Cycloaddition Reactions across the Ti=O Bond of (tmtaa)Ti=O (tmtaa = dianion of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine)

Chris E. Housmekerides,[a] **Robert S. Pilato,**[a] **Gregory L. Geoffroy***[a] **and Arnold L. Rheingold**[b]
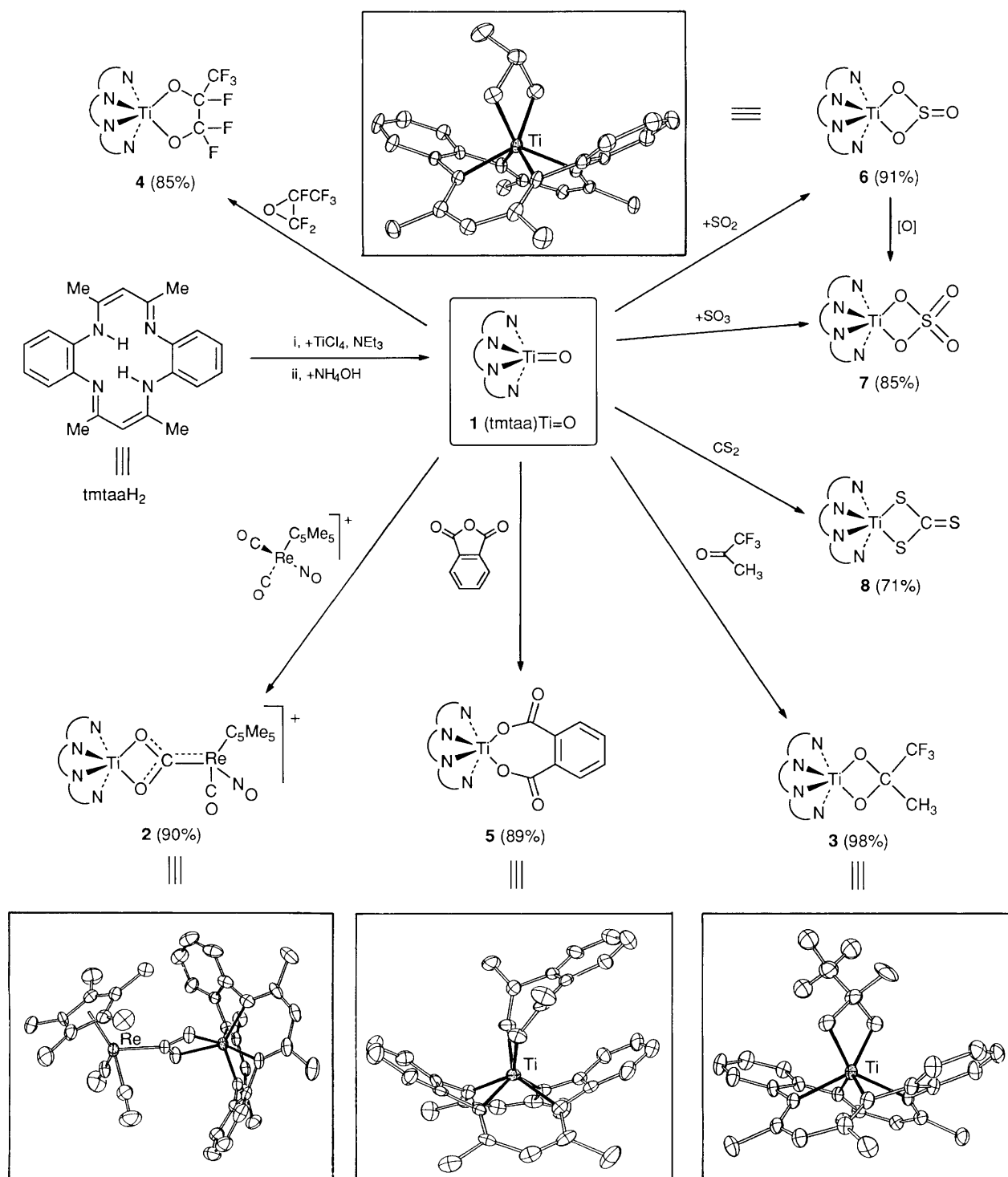
[a] *Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Department of Chemistry, The University of Delaware, Newark, DE 19716, USA*

The complex (tmtaa)Ti=O undergoes [2 + 2] cycloaddition of the Ti=O bond across the C=O bond of ketones and $[(C_5Me_5)Re(CO)_2(NO)]^+$, the S=O bonds of SO_2 and SO_3, the C=S bond of CS_2, and ring opens epoxides and cyclic anhydrides to give metallacycles.

