]$^-$ with (tmtaa)TiCl$_2$. Complex **1** was observed to react instantly with Cp*W(O)$_2$Cl to form the oxo-bridged heterobimetallic complex **39** (eq 16). Note that in this reaction a chloride ligand has transferred from tungsten to titanium. In other work[6] we have shown that the anionic complex [Cp*WO$_3$]$^-$ (**40**) readily displaces halides from other metal centers to form μ_2-oxo complexes, and as illustrated in eq 16, we have similarly found that this complex reacts with [tmtaa]TiCl$_2$ to form complex **39**. Complex **39** was obtained in 85% yield from both reactions as a spectroscopically characterized microcrystalline solid. It showed a parent ion at m/z = 793 (M + 1)$^+$ in its positive ion FAB mass spectrum along with ions corresponding to the fragments [(tmtaa)-Ti(μ-O)WO$_2$Cp*]$^+$, [(tmtaa)Ti(Cl)(μ-O)WO$_2$]$^+$, [(tmtaa)Ti-(Cl)(OH$_2$)]$^+$, [tmtaa]TiCl$^+$, and [(tmtaa)TiOH]$^+$. The ^{1}H NMR spectrum of **39** showed a typical tmtaa resonance pattern and a Cp* resonance at δ 1.65.



(16)

Discussion

The reactions reported herein demonstrate the remarkably high nucleophilicity of the Ti=O and Ti=S linkages of [tmtaa]Ti=O (**1**) and [tmtaa]Ti=S (**2**) and significantly extend the state of knowledge of the reactivity of metal–oxo and metal–sulfido bonds. The observed cycloaddition reactions of **1** and **2** with SO$_2$, SO$_3$, and hexafluoropropylene oxide are new transformations of M=O and M=S linkages in coordination compounds, and the acylation reactions with acetyl chloride and the three anhydrides studied have little precedent in other systems. Particularly striking are the cycloaddition reactions with ketones to form the dioxatitanacyclobutane complexes **15**–**17** and the corresponding cycloaddition reactions of [tmtaa]Ti=S with ketones to form the metallacycles **18** and **19**. The only precedent for these ketone cycloaddition reactions of which we are aware is the previously reported cycloaddition of Cp$_2$W=O with O=C(CF$_3$)$_2$ to form a similar metallacycle,[4b] and to our knowledge there are no prior examples of ketone cycloadditions with M=S linkages. The titanium oxo complex **1** is substantially more reactive toward ketones than is Cp$_2$W=O since this latter compound failed to give stable metallacycles with O=C(CF$_3$)CH$_3$ and O=C(CF$_3$)Ph although **1** did.[38] Related to the ketone cycloadditions is the reaction of **1** with [Cp*Re(CO)$_2$(NO)]$^+$ to form the bimetallic μ_2,η^3-CO$_2$ complex **21** (eq 7), a reaction that also has precedent in the reactions of Cp$_2$W=O with electrophilic carbonyl complexes.[4] We have assumed that the cycloaddition reactions of **1** and **2** with

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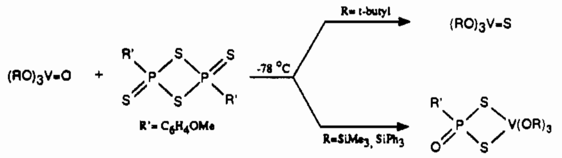
[33] (a) Mays, M. J.; Gavens, P. D. *J. Chem. Soc., Dalton Trans.* **1980**, 911. (b) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 233. (c) Bruce, M. I.; Matisons, J. G.; Wallis, R. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2365. (d) Bruce, M. I.; Pain, G. N.; Hughes, C. A.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1986**, *307*, 343. (e) Zuffa, J. L.; Kivi, S. J.; Gladfelter, W. L. *Inorg. Chem.* **1989**, *28*, 1888.

[34] (a) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403. (b) Bruce, M. I.; Liddell, M. J.; Hughes, C. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1988**, *347*, 157.

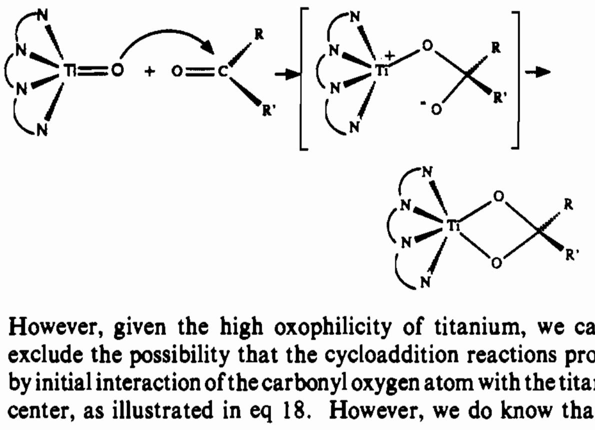
[35] Parshall, G. W. *Inorg. Synth.* **1970**, *7*, 27.

[36] Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1365.

Scheme XII

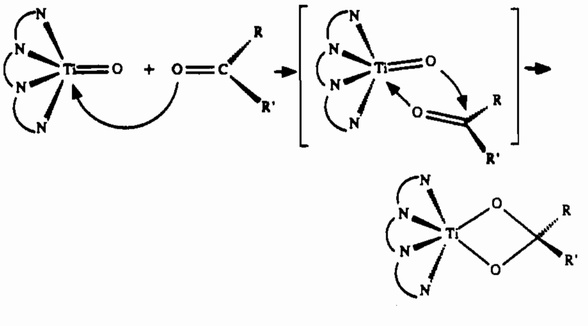


ketones and with $[Cp^{*}Re(CO)_2(NO)]^+$ proceed by initial nucleophilic addition of the electron-rich oxo and sulfido ligands to the electrophilic carbonyl carbon in these substrates (eq 17).



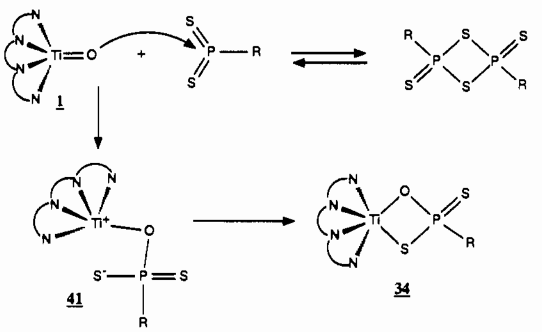
(17)

However, given the high oxophilicity of titanium, we cannot exclude the possibility that the cycloaddition reactions proceed by initial interaction of the carbonyl oxygen atom with the titanium center, as illustrated in eq 18. However, we do know that the oxygen atom of **1** is nucleophilic as evidenced by its ability to coordinate to low-valent Os, Ir, and Pt atoms in the bimetallic complexes **36–38**[37] as well as the more electrophilic metal atoms in the complexes earlier prepared by Goedkin,[13b] by its facile acylation to form the carboxylate intermediate **9**, by its reactions with anhydrides to form the bis(carboxylate) complexes **10–12**, and by its facile protonation reactions summarized in Scheme II. Thus, nucleophilic addition of the oxygen atom of **1** to ketones and to $[Cp^{*}Re(CO)_2(NO)]^+$ appears to be a plausible pathway.



