Cycloaddition and Cycloreversion Reactions of a Monomeric Ti(IV) Oxo Complex with Terminal and Internal Alkynes. A Reversible Oxametallacyclobutene/Hydroxoacetylide Interconversion

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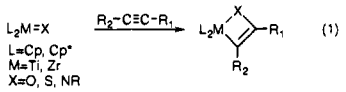
In most isolable mononuclear metal oxo complexes, the majority of which are formed from metals in the middle of the transition series (e.g., Mo, W, Re), the metal−oxygen bond does not interact directly with external reagents and functions only as a "spectator" for reactions that typically take place at other coordination sites in the molecule.[1] The synthesis and structure of $Cp^*_2Ti(O)(pyr)$ ($Cp^* = \eta^5$-C_5Me_5; pyr = pyridine) (**1**) were described recently.[2] We have found that the Ti=O bond in this compound, a rare example of a simple mononuclear oxotitanium complex, reacts with unsaturated CC and CX bonds (X = N, O, S). We report here on the [2 + 2] cycloaddition of **1** with terminal alkynes and the novel rearrangement of the resulting oxametallacyclobutenes to hydroxoacetylide complexes. In at least one case the rearrangement is reversible, and we have obtained information on its mechanism.

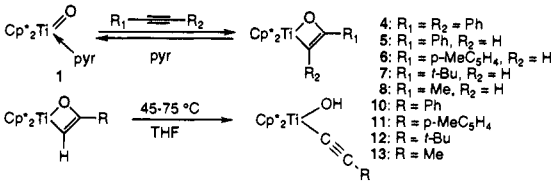
Like its cyclopentadienyl (Cp) and Cp* imido-[3] and oxozirconium[4] analogs, **1** undergoes overall [2 + 2] cycloaddition reactions with alkynes to give metallacyclobutene complexes (eq 1).[5] However, in contrast to those systems, **1** favors reaction



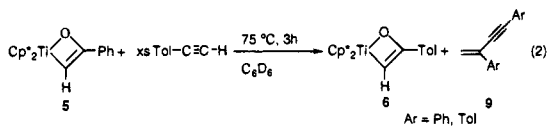
(1)

with terminal rather than internal alkynes. Thus, treatment of a toluene solution of **1** with diphenyl-, phenyl-, *p*-tolyl-, *tert*-butyl-, or methylacetylene gave the oxametallacyclobutene complexes **4**−**8** (Scheme 1) in good to moderate yield.[6] Furthermore, the cycloaddition reactions were found to be reversible; thermolysis of the oxametallacycles in the presence of pyridine resulted in quantitative conversion to **1**. Similarly, heating oxametallacycle **5** to 75 °C in the presence of excess

Scheme 1



p-tolylacetylene resulted in formation of **6**, along with an organic product, subsequently identified as the enyne **9** (eq 2).[7]



(2)

The cycloaddition reactions of **1** with terminal alkynes are highly regioselective. On the basis of ^1H and $^{13}C\{^1H\}$ NMR experiments, as well as hydrolysis with 5% HCl to the corresponding ketones, we have determined that the regioisomers formed have the original terminal alkynyl carbon bound to titanium (Scheme 1). Possibly due to the more crowded Ti center, the regiochemistry of alkyne additions to **1** is the opposite of that observed in the zirconium systems.[3,4] To confirm the proposed connectivity, a single crystal X-ray diffraction study of **5** was performed.[8] An ORTEP diagram, along with selected bond lengths and angles, is included in Figure 1. The titanium−oxygen distance of 1.978(5) Å is consistent with the presence of a Ti−O single bond (estimated using covalent radii).[9] However, the observed Ti−O distance is longer than the Ti−O distance of 1.866 Å observed in a related oxametallacyclopentane complex synthesized by Mashima and co-workers.[10]

Thermolysis of oxametallacyclobutenes **5**−**8** at 45−100 °C in benzene or THF solution resulted in conversion to the corresponding hydroxoacetylide complexes **10**−**13** in good yield (Scheme 1), identified by NMR spectroscopy and X-ray crystallography for **10**.[8] The acetylide complexes show a sharp OH stretch in the infrared spectrum at ~3600 cm^{-1} and in most cases a C≡C stretch at ~2000 cm^{-1}.[11,12] An ORTEP drawing, along with selected bond lengths and angles, is shown in Figure 1. In the solid state, no intra- or intermolecular hydrogen bonding to the OH group is observed. In addition, the hydrogen atom of the hydroxide group points away from the Ti and the triple bond of the acetylide ligand.