There has been considerable recent interest in the chemistry of transition metal oxo ligands, in part because of the relevance of this functional group to catalytic oxiation processes.[1] Particularly interesting targets of study have been the complexes cp₂Ti=O and cp₂Zr=O (cp = cyclopentadienyl) which
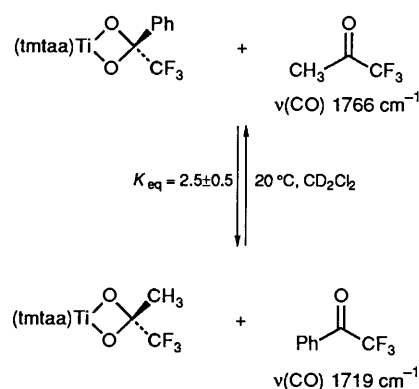
Bergman *et al.* have shown to be unstable but able to be generated as reactive transients.[2] Our interest has focused on the earlier reported[3] compound (tmtaa)Ti=O **1** (tmtaa = dianion of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecine), which is isoelectronic

4 (85%)

tmtaaH₂

6 (91%)

7 (85%)

8 (71%)

i, +TiCl₄, NEt₃

ii, +NH₄OH

1 (tmtaa)Ti=O

+SO₂

+SO₃

CS₂

[O]

2 (90%)

5 (89%)

3 (98%)

Scheme 1

with $cp_2Ti=O$ but which has the advantage of being sufficiently stable for it to be isolated and studied under controlled conditions. We have found the oxo ligand of this complex to be remarkably nucleophilic and to undergo a variety of addition and cycloaddition reactions with organic and inorganic substrates, as illustrated in Scheme 1. The new complexes 2, 3, 5 and 6 have been crystallographically characterized,† and spectroscopic data‡ for all the new complexes are consistent with their proposed or crystallographically determined structures. All reactions were conducted at 22 °C in CH_2CL_2 and pyridine (for 4), and were complete within minutes of mixing (except for 8 which required 2 days).

An initial test of the nucleophilicity of the oxo ligand of 1 showed that it is sufficiently reactive to attack a carbonyl ligand of the electrophilic complex $[(C_5Me_5)Re(CO)_2(NO)]^+$ and induce cycloaddition to form the bimetallic complex 2. This species possesses a μ_2, η^3-CO_2 ligand, and its formation is similar to the earlier reported cycloaddtion of $[(C_5Me_5)$-$Re(CO)_2(NO)]^+$ with $cp_2M=O$ (M = Mo, W).[4] Complex 1 also undergoes rapid cycloaddition of the Ti=O bond across the C=O bond of electron-deficient ketones, as illustrated in Scheme 1 by the reaction with $(CF_3)MeC=O$ to form the metallacycle 3. Similar cycloaddition occurred with $(CF_3)_2C=O$, $(CHCl_2)MeC=O$, $(CH_2Cl)MeC=O$ and

Scheme 2

---

† Crystal data for 2: $C_{34}H_{37}BF_4N_5O_4ReTi$, $M = 900.58$, triclinic, $P\bar{1}$, $a = 8.7772(11)$, $b = 12.1983(17)$, $c = 16.8154(23)$ Å, $\alpha = 90.122(11)$, $\beta = 93.357$, $\gamma = 91.902°$, $U = 1796.2(4)$ Å^3, $Z = 2$, $T = 297$ K, $D_c = 1.665$ g cm^{-3}, μ(Mo-Kα) = 38.50 cm^{-1}. Intensity data were collected on a Nicolet R3m diffractometer, by Wyckoff ω scan technique ($4° \leqslant 2\theta \leqslant 44°$). From 4637 measured data, 3481 with $F_o \geqslant 5\sigma(F_o)$ were considered observed. The structure was solved by direct methods. $R_F = 4.54\%$ and $R_{wF} = 4.61\%$.