(18)

Scheme XIII



Another interesting aspect of the reactivity of [tmtaa]Ti=O is its behavior with Lawesson's reagent where it gives the metallacyclic complex **34** having a -Ti–O–P–S– linkage (eq 14). This differs from the earlier reported reaction of the oxo complexes $(RO)_3V{=}O$ ($R{=}Bu^t$, $SiMe_3$, and $SiPh_3$) with this reagent (Scheme XII).[39] Lawesson's reagent is known to be useful for replacing an oxygen atom with sulfur in organic carbonyl compounds,[30] and a similar reaction was observed with $(Bu^tO)_3V{=}O$ to form $(Bu^tO)_3V{=}S$ without the detection of an intermediate metallacycle.[39] However, metallacycles were obtained with the complexes $(Me_3SiO)_3V{=}O$ and $(Ph_3SiO)_3V{=}O$, but these had two sulfur atoms in the metallacyclic framework instead of one oxygen and one sulfur as in **34**.[39] However, the rearrangement of an intermediate species like **34** with a -V–O–P–S– linkage is a logical step in these reported transformations. It has been proposed that Lawesson's reagent induces the sulfur for oxygen exchange in carbonyl compounds by nucleophilic addition of a carbonyl oxygen to the electrophilic phosphorus atom in $ArPS_2$ monomers formed from Lawesson's reagent.[40] In a similar manner, we suggest that the nucleophilic oxygen atom of **1** adds to the phosphorus atom in an $ArPS_2$ monomer to form **41** which collapses to the observed [2 + 2] cycloaddition product **34** (Scheme XIII). The high oxophilicity of titanium may account for the fact that **34** does not undergo a *retro*-[2 + 2] cycloaddition to form [tmtaa]Ti=S and $(ArP({=}O)S)_x$ or rearrange to a -Ti–S–P–S– metallacycle.

Experimental Section

General Data. Hexafluoroacetone, 1,1,1-trifluoroacetone, 1,1-dichloroacetone, chloroacetone, 2,2,2-trifluoroacetophenone, pyridine (Gold Label), sulfur dioxide, sulfur trioxide, carbonyl sulfide, maleic anhydride, dimethyl maleic anhydride, *N*-methylmaleimide, phthalic anhydride, hexafluoropropylene oxide, acetyl chloride, and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson's reagent) were purchased from Aldrich Chemical Co., iodosobenzene was purchased from Pfaltz and Bauer, Inc., carbon disulfide was purchased from Sargent-Welch Co., and samples of enriched H_2O (^{17}O, 10%; ^{18}O, 10%) were purchased from Cambridge Isotope Laboratories. The complexes [tmtaa]Ti=O,[13a,b] $[Cp^{*}Re(CO)_2(NO)][BF_4]$,[41] $Os_3(CO)_{11}(CH_3CN)$,[32] $[tmtaa]TiCl_2$,[13] $[t\text{-}BuNH_3][Cp^{*}WO_3]$,[6] *cis*-$PtCl_2(PEt_3)_2$,[35] and *trans*-$Ir(CO)(CH_3CN)(PPh_3)_2$[36] and the ligands $[tmtaa]H_2$[13c] and $[omtaa]H_2$[42] were prepared according to published methods. $Os_3(CO)_{12}$ was prepared from osmium waste solutions,[43] and ^{13}CO-enriched $Os_3(CO)_{12}$ was prepared according to the literature.[33e] Hexane, pentane, benzene, and CH_2Cl_2 were dried over CaH_2, THF was distilled over Na/benzophenone, and acetone was dried over K_2CO_3 prior to use. Unless otherwise specified, standard Schlenk techniques were used for the synthesis and handling of all compounds under prepurified Ar or N_2 atmospheres. NMR spectra were recorded on a Bruker AM 300 FT NMR spectrometer, IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode, and fast atom bombardment (FAB) mass spectra were recorded on a Kratos AFAB-MS9 spectrometer. ^{31}P and ^{17}O NMR spectra were referenced to external CD_2Cl_2 solutions of H_3PO_4 and $^{17}OH_2$, respectively. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY, from the Penn State Materials Characterization Laboratories, University Park, PA, and from Galbraith Laboratories, Inc., Knoxville, TN.

General Procedure for the Generation of [tmtaa]Ti=S (2).[13a] One equivalent of the complex $[tmtaa]TiCl_2$ and 2 equiv of well-dried n-Bu_3N or Et_3N were added to freshly distilled CH_3CN, and H_2S gas was slowly

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(37) (a) For other examples of the formation of bimetallic μ-oxo complexes via the coordination of a M=O unit to another metal see refs 6, 13b, and 37b–h and the references contained therein. (b) Pilato, R. S.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 1986. (c) Carofiglio, T.; Floriani, C.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 3245. (d) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G. *Inorg. Chem.* **1985**, *24*, 4055. (e) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (f) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345. (g) Klemperer, W. G.; Main, D. J. *Inorg. Chem.* 2355. (h) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1990**, *45B*, 619.

(38) Pilato, R.; Housmekerides, C.; Geoffroy, G. L. Unpublished observations.

(39) Preuss, F.; Noichl, H. *Z. Naturforsch.* **1987**, *42B*, 121.

(40) Rauchfuss, T. B.; Zank, G. A. *Tetrahedron Lett.* **1986**, *27*, 3445.

(41) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

(42) Place, D. A.; Ferrara, G. P.; Harland, J. J.; Dabrowiak, J. C. *Heterocycl. Chem.* **1980**, *17*, 439.

(43) (a) Keister, J. B. Ph.D. Thesis, University of Illinois, 1978. (b) Frake, S. R.; Loveday, P. A. *Inorg. Synth.* **1990**, *28*, 230.

bubbled through the solution for 30 s. The flask was sealed, and the reaction mixture was stirred for 5 min as [tmtaa]Ti=S precipitated as a red solid in essentially quantitative yield. The CH_3CN solution was decanted, and the solid was washed once with CH_3CN and then dissolved in the solvent to be used in the next reaction followed by bubbling H_2S through the solution for ~1 s. Because of the water sensitivity of **2** and its tendency to hydrolyze to **1**, all manipulations of the compound and its reactions were conducted with solutions containing a slight excess of H_2S.

Preparation of [tmtaa]Ti=^{17}O. Complex **1** (406 mg, 1.00 mmol) was dissolved in CH_2Cl_2 (100 mL), and 200 μL of 10% ^{17}O-enriched water was added followed by stirring at 20 °C for 24 h. Some decomposition occurred during the exchange process, as evidenced by a darkening of the color to brownish-red, but a drop of *n*-Bu_3N immediately induced the color to change back to yellow and ^1H NMR analysis indicated the complete formation of **1**. The CH_2Cl_2 solvent was removed under vacuum, and the resultant yellow solid was washed with CH_3CN (30 mL) and then dissolved in CH_2Cl_2 (2 × 30 mL). This solution was dried over $MgSO_4$ and filtered, and the solvent was evaporated under vacuum to leave ^{17}O enriched **1** in 93% yield (378 mg, 0.93 mmol; ^{17}O NMR δ 965).

Reaction of 1 with HO_3SCF_3, $Me_3SiO_3SCF_3$, and MeO_3SCF_3 To Form [tmtaa]Ti[OSO_2CF_3]$_2$ (4). Complex **1** (203 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (30 mL), and CF_3SO_3H (88 μL, 0.99 mmol) was added to induce a color change from yellow to dark red-brown. The solution was stirred for 1 h, and the CH_2Cl_2 solvent was evaporated under vacuum. The remaining brown solid was recrystallized from CH_2Cl_2/pentane (1:10) and was dried under vacuum overnight to yield **4** as a microcrystalline red-brown solid in 96% yield (330 mg, 0.48 mmol). The addition of excess $Me_3SiO_3SCF_3$ or MeO_3SCF_3 to **1** in CD_2Cl_2 in a resealable NMR tube induced, by ^1H NMR, an instant color change from yellow to dark red-brown and the quantitative formation of **4**. Also observed were the formation of $(Me_3Si)_2O$ (δ 0.07) and Me_2O (δ 3.34) from the respective reactions with $Me_3SiO_3SCF_3$ or MeO_3SCF_3.

