J. Am. Chem. Soc. **1995,** *117,* 6382−6383

Synthesis and Structure of a Terminal Metal Azide Complex: An Isolated Intermediate in the Formation of Imidometal Complexes from Organic Azides

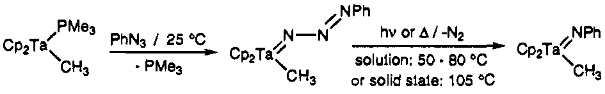
Grant Proulx and Robert G. Bergman*

Department of Chemistry, University of California
Berkeley, California 94720

Received February 8, 1995

Organic azides (RN_3) often undergo reactions in which dinitrogen is extruded, and it is this reactivity that has long caused chemists to use them as convenient sources of "RN:" or nitrene fragments.[1] In organometallic chemistry, azides are commonly used as precursors for nitrene (or, more correctly, terminal imido) complexes (M═NR).[2] In the synthesis of imido species, organoazidometal complexes have been proposed as intermediates formed in the initial interaction of a coordinatively unsaturated metal complex with RN_3.[3-7] However, there are few examples of reactions of this type that yield observable organoazidometal complexes, presumably due to their rapid loss of N_2.[4,5] Although there are some examples of RN_3 complexes that are stabilized by insertion of the R−N_3 group into a M−X bond,[6] there do not appear to be any monometallic M−N_3R complexes whose structures have been established by X-ray diffraction.[7] This report describes the synthesis and structure determination of the first fully characterized terminal organoazidometal complex, $Cp_2Ta(N_3Ph)(CH_3)$ (**1**).[8] We also report preliminary mechanistic experiments that bear on the pathway for conversion of this complex to the corresponding imidometal complex $Cp_2Ta(NPh)(CH_3)$ (**2**).

Treatment of a toluene solution of the red Ta(III) species $Cp_2Ta(PMe_3)(CH_3)$[9] (Cp = η^5-C_5H_5) with PhN_3 at room temperature results in a rapid color change to deep orange. Monitoring this addition by ^{1}H and ^{31}P NMR spectroscopy shows formation of free PMe_3 and a new species in essentially quantitative yield with the formula $Cp_2Ta(N_3Ph)(CH_3)$ (**1**) (eq 1).[10] Crystallization from benzene/pentane gave orange needlelike crystals of pure $Cp_2Ta(N_3Ph)(CH_3)$ in 88% yield. The IR spectrum of these crystals in KBr showed a strong absorbance for a N═N double bond at 1730 cm^{-1}. However, we could not determine conclusively whether the Ta center was bound to the α- or γ-nitrogen atom in the coordinated organoazide or the mode in which the RN_3 fragment was bound.



(1)

In order to resolve this ambiguity, a single-crystal X-ray diffraction study of **1** was undertaken. The structure was solved by Patterson methods in space group $P2_1$ and refined via standard least-squares and Fourier techniques. An ORTEP drawing is shown in Figure 1. As the structure shows, the azide ligand adopts an η^1-terminal configuration in the solid state.[11] It does not prefer a cyclic configuration that would allow the metal to interact with two nitrogens of the ligand, nor does the molecule opt for an olefinic type bonding mode analogous to the previously characterized η^2-S_2 and η^2-C_2H_4 complexes in this series.[9,12]

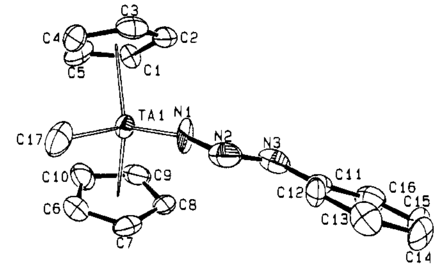


Figure 1. ORTEP diagram for one of the two crystallographically independent molecules of complex **1**.

