A Dimeric Niobium(I) Complex formed by Electrochemical Reduction of a Niobium(III) Dimethylphosphane Adduct

LILIANE G. HUBERT-PFALZGRAF*

Laboratoire de Chimie de Coordination, Parc Valrose, 06034 Nice Cedex, France

ANNIE CHALOYARD and NABIL EL MURR*[†]

Laboratoire de Synthèse et d'Electrosynthèse Organométallique, 6 Boulevard Gabriel, 2100 Dijon, France

The molecular chemistry of niobium in oxidation states lower than 3 is very limited, especially for non-carbonyl derivatives [1]. In fact, the only niobium(I) species reported so far are an impure dinitrogen compound $\{NbCl(dmpe)_2\}(\mu\text{-}N_2)$ [2] (dmpe = 1,2-bis-(dimethylphosphino)ethane) and an allyl derivative, $(\eta^3\text{-}CH_3C_3H_4)(C_4H_6)_2Nb$ [3] obtained by metal vapor synthesis. On the other hand, the unstable Cp_2Nb, which could not be isolated, was characterized only by its EPR spectra and by its derivatives resulting from oxidative addition reactions [4]; this suggests a low stability for oxidation state 2.

Starting from the niobium(III) complex Nb_2Cl_6-$(PhPMe_2)_4$ for which a metal–metal bond of order 2 was assumed [5], we undertook electrochemical investigations in order to gain more information about the relative stability of oxidation states 2 and 1 and to generate stable niobium species having triple or quadruple metal–metal bonding. We now report the salient features of this investigation.

Experimental

All manipulations were performed using Schlenk tubes or vacuum line techniques under dry deoxygenated argon with purified CH_2Cl_2. Tetra-n-butylammonium hexafluorophosphate (from Fluka) was recrystallized from aqueous ethanol and dried *in vacuo*; it was deoxygenated and dehydrated by melting under vacuum prior to use. The complex Nb_2-$Cl_6(PhPMe_2)_4$ was prepared according to the literature [5].

---

*Authors to whom correspondence should be addressed.

[†]New address: Institut de Recherches sur la Catalyse, 79 Boulevard du 11 Novembre 1918, 69226 Villeurbanne Cedex, France.

EPR spectra were obtained on a Varian E4 spectrometer. ^{31}P NMR spectra were registered on a Bruker WH-90 machine operating in the Fourier transform mode, and the ^{31}P chemical shifts are given as positive when they occur at low fields relatively to 85% H_3PO_4 as external reference. UV spectra were made on a CARY 14 spectrometer and the mass spectra on a Nermag R 10-10 operating by chemical ionization with NH_3.

Electrochemical measurements were made under argon at room temperature on dichloromethane solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte. Polarography and cyclic voltammetry were performed with a Tacussel Model TipoL in conjunction with a Tacussel Model EPL 2 X–Y recorder. Potential control for coulometric experiments was maintained with an Amel Model 552-potentiostat. Potential values were referenced to the saturated potassium chloride calomel electrode (SCE) at 20 ± 2 °C and were uncorrected for junction potentials. Polarographic measurements were made at a dropping mercury electrode with a dropping time of 0.5 s. Cyclic voltammetry experiments were made at a platinum or glassy carbon electrode, coulometry and preparative experiments were carried out at a 50 cm^3 mercury pool or 35 cm^3 platinum plate.

Mass spectrum (150 °C chemical ionization) (obtained on the crude product) (m/e[+]) Nb_2-$(PhPMe_2)_2(PhPMe)(PC_6H_3)$ 1%, $Nb_2(PhPMe_2)_2$-$(PhPMe)$ 3%, $Nb_2(PMe)_2C$ 4%, $Nb_2(C_4H_9)$ 8%, $Nb_2(C_4H_8)$ 39%, Nb_2H 13%, Nb_2 100%.

Results and Discussion

The best conditions for the electrochemical measurements on $Nb_2Cl_6(PhPMe_2)_4$ solutions were found using dichloromethane as a solvent, and Bu_4-NPF_6 as the supporting electrolyte; ether media – tetrahydrofuran and dimethoxyethane – led to side reactions.

Polarography of $Nb_2Cl_6(PhPMe_2)_4$ shows only one well-defined reduction step at -0.28 V SCE. Scaling with the $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ couple indicates that the preceding wave corresponds to a transfer of two electrons per dimer, and thus probably corresponds on the electrochemical time scale to the generation of a niobium(II) species. Cyclic voltammetry measurements at platinum or glassy carbon electrodes indicate also only one reduction peak of $Nb_2Cl_6(PhPMe_2)_4$ at $E_{1/2} = -0.8$ V SCE, which was found to be irreversible.