Anal. Calcd for $C_{24}H_{22}F_6N_4O_6S_2Ti\cdot CH_2Cl_2$: C, 38.83; H, 3.13. Found: C, 39.01; H, 3.64. *m/z* (FAB) = 688 (M^+), 539 $(MO_3SCF_3)^+$. ^1H NMR (CD_2Cl_2): δ 2.76 (s, tmtaa-C*H*$_3$, 12 H), 6.15 (s, tmtaa-C*H*, 2 H), 7.7–7.9 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.8 (tmtaa-*C*H$_3$), 108.8 (tmtaa-MeC*C*H), 125.8 (tmtaa-Me*C*), 127.6, 131.1, 158.9 (tmtaa-Ar*C*), 123.3 (q, *C*F$_3$, J_{CF} = 312 Hz).

Reaction of 4 with Water To Form [(tmtaa)Ti(OH_2)$_2$][O_3SCF_3]$_2$ (5). Complex **5** precipitates in quantitative yield when CH_2Cl_2 solutions of **4** are permitted to stand for several days in the presence of moist air. This reaction can be performed in a variety of ways, but it was first observed to occur when a CD_2Cl_2 (1 g) solution of **4** (5 mg, 0.007 mmol) was allowed to stand in a poorly sealed NMR tube for 4 days which gave slow deposition of crystalline **5** on the sides of the NMR tube.

Anal. Calcd for $C_{24}H_{26}N_4O_8F_6TiS_2$: C, 39.79; H, 3.62. Found: C, 39.49; H, 4.11. ^1H NMR (CD_2Cl_2): δ 1.7–2.4 (br, *H*$_2$O, 4 H), 2.77 (s, tmtaa-C*H*$_3$, 12 H), 6.17 (s, tmtaa-C*H*, 2 H), 7.8–7.9 (m, tmtaa-Ar*H*, 8 H).

Reaction of 5 with Et_3N To Form 1. Complex **5** (223 mg, 0.33 mmol) was dissolved in CH_2Cl_2 (40 mL), and Et_3N (0.50 mL, 4.95 mmol) was added to induce a color change from brown to yellow. The reaction mixture was stirred for 4 h, the CH_2Cl_2 solvent was removed under vacuum, and the yellow residue was washed with CH_3CN (20 mL) to yield complex **1** in 92% yield (120 mg, 0.30 mmol).

Formation of [(tmtaa)Ti–O–Ti(tmtaa)][O_3SCF_3]$_2$ (8) from the Reaction of [tmtaa]Ti=O with One Equivalent of HO_3SCF_3. Treatment of a CH_2Cl_2 (40 mL) solution of complex **1** (414 mg, 1.02 mmol) with HO_3SCF_3 (90 μL, 1.02 mmol) gave by ^1H NMR a 57:43 mixture of **8** and a presently unidentified compound [δ 2.75 (s, tmtaa-C*H*$_3$, 12 H), 6.12 (s, tmtaa-C*H*, 2 H), 7.85 (br, tmtaa-Ar*H*, 8 H)]. Addition of 1 drop of water to this solution followed by stirring for 12 h induced the complete conversion to **8**. Addition of an additional equivalent of HO_3SCF_3 (90 μL, 1.02 mmol) induced the quantitative formation of complex **4** (^1H NMR).

Anal. Calcd for $C_{46}H_{44}F_6N_8O_7S_2Ti_2\cdot CH_2Cl_2$: C, 47.85; H, 3.93. Found: C, 47.75; H, 3.95. ^1H NMR (CD_2Cl_2): δ 2.55 (s, tmtaa-C*H*$_3$, 12 H), 5.76 (s, tmtaa-C*H*, 2 H), 7.52–7.85 (m, tmtaa-Ar*H*, 8 H).

Reaction of 1 with Water. Upon standing in moist air, yellow CH_2Cl_2 solutions of complex **1** slowly turned red over a several day period, and ^1H NMR monitoring indicated the formation of a new species [δ 2.39 (s, tmtaa-C*H*$_3$, 12 H), 2.54 (s, tmtaa-C*H*, 2 H), 7.32–7.58 (m, tmtaa-Ar*H*, 8 H)]. Evaporation of solvent from such solutions left a red-brown residue that failed to give an interpretable mass spectrum and this species has not been further characterized.

Reaction of [tmtaa]Ti=S with $Me_3SiO_3SCF_3$ To Form 4. Complex **2** (1.00 mmol) was dissolved in CH_2Cl_2 (40 mL) and $Me_3SiO_3SCF_3$ (390 μL, 2.02 mmol) was added via microsyringe to induce an instantaneous color change from red to dark red-brown. After the reaction was stirred for 10 min, the CH_2Cl_2 solvent was removed under vacuum, and the remaining brown solid was recrystallized from CH_2Cl_2/pentane (1:10) and washed with hexane (40 mL) to leave analytically pure **4** as a microcrystalline brown solid in 87% yield (597 mg, 0.87 mmol). The $Me_3SiSSiMe_3$ byproduct was detected by ^1H NMR as follows.

Reaction of 1 with Acetyl Chloride. Complex **1** (203 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (40 mL), and 2 equiv of acetyl chloride (71 μL, 1.00 mmol) were added to give an immediate color change from yellow to red-brown. After 5 min of stirring, the CH_2Cl_2 solvent was evaporated under vacuum, and the resultant solid was recrystallized from CH_2Cl_2/pentane followed by a pentane (30 mL) wash to leave the brown complex [tmtaa]$TiCl_2$[13a] in 90% yield (208 mg, 0.45 mmol). Reaction of complex **1** (20 mg, 0.049 mmol) with 1 equiv of $CH_3C(O)Cl$ (4 μL, 0.056 mmol) in CD_2Cl_2 (1 g) in a resealable NMR tube gave an immediate yellow to red-brown color change as the intermediate complex **9** formed (see text). After recording the NMR spectra, the solution was transferred to a 25 mL Schlenk flask, the solvent was evaporated to dryness, and the FAB mass spectrum of the residue was recorded.

Characterization data are as follows for **9**. *m/z* (FAB) = 485 $(M + 1)^+$, 425 ([tmtaa]$TiCl^+$). ^1H NMR (CD_2Cl_2): δ 1.75 (s, O_2CCH_3, 3 H), 2.40 (s, tmtaa-C*H*$_3$, 12 H), 5.53 (s, tmtaa-C*H*, 2 H), 7.26–7.55 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 21.0 (s, O_2CCH_3), 23.5 (tmtaa-*C*H$_3$), 106.9 (tmtaa-MeC*C*), 124.4 (tmtaa-Me*C*), 124.4, 128.1, 133.8, 159.3 (tmtaa-Ar*C*).

Reaction of 1 with Phthalic Anhydride To Form 11. Complex **1** (500 mg, 1.23 mmol) was dissolved in CH_2Cl_2 (40 mL), and phthalic anhydride (200 mg, 1.35 mmol) was added to the solution. This induced an instantaneous change of color from yellow to dark red. After being stirred for 20 min, the solution was concentrated to 10 mL under vacuum, and pentane (40 mL) was added to induce precipitation of **11** as a brownish-red microcrystalline solid which was recrystallized twice from CH_2Cl_2/pentane (1:6). To remove any solid remaining on the sides of the recrystallization flask, hexane (50 mL) was added to the solid and the flask was immersed in a liquid N_2 bath until the hexane froze. The flask was then warmed to room temperature by running lukewarm water around the flask and continuously shaking it to induce the solid to flake off the sides of the flask. The hexane solvent was then decanted to leave analytically pure **11** in 82% yield (556 mg, 1.00 mmol).

