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Communications

Tantalum-Mediated Cleavage of an N=N Bond in an Organic Diazene (Azoarene) to Produce an Imidometal (M=NR) Complex: An η^2-Diazene Complex Is Not an Intermediate

Mark A. Aubart[‡] and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720

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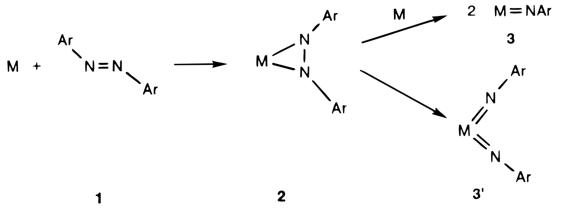
Summary: Treatment of methyl tantalocene complexes $Cp_2Ta(L)CH_3$ *(**4**,* $L = Cp_2Ta({=}S)CH_3$, PMe_3, *ethylene) with azobenzene or azotoluene (ArN=NAr) leads to loss of L and formation of* $Cp_2Ta(\eta^2\text{-}ArN{=}NAr)CH_3$ *(**5**; the first structurally characterized group V azoarene complex) and* $Cp_2Ta({=}NAr)CH_3$ *(**6**). Mechanistic studies show that complex **5** cannot be an intermediate in the formation of **6**; an* η^1*-azoarene complex (**8**) is suggested as an alternative.*

Metal-mediated atom- and group-transfer reactions are important fundamental processes because they provide a means of utilizing metals to cleave the very strong multiple bonds between second-row atoms in the periodic table. An important example of such a reaction is the cleavage of the N=N bond in organic diazenes (azo compounds **1** in eq 1) to give metal imido (nitrene) complexes (**3**, **3′**).[1−13]



(1)

Several authors who have observed this type of reaction have made the assumption that it proceeds by initial formation of an η^2-diazene or diazametallacyclopropane complex (**2**),[7,14−17] which "activates" the N=N bond by reducing its multiplicity, thus promoting its conversion to **3**.[2,5,9,10] We report here that, in at least one case, this assumption is incorrect.

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* E-mail: bergman@cchem.berkeley.edu.

[‡] Present address: Elf-Atochem North America, 900 First Ave., King of Prussia, PA 19406. E-mail: maubart@ato.com.

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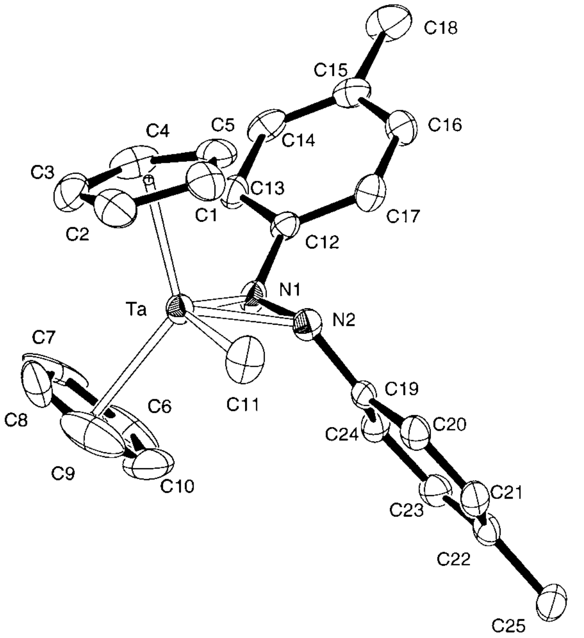
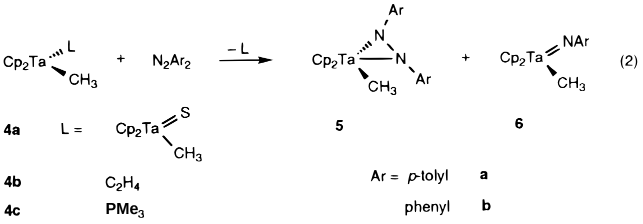


Figure 1. ORTEP diagram of $Cp_2Ta(\eta^2\text{-}C_7H_7NNC_7H_7)CH_3$ (**5a**).

