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Synthesis, Structure, and Reactivity Studies of an η^2-N_2-Titanium Diazoalkane Complex. Generation and Trapping of a Carbene Complex Intermediate

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Organic diazoalkanes have long been used as synthons for metal carbene complexes.[1−4] It is generally assumed that an intermediate diazoalkane complex is involved in the carbene transfer process.[3] Diazoalkane complexes have also been implicated as intermediates in the metal-catalyzed cyclopropanation of olefins by organic diazoalkanes.[2,3] Unfortunately, while there are numerous examples of isolable transition metal diazoalkane complexes, they are typically quite resistant to N_2 loss;[3,4] as a result there are few isolable diazoalkane complexes known to generate metal carbene complexes.[5−9] We report here on the synthesis of a titanocene diazoalkane complex which undergoes facile N_2 loss and on the mechanism of its reaction with olefins to give titanacyclobutane complexes.

Treatment of a benzene solution of $Cp^*{}_2Ti(C_2H_4)$[10] ($Cp^* = C_5Me_5$) with 1 equiv of Me_3SiCHN_2 results in an immediate color change from lime to forest green. Removal of the solvent gives a green powder, which may be recrystallized from hexanes at −50 °C to give $Cp^*{}_2TiN_2CHSiMe_3$ (**1**) in 60−70% yield (Scheme 1). The modest isolated yield reflects the high solubility of the complex rather than the formation of any byproducts. When the reaction is performed in C_6D_6 and followed by ^1H NMR spectroscopy, 1 equiv of free C_2H_4 is produced in addition to **1**, which is the only observable titanium-containing product and is formed in >98% yield. Retention of the nitrogen was confirmed by elemental analysis.[11]

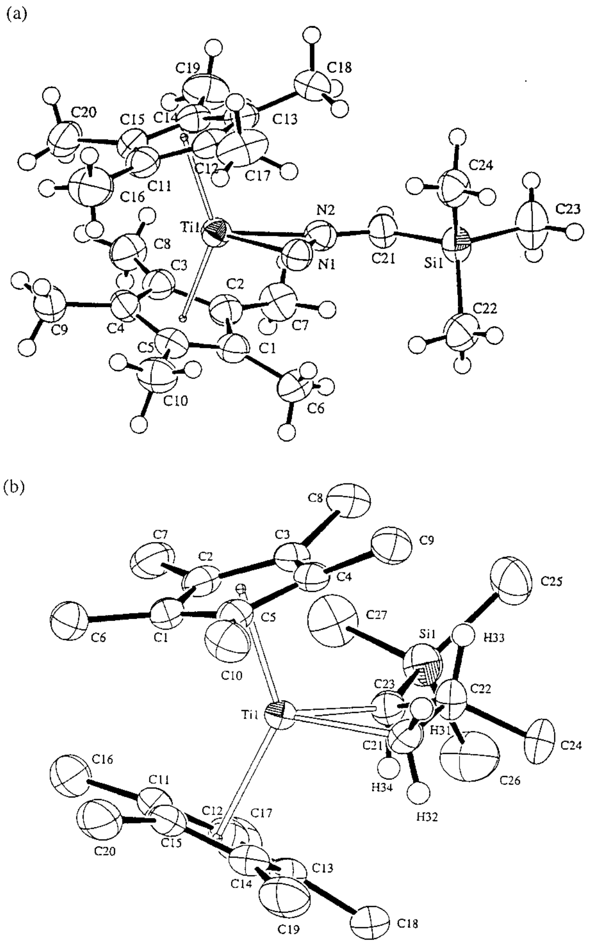
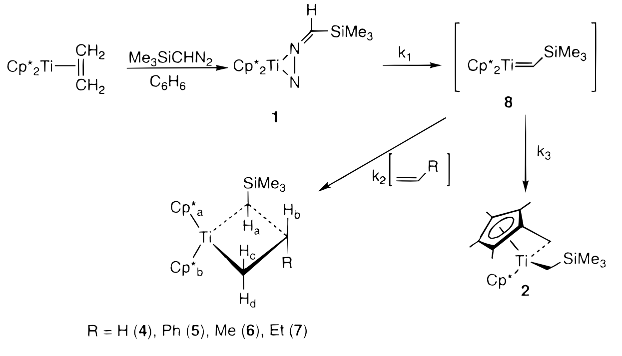