Anal. Calcd for $C_{30}H_{26}N_4O_4Ti\cdot C_8H_6O_4\cdot 2CH_2Cl_2$: C, 53.95; H, 4.08. Found: C, 54.01; H, 4.54 (the occluded solvent molecules were also observed in the X-ray diffraction study, see below). IR (CH_2Cl_2): ν_{CO} = 1652 cm^{-1}. *m/z* (FAB) = 555 $(M + 1)^+$. ^1H NMR (CD_2Cl_2): δ 2.60 (s, tmtaa-C*H*$_3$, 12 H), 5.85 (s, tmtaa-C*H*, 2 H), 6.9–7.2 (br, phthalic, Ar*H*, 4 H), 7.31–7.50 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.4 (tmtaa-*C*H$_3$), 106.2 (tmtaa-MeC*C*), 124.6 (tmtaa-Me*C*), 129.6, 130.1, 157.7 (tmtaa-Ar*C*), 123.3, 124.4, 134.1 (phthalic Ar*C*), 171.4 (*C*=O).

Reaction of 1 with Maleic Anhydride To Form 10. Complex **10** was prepared similarly to **11** using [tmtaa]Ti=O (300 mg, 0.74 mmol) and maleic anhydride (78 mg, 0.80 mmol) in CH_2Cl_2 (40 mL) and was isolated as a red microcrystalline solid in 89% yield (330 mg, 0.66 mmol).

Anal. Calcd for $C_{26}H_{24}N_4O_4Ti\cdot CH_2Cl_2$: C, 55.03; H, 4.44. Found: C, 54.41; H, 4.80. IR (CH_2Cl_2): ν_{CO} = 1658 cm^{-1}. *m/z* (FAB) = 505 $(M + 1)^+$. ^1H NMR (CD_2Cl_2): δ 2.64 (s, tmtaa-C*H*$_3$, 12 H), 3.96 (br, maleic *H*, 2 H), 5.89 (s, tmtaa-C*H*, 2 H), 7.60–7.69 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.5 (tmtaa-*C*H$_3$), 106.6 (tmtaa-MeC*C*), 125.0 (tmtaa-Me*C*), 129.9, 130.1, 157.9 (tmtaa-Ar*C*), 128.5 (maleic *C*=*C*), 168.2 (*C*=O).

Reaction of 1 with $(CF_3CO)_2O$ To Form 12. Complex **12** was prepared similarly to **11** using [tmtaa]Ti=O (203 mg, 0.50 mmol) and $(CF_3CO)_2O$ (350 μL, 2.46 mmol) in CH_2Cl_2 (50 mL) and was isolated as a brown microcrystalline solid in 82% yield (250 mg, 0.41 mmol).

Anal. Calcd for $C_{26}H_{22}F_6N_4O_4Ti$: C, 50.67; H, 3.60. Found: C, 50.05; H, 4.22. IR (CH_2Cl_2): ν_{CO} = 1680 cm^{-1}. *m/z* (FAB) = 616 $(M)^+$. ^1H NMR (CD_2Cl_2): δ 2.69 (s, tmtaa-C*H*$_3$, 12 H), 5.95 (s, tmtaa-C*H*, 2 H), 7.66–7.78 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.6 (tmtaa-*C*H$_3$), 107.5 (tmtaa-MeC*C*), 125.2 (tmtaa-Me*C*), 129.7, 129.9, 158.4 (tmtaa-Ar*C*), 115.7 (q, $^1J_{CF}$ = 290 Hz, *C*F$_3$), 159.1 (q, $^2J_{CF}$ = 38 Hz, *C*O).

Reaction of 1 with Hexafluoropropylene Oxide To Form 13. Complex **1** (300 mg, 0.74 mmol) was dissolved in pyridine (40 mL), and hexafluoropropylene oxide was bubbled through the solution for 15 s to induce an immediate yellow to brownish-red color change. The solution was stirred for 12 h, the pyridine and excess epoxide were evaporated under vacuum, and the resultant solid was recrystallized twice from CH_2Cl_2/pentane (1:6) to leave a grayish-brown solid. A freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure **13** in 85% yield (359 mg, 0.63 mmol).

Anal. Calcd for $C_{25}H_{22}F_6N_4O_2Ti{\cdot}CH_2Cl_2$: C, 47.51; H, 3.68. Found: C, 47.07; H, 3.23. m/z (FAB) = 573 $(M + 1)^+$, 503 $(M - CF_3)^+$. ^{1}H NMR (CD_2Cl_2): δ 2.56 (s, tmtaa-CH_3, 12 H), 5.69 (s, tmtaa-CH, 2 H), 7.41–7.57 (m, tmtaa-ArH, 8 H).

Reaction of 1 with Hexafluoroacetone To Form 15. Complex **1** (201 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (30 mL), and $(CF_3)_2C{=}O$ was bubbled through the solution for 15 s to induce an immediate yellow to brown color change. The solution was stirred for 1 h, the CH_2Cl_2 and excess ketone were evaporated under vacuum, and the resultant solid was recrystallized from CH_2Cl_2/pentane (1:6) to give a grayish-brown product. A freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure **15** as a gray-brown microcrystalline solid in 96% yield (273 mg, 0.48 mmol).

Anal. Calcd for $C_{25}H_{22}F_6N_4O_2Ti{\cdot}CH_2Cl_2$: C, 47.51; H, 3.68. Found: C, 47.26; H, 3.66. m/z (FAB) = 573 $(M + 1)^+$. ^{1}H NMR (CD_2Cl_2): δ 2.60 (s, tmtaa-CH_3, 12 H), 5.77 (s, tmtaa-CH, 2 H), 7.45–7.63 (m, tmtaa-ArH, 8 H).

Reaction of 1 with Trifluoroacetone To Form 16. Complex **16** was prepared similarly to **15** using **1** (203 mg, 0.50 mmol) and $(CF_3)(CH_3)C{=}O$ (50 μL, 0.56 mmol) in CH_2Cl_2 (30 mL) and was isolated as a light red solid in 98% yield (254 mg, 0.49 mmol).

Anal. Calcd for $C_{25}H_{25}F_3N_4O_2Ti{\cdot}CH_2Cl_2$: C, 51.76; H, 4.51. Found: C, 50.76; H, 4.82 (the occluded solvent molecule was observed in the X-ray diffraction study). m/z (FAB) = 519 $(M + 1)^+$. ^{1}H NMR (CD_2Cl_2): δ 0.11 (q, C(CF_3)(CH_3), 3 H, $^4J_{HF}$ = 1.31 Hz), 2.56 (s, tmtaa-CH_3, 12 H), 5.66 (s, tmtaa-CH, 2 H), 7.35–7.55 (m, tmtaa-ArH, 8 H).

Reaction of 1 with Trifluoroacetophenone To Form 17. Complex **17** was prepared similarly to **15** using **1** (406 mg, 1.00 mmol) and $(CF_3)(Ph)C{=}O$ (150 μL, 1.07 mmol) in CH_2Cl_2 (30 mL) to give **17** as a red microcrystalline solid in 85% yield (490 mg, 0.85 mmol).

Anal. Calcd for $C_{30}H_{27}F_3N_4O_2Ti{\cdot}CH_2Cl_2$: C, 55.96; H, 4.39. Found: C, 55.88; H, 4.67. m/z (FAB) = 581 $(M + 1)^+$. ^{1}H NMR (CD_2Cl_2): δ 2.55 (s, tmtaa-CH_3, 12 H), 5.68 (s, tmtaa-CH, 2 H), 6.59–6.98 (m, C_6H_5, 5 H), 7.12–7.39 (m, tmtaa-ArH, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.5 (tmtaa-CH$_3$), 105.8 (tmtaa-MeCC), 123.9 (tmtaa-MeC), 126.8, 135.1, 158.8 (tmtaa-ArC), 100.37 (q, CO$_2$, $^2J_{CF}$ = 30 Hz), 124.5 (q, CF$_3$, $^1J_{CF}$ = 292 Hz).