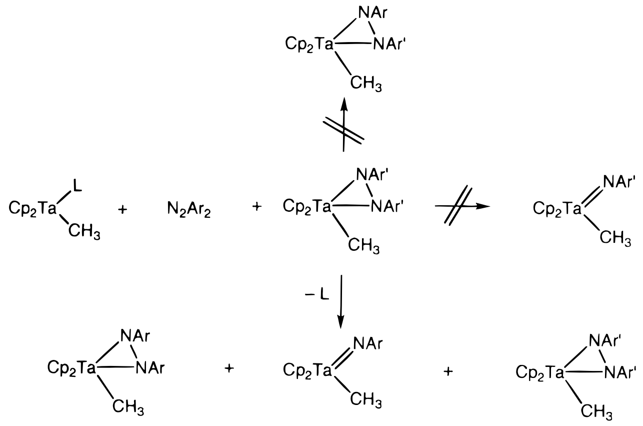
Methyl tantalocene complexes [$Cp_2Ta(L)CH_3$] (**4**) can be used as thermal or photochemical sources of the Ta(III) reactive intermediate [Cp_2TaCH_3]. Several complexes of this general structure have been known for some time;[18] bimetallic bridging sulfido complex **4a** was synthesized recently,[19] and we have now confirmed its structure by X-ray diffraction.[20] Treatment of complexes **4**[18,19] with azobenzene or azotoluene under thermal (L = trimethylphosphine (75 °C) or $Cp_2Ta({=}S)CH_3$ (60 °C)) or photochemical (L = ethylene) conditions leads cleanly to a mixture of *both* η^2-azoarene complex **5** and imido complex **6** (eq 2). The ratio of products is very sensitive to the concentration of azoarene and **4**: complex **5** is favored at low concentrations of **4** and high concentrations of azoarene, and formation of **6** is favored under the opposite conditions.



(2)

The imido complexes **6** were identified by their known spectral characteristics.[21] The structure of **5a** was determined by X-ray diffraction (see ORTEP diagram in Figure 1). To our knowledge, η^2-adduct **5a** represents the first group V azoarene complex to be isolated and structurally characterized. The most notable features of the structure are that the N−N bond length of 1.435(4) Å is consistent with a single N−N bond, and the C12−N1−N2−C19 torsion angle is 97.0(4)°. The azotoluene ligand has metrical parameters similar to those observed in several related group IV d^0 metal complexes.[15,22−24]

Scheme 1



Heating η^2-azoarene adduct **5** did not lead to significant amounts of imido complex **6.** To determine whether the presence of **4** mediates imide formation from **5**, azobenzene adduct **5b** was treated with 1 equiv of **4a** at 60 °C for approximately 14 h. A negligible amount of phenyl imido complex **6b** was observed (presumably from slow decomposition of **5b** to azobenzene and intractable products). However, addition of 0.3 equiv of azotoluene to this mixture and heating at 75 °C for approximately 1.5 h led to azotoluene adduct **5a** and tolyl imide **6a** only, with complete consumption of azotoluene. Similar results were obtained when the substituents were reversed, illustrating that this observation was not a result of **4a** reacting with azotoluene adduct **5a** faster than with azobenzene adduct **5b**. From these observations (illustrated in Scheme 1), we conclude that there must be a direct path from **4** + N_2Ar_2 to **6** that avoids passing through **5**.

Initial attempts to conduct kinetic studies on the reaction of **4** with azobenzene were carried out with **4c** in the presence of trimethylphosphine. However, these were complicated by the reaction of azo compounds with the phosphine to give betaines.[25] We therefore turned to sulfido complex **4a**. This system gave clean kinetic behavior, and we were able to find concentration regimes under which only phenyl imide complex **6b** was formed, as well as regimes under which only η^2-adduct **5b** was observed. The rate studies were carried out in both of these regimes, in the presence of excess, but variable, concentrations of added azoarene and terminal sufido complex $Cp_2Ta(S)CH_3$. At high [$Cp_2Ta(S)CH_3$]/[azobenzene] ratios, the rates were cleanly first order in **4a** and azoarene and were inhibited by the added monomeric sulfido complex. Using low [$Cp_2Ta(S)CH_3$]/[azobenzene], we were not able to reach saturation