Figure 1. ORTEP drawings of (a) **1** and (b) **6**. Selected bond distances (Å) and angles (deg) for 1: Ti−N1, 1.979(2); Ti−N2, 2.012(2); N1−N2, 1.276(3); N2−C21, 1.342(3); C21−H, 0.96 (3); C21−Si, 1.840(3); N1−Ti−N2, 37.27(9); N1−N2−C21, 131.3(2); N2−C21−Si, 122.6(2); Cp*1−Ti−Cp*2, 140.72(2). Selected bond distances (Å) and angles (deg) for **6**: Ti−C23, 2.192(4); Ti−C21, 2.155(4); C23−C22, 1.557(5); C21−C22, 1.551(5); C23−Si, 1.873(4); C23−Ti−C21, 71.2(1); Ti−C23−C22, 86.1(2); Ti−C21−C22, 87.6(2); C23−C22−C21, 109.0(3); Cp*1−Ti−Cp*2 135.78(3).

Scheme 1



Because of the wide variety of coordination modes possible for diazoalkane complexes, it is often difficult to predict their structures on the basis of spectroscopic data. We therefore undertook an X-ray diffraction study to determine the coordination mode of the diazoalkane fragment in **1**. An ORTEP diagram and selected bond lengths and angles are shown in Figure 1a.[11] The Me_3SiCHN_2 group is bound to the titanium in a side-on fashion through the two nitrogen atoms. Although side-on coordination is far less common than end-on or bridging coordination modes, it is not unprecedented.[7,12,13] The bonding situation in **1** is similar to that in an olefin adduct. The relatively long N−N bond distance (1.276(3) Å) compared with that of uncomplexed diazoalkanes (1.12−1.13 Å)[14] indicates substantial π-back-bonding from the b_2 orbital of the titanocene fragment to the diazoalkane LUMO, which is N−N antibonding.[15] However, the N−N distance is still indicative of a partial N−N double bond.[16]

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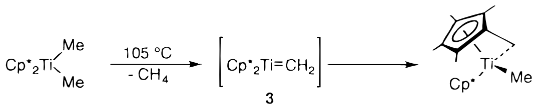
Compound **1** is thermally unstable in both the solid and solution states. It decomposes in the solid state with a half-life of ~12 h to give an insoluble red powder. This powder has not been identified, but on the basis of its low solubility it is presumed to be polymeric in nature. In benzene and toluene solution **1** decomposes to the fulvene complex $Cp^*FvTiCH_2SiMe_3$ (**2**) with a half-life of 12 h at 25 °C (Scheme 1). Complex **2** was identified on the basis of its NMR spectral data, elemental analysis,[11] and independent synthesis from $Cp^*FvTiCl$[17] and Me_3SiCH_2MgCl. This reaction is assumed to proceed *via* initial N_2 loss to give a transient carbene complex (**8**) which then undergoes hydrogen transfer from the Cp^* ligand. The formation of a carbene complex intermediate during thermolysis of **1** is strongly suggested by a mechanistic study of the reaction of **1** with alkenes (*vide infra*). In related work, Bercaw and coworkers have described the thermolysis of $Cp^*_2TiMe_2$ to give the fulvene complex $Cp^*FvTiMe$ (eq 1).[18] A detailed labeling study showed that methylidene complex **3** was the likely intermediate, although it could not be trapped at the high temperature needed for its generation.[19]



(1)