Reaction of [tmtaa]Ti=S with Hexafluoroacetone To Form 18. Hexafluoroacetone was slowly bubbled through a CH_3CN (30 mL) solution of complex **2** (1.00 mmol) for 10 s to induce an immediate color change from red to dark red-brown. After the mixture was stirred for 5 min, the acetonitrile solvent was pumped off under vacuum, and the remaining solid was recrystallized twice from CH_2Cl_2/pentane (1:10). A freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure microcrystalline **18** as a brown solid in 79% yield (467 mg, 0.79 mmol).

Anal. Calcd for $C_{25}H_{22}F_6N_4OSTi{\cdot}CH_2Cl_2$: C, 46.38; H, 3.59. Found: C, 46.36; H, 3.53. MS (FAB): m/z = 589 $(M + 1)^+$. MS (EI): m/z = 406, 182, 113, 69. ^{1}H NMR (CD_2Cl_2): δ 2.62 (s, tmtaa-CH_3, 12 H), 5.78 (s, tmtaa-CH, 2 H), 7.47–7.62 (m, tmtaa-ArH, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.8 (tmtaa-CH$_3$), 106.7 (tmtaa-MeCC), 124.6 (tmtaa-MeC), 128.0, 133.7, 159.0 (tmtaa-ArC), 123.6 (q, CF$_3$, $^1J_{CF}$ = 288 Hz).

Reaction of [tmtaa]Ti=S with α,α,α-Trifluoroacetone To Form 19. Complex **19** was prepared similarly to **18** with [tmtaa]Ti=S (1.00 mmol) and α,α,α-trifluoroacetone (0.3 mL, 3.35 mmol) except that the reaction was stirred for 12 h to give a gradual color change from red to dark red-brown. The product was recrystallized from CH_2Cl_2/pentane and a freeze–thaw cycle using hexane (50 mL) was applied, as described above for the preparation of **11**, to leave analytically pure **19** in 84% yield (449 mg, 0.84 mmol).

Anal. Calcd for $C_{25}H_{25}F_3N_4OSTi$: C, 56.19; H, 4.71. Found: C, 56.02; H, 4.66. MS (FAB): m/z = 535 $(M + 1)^+$. MS (EI): m/z = 406, 256, 187, 128, 113. ^{1}H NMR (CD_2Cl_2): δ 0.40 (q, C(CF_3)(CH_3), 3 H, $^4J_{HF}$ = 1.22 Hz), 2.58 (s, tmtaa-CH_3, 6 H), 2.59 (s, tmtaa-CH_3, 6 H), 5.71 (s, tmtaa-CH, 2 H), 7.40–7.54 (m, tmtaa-ArH, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.5 (tmtaa-CH$_3$), 27.4 (s, C(CF_3)(CH$_3$)), 85.3 (q, C(CF_3)(CH_3), $^2J_{CF}$ = 31 Hz), 105.7 (tmtaa-MeCC), 124.1, 124.5 (tmtaa-MeC), [127.2, 127.3], [133.8, 134.0], 158.6 (tmtaa-ArC), 123.5 (q, CF$_3$, $^1J_{CF}$ = 285 Hz).

Reaction of 1 with [Cp*Re(CO)$_2$(NO)][BF$_4$] To Form 21. Complex **1** (0.500 g, 1.23 mmol) and [Cp*Re(CO)$_2$(NO)][BF$_4$] (670 mg, 1.35 mmol) were dissolved in CH_2Cl_2 (40 mL). The resultant red solution was stirred for 1 h and then concentrated to 10 mL under vacuum. Pentane (40 mL) was then added to induce precipitation of **21** as a red microcrystalline solid which was recrystallized twice from CH_2Cl_2/pentane (1:6) to give **21** as a dark red microcrystalline solid in 90% yield (998 mg, 1.11 mmol).

Anal. Calcd for $C_{34}H_{37}BF_4N_5O_4ReTi$: C, 45.35; H, 4.14. Found: C, 45.12; H, 4.18. IR (KBr) ν_{CO} = 1990, ν_{NO} = 1715 cm^{-1}. m/z (FAB) = 814 $(M)^+$. ^{1}H NMR (CD_2Cl_2): δ 1.65 (s, C_5(CH_3)$_5$, 15 H), 2.73 (s, tmtaa-CH_3, 12 H), 6.05 (s, tmtaa-CH, 2 H), 7.77 (br, tmtaa-ArH, 8 H). ^{13}C NMR (CD_2Cl_2): δ 9.9 (C_5(CH$_3$)$_5$), 23.3 (tmtaa-CH$_3$), 105.1 (tmtaa-MeCC), 125.2 (tmtaa-MeC), 130.0, 130.6, 158.7 (tmtaa-ArC), 108.3 (C_5(CH_3)$_5$), 226.2 (Re=CO$_2$), 202.7 (CO).

Formation of [Cp*Re(CNPh)$_2$(NO)][BF$_4$] (22) from the Reaction of 20 with Ph$_3$P=NPh. The complex [Cp*Re(CO)$_2$(NO)][BF$_4$] (**20**) (494 mg, 1.00 mmol) and Ph$_3$P=NPh (777 mg, 2.20 mmol) were stirred in CH_2Cl_2 (40 mL) at room temperature for 4 h. The CH_2Cl_2 solvent was then removed under vacuum to leave a yellow residue which was washed seven times with CH_2Cl_2/pentane (1:10) to remove the Ph$_3$P=O. This left **22** as a yellow solid in 82% yield (525 mg, 0.82 mmol).

Anal. Calcd for $C_{24}H_{25}BF_4N_3ORe$: C, 44.73; H, 3.91. Found: C, 45.33; H, 3.88. IR (CH_2Cl_2): ν_{CN} = 2159, 2120 cm^{-1}; ν_{NO} = 1730 cm^{-1}. m/z (FAB) = 555 $(M)^+$. ^{1}H NMR (CD_2Cl_2): δ 2.28 (s, C_5(CH_3)$_5$, 15 H), 7.4–7.6 (m, ArH, 10 H).

Reaction of 21 with Ph$_3$P=NPh To Give 22. Complex **21** (450 mg, 0.50 mmol) and Ph$_3$P=NPh (388 mg, 1.1 mmol) were stirred in CH_2Cl_2 (40 mL) for 4 h. The CH_2Cl_2 solvent was evaporated under vacuum, and the remaining solid was extracted with CH_3CN (2 × 20 mL). The CH_3CN solvent was then evaporated under vacuum to leave a mixture of Ph$_3$P=O and complex **22**.

Reaction of 1 with SO$_2$ To Form Complex 23. Complex **1** (1.000 g, 2.46 mmol) was dissolved in CH_2Cl_2 (40 mL), and sulfur dioxide was bubbled through the solution for 15 s to induce an immediate yellow to red-brown color change. The solution was stirred for 5 min, the CH_2Cl_2 and excess sulfur dioxide were evaporated under vacuum, and the solid was recrystallized twice from CH_2Cl_2/pentane (1:6) to give a dark red-brown product. A freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure **23** in 91% yield (1.055 g, 2.25 mmol).

Anal. Calcd for $C_{22}H_{22}N_4O_3STi{\cdot}CH_2Cl_2$: C, 49.75; H, 4.36; S, 5.77. Found: C, 49.36; H, 4.67; S, 5.84 (the included solvent molecule was observed in the X-ray diffraction study). IR (KBr): ν_{SO} 1161, 1148, 1128, 939, and 656 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.64 (s, tmtaa-CH_3, 12 H), 5.84 (s, tmtaa-CH, 2 H), 7.57–7.70 (m, tmtaa-ArH, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.5 (tmtaa-CH$_3$), 106.9 (tmtaa-MeCC), 124.6 (tmtaa-MeC), 128.8, 132.1, 158.6 (tmtaa-ArC).