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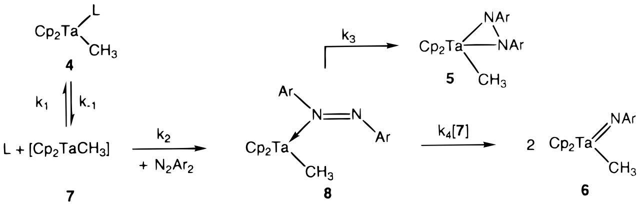
Scheme 2



behavior in the phenyl imide regime, but saturation rates were achieved in the η^2-adduct experiments. The rate law most consistent with our combined data is given in eq 3. The η^2-adduct regime data led to a linear

$$\frac{d[2b]}{dt} = k_{obs}[4a] = \frac{k_1k_2[4a][\text{azobenzene}]}{k_{-1}[Cp_2Ta(S)CH_3] + k_2[\text{azobenzene}]} \quad (3)$$

plot of $1/k_{obs}$ vs $[Cp_2Ta(S)(CH_3)]/[\text{azobenzene}]$ which yielded values of $k_1 = (6.7 \pm 0.1) \times 10^{-3}\ s^{-1}$ and $k_{-1}/k_2 = 2.17 \pm 0.05$. The imide regime data yielded a linear plot of k_{obs} vs $[\text{azobenzene}]/[Cp_2Ta(S)(CH_3)]$, which yielded a value of $k_1k_2/k_{-1} = (2.2 \pm 0.3) \times 10^{-3}\ s^{-1}$ (compare to the η^2-adduct value, $k_1k_2/k_{-1} = (3.1 \pm 0.1) \times 10^{-3}\ s^{-1}$).

To probe the mechanistic steps that occur after the rate-determining transition state of the reaction, we examined the dependence of the kinetic product ratio on the concentration of **4a**. The poor solubility of **4a** in organic solvents limited the concentration range over which this study could be conducted, but the reaction of azobenzene in the presence of 0.99 equiv of $[Cp_2Ta(S)CH_3]$ in tetrahydrofuran-d_8 with varying amounts of **4a** (1.3−5.2 equiv) at 60 °C could be monitored by ^1H NMR spectroscopy. A plot of the product ratio **6b**/**5b** vs [**4a**] (data taken at approximately 10% conversion) was linear (see Supporting Information). The relationship clearly demonstrates that the imide-forming step has one higher order dependence on [**4a**] than does the η^2-adduct-forming step.

Taken together, our data are most consistent with the mechanism illustrated in Scheme 2. We propose that η^1-adduct **8** is the common intermediate from which branching to the final products occurs.[26] Unimolecular, irreversible rearrangement of **8** to generate η^2-adduct **5** then competes with attack on **8** by another molecule of 16-electron Ta(III) intermediate **7**. This is supported by the linear dependence of the product ratio (**6b**/**5b**) on the concentration of **4a**. Azoarene complexes in which the ligand is η^1-bound are rare but have been isolated, especially from the reaction of benzo[*c*]cinnoline with metal carbonyl complexes.[27−31] The *unimolecular* rearrangement of η^1-adduct **8** to give π-adduct **5** must require a significant enthalpy activation barrier, relative to that for the *bimolecular* attack of **7** on **8,** in order for these two steps to be kinetically competitive. This is reasonable, since the rearrangement demands that the azobenzene ligand swing toward the metal center and rotate 90° so as to allow the nitrogen lone-pair-based σ-bond to dissociate and the π and π^* ligand orbitals to effectively overlap with the metal-based molecular orbitals.[32]

In summary, rather than being an intermediate on the way to azoarene cleavage product, the η^2-adduct **5** is a mechanistic "dead end". This is reminiscent of an observation we made several years ago, which established that reaction of Ir(I) intermediates capable of reacting with alkene C−H bonds led to both η^2-adducts and vinyl hydrides, but that the η^2-adducts were stable to the reaction conditions and therefore not viable intermediates in the C−H oxidative addition process.[33] The present η^2-diazene system appears to be another case in which the term "activation" does not properly describe the properties of a metal-complexed organic molecule.

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Supporting Information Available: Spectroscopic and analytical data for complexes **5a** and **5b**, tables containing complete crystal and data collection parameters, positional parameters with estimated standard deviations, intramolecular distances and angles for compound **5a**, and representative kinetic data for the reaction of **4a** with azobenzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) We also considered the possibility that an η^2-*cis*-azoarene adduct is an intermediate. However, treatment of **4** with a *cis*-constrained azoarene, benzo[*c*]cinnoline,[33] led to formation of $Cp_2Ta(\eta^2\text{-benzo}[c]\text{cinnoline})CH_3$ as the sole product under all reaction conditions. The formation and inertness of this complex imply that the important branching intermediate is not an η^2-*cis*-azoarene adduct. The full details of this study, including an X-ray diffraction study of this new adduct, will be presented in a full paper.

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