Crystal data for 3: $C_{25}H_{25}F_3N_4O_2Ti\cdot CH_2Cl_2$, $M = 600.28$ triclinic, $P\bar{1}$, $a = 10.410(6)$, $b = 10.487(6)$, $c = 13.993(7)$ Å, $\alpha = 67.19(4)$, $\beta = 85.28(4)$, $\gamma = 73.83(4)°$, $U = 1352.0(13)$ Å^3, $Z = 2$, $T = 297$ K, $D_c = 1.474$ g cm^{-3}, μ(Mo-Kα) = 5.68 cm^{-1}. Intensity data were collected as for 2 ($4° \leqslant 2\theta \leqslant 48°$). From 4409 measured data, 3243 were considered observed, $F_o \geqslant 5\sigma(F_o)$. The structure was solved by direct method. $R_F = 10.08\%$ and $R_{wF} = 10.91\%$. There was a 50% disorder between the methyl group and the trifluoromethyl group.

Crystal data for 5: $C_{30}H_{26}N_4O_4Ti\cdot C_8H_6O_4\cdot 2CH_2Cl_2$, $M = 888.42$, monoclinic, $P2_1/c$, $a = 15.519(9)$, $b = 12.529(6)$, $c = 22.110(11)$ Å, $\beta = 104.25(4)°$, $U = 4167.1(38)$ Å^3, $Z = 4$, $T = 297$ K, $D_c = 1.416$ g cm^{-3}, μ(Mo-Kα) = 5.21 cm^{-1}. Intensity data were collected as for 2 ($4° \leqslant 2\theta \leqslant 45°$). From 5822 measured data, 2674 with $F_o \geqslant 5\sigma(F_o)$ were considered observed. The structure was solved by a Patterson synthesis. $R_F = 8.68\%$ and $R_{wF} = 9.48\%$.

Crystal data for 6: $C_{22}H_{22}N_4O_3STi\cdot CH_2Cl_2$, $M = 555.25$, monoclinic, $P2_1/n$, $a = 11.233(6)$, $b = 12.9637(7)$, $c = 17.444(7)$ Å, $\beta = 106.40(4)°$, $U = 2436(22)$ Å^3, $Z = 4$, $T = 297$ K, $D_c = 1.513$ g cm^{-3}, μ(Mo-Kα) = 6.91 cm^{-1}. Intensity data were collected as for 2 ($4° \leqslant 2\theta \leqslant 45°$). From 3501 measured data, 3481 were considered observed with $F_0 \geqslant 5\sigma(F_o)$. The structure was solved by direct methods. $R_F = 6.22\%$ and $R_{wF} = 6.93\%$.

Atom coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Spectroscopic data for 2: IR (KBr) v_{CO} 1990, v_{NO} 1715 cm^{-1}; m/z (FAB) 814(M$^+$); ^{1}H NMR (CD$_2$Cl$_2$): δ 7.77 (tmtaa-ArH), 6.05 (tmtaa-CH), 2.73 (tmtaa-Me) and 1.65 (C$_5$Me$_5$); ^{13}C NMR (CD$_2$Cl$_2$): δ 226.20 (Re=CO$_2$) and 202.68 (CO). For 3: m/z (FAB) 519(M$^+$); ^{1}H NMR (CD$_2$Cl$_2$): δ 7.55 −7.35 (tmtaa-ArH), 5.66 (tmtaa-CH), 2.56 (tmtaa-Me) and 2.45 (CF$_3$COCH$_3$). For 4: m/z (FAB) 573(M$^+$); ^{1}H NMR ($[^2$H$_5]$pyridine): δ 7.50–7.42 (tmtaa-ArH), 5.69 (tmtaa-CH) and 2.56 (tmtaa-Me). For 5: m/z (FAB) 555(M$^+$); ^{1}H NMR (CD$_2$Cl$_2$): δ 7.50–6.1 (aryl), 5.85 (tmtaa-CH) and 2.60 (tmtaa-Me). For 6: IR (KBr) v_{SO} 1188, 1161, 1148 and 1128 cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ 7.70–7.57 (tmtaa-ArH), 5.84 (tmtaa-CH) and 2.64 (tmtaa-Me). For 7: IR (KBr) v_{SO} 912(v_1), 558(v_2), 1276(v_3), 1172(v_3), 922(v_3), 712(v_4) and 671(v_4) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$): δ 7.73–7.71 (tmtaa-ArH), 5.97 (tmtaa-CH) and 2.70 (tmtaa-Me$_3$). For 8: IR (KBr) v_{cs} 1020 cm^{-1}. Satisfactory C, H analyses were obtained for 2–8.

