(3) Pola, J.; Leven, G.; Szwarc, M. *J. Phys. Chem.* **1976,** *80,* 1690.
(4) Stevenson, G. R.; Ocasio, I.; Bonilla, A. B. *J. Am. Chem. Soc.* **1976,** *98,* 5469.
(5) The calibration factor for the calorimeter is −119.3 ± 0.8 kcal/deg. This factor was multiplied by the slopes of the lines obtained in Figures 1 and 2 to obtain the enthalpy of reaction of the salt with water. The errors in the slopes of these lines (standard deviations) were propagated with the error in the calibration factor to obtain the errors in the enthalpies of reaction.
(6) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, New York, 1960; p 509.
(7) Huheey, J. E. "Inorganic Chemistry Principles of Structure and Reactivity"; Harper and Row: New York, 1972; p 62.
(8) Gunn, S. R. *J. Phys. Chem.* **1976,** *71,* 1386.
(9) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds", Academic Press: London, 1970.
(10) Hicks, W. T. *J. Chem. Phys.* **1963,** *38,* 1873.
(11) Lotz, W. *J. Opt. Soc. Am.* **1967,** *57,* 873.
(12) Becker, R. S.; Chen, E. *J. Chem. Phys.* **1966,** *45,* 2403.
(13) Shaw, R.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1977,** *81,* 1716.
(14) Thomas, L. H. *J. Chem. Soc.* **1959,** 2132.
(15) Stevenson, G. R.; Caldwell, G.; Williams, E. *J. Phys. Chem.* **1979,** *83,* 643.

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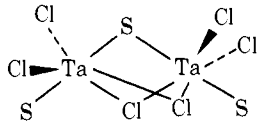
Reactions of Tantalum(III) with Alkynes and Nitriles

Sir:

There has lately been an upsurge of interest in the chemistry of the early transition elements, especially with respect to organometallic reactions and possible catalytic applications thereof. Most of the work reported so far, however, deals with cyclopentadienyl derivatives, and the noncyclopentadienyl chemistry of tantalum and niobium in their intermediate oxidation states, e.g., III, is still practically unknown. This is particularly true of reactions with unsaturated organic molecules and the main reason appears to be a lack of convenient reactants. We report here that the compound $Ta_2Cl_6(SC_4H_8)_3$, **1**,[1] serves as a convenient source of Ta(III) and we describe several interesting reactions that adumbrate a large and interesting chemistry of Ta (and, presumably, also Nb) with unsaturated organic compounds.

Compound **1** reacts with acetonitrile to form **2a,** the structure of which has been inferred from a crystallography study. The only previous synthesis of **2a** was by an indirect route which gave a poor yield. We have found that direct synthesis from **1** proceeds quickly and in high yield and report a method that is applicable to alkyl cyanides in general. We have also found that **1** reacts with alkynes to give products of unusual properties.



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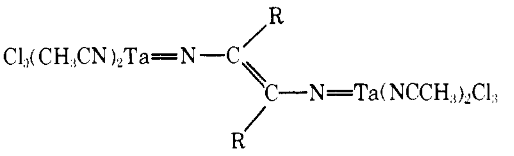


2a, R = CH_3
b, R = C_2H_5

Reaction of **1** with acetonitrile, propionitrile, or isobutyronitrile, gives a green product within a few minutes.[3] The infrared spectrum of the MeCN product is identical with that of **2a.** IR, analysis, and chemical properties show that the compounds from EtCN (**2b**) and Pr^iCN are of the same type. Neither $(CH_3)_3CCN$ nor $C_6H_5CH_2CN$ reacts with **1** to give reductively coupled products.

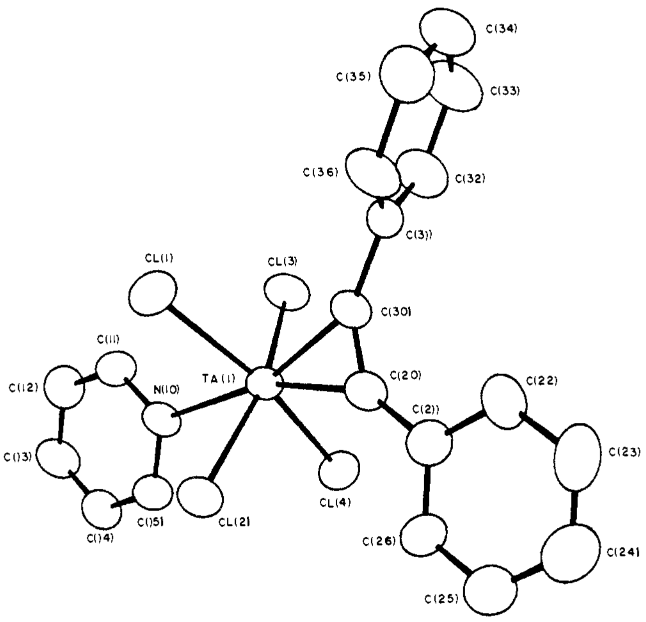
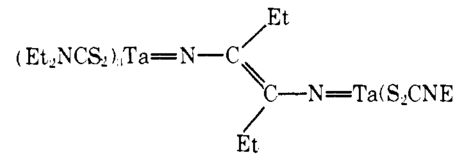


Figure 1. A computer-generated drawing of the $[TaCl_4(py)(PhCCPh)]^-$ anion.