Reaction of 1 with SO$_3$ To Form Complex 24. Sulfur trioxide was received as a solid mixture of the monomer and some low-boiling solid polymer. This solid (150 mg, 1.88 mmol) was placed in a 100-mL Schlenk flask and warmed by running lukewarm water around the flask to liquefy and convert all the solid into SO$_3$ monomer. Complex **1** (500 mg, 1.23 mmol) was dissolved in CH_2Cl_2 (40 mL) and transferred via cannula to the flask containing the SO$_3$. This induced an instantaneous change of color from yellow to dark red-brown. After being stirred for 5 min, the solution was concentrated to 10 mL under vacuum, and pentane (40 mL) was added to induce precipitation of **24** as a grayish-brown microcrystalline solid which was recrystallized twice from CH_2Cl_2/pentane (1:6). A freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure **24** as a gray-brown microcrystalline solid in 85% yield (508 mg, 1.05 mmol).

Anal. Calcd for $C_{22}H_{22}N_4O_4STi{\cdot}CH_2Cl_2$: C, 48.35; H, 4.23; N, 9.81. Found: C, 47.91; H, 4.57; N, 10.49. IR (KBr): ν_{SO} 912 (ν_1), 558 (ν_2), 1276 (ν_3), 1172 (ν_3), 922 (ν_3), 712 (ν_4), 671 (ν_4) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.70 (s, tmtaa-CH_3, 12 H), 5.96 (s, tmtaa-CH, 2 H), 7.72–7.73 (m, tmtaa-ArH, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.6 (tmtaa-CH$_3$), 107.9 (tmtaa-MeCC), 124.9 (tmtaa-MeC), 130.2, 130.6, 158.5 (tmtaa-ArC).

Reaction of 23 and 24 with [NH$_4$]OH To Form 1. Addition of one drop of aqueous [NH$_4$]OH (28%) to complex **23** (10 mg, 0.021 mmol) in CD_2Cl_2 (1 g) induced an immediate change in color from red-brown to yellow, and the ^{1}H NMR spectrum showed quantitative conversion to [tmtaa]Ti=O. To show the formation of the [NH$_4$]$_2$SO$_3$ byproduct, complex **23** (1.000 g, 2.13 mmol) was dissolved in CH_2Cl_2 (50 mL), and

15 drops of (aqueous) NH_4OH (28%) were added. The solution was stirred for 20 min, and the solvent was evaporated under vacuum. The residue was extracted with H_2O (15 mL), and then the aqueous solution was evaporated to dryness on a hot plate. IR (KBr) analysis of the resultant salt showed bands for $[NH_4]_2SO_3$ which compared well to those of an authentic sample. A similar reaction with **24** showed the formation of **1** and $[NH_4]_2SO_4$.

Reaction of [tmtaa]Ti=S with SO_2 To Form 23. Sulfur dioxide was bubbled through a CH_2Cl_2 (40 mL) solution of complex **2** (1.00 mmol) for 10 s to induce a color change from red to red-brown. The solution was stirred for 30 min, the CH_2Cl_2 solvent and SO_2 were evaporated under vacuum, and the remaining solid was recrystallized twice from CH_2Cl_2/pentane (1:6). A freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure **23** in 85% yield (398 mg, 0.85 mmol).

Reaction of [tmtaa]Ti=S with SO_3 To Form 24. As received the sulfur trioxide was a solid mixture of the monomer and low-boiling solid polymer. This solid (150 mg, 1.88 mmol) was placed in a 100-mL Schlenk flask and liquefied and depolymerized by running lukewarm water around the sides of the flask. The solvent CH_2Cl_2 (40 mL) was added to the flask, and then the SO_3 solution was transferred via cannula to a flask containing complex **2** (1.00 mmol). An instantaneous reaction occurred, as evidenced by the color change from red to dark red-brown. The solution was stirred for 30 min, and then the CH_2Cl_2 solvent was evaporated under vacuum. The residue was recrystallized from CH_2Cl_2/pentane (1:10), and a freeze–thaw cycle using hexane (50 mL) was applied, as described above for the preparation of **11**, to leave analytically pure **24** as a microcrystalline brown solid in 78% yield (369 mg, 0.78 mmol).

Oxidation of 23 To Form 24. An NMR tube was equipped with a solution of complex **23** (10 mg, 0.021 mmol) in CD_2Cl_2 (1 g), and O_2 was slowly bubbled through the solution via a thin needle. After the solution was exposed to sunlight for 4 h, its ^1H NMR spectrum was recorded and showed complete conversion to complex **24**. In the absence of sunlight, only 10% conversion occurred over the course of 1 day. Alternatively, complex **23** (10 mg, 0.021 mmol) was dissolved in CD_2Cl_2 (1 g), and PhIO (6 mg, 0.028 mmol) was added to the NMR tube. ^1H NMR analysis after 1 h showed complete conversion to **24**.

Reaction of 1 with Carbon Dioxide To Form 27. Complex **1** (10 mg, 0.025 mmol) was dissolved in CD_2Cl_2 (1 g) in a resealable NMR tube, and the sample was cooled to −78 °C. Using a very thin needle, CO_2 was bubbled slowly through the solution in the NMR tube for 15 s, and the NMR tube was immediately sealed. The NMR tube was warmed to 20 °C in a closed hood in case the increased CO_2 pressure would cause detonation. It was observed that during the CO_2 addition step, the yellow color of complex **1** changed quickly to red. The ^1H NMR spectrum of the warmed sample showed the quantitative formation of the carbonate complex **27** [^1H NMR (CD_2Cl_2): δ 2.64 (s, tmtaa-CH_3, 12 H), 5.83 (s, tmtaa-C*H*, 2 H), 7.55–7.66 (m, tmtaa-Ar*H*, 8 H)]. The NMR tube was slowly opened to release the excess CO_2 pressure in order to achieve 1 atm of CO_2 in the NMR tube, and the ^1H NMR spectrum was recorded. Under these conditions, the ^1H NMR spectrum showed approximately equal amounts of complex **1** (52%) and **27** (48%).

Preparation of [omtaa]Ti=O (28). Complex **28** was prepared similarly to the reported[13] preparation of complex **1** using [omtaa]H_2 as the ligand source.

Anal. Calcd for $C_{26}H_{30}N_4OTi\cdot CH_3CN$: C, 66.80; H, 6.61. Found: C, 66.52; H, 6.61. IR (KBr): $\nu_{Ti=O}$ = 916 cm^{-1}. *m*/*z* (FAB) = 463 (M + 1)$^+$. ^1H NMR (CD_2Cl_2): δ 2.36 (s, omtaa-ArCH_3, 12 H), 2.44 (s, omtaa-NCCH_3, 12 H), 5.30 (s, omtaa-C*H*, 2 H), 7.27 (s, omtaa-Ar*H*, 4 H). ^{13}C NMR (CD_2Cl_2): δ 20.1 (omtaa-Ar*C*H_3), 22.8 (omtaa-NC*C*H_3), 103.7 (omtaa-MeC*C*), 124.9 (omtaa-Me*C*), 135.4, 136.2, 161.0 (omtaa-Ar*C*).

Reaction of [omtaa]Ti=O with Carbon Dioxide To Form 29. Complex **29** was prepared as described above for complex **27** using [omtaa]Ti=O (7 mg, 0.015 mmol). ^1H NMR analysis using 1 atm of CO_2 showed the presence of complex **1** and **29** in a 7:93 ratio.

IR (CH_2Cl_2): ν_{CO} = 1618 cm^{-1}; ^1H NMR (CD_2Cl_2): δ 2.42 (s, omtaa-ArCH_3, 12 H), 2.62 (s, omtaa-NCCH_3, 12 H), 5.78 (s, omtaa-C*H*, 2 H), 7.42 (br, omtaa-Ar*H*, 4 H). ^{13}CNMR (CD_2Cl_2): δ 20.6 (omtaa-Ar*C*H_3), 23.5 (omtaa-NC*C*H_3), 106.5 (omtaa-MeC*C*), 124.3 (omtaa-Me*C*), 130.8, 138.7, 158.1 (omtaa-Ar*C*), 163.2 (O_2*C*O).