There are a total of four molecules of the compound and two molecules of benzene in the unit cell, and there are no abnormally short intermolecular contacts between the molecules. The bonding of the methyl and the Cp ligands to tantalum appears to be normal, but the formal bonding arrangement of the N_3 ligand is a little less obvious.[13,14] The Ta−N−N angle in **1** (166.0(10)°) is more strongly bent than in the tantalum phenylimido species, $Cp^*_2Ta({=}NPh)(H)$, where ∠Ta−N−C is 177.8(9)°.[13] The Ta═N bonding distance (the two independent molecules in the unit cell are similar at 1.830(11) and 1.845(10) Å) is also significantly shorter than in those compounds viewed as having "true" Ta═N double bonds (estimated by Bercaw and co-workers as ca. 1.89 Å) and significantly longer than for those having "true" Ta≡N triple bonds (1.75 Å).[13,15] It therefore appears that the most reasonable picture of the bonding situation at the metal center postulates a situation intermediate between double and triple bonding. The PhN−N bond length of 1.267(15) Å is slightly longer than typical N═N double bonds, such as *trans*-azobenzene (1.247(2) Å).[16]

Variable temperature NMR experiments showed no significant changes in the ^{1}H NMR spectrum (THF-d_8), and all resonances remained sharp from room temperature to −50 °C. Addition of excess PhN_3 to the reaction mixture at ambient temperatures leads only to the extrusion of N_2 (evident by effervescence during addition) and the formation of PhN═PMe_3. Heating a C_6D_6 solution of **1** to 70 °C also causes evolution of N_2. Formed in this reaction is the previously characterized, oily yellow imido species, $Cp_2Ta(NPh)(CH_3)$ (**2**)[12] in quantitative

---

(1) Lwowski, W. *Nitrenes*; Interscience Publishers: New York, 1970.

(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988.

(3) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537.

(4) Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213.

(5) Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49.

(6) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1982**, *21*, 2064.

(7) Rosen, R. K. Ph.D. Thesis, U. C. Berkeley, 1989.

(8) A terminal vanadium azide complex was discovered simultaneously and independently by Cummins and co-workers; see: Fickes, M. G.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6384−6385.

(9) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(10) Anal. Calcd for $C_{17}H_{18}N_3Ta{\cdot}0.5C_6H_6$: C, 49.60; H, 4.37; N, 8.68. Found: C, 49.37; H, 4.22; N, 8.31. Mp = 105-8 °C dec. NMR data for $Cp_2Ta(N_3Ph)(CH_3)$ (**1**): ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.03 (dd, 2H, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 8.5 Hz, *o*-C_6H_5), 7.30 (t, 2H, $^3J_{HH}$ = 7.9, *m*-C_6H_5), 6.98 (t, 1H, $^3J_{HH}$ = 7.3 Hz, *p*-C_6H_5), 5.21 (s, 10H, C_5H_5), 0.54 (s, 3H, TaCH_3); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 153.8 (s, *i*-C_6H_5), 129.2 (s, *o*-C_6H_5), 124.2 (s, *p*-C_6H_5), 121.0 (s, *m*-C_6H_5), 104.7 (s, C_5H_5), 4.1 (s, CH_3); ^{13}C NMR (101 MHz, C_6D_6) Ta$^{13}CH_3$ δ 4.1 (q, $^1J_{CH}$ = 124.3 Hz); IR [KBr] 1730 ($\nu_{N=N}$) cm^{-1}; MS (FAB) *m/z* 418 (M^+ + H − N_2), 402 (M^+ − N_2 − CH_3).

(11) Inspection of the thermal parameters for the N_3 ligand shows some peculiar "thermal motion" that is observed with respect to the organoazide ligand on one of the two crystallographically independent molecules in the structure. This may represent the effect of the interaction of the molecule with the X-rays passing through the structure (possibly extruding N_2 at −115 °C but not allowing the molecule to escape from the lattice) plus damage to the crystal that occurred during its brief exposure to the warm Paratone N during attempts to mount the crystal. For this reason, we recommend that the distances and angles in the region of the molecule with respect to N5 and N6 be interpreted with some care. The final residuals, however, were quite good for 427 variables refined against the 2277 accepted data for which $F^2 > 3\sigma(F^2)$ at R = 2.36% and R_w = 2.82% with a GOF of 1.297. We have also obtained a crystal structure of the $TaN_3C_6H_4$-*p*-NMe_2-substituted species that does not have the peculiar thermal motion of the N_3Ar ligand. The full details of the structure will be reported in an upcoming full paper.

(12) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7953.

(13) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82.