The tantalum(V)-nitrene complexes formed in these reactions are relatively resistent to protic attack. When an HCl/Et_2O solution was added to **2a,** no reaction was observed even after several hours. However, if, instead, acetone was added to **2a,** $TaOCl_3(MeCN)_2$ was formed on standing overnight. We are attempting to learn what happens to the organic fragments. This sort of exchange of oxygen for nitrogen was suggested in the reaction of $[(CH_3)_2N]_3Ta{=}NBu^t$ and benzaldehyde.[4]

Compound **2b** reacts with the diethyl dithiocarbamate anion producing an air-stable crystalline compound shown by X-ray crystallography to be **3**, in which the Ta atoms are seven coordinate. The details of this structure will be reported elsewhere, since they are not pertinent to the main thrust of this communication.



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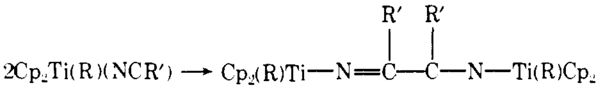
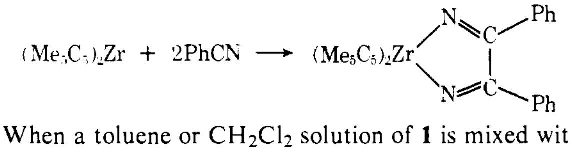
To our knowledge, this type of facile reductive coupling of nitriles (accompanied by oxidation of the metal atoms) is unprecedented. The closest related reactions we know of are eq 1 and 2, recently described by DeBoer and Teuben[5] and by Bercaw.[6]



$$2\mathrm{Cp_2Ti(R)(NCR')} \longrightarrow \mathrm{Cp_2(R)Ti{-}N{=}\overset{R'}{\overset{|}{C}}{-}\overset{R'}{\overset{|}{C}}{-}N{-}Ti(R)Cp_2} \quad (1)$$

$$\mathrm{Cp} = \eta^5\text{-}\mathrm{C_5H_5};\ \mathrm{R} = \mathrm{C_6H_5};\ \mathrm{R'} = \mathrm{C_6H_5CH_3}$$



(2)

When a toluene or CH_2Cl_2 solution of **1** is mixed with 3-hexyne, hexaethylbenzene is formed in a rapid, exothermic reaction that is clearly catalytic at 25 °C. Such catalytic ac-

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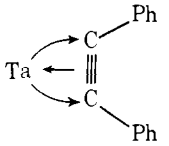
tivity by a group 5 metal is unprecedented and further study of this and related reactions is underway.

Under comparable conditions diphenylacetylene (tolane) reacts stoichiometrically to give mononuclear complexes of composition $TaCl_3L_2$(tolane), where L represents a neutral donor such as tetrahydrothiophene (THT), tetrahydrofuran (THF), CH_3CN, or pyridine. When $TaCl_3(THT)_2$(tolane) was dissolved in acetone containing some water, hydrous Ta_2O_5 precipitated within minutes and *cis*-stilbene was detected in the acetone. This suggests that the attachment of the tolane to the Ta is in the nature of an oxidative addition. In this respect the product would be similar to some isoelectronic Mo(IV) species obtained by addition of alkynes to $(R_2NCS_2)_2MoO$, some of which have been compared to the active site in nitrogenase.[7,8]

We have obtained crystals of a derived compound, **4**, with the formula (pyH)[$TaCl_4$(py)(tolane)][9] and determined its structure by X-ray crystallography.[10] The anion is shown in Figure 1. The binding of the tolane to the tantalum is very strong and symmetrical. The Ta–C distances are 2.066 (8) and 2.069 (8) Å, the C–C distance is 1.325 (12) Å, and the two C(phenyl)CC angles are 138.24 (80) and 141.16 (82)°. The Ta–C distances are only slightly longer than the average for the C=Ta double bonds found in several tantalum alkylidene compounds,[11] namely, 2.04 Å, and thus a simple μ-bond representation, **5**, or one with two single bonds, **6**, does not seem adequately to account for the structure. We therefore suggest **7** which has C=Ta double bonds and is a kind of dialkylidene. Perhaps, in resonance terms, a mixture of **6** and **7**, with an appreciable contribution from **7** would best accommodate all of the chemical and structural evidence. The bond lengths and angles that occur in a compound[12] with arrangement **8** make a useful comparison. Here each acetylenic carbon atom is forming two single bonds to metal atoms. Thus, we might expect the C–C distance to be similar to that in the present case, and it is, 1.329 (6) Å. On the other hand, the C–Mo distances should be much longer than our C–Ta distances, and they are, averaging 2.18 ± 0.02 Å. The Ta–C distances here are similar to those in the benzyne complex $Ta(\eta^5\text{-}C_5Me_5)(CH_3)_2(C_6H_4)$[13] but very much shorter than those in $[\eta^5\text{-}C_5H_5]_2Nb(O_2CCH_3)$(tolane).[14]