Reaction of 1 with COS To Form 2. Complex **1** (5 mg, 0.012 mmol) was added to CD_2Cl_2 (1 g) in a resealable NMR tube, and gaseous COS was added in a manner similar to that used to prepare **27**. The room-temperature ^1H NMR spectrum recorded after 30 min at 20 °C showed the presence of only [tmtaa]Ti=S.

Reaction of 1 with CS_2 To Form 31. Complex **1** (406 mg, 1.00 mmol) and CS_2 (0.6 mL, 10.0 mmol) were dissolved in CH_2Cl_2 (40 mL), and the reaction mixture was stirred for 2 days as the color slowly changed from yellow to red ([tmtaa]Ti=O and [tmtaa]Ti=S) to deep red ([tmtaa]-Ti=S plus some complex **31**) and then to gray-brown as **31** precipitated. The product **31** was isolated in 71% yield (342 mg, 0.71 mmol) by filtering the solution and washing the remaining solid with CH_2Cl_2 (30 mL), CH_3CN (20 mL), and petroleum ether (2 × 50 mL) in that order.

Anal. Calcd for $C_{23}H_{22}N_4S_3Ti\cdot CH_2Cl_2$: C, 49.41; H, 4.15. Found: C, 49.50; H, 4.56. IR (KBr): ν_{CS} 1025, 1014, and 861 cm^{-1}.

Reaction of [tmtaa]Ti=S with CS_2 To Form 31. Carbon disulfide (0.5 mL, 30 mmol) was added to a CH_2Cl_2 (40 mL) solution of **2** (1.00 mmol), and the reaction mixture was stirred vigorously for 2 days during which time the red color slowly changed to dark brown as a brown precipitate deposited. The solution was filtered, and the residue was washed with CH_2Cl_2 (30 mL), CH_3CN (20 mL), and hexane (2 × 50 mL) in that order to yield complex **31** as a gray-brown microcrystalline solid in 62% yield (310 mg, 0.62 mmol).

Reaction of 1 with Lawesson's Reagent To Form 34. Complex **1** (1.000 g, 2.46 mmol) was dissolved in CH_2Cl_2 (40 mL), and Lawesson's reagent (404 mg, 1.24 mmol) was added to induce an instantaneous change of color from yellow to red. After being stirred for 20 min, the solution was concentrated to 10 mL under vacuum, and pentane (40 mL) was added to induce precipitation of **34** as a brown microcrystalline solid which was recrystallized twice from CH_2Cl_2/pentane (1:6). A single freeze–thaw cycle using hexane (50 mL), as described above for the preparation of **11**, left analytically pure **34** as a brown-red microcrystalline solid in 94% yield (1.407 g, 2.31 mmol).

Anal. Calcd for $C_{29}H_{29}N_4O_2PS_2Ti\cdot CH_2Cl_2$: C, 51.96; H, 4.51. Found: C, 52.33; H, 4.79 (the included solvent molecule was observed in the X-ray diffraction study). *m*/*z* (FAB) = 609 (M + 1)$^+$. ^1H NMR (CD_2Cl_2): δ 2.65 (s, tmtaa-CH_3, 12 H), 3.71 (s, CH_3O, 3 H), 5.85 (s, tmtaa-C*H*, 2 H), 6.41–6.70 (m, $C_6H_4OCH_3$, 4 H), 7.58–7.66 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 23.7 (tmtaa-*C*H_3), 55.8 (*C*H_3O), 106.9 (tmtaa-MeC*C*), 124.9 (tmtaa-Me*C*), 129.1, 131.7, 158.4 (tmtaa-Ar*C*), 127.1 (d, Law.-ArC_α, $^1J_{PC}$ = 121.1 Hz), 131.2 (d, Law.-ArC_β, $^2J_{PC}$ = 13.9 Hz), 112.7 (d, Law.-ArC_γ, $^3J_{PC}$ = 14.8 Hz), 161.0 (d, Law.-ArC_δ, $^4J_{PC}$ = 3.7 Hz). ^{31}P NMR (CD_2Cl_2): δ 87.7.

Reaction of [tmtaa]Ti=O with $Os_3(CO)_{11}(NCCH_3)$ To Form 36. The complex $Os_3(CO)_{11}(NCCH_3)$, prepared from $Os_3(CO)_{12}$ (495 mg, 0.55 mmol), was dissolved in CH_2Cl_2 (30 mL), and solid [tmtaa]Ti=O (199 mg, 0.49 mmol) was added. The solution was stirred at 20 °C for 6 h, the CH_2Cl_2 solvent was removed under vacuum, and the resultant residue was washed three times with CH_2Cl_2/pentane (1:7) and then dissolved in THF and filtered through a Celite filter pad. The THF solvent was removed under vacuum to leave orange-red [tmtaa]Ti=O→$Os_3(CO)_{11}$ (**36**) in 58% yield (365 mg, 0.28 mmol). Approximately 17% ^{13}CO enriched **36** was prepared as above using ~17% ^{13}CO enriched $Os_3(CO)_{12}$.

Anal. Calcd for $C_{33}H_{22}N_4O_{12}Os_3Ti\cdot CH_2Cl_2$: C, 29.81; H, 1.77. Found: C, 29.87; H, 1.74. MS (FAB): *m*/*z* = 1286 (M)$^+$, and fragment ions corresponding to the consecutive loss of 10 carbonyls. IR (THF): ν_{CO} = 2098 (vw), 2066 (vw), 2044 (m), 2027 (s), 2007 (vs), 1985 (m), 1964 (m), 1937 (w) cm^{-1}. IR (KBr): $\nu_{Ti=O}$ = 896 cm^{-1}. ^{13}C NMR (THF-d_8, ~17% ^{13}CO, −58 °C): δ 187.6 (s with ^{13}C satellites, $^2J_{CC}$ = 34.2 Hz, 2 C, *ax*-Os–*C*O), 184.8 (s with ^{13}C satellites, $^2J_{CC}$ = 34.8 Hz, 2 C, *ax*-Os–*C*O), 183.8 (s, 2 C, *eq*-Os–*C*O), 182.6 (s, 1 C, *trans*-Ti=O→Os–*C*O), 179.0 (s, 2 C, *eq*-Os–*C*O), 177.5 (s, 2 C, *eq*-Os–*C*O). ^{13}C NMR {^1H} (CD_2Cl_2, 20 °C): δ 23.0 (tmtaa-*C*H_3), 107.0 (tmtaa-MeC*C*), 137.2 (tmtaa-Me*C*), 126.2, 127.9, 161.9 (tmtaa-Ar*C*), 182.1 (s, *trans*-Ti=O→Os–*C*O), 180–184 (br, Os–*C*O). ^1H NMR (CD_2Cl_2): δ 2.52 (s, tmtaa-CH_3, 12 H), 5.53 (s, tmtaa-C*H*, 2 H), 7.49–7.59 (m, tmtaa-Ar*H*, 8 H).