Compound **1** reacts with α-olefins $H_2C{=}CHR$ (R = H, Ph, Me, Et) over a period of 2 d at rt to give the deep red metallacyclobutane complexes **4**−**7** (Scheme 1) in excellent yield.[11] The ^1H NMR spectra of these materials show the expected features, including inequivalent Cp^* ligands. In the case of substituted olefins the reaction is regio- and stereospecific; NMR experiments indicate that only the trans-α,β-disubstituted diastereomer is formed (Scheme 1). The ^1H and $^{13}C\{^1H\}$ NMR spectra of these materials were fully assigned using a combination of COSY and HMQC experiments.[11] In addition to the resonances for the Cp*, R, and Me_3Si groups, the $^{13}C\{^1H\}$ NMR spectra of these compounds display a methylene signal at ~70 ppm, as well as methine peaks at ~70 and ~30 ppm. The downfield resonances are characteristic of the α-carbons of titanacyclobutanes,[20−24] indicating that the complexes are α,β-disubstituted. The stereochemistry was determined by 2D NOESY experiments.[11] Cross peaks were observed (see Scheme 1 for substituent labeling) between Cp^*_a and the Me_3Si group, H_b, and H_c. Cp^*_b showed NOEs to H_d, the R group, and H_a. *No* NOEs were observed between the ring protons and the Cp^* on the opposite side of the ring from them. This is consistent with a trans arrangement of the two ring substituents as shown in Scheme 1.

The stereochemical assignment has been confirmed by X-ray crystallography in the case of **6**. An ORTEP diagram along with selected bond lengths and angles is shown in Figure 1b.[11] As expected from the NMR experiments, the two substituents are on adjacent carbons, and are trans to one another. The Ti−C and C−C distances are similar to those observed in other titanacyclobutane complexes.[21] The ring is puckered with a dihedral angle of 28° between the $C_{21}TiC_{23}$ and $C_{21}C_{22}C_{23}$ planes. Although the vast majority of structurally characterized titanacyclobutanes are planar,[21] puckering of the ring has been observed previously in an α,β-disubstituted titanacyclobutane derived from Tebbe's reagent and a norbornene diester.[25] The distortion in this case is probably a result of the extreme steric congestion between the metal center and the two ring substituents.

The metallacyclobutane complexes are thermally stable up to 75 °C in solution. Heating benzene solutions of **4**−**7** at temperatures at or above 75 °C gives complicated product mixtures. The major organometallic product is **2**, suggesting that cycloreversion of the metallacycle to the transient (trimethylsilyl)methylidene complex is the principal thermal decomposition route. Curiously, **4**−**7** are far more thermally stable than the α,β-disubstituted metallacycles reported by Grubbs in the parent Cp system.[24] This greater stability is clearly electronic in nature, since the Cp^* system is far more sterically encumbered than the parent system.

The kinetics of the reaction of **1** with styrene in toluene-d_8 have been examined by ^1H NMR spectroscopy at a variety of temperatures and styrene concentrations.[11] These studies show that the reaction is first order in metal complex and the rate is independent of styrene concentration. From an Eyring plot (30−60 °C) we have measured $\Delta H^‡ = 22.5 \pm 0.3$ kcal/mol, $\Delta S^‡ = -3.1 \pm 1.0$ eu, and $\Delta G^‡ = 23.4 \pm 0.4$ kcal/mol (calculated at 25 °C). Since we observe no rate dependence on alkene concentration, any mechanism that involves initial attack or precoordination of the alkene may be ruled out. We have also found that at 45 °C **1** rearranges to fulvene complex **2** with a k_{obs} ($5.17 \times 10^{-4} \pm 0.10 \times 10^{-4}$ s^{-1}) identical to that for the reaction with of **1** with styrene at 45 °C ($5.02 \times 10^{-4} \pm 0.04 \times 10^{-4}$ s^{-1}) Our data are consistent with a mechanism in which the rate-determining step is N_2 loss to give carbene intermediate **8** (Scheme 1).

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Supporting Information Available: Spectroscopic and analytical data for complexes **1**, **2**, and **4**−**7**, structural data for **1** and **6**, HMQC and NOESY spectra of **7**, and representative kinetic data for the reaction of **1** and styrene, including plots of concentration vs time, k_{obs} vs [styrene], and ln(*k*/*T*) vs 1/*T* (Eyring plot) (25 pages). See any current masthead page for ordering and Internet access instructions.

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