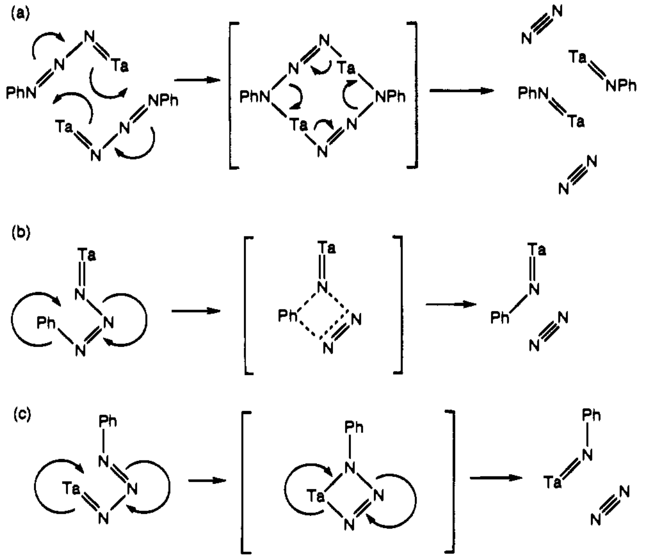
(14) Jørgensen, K. A. *Inorg. Chem.* **1993**, *32*, 1521.

(15) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579.

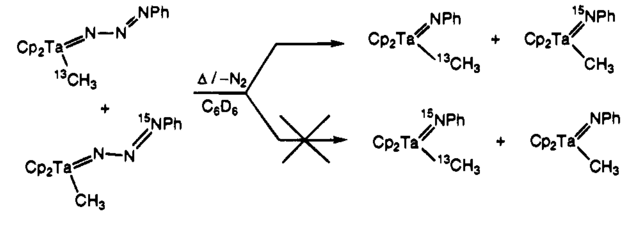
(16) Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr., Sect. C* **1983**, *39*, 1121.

0002-7863/95/1517-6382$09.00/0

Scheme 1



Scheme 2



isolated yield (>95% by ^{1}H NMR vs Cp_2Fe internal standard). The decomposition to **2** could be effected easily in the solid state by heating the orange crystals to 105 °C. Photolysis (10 min) of a solution of **1** also readily gives **2** in essentially quantitative yield (eq 1).

Three possible nitrogen-extrusion pathways for the conversion of **1** to **2** are illustrated in Scheme 1. It has been known for some time that treatment of tertiary phosphines with organic azides is known to proceed via a reactive intermediate, $R'NNNPR_3$, which decomposes in a unimolecular process to dinitrogen and the corresponding phosphoranimine.[17-19] One potential mechanism for the **1** to **2** conversion would involve the bimolecular interaction and transition state shown as path a in Scheme 1. Two other possibilities involve (b) transfer of the γ-nitrogen-bound phenyl group to the α-nitrogen atom with extrusion of N_2 and (c) Ta−N_γ coordination with extrusion of N_2.

Isotopic labeling and kinetic studies have helped to distinguish between these paths. On treatment of the (>98%) α-^{15}N-labeled azide $Ph^{15}N{=}N{=}N$ with $Cp_2Ta(PMe_3)(CH_3)$, we were able to isolate the ^{15}N-labeled $Cp_2Ta(NN^{15}NPh)(CH_3)$ product and watch the further decomposition of this complex to the labeled imido species **2-^{15}N** (>98% by FAB MS). This shows conclusively that the nitrogen atom that is originally bound to the Ta center is extruded as free N_2, and thus, the phenyl migration route (b) is eliminated as a major mechanistic pathway. Also, a double-labeling experiment was undertaken in which $Cp_2Ta(^{13}CH_3)(NNNPh)$ (99% ^{13}C) was thermally decomposed in the presence of 1 equiv of $Cp_2Ta(CH_3)(NN^{15}NPh)$ (>98% ^{15}N) (Scheme 2). The only products detected were the singly-labeled imido species, $Cp_2Ta(CH_3)(^{15}NPh)$ and $Cp_2Ta(^{13}CH_3)(NPh)$, in >97% yields determined by NMR and MS analysis. No evidence of either the unlabeled ($Cp_2Ta(CH_3)(NPh)$) or doubly-labeled ($Cp_2Ta(^{13}CH_3)(^{15}NPh)$) species in significant amounts was found. These experiments essentially rule out any bimolecular pathway (a), leaving path c as the most likely alternative consistent with our observations.[20]

Our initial attempts to measure the rate of the **1** to **2** reaction gave perplexing results. Although the reactions appeared to be approximately first order, erratic and irreproducible concentration vs time plots were obtained. Significantly, we found that exceedingly brief exposure of reaction solutions to the atmosphere caused significant accelerations in the rate, suggesting that the conversion was catalyzed by very small traces of air or water.

