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A Single Step Synthesis of a Convenient Niobium(III) Starting Material: Bis(dimethylphenylphosphine)niobium(III) Trichloride

L. HUBERT-PFALZGRAF and J. G. RIESS

Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034 Nice, France

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The chemistry of the lower oxidation states of niobium and tantalum is still limited in its development [1] by the tendency of these metals to give strong metal–metal bonding in their reduced species, which results in the formation of insoluble, inert, intractable, solid materials, and by the lack of convenient starting materials. The anhydrous trihalides are difficult to obtain, ill-defined, non-stoichiometric, and too inert to be used for this purpose. Only a limited range of *molecular* adducts of the niobium(III) halides have been reported: $Nb_2X_6(SC_4H_8)_3$ (X = Cl, Br, I), $[Nb_2Cl_8(SC_4H_8)]^{2-}$ [2], $Nb_2Cl_6(CH_3CN)(C_4H_6N_2)$ [3], and more recently $Nb_2Cl_6(SMe_2)_3$ and $Nb_2Cl_6(L–L)_2$ where L–L is $(Ph_2PCH_2)_2$, $MeC(CH_2AsMe_2)_2$ and o-$C_6H_4(AsMe_2)_2$ [4]. These were obtained from $NbCl_5$ either through a two-step reductive process or reduction of an isolated niobium(IV) intermediate, but these methods generally resulted in poor yields.

We wish now to report an easy, one-step synthesis of bis(dimethylphenylphosphine)niobium(III) trichloride, a highly soluble molecular niobium(III) derivative, by reduction of niobium pentachloride by magnesium in the presence of the ligand.

Results and Discussion

Reduction of $NbCl_5$ by metals such as zinc or aluminium in the presence of a ligand usually resulted in niobium(IV) derivatives of type $NbCl_4 \cdot L_2$ or $NbCl_4 \cdot L_3$ [5]; the yields were low as a result of difficulties in separating the by-product issued from the reducing agent. Magnesium, on the other hand, appears to have an attractive potential as a reducing agent of early transition metals (Ti, Cr, Mo [6] and recently Nb [7]) as well as of other transition metal (Co) compounds [8].

Compound $NbCl_3 \cdot 2PhPMe_2$ (I) was obtained by treating $NbCl_5$ with an excess of magnesium in CH_2Cl_2 in the presence of 3 equivalents of phenyldimethylphosphine at room temperature. The excess magnesium and its derivatives are easily separated by filtration, and the dark-brown crystalline niobium(III) compound was isolated in *ca.* 80% yield by low-temperature crystallization. Solvent effects were also seen to be important, for example no reduction was observed in toluene.

The new compound, which is highly air and oxygen sensitive, especially when dissolved, was characterized by its elemental analysis and infra-red, ^1H and ^{31}P NMR spectroscopy. It is soluble in the common organic solvents, including benzene, dichloromethane, acetonitrile and tetrahydrofurane; however, slow decomposition reactions, presumably of a photochemical nature [9], were noted in the chlorinated hydrocarbons. No further coordination by acetonitrile was observed, since compound I is recovered unchanged after recrystallization from that solvent.

Adduct I was found to be diamagnetic by Evans' method [10] suggesting a dimeric structure with a strong metal–metal interaction. This was confirmed by the determination of its molecular weight by vapor pressure osmometry in benzene (found 810, calc. for $[NbCl_3(PhPMe_2)_2]_2$ 951). The metal–chlorine stretching frequencies observed at 438, 400, 360, 303 cm^{-1} in the infra-red on the solid further support a dimeric structure.

The proton decoupled ^{31}P NMR spectra measured at 30 °C on a 0.40 molar solution of $Nb_2Cl_6 \cdot 4PhPMe_2$ in acetonitrile exhibits three sharp singlets, a, b and c at 21.7, 31.7 and 47.8 ppm respectively. No free ligand was detected. Six geometrical isomers can be expected for a dimeric μ-dichloro compound of formula $[NbCl_3(PhPMe_2)_2]_2$, and it is now well established that adducts derived from early transition metals easily give complex mixtures of isomers in solutions [11].

The ^1H NMR spectra consist primarily of two doublets for PMe_2 groups at $\delta = 2.11$ ppm, $J_{P–CH_3} = 14$ Hz; $\delta = 1.88$ ppm, $J_{P–CH_3} = 13$ Hz, which represent 80% of the methyl peak area. These doublets remain of equal area independently of the experimental conditions, and are therefore likely to belong to a same molecular species in which the two ligands would occupy non-equivalent sites. This hypothesis is further borne out by quantitative data from non-decoupled ^{31}P NMR spectra, which show that the two principal signals (a and c) also have comparable area. No change in the $^{31}P\{^1H\}$ spectra was noted between –30 and +70 °C.

Investigation into the reactivity of $Nb_2Cl_6[PhPMe_2]_4$ as well as further studies on the reduction of niobium and tantalum pentahalides by magnesium in various complexing media are under way.

Experimental

All handling was achieved under dry argon using Schlenk tubes or vacuum line techniques. Solvents were purified by standard methods and carefully deoxygenated by purging with argon for several hours. Niobium pentachloride was prepared by chlorination of the metal (gift from Péchiney Ugine Kuhlmann). Infra-red spectra were recorded as Nujol mulls on a Perkin–Elmer 577 spectrometer. NMR spectra were recorded on a WH-90 Bruker spectrometer operating in the Fourier transform mode. The ^{31}P chemical shifts are given positively towards lower fields relative to 85% H_3PO_4 as external reference. Molecular weight data were obtained on a Knauer vapor pressure osmometer. The elemental analyses were performed by the Centre de Microanalyse of the CNRS.

Preparation of $NbCl_3(PhPMe_2)_2$

Phenyldimethylphosphine (1.6 ml, 11.21 mmol) is progressively added while stirring to a suspension of $NbCl_5$ (880 mg, 3.28 m*M*) and of an excess of Mg turnings (200 mg) in 20 ml CH_2Cl_2 at room temperature. The mixture turns dark red when about one equivalent of phosphine is added, and a red crystalline product is formed, which dissolves again when more phosphine is added. The colour of the solution then turns to red–brown and later to green–brown, while the attack of the magnesium is observed and $MgCl_2$ starts precipitating. The mixture is stirred for about 36 hours, until a stable black–brown coloration is obtained. The excess magnesium and its derivatives are filtered and carefully washed with CH_2Cl_2 until the precipitate of $MgCl_2$ is fully decoloured. The filtrate is concentrated to about 4 ml. The crystallisation of the niobium(III) adduct is improved by adding a small amount (*ca.* 1 ml) of hexane. After 3 days at –30 °C, 970 mg (87%) of brown-black air-sensitive crystals (m.p. 76 °C) are obtained. The compound is slightly soluble in toluene, and very soluble in methylene chloride, acetonitrile and methanol. *Anal.* Found: C 39.9, H 4.88, Cl 22.54%. Calc. for $C_{16}H_{22}Cl_3NbP_2$: C 40.35, H 4.99, Cl 22.38%. Ir (Nujol, cm^{-1}): 1585 (νC=C); 1295 (ν_sP–CH$_3$), 1140, 1131, 1115, 1090, 1070; 962, 940, 912(νP=CH$_3$); 870, 833, 735, 690, 490(P–Ph); 438, 400, 360, 303 (νNb–Cl).

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