When a controlled potential electrolysis was carried out at -0.8 V *vs.* SCE at a platinum electrode, the dark green solution of $Nb_2Cl_6(PhPMe_2)_4$ turned

to black and the resulting solution was found to be relatively air stable. Coulometric values obtained from such controlled-potential experiments indicate that about 4 electrons ($n = 4.2$) were involved per dimer. The polarogram of the resulting solution confirmed the absence of the starting material. The presence of an excess of dimethylphenylphosphane in the dichloromethane solutions of Nb_2Cl_6-$(PhPMe_2)_4$ has no influence on the various voltammograms, nor on the course of the electrolysis. Comparison of polarographic (two-electron wave) and coulometric results (four electrons) shows that the niobium(II) species is not stable on the electrolysis time scale, despite the polarographic data indicating that such species could exist, and bulk electrolytes then led to the formation of a niobium(I) complex. Moreover, the absence of an EPR signal during and at the end of electrolyses suggests that the dimeric structure is preserved during the reduction of the metal, and that $Nb_2Cl_6(PhPMe_2)_4$ has a metal–metal bond-order higher than one [6].

The solutions resulting from electrolysis shows no free dimethylphenylphosphate but liberation or four chloro substituents (identified by their oxidation waves). These observations exclude the formation of a niobium chloro anion, but support the obtention of a neutral derivative, and the formula Nb_2Cl_2-$(PhPMe_2)_4$ seems likely. Unfortunately, this species could not be isolated in the chemically pure state as a result of solubility properties similar to tetra-butylammonium hexafluorophosphate. It should be mentioned that the replacement of the preceding supporting electrolyte by any other — which would be dissociated in CH_2Cl_2 as tetraethylammonium perchlorate for instance — does not overcome these difficulties. On the other hand, despite the notable stability of the niobium(I) compound (decomposition started at about 160 °C), separations by high vacuum sublimation were also unsuccessful. Furthermore we have not been able to prepare this niobium compound using chemical reduction methods. The crude niobium(I) $Nb_2Cl_2(PhPMe_2)_4$ could however be characterized unambiguously by ^{31}P NMR, mass spectrometry and UV data. The $^{31}P\{^1H\}$ spectra obtained at room temperature on CH_2Cl_2 solutions exhibit a singlet at 22 ppm, shifted to high fields as compared with $Nb_2Cl_6(PhPMe_2)_4$, as expected when the electronic density of the metal increases. The existence of only one peak (even at −70 °C), without free ligand, indicates that probably only one molecular species, having an equivalent phosphorus ligand, is present in solution. It should be noted that as no high field signals (compared to the free ligand) were observed, cyclometallation reactions [7] or formation of π complexes [8] seems unlikely. The mass spectrum (see experimental section) shows only fragments derived from a dinuclear niobium species. Furthermore, the peak of 100% abundance corresponds to the Nb_2 fragment, which illustrates the high stability of the metal–metal bond in Nb_2-$Cl_2(PhPMe_2)_4$ and the fact that the reduction of $Nb_2Cl_6(PhPMe_2)_4$ occurs with retention of the metal–metal bond. The electronic spectroscopic data on CH_2Cl_2 solutions of the new compound — strong absorption at 37 880 cm^{-1} with a vibrational progression of 166 cm^{-1} and weak absorptions at 31 746 cm^{-1} and at 27 700 cm^{-1} — also confirm the metal–metal bonding [9] but exclude a cluster core [10].

References

1 D. L. Kepert, 'The early transition metals', Academic Press, London (1972).
2 R. J. Burt, G. J. Leigh and D. L. Hughes, *J. Chem. Soc.,* *Dalton Trans.*, 793 (1981).
3 R R. Brown, C. N. Coke and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1126 (1980).
4 D. A. Lemenovski and V. P. Fedin, *J. Organometal Chem., 132,* C14 (1977).
5 L. G. Hubert-Pfalzagraf and J. G. Riess, *Inorg. Chim. Acta, 29,* L251 (1980);
   L. G. Hubert-Pfalzgraf, M. Tsunoda and J. G. Riess, *Inorg. Chim. Acta, 41,* 283 (1980).
6 F. A. Cotton, W. H. Isley and W. Kaim, *J. Am. Chem. Soc., 102,* 1918 (1980).
7 K. I. Gell, *J. Chem. Soc., Chem. Commun.*, 244 (1979),
   K. I. Gell and J. Schwartz, *J. Am. Chem. Soc., 103,* 2687 (1981).
8 R. Mason, K. M. Thomas and G. A. Heath, *J Organometal. Chem., 90,* 195 (1975).
9 J. E. Templeton, *Progr. Inorg Chem.*, Ed, S. J. Lippard, Vol. 26, New-York (1979),
   W. C. Trogler and H. B. Gray, *Acc. Chem. Res., 11,* 232 (1978).
10 D. D. Klendworth and R. A. Walton, *Inorg Chem., 20,* 1151 (1981).