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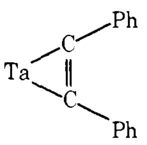

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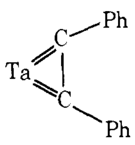

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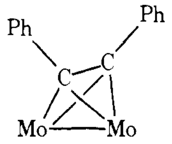

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Comparison with the recently reported work of Weiss et al.[15] is especially pertinent. They find a W(HCCH) unit with W–C distances of 2.03 Å and a C–C distance of 1.29 Å and on the basis of these facts and other reasoning propose that the acetylene is acting as a four-electron donor. In their case this, allows the metal to achieve an 18-electron configuration, whereas for our compound Ta reaches only a 16-electron configuration. However, this is not unusual for group 5 metals.[16]

Supplementary Material Available: Tables of atomic positional and thermal parameters for (pyH)[$TaCl_4$(py)(tolane)] (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978,** *17,* 2293.

(2) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978,** *17,* 3527.

(3) All manipulations were conducted under anaerobic and anhydrous conditions.

(4) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978,** 578.

(5) DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1978,** *153,* 53.

(6) Bercaw, J. "Abstracts of Papers", ACS/CSJ Chemical Congress, Honolulu, April 1979; American Chemical Society: Washington, D.C., 1979; INOR 280.

(7) Maata, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979,** *18,* 524.

(8) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972,** *94,* 8640.

(9) Excess pyridine was added to a solution of $TaCl_3(THT)_2$(tolane) in CH_2Cl_2. Traces of adventitious water caused partial hydrolysis creating some (pyH)Cl which then allowed the formation of crystals of (pyH)[$TaCl_4$(py)-(tolane)] over a period of 2 days.

(10) The compound crystallized in the space group $P\bar{1}$ with a = 11.375 (8), b = 12.335 (5), c = 9.352 (4) Å; α = 101.12 (3), β = 106.82 (4), γ = 87.07 (4)°; V = 1232.5 (1.0) Å^3; and Z = 2. Data were collected for $0° < 2\theta < 45°$, and 3340 reflections were found to be greater than 3σ. Least-squares refinement has yielded final discrepancy indices of R_1 = 0.031 and R_2 = 0.051. Methods of data collection and structure refinement have been described previously.[2] Tables of atomic positional and thermal parameters is available as supplementary material. See paragraph at the end of paper regarding supplementary material.

(11) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellman, J. D. *J. Am. Chem. Soc.* **1979,** *101,* 1593 and ref 5 therein.

(12) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Randel, L. A. *J. Am. Chem. Soc.* **1978,** *100,* 5764.

(13) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979,** *101,* 263.

(14) Passynskii, A. A. *J. Organomet. Chem.* **1979,** *165,* 39.

(15) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978,** *100,* 1318.

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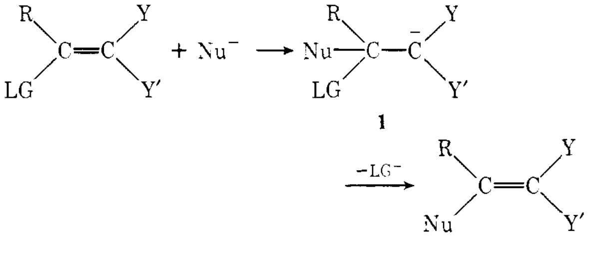
The Importance of Hyperconjugation in Nucleophilic Vinylic Substitution

Sir:

Nucleophilic vinylic substitution via addition-elimination[1,2] (eq 1: LG = leaving group, Nu = nucleophile, Y,Y′ = activating groups) proceeds via an intermediate carbanion as indicated by the "element effect"[1-3] and by base catalysis found in several substitutions by amines.[3,4] The substitution of a good leaving group, e.g., Cl, Br, proceeds in most cases exclusively or predominantly with retention.[1,2] "Convergence",[2] i.e., approach to a similar product composition starting from either of the two isomers, is sometimes found when LG = F,[5] but mostly results from postisomerization of retained products.[1a] Two mechanisms were proposed to explain the observed retention: (a) a concerted bond formation and cleavage,[6] which was recently criticized for neglecting the other evidence above;[2] (b) formation of a planar carbanion where LG expulsion (F excluded) is faster than internal rotation, and a 60° rotation which gives retention is preferred over 120° rotation which gives inversion.[1] A related explanation was given for tetrahedral carbanions.[2] The source of the rotational barrier and the reason for the preference of a 60° rotation are not fully un-



(1)

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