To deal with this problem, we added varying amounts of Cp_2ZrMe_2 to the solutions used for kinetic runs. This material reacts rapidly with O_2 and H_2O to give soluble and NMR-observable $Cp_2(CH_3)ZrOZr(CH_3)Cp_2$, and so the presence of unreacted Cp_2ZrMe_2 remaining in solution provides strong assurance that the concentrations of air and water are extremely low. Under these conditions, no reaction of Cp_2ZrMe_2 with either **1** or **2** was observed, and the rates for the **1** to **2** conversion became slower and very well behaved. Rigorous first-order behavior (independent of the concentration of Cp_2ZrMe_2) was observed over a 30 °C temperature range; an Eyring plot gave $\Delta H^\ddagger = 25.4 \pm 0.4$ kcal/mole and $\Delta S^\ddagger = -0.7 \pm 1.3$ eu. The nearly zero activation entropy is consistent with a unimolecular reaction in which little free rotation is frozen out in proceeding from **1** to the transition state.[21] The crossover experiments described above were also carried out in the presence of Cp_2ZrMe_2 and the results shown to be independent of the additive. We have carried out a preliminary Hammett σ/ϱ study using azidoaryl complexes having H, NMe_2, and CF_3 substituents in the para positions of the aromatic ring. An excellent linear log k vs σ plot was obtained. Somewhat surprisingly, ϱ_{para} for the reaction is +0.66, indicating that the reaction is accelerated by electron-withdrawing substituents. If Ta−N bond formation is involved in the rate-determining step, the electronic effect could be due to the ability of the ring to withdraw electron density from the Ta center through the Ta−N_3−aryl π system, facilitating attack of the orthogonal aryl-substituted nitrogen lone pair at the metal center. Alternatively, a (electron-withdrawing group stabilized) conformational isomer of **1**, such as the cis isomer,[22] may be formed initially, followed by fast attack of N at Ta. The results of experiments now under way designed to distinguish these hypotheses, as well as the complete details of the work described here, will be reported in a full paper.

Acknowledgment. We wish to thank Prof. Christopher C. Cummins and his co-workers for helpful discussions and for their willingness to disclose results of their independent investigation prior to publication. We acknowledge the National Science Foundation (Grant No. CHE-9416833) for generous financial support of this work and Dr. F. J. Hollander, director of the U. C. Berkeley X-ray diffraction facility (CHEXRAY), for determination of the X-ray structure. G.P. wishes to thank the Department of Education for a predoctoral fellowship, and we are grateful to a referee for calling our attention to ref 5.

Supplementary Material Available: Tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, and intramolecular distances and angles for **1** with selected kinetic data for the decomposition of **1** to **2** and MS and NMR spectra for **1** (19 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.

JA9504193

---

(17) Although there is some ambiguity in the literature regarding the molecularity of the decomposition of the Staudinger phosphazides ($R_3PNNNAr$), the more recent literature points toward a unimolecular pathway. See: Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353 and references therein.

(18) Mosby, W. L.; Silva, M. L. *J. Chem. Soc.* **1965**, 1003.

(19) Horner, L.; Gross, A. *Justus Liebigs Ann. Chem.* **1955**, *591*, 117.

(20) Similarly, we have so far found no evidence for exchange of free and bound organic azides.

(21) It is interesting that the analogous (arylazido)vanadium complex discovered by Cummins is also converted to the corresponding arylimido complex, but the kinetics are second- rather than first-order. It is possible that this is due to the different electronic character of the vanadium species.

(22) It has been shown that in small and medium-sized cyclic azo compounds, in which cis stereochemistry is enforced by the ring structure, loss of dinitrogen occurs 100 times faster than it does in the analogous acyclic trans species. See: Wang, C. H.; Hsiao, S. H.; Saklad, E.; Cohen, S. G. *J. Am. Chem. Soc.* **1957**, *79*, 2661.