Reaction of [tmtaa]Ti=O with *cis*-$[PtCl(PEt_3)_2(acetone)]^+$ To Form 37. The complex *cis*-$[PtCl_2(PEt_3)_2]$ (502 mg, 1.00 mmol) was dissolved in acetone (40 mL), and the solution was cooled to −78 °C. Solid $AgBF_4$ (250 mg, 1.28 mmol) was then added. The solution was slowly warmed to 20 °C, stirred for 1 h, and filtered through a glass wool pad. The filtrate was cooled to −78 °C, and [tmtaa]Ti=O (406 mg, 1.00 mmol) was added. The solution was warmed to 20 °C as the color changed from yellow to red. After being stirred for 2 h, the solution was filtered through a Celite filter pad, and the solvent was evaporated under vacuum. The resultant residue was dissolved in THF (3 × 25 mL), and the solution was filtered through a Celite filter pad into a flame-dried flask. The THF solvent was evaporated under vacuum, and the remaining solid was recrystallized with CH_2Cl_2/pentane (1:15) and washed twice with cold benzene (10 mL) to isolate the very soluble microcrystalline orange-red complex **37** in 38% yield (364 mg, 0.38 mmol). Complex **37** can be separated from any remaining *cis*-$[PtCl_2(PEt_3)_2]$ by photolyzing the mixture of products for 2 h in benzene, and then decanting the benzene layer. Photolysis causes isomerization of *cis*-$[PtCl_2(PEt_3)_2]$ to its more soluble trans isomer which dissolves in benzene.

Anal. Calcd for $C_{34}H_{52}BClF_4N_4OP_2PtTi\cdot{}^1/_2CH_2Cl_2$: C, 41.39; H, 5.34. Found: C, 41.33; H, 4.98. MS (FAB): $m/z = 873\ (M)^+$. IR (KBr): $\nu_{Ti=O} = 894\ cm^{-1}$. ^{1}H NMR ($CD_2Cl_2$): δ 0.63–0.74 (m, $P(CH_2CH_3)_3$, 9 H), 0.79–0.90 (m, $P(CH_2CH_3)_3$, 9 H), 1.26–1.32 (m, $P(CH_2CH_3)_3$, 6 H), 1.57–1.62 (m, $P(CH_2CH_3)_3$, 6 H), 2.58 (s, tmtaa-C*H*$_3$, 12 H), 5.64 (s, tmtaa-C*H*, 2 H), 7.50–7.65 (m, tmtaa-Ar*H*, 8 H). ^{31}P NMR (CD_2Cl_2): δ 0.35 (d, $^2J_{P-P} = 20$ Hz, $^1J_{Pt-P} = 3550$ Hz), 13.24 (d, $^2J_{P-P} = 20$ Hz, $^1J_{Pt-P} = 3582$ Hz).

Reaction of Complex 1 with *trans*-$[Ir(PPh_3)(CO)(CH_3CN)]BF_4$ To Form 38. The yellow complexes [tmtaa]Ti═O (186 mg, 0.46 mmol) and *trans*-$[Ir(CO)(CH_3CN)(PPh_3)_2][BF_4]$ (380 mg, 0.46 mmol) were added to CH_2Cl_2 (30 mL) and an instant color change to red was observed. After the red solution was stirred for 15 min, the CH_2Cl_2 solvent was evaporated under vacuum and the remaining red solid was recrystallized twice with CH_2Cl_2/pentane (1:10) and washed with hexane (40 mL) to leave the microcrystalline complex **38** in 85% isolated yield (483 mg, 0.39 mmol).

MS (FAB): $m/z = 1152\ (M + 1)^+$. IR (KBr): $\nu_{C=O} = 1959\ cm^{-1}$, $\nu_{Ti=O}$ 883 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.19 (s, tmtaa-C*H*$_3$, 12 H), 5.14 (s, tmtaa-C*H*, 2 H), 7.1–7.5 (m, tmtaa-Ar*H* and PPh_3, 38 H). ^{31}P NMR (CD_2Cl_2): δ 27.2.

Reaction of [tmtaa]Ti═O with Cp*W(O)$_2$Cl To Form 39. Complex **1** (131 mg, 0.32 mmol) and Cp*W(O)$_2$Cl (125 mg, 0.32 mmol) were added to CH_2Cl_2 (20 mL), and the red-brown solution was stirred for 5 min. The CH_2Cl_2 solvent was then evaporated, and the remaining light brown solid was washed with pentane to leave complex **39** in 85% yield (215 mg, 0.27 mmol). This reaction is very sensitive to the presence of chloride impurities, which can cause the formation of [tmtaa]TiCl$_2$, so extra care needs to be exercised in the preparation and purification of Cp*W(O)$_2$Cl. Complex **39** was found to decompose readily and this diminished the overall yield in attempts to isolate pure samples.

Anal. Calcd for $C_{32}H_{37}ClN_4O_3TiW$: C, 48.48; H, 4.70. Found: C, 48.73; H, 4.93. MS (FAB): $m/z = 793\ (M + 1)^+$. IR (KBr): 940 (w), 918 (m), 763 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.64 (s, $C_5(CH_3)_5$, 15 H), 2.57 (s, tmtaa-C*H*$_3$, 12 H), 5.76 (s, tmtaa-C*H*, 2 H), 7.49–7.72 (m, tmtaa-Ar*H*, 8 H). ^{13}C NMR (CD_2Cl_2): δ 10.4 ($C_5(CH_3)_5$), 23.3 (tmtaa-*C*H$_3$), 105.1 (tmtaa-MeC*C*H), 157.7 (tmtaa-Me*C*), 124.7, 128.3, 130.4 (tmtaa-Ar*C*), 117.3 $C_5(CH_3)_5$.

Reaction of [tmtaa]TiCl$_2$ with [Cp*WO$_3$]$^-$ To Form 39. The salt $[Bu^tNH_3][Cp^*WO_3]$ (145 mg, 0.33 mmol) and [tmtaa]TiCl$_2$ (150 mg, 0.33 mmol) were combined in CH_2Cl_2 (50 mL), and the solution was stirred for 3 h. The solvent was evaporated to leave an orange-brown residue which was washed with pentane (5 × 20 mL) to give **39** as a light brown solid in 85% yield (222 mg, 0.28 mmol).

Crystal and Molecular Structures of 5, 8, 11, 16, 21, 23, and 34. Crystal, data collection, and refinement parameters are collected in Table I. Crystals of each were mounted on fine glass fibers with epoxy cement, and the unit-cell parameters were obtained from the least-squares fit of 25 reflections ($20° \le 2\theta \le 25°$). Preliminary photographic characterization showed $2/m$ Laue symmetry for **5**, **8**, **11**, **23**, and **34**. The systematic absences in the diffraction data for **5**, **8**, and **34** uniquely established the space group as $P2_1/n$, and for **11** and **23** as $P2_1/c$. For **16** and **21**, $\bar{1}$ Laue symmetry was found, and all processing of their data was confined to the centrosymmetric space group $P\bar{1}$, which resulted in the chemically reasonable structures reported. A semiempirical absorption correction was applied to the data set for **21**, and the semiempirical absorption program XABS was applied to the data sets of **5**, **8**, and **34**. No absorption correction was used for **11**, **16**, or **23** ($T_{max}/T_{min} = 1.012$, 1.113, and 1.110, respectively).

The structures were all solved by direct methods, which located the Ti atoms for **5**, **8**, **11**, **16**, **23**, and **34** and the Ti and Re atoms for **21**. The remaining non-hydrogen atoms were located through subsequent least squares and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (dCH = 0.960 Å, $U = 1.2U$ for attached C). For **5**, **11**, **21**, **23**, and **34**, all non-hydrogen atoms were refined with anisotropic thermal parameters. For **5**, all non-carbon and non-hydrogen atoms were refined with anisotropic thermal parameters, and for **16**, all non-hydrogen atoms except the fluorine atoms were refined with anisotropic thermal parameters. The fluorine atoms were refined isotropically due to the disorder between the $-CH_3$ and $-CF_3$ groups.

All computer programs and the sources of the scattering factors are obtained in the SHELXTL program library (Version 5.1; G. Sheldrick; Nicolet (Siemens), Madison, WI).

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Supplementary Material Available: For **5**, **8**, **11**, **16**, **21**, **23**, and **34**, tables of crystal data, atomic coordinates, anisotropic temperature factors, complete bond lengths and bond angles, and calculated hydrogen atom positions (51 pages). Ordering information is given on any current masthead page.