We have carried out the following experiments designed to investigate the mechanism of the oxametallacycle-to-hydroxoacetylide rearrangement. Thermolysis of $Cp^v_2Ti(OCTolCH)$ ($Cp^v = Me_4EtC_5$) (**14**) and **5** in C_6D_6 resulted in complete scrambling to all four metallacycle products before any conversion to the hydroxoacetylide complexes had occurred. This is clearly due to the fact that retrocyclization occurs more rapidly than rearrangement and is consistent with the reversion of **4**−**8**

(1) Nugent, W. A.; Mayer, J. A. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.
(2) Smith, M. R.; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049.
(3) (a) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 1753. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (c) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. (d) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.
(4) (a) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (b) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. (c) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761. (d) Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6343.
(5) Cycloaddition reactions of a Ti=O linkage with organic and metal carbonyls have been reported previously. See: (a) Housmekerides, C. E.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 563. (b) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453.
(6) For similar oxametallacyclobutenes of zirconium, see: (a) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491. (b) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994. Also see ref 4.
(7) We believe the enyne results from dimerization of excess alkyne catalyzed by trace amounts of hydroxoacetylide, which is formed from the metallacycle during the thermolysis. Treatment of isolated hydroxoacetylides **12** and **13** with terminal alkynes results in rapid dimerization of the alkynes. This catalysis will be the subject of a future publication. For examples of other metal acetylide-catalyzed alkyne dimerizations, see: (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Bolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Heeres, H. J.; Teuben, J. H.; *Organometallics* **1991**, *10*, 1980.
(8) A single crystal X-ray diffraction study of **4** has also been performed. See supplementary material for details of the X-ray studies on **5**, **10**, and **4**.
(9) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.
(10) Mashima, K.; Haraguchi, H.; Ohyoshi, A.; Sakai, N.; Takaya, H. *Organometallics* **1991**, *10*, 2731.
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(12) Teuben, J. H.; Meijer, H. J. D. L. *J. Organomet. Chem.* **1969**, *17*, 87.

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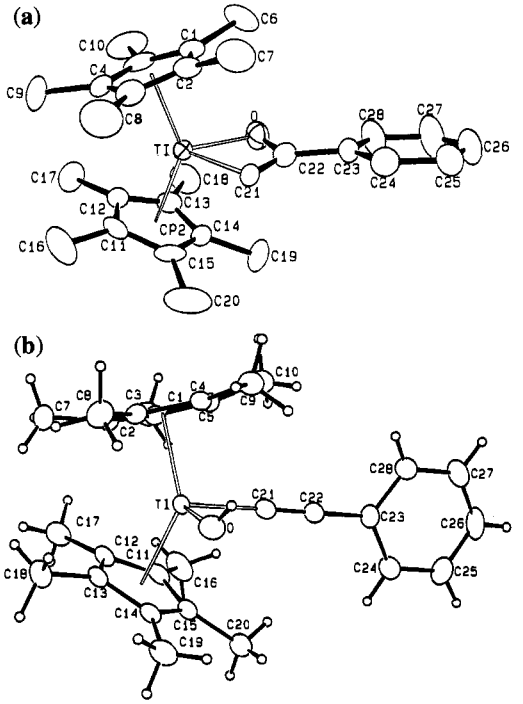


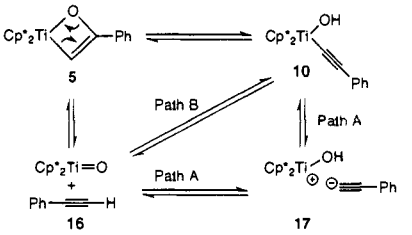
Figure 1. ORTEP drawings of (a) **5** and (b) **10**. Selected bond distances (Å) and angles (deg): for **5**, Ti−O 1.978(5), Ti−C21 2.041(6), C22−O 1.370(8), C22−C21 1.313(9), O−Ti−C21 68.35(23), Ti−O−C22 89.0-(4), Ti−C21−C22 87.9(5); and for **10**, Ti−O 1.870(2), Ti−C21 2.117-(2), C21−C22 1.218(3), O−H(O) 0.67(3), O−Ti−C21 94.10(8), Ti−O−H(O) 118.3(30).

to **1** in the presence of pyridine. The kinetics of the rearrangement of **5** to **10** in toluene-d_8 have been examined by ^{1}H NMR spectroscopy at a variety of temperatures. These studies show that the reaction is first order in metal complex and is *reversible*.[13] A typical plot of concentration vs time is provided as supplementary material. From the temperature dependence of K_{eq} over a 73−101 °C temperature range, we have determined that $\Delta H° = 2.7 \pm 0.4$ kcal/mol, $\Delta S° = 8.7 \pm 1$ eu, and $\Delta G° = 0.11 \pm 0.5$ kcal/mol at 25 °C. From an Eyring plot (73−101 °C), we have measured $\Delta H^‡ = 33.6 \pm 0.8$ kcal/mol, $\Delta S^‡ = 15.3 \pm 0.6$ eu, and $\Delta G^‡ = 29.0 \pm 2.0$ kcal/mol (calculated at 25 °C).