$(CF_3)(Ph)C=O$, but metallacycle formation was not detected with $Me_2C=O$, $Et_2C=O$, and methyl styryl ketone. The correlation observed is that ketones with $v(CO) \geqslant 1719$ cm^{-1} give metallacyles but those with $v(CO) \leqslant 1712$ cm^{-1} do not. These metallacycles have also been observed to undergo slow ketone exchange at 22 °C to give an equilibrium favouring the metallacycle formed from the more electron-deficient ketone (Scheme 2).

The only reported precedent for these ketone cycloaddition reactions is that which occurs between $cp_2W=O$ and the highly electrophilic $(CF_3)_2C=O$.[4] The observation that 1 reacts with ketones less electrophilic than $(CF_3)_2C=O$ to give stable metallacycles, whereas $cp_2W=O$ does not, implies the nucleophilic ordering $1 > cp_2W=O$.

The nucleophilic oxygen atom of complex 1 also ring opens hexafluoropropene oxide and phthalic anhydride to form the metallacycles 4 and 5, respectively. Maleic anhydride gave a product similar to 5, but the only epoxide which has been found to react with 1 is the highly electron-deficient $CF_3\overline{CFCF_2O}$ just mentioned. The ring opening of epoxides by metal oxides is believed to be an important step in the metal oxide catalysed hydrolysis of epoxides,[9] and the reverse of this reaction may be an important step in metal oxide catalysed epoxidation reactions.[6]

Complex 1 also undergoes cycloaddition with SO_2 and SO_3 to give the new metallacycles 6 and 7, and metallacycle 6 can be quantitatively converted into 7 by oxidation with PhIO or O_2 in the presence of sunlight.[5] Although $\eta^2(O_2)$-sulphito complexes are known for several transition metals, early transition-metal complexes of this ligand are rare and to our knowledge complex 6 is the first reported $\eta^2(O_2)$-sulphito complex of titanium. The formation of 6 and its subsequent oxidation to 7 mimics steps proposed in the catalysis of SO_2 oxidation by metal oxides (e.g., V_2O_5).[7] Relevant to this work is Herrmann's report of a similar [2 + 2] cycloaddition of SO_2 across a Re=O bond on each rhenium atom of $(C_5Me_5)_2Re_2O_4$,[8] although this reaction is reported to be slower (1 h) than the essentially instantaneous addition of SO_2 to 1. We can find no precedent for the cycloaddition of SO_3 with a metal oxo complex. Complex 1 also reacts with CS_2 to form as the ultimate product the thiocarbonate complex 8, formed by initial metathesis between CS_2 and 1 to yield COS and (tmtaa)Ti=S which then cycloadds another equivalent of CS_2 to form 8. Complex 8 was also formed by the direct reaction of the known[3] complex (tmtaa)Ti=S and CS_2.

Complex 1 appears to be the most nucleophilic oxo complex yet reported and it presents an opportunity to define further the chemistry of the relatively neglected oxo ligand. Further explorations are in progress.

References

1 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981; W. A. Herrmann, *J. Organomet. Chem.*, 1990, **382**, 1; W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1297; G. Parkin and J. E. Bercaw, *J. Am. Chem. Soc.*, 1989, **111**, 391; J. K. Felixberger, J. G. Kuchler, E. Herdtweck, R. A. Paciello and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 946; W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, 1988.

2 M. J. Carney, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1990, **112**, 6426; M. J. Carney, P. J. Walsh, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 8751.

3 V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 1982, 142.

4 R. S. Pilato, C. E. Housmekerides, P. Jernakoff, D. Rubin, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1990, **9**, 23333.

5 A. R. Miksztal and J. S. Valentine, *Inorg. Chem.*, 1984, **23**, 3548.

6 K. A. Jorgensen, *Chem. Rev.*, 1989, **89**, 431.

7 U. H. F. Sander, H. Fischer, U. Rothe and R. Kola, *Sulfur, Sulfur Dioxide and Sulfuric Acid*, The British Sulfur Corporation, London, 1984; B. Meyer, *Sulfur, Energy, and Environment*, Elsevier, Amsterdam, 1977; A. Muller and B. Krebs, *Sulfur*, Elsevier, Amsterdam, 1984.

8 W. A. Herrmann, K. A. Jung and E. Herdtweck, *Chem. Ber.*, 1989, **122**, 2041.

9 J. R. Briggs, A. M. Harrison and J. H. Robson, *Polyhedron*, 1986, **5**, 281.