Inorganica Chimica Acta, 100 (1985) L21–L22

Reactions of Niobium(III) Trichloride Adducts with Organic Azides: Access to Nitrenes, Azides or Nitrides

L. G. HUBERT-PFALZGRAF* and G. AHARONIAN

Laboratoire de Chimie de Coordination, UA 428, Université de Nice, Parc Valrose, 06034 Nice, France

Received January 5, 1985

Transition metal organoimido complexes are currently of considerable interest in inorganic and organometallic chemistry, owing to their potential importance industrially and the formal similarity of the RN^{2-} ligand with carbene or oxo groups [1].

Group V nitrenes are accessible by several routes, mainly involving reactions, between alkylidenes and organic imines [2] or hydrogen abstraction reactions – often promoted by thermolysis [3] or addition of various reactants [4] – from pentavalent mono or dialkylamides. The unusual reactivity of the low valent niobium or tantalum derivatives toward dinitrogen [5], or the reductive coupling of nitriles [6], illustrates the propensity of these elements to form metal nitrogen multiple bonds [7] and provides an alternate synthesis of M(V) nitrenes.

Covalent azides RN_3 are useful reagents in the synthesis of stable nitrene derivatives [8] and their reactions with various Nb(III) and Ta(III) chloride adducts were investigated. The recent synthesis of $[NbCl_2(NPh)(SMe_2)]_2(\mu\text{-}Cl)_2$, (1), by Cotton [9] through a double metathesis reaction between the metal–metal double-bonded dimer $Nb_2Cl_6(SMe_2)_3$ and azobenzene PhN=NPh, prompts us to report our observations.

The air-sensitive $Nb_2Cl_6(NPh)_2(SMe_2)_2$ (1) was independently obtained in our laboratory by smooth oxidative addition of phenyl azide to $Nb_2Cl_6(SMe_2)_3$ in toluene at 0 °C. The spectroscopic data (^1H NMR, IR) of (1) are in agreement with those reported by Cotton. No molecular peak of the dimer could be observed by mass spectrometry even through chemical ionization.

The reactivity of (1) was investigated. $Nb_2Cl_6(NPh)_2(PhPMe_2)_2$ (2) (^1H NMR: δ_{PMe_2}: 1.70 ppm(d), $^2J_{P-H}$ = 9 Hz. ^{31}P NMR: +26 ppm; IR: $\nu_{Nb=NPh}$: 1130 cm^{-1}, ν_{Nb-Cl}: 300 vs, 290sh) was quantitatively obtained as a brown compound by ligand exchange between (1) and phenyldimethylphosphane. This reaction constitutes an alternative route to the synthesis of (2) by oxidative addition of phenylazide to $Nb_2Cl_6(PhPMe_2)_4$.

No alkylation between $Nb_2Cl_6(NPh)_2(PhPMe_2)_2$ and $SnMe_4$ was observed, but it reacts with excess methyllithium in diethylether at −50 °C to give the crystalline oxo-imido derivative $Nb_2Cl_4Me_2(NPh)(\mu\text{-}O)(PhPMe_2)_2$ (50%) ($\nu_{Nb=Ph} \simeq 1100$ cm^{-1}, $\nu_{Nb-O-Nb}$: 750–650 cm^{-1}. A comparable loss of the phenylimido group was also observed during the methylation of $W(NPh)Cl_4$ [10]. Although the niobium methyl imido derivative was relatively stable in the solid ($t_{dec.} \simeq 60$ °C), rapid decomposition occurred in solutions above −40 °C.

The reactions of various azides with niobium(III) or tantalum(III) chloride complexes offer a diverse array of products, and the isolated products sometimes result from the cleavage of the R–N bond. Thus, the reactions between trimethylsilylazide and $Nb_2Cl_6(SMe_2)_3$ led to the elimination of trimethylchlorosilane and synthesis of a metal azide complex, $Nb_2Cl_4(N_3)_2(SMe_2)_2$ (3), (ν_{asN_3}: 2130 cm^{-1}). Although the oxidative addition of the $NSiMe_3$ group was successful with a Ta(III) alkylidene [11], formation of pseudohalide complexes was also observed on allowing Me_3SiN_3 to react with Ta(V) [12] or Mo(IV) derivatives [13]. ^1H monitoring experiments established that the reaction between Me_3SiN_3 and $Nb_2Cl_6(PhPMe_2)_4$ was even more complex than those with $Nb_2Cl_6(SMe_2)_3$, as Staudinger-type reactions are also observed.

The niobium(III) or tantalum(III) azide adducts are unstable even in the solid state, and behave as nitrido precursors, giving rise for instance to poorly soluble $[NbNCl_2(SMe_2)]_n$. The niobium(V) or tantalum(V) azides have not yet been thermally converted into nitrido complexes [7], and such compounds, generally obtained by thermolysis of the ammonium salts of niobium or tantalum, remain scarce [14]. The sensitivity of the niobium(III) or tantalum(III) azides to redox reductions may therefore be a useful synthetic route to their pentavalent nitrides.