Deuterium substitution at the α-position of **5** has allowed us to measure both an equilibrium and a kinetic isotope effect for the rearrangement. At 101 °C, the equilibrium isotope effect K_H/K_D is 0.781 ± 0.014, which is consistent with the conventional prediction that the deuterium should favor a location at the higher frequency O−H bond[14] over the C−H bond of the metallacycle. The normal kinetic isotope effect on $k_{forward}$ [k_{1H}/k_{1D} (101 °C)] is 2.94 ± 0.06, indicating that C−H bond cleavage takes place before or during the rate-determining transition state. From the equilibrium and forward reaction isotope effects, we can calculate an isotope effect for the reverse reaction of 3.77 ± 0.28.

Finally, we have found that the ring (alkynyl) substituents have a profound effect on the rate of the rearrangement. The relative rates of rearrangement are Ph ≈ Tol < Me ≪ *tert*-butyl. When R = Me_3Si, the oxametallacycle is not isolable; treatment of **1** with (trimethylsilyl)acetylene results in direct conversion to $Cp^*_2Ti(OH)C{\equiv}CSiMe_3$ (**15**). The relative rates of formation of **10**, **13**, and **12** normalized to 45 °C[15] are 1:35:240. Phenylacetylene has the lowest pK_a of the three alkynes,[16] and so the relative rates do not show a simple correlation with the acidity of the uncomplexed alkyne. The rates increase most dramatically for the largest substituents, indicating that steric effects play a significant role in determining the rates. We attribute the rate acceleration primarily to the relative ground state energies of the metallacycles. We find, for example, that at 45 °C, **5** is 2.5 kcal/mol more stable than **8**. This difference completely accounts for the 35-fold rate acceleration observed for formation of **13** relative to **10**.

Scheme 2



Two possible mechanisms, consistent with our observations, for the interconversion of **5** and **10** are shown in Scheme 2. Common to both mechanisms is initial cycloreversion to generate **16** and phenylacetylene,[17] an occurrence that is documented by the reconversion of **4**−**8** to **1** and by the rapid exchange of one alkyne fragment for another in the metallacycles. After the initial step, path A postulates abstraction of the weakly acidic alkynyl proton by the titanium-bound oxygen, followed by collapse of the resulting ion pair **17** to give the observed product. Alternatively, proton transfer and Ti−C bond formation could take place in a concerted step, as is illustrated in path B. We observe no rate acceleration when the reaction is run in THF rather than in toluene or benzene. This argues against path A, since it would be expected to show a large solvent effect. The influence of the alkyne substituent on the rate provides evidence against path A because one would expect that more acidic alkynes should undergo proton transfer most rapidly. Because the opposite is observed, it is more likely that C−H bond breaking and O−H bond-making are synchronous processes with negligible or modest development of negative charge at the terminal alkyne carbon in the transition state for the rearrangement.

Further studies of the chemistry of **1** and its analogues, as well as of the catalyzed dimerization of alkynes by this material, are underway in our laboratories.

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Supplementary Material Available: Spectroscopic and analytical data for **4**−**8**, **10**, **12**, **14**, and **15**; details of the structure determination for **4**, **5**, and **10**, including ORTEP drawings showing full atomic numbering, crystal and data collection parameters, positional parameters and their esds, and intramolecular distances and angles; representative kinetic data for the rearrangement of **5** to **10** including a plot of concentration vs time, an Eyring plot ($\ln(k_1/T)$ vs $1/T$), and a van't Hoff plot ($\ln(K_{eq})$ vs $1/T$) (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) Preliminary studies of the rearrangement of **7** indicate that it is first order and nonreversible. Studies are underway to determine whether the differences between the two systems are due to electronic or steric effects.

(14) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987; p 1090.

(15) Because K_{eq} is too small to allow direct measurement of the rate of conversion of **5** to **10** at 45 °C, the rate was calculated from the Eyring plot.

(16) Streitwieser, A., Jr.; Reuben, D. M. E. *J. Am. Chem. Soc.* **1971**, *93*, 1794.

(17) Because **10** dimerizes excess alkyne, studies of alkyne inhibition on the rate could not be performed. We therefore cannot rule out the possibility that **16** actually exists as an alkyne complex or that such a complex is formed on the reaction coordinate between **5** or **10** and **16**.