Further study on the reactions between organic azides and low-valent niobium and tantalum derivatives is in progress.

Experimental

All manipulations were routinely performed under argon, using solvents purified by standard methods. The low valent niobium or tantalum compounds [15] and triphenylazides [16] were obtained as reported in the literature. Trimethylsilylazide (Fluka) was purified by chromatography over silica. The

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

IR, NMR and mass spectra were measured on a 577 Perkin-Elmer, a Bruker WH-90 or a Ribber R-10-10 spectrometer, respectively. Microanalyses were obtained from the Centre de Microanalyses du CNRS.

Synthesis of $Nb_2Cl_6(NPh)_2(SMe_2)_2$ *(1)*

Freshly distilled triphenylazide (0.16 ml, 1.44 mmol) in 5 ml toluene was slowly added to a solution of $Nb_2Cl_6(SMe_2)_3$ (420 mg, 0.72 mmol) in 20 ml toluene cooled at 0 °C. The addition was followed by an immediate gaseous evolution while the solution turned dark red. After 30 min the reaction mixture was filtered. The filtrate was concentrated to about 3 ml and precipitation of $Nb_2Cl_6(NPh)_2(SMe_2)_2$ was achieved by adding hexane (210 mg, 45%). *Anal.* $NbC_8H_{11}NS$: Found C, 27.03; H, 3.05; N, 3.88%. Calcd. C, 27.23; H, 3.14; N, 3.97. IR (cm^{-1}): 320sh, 290s, 250m, 230w (ν_{Nb-Cl}). NMR ($CDCl_3$) (δ, ppm): 2.16 (SMe_2, 6 H), 7.18m (NPh, 10 H).

References

1 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev., 31,* 123 (1980);
J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun and J. W. Kang, *J. Am. Chem. Soc., 90,* 5430 (1968);
S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Gusastini, *J. Chem. Soc., Chem. Commun.,* 1015 (1982);
J. D. Burrington and R. K. Graselli, *J. Catal., 59,* 79 (1979);
A. K. Rappe and W. A. Goddard, *J. Am. Chem. Soc., 104,* 448 (1982).

2 S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc., 104,* 3077 (1982).

3 Y. Takahaskii, N. Onoyama, Y. Ishikawa, S. Motojima and K. Sugiyama, *Chem. Lett.,* 525 (1978).

4 J. R. Dilworth, S. J. Harrison, R. A. Henderson and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.,* 176 (1984);
D. C. Bradley, M. B. Hursthouse, K. M. Abdul Malik, A. J. Nielson and G. B. Chotavuru, *J. Chem. Soc., Dalton Trans.,* 1069 (1984).

5 S. M. Rocklage, H. W. Turner, J. D. Fellmann and R. R. Schrock, *Organometallics, 1,* 703 (1982);
L. Seng Tan, G. U. Goeslen and B. L. Haymore, *Inorg. Chem., 22,* 1744 (1983);
W. A. Nugent, *Inorg. Chem., 22,* 965 (1984).

6 P. A. Finn, M. S. King, P. A. Kilty and R. E. McCarley, *J. Am. Chem. Soc., 97,* 220 (1975);
F. A. Cotton and W. T. Hall, *Inorg. Chem., 17,* 3525 (1978).

7 K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl., 20,* 413 (1981)

8 S. Cenini and G. La Monica, *Inorg. Chim. Acta, 18,* 279 (1976).

9 F. A. Cotton, S. A. Duraj and W. J. Roth, *J. Am. Chem. Soc., 106,* 4749 (1984).

10 D. C. Bradley, M. B. Hursthouse, K. M. Abdul Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc., Dalton Trans.,* 2651 (1983).

11 S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc., 102,* 7808 (1980).

12 R. A. Andersen, *Inorg. Nucl. Chem. Lett., 16,* 31 (1980).

13 E. Schweda and J. Strähle, *Z. Naturforsch., Teil B:, 35,* 1146 (1980).

14 K. P. Frank, J. Strähle and J. Weidlein, *Z. Naturforsch., Teil B:, 35,* 300 (1980).

15 L. G. Hubert-Pfalzgraf, M. Tsunoda and J. G. Riess, *Inorg. Chim. Acta, 41,* 283 (1980);
L. G. Hubert-Pfalzgraf and J. G. Riess, *Inorg. Chim. Acta, 29,* L251 (1978);
J. L. Morançais, L. G. Hubert-Pfalzgraf and P. Laurent, *Inorg. Chim. Acta, 71,* 119 (1983).

16 R. O. Lindsay and C. F. H. Allen, 'Organic Synthesis, Vol. 3', Wiley, New York, p. 710.