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Synthesis and Characterization of Niobium(III) β-Diketonate Derivatives; Molecular Constitution of their Solutions

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The niobium(III) molecular derivatives $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ *(acacH = acetylacetone),* $Nb_2Cl_5(dpm)(PhPMe_2)_2$ *and* $Nb_2Cl_3(dpm)_3$ *(dpmH = dipivaloylmethane) were isolated in high yields by reacting the corresponding β-diketone with* $Nb_2Cl_6(PhPMe_2)_4$ *or* $Nb_2Cl_6(SMe_2)_3$*. These products were characterized by elemental analysis, mass spectra, infra-red and* ^1H *and* ^{31}P *NMR spectroscopy. Unlike the dipivaloylmethanato derivatives, extensive dissociation reactions were observed for* $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ *in solution, which therefore contains mainly* $Nb_2Cl_4(acac)_2(PhPMe_2)_2$ *species.*

Introduction

We are currently investigating the reactivity of the molecular niobium(III) halide adducts $Nb_2Cl_6(PhPMe_2)_4$ and $Nb_2Cl_6(SMe_2)_3$ which are among the few convenient starting materials now available [1, 2] for developing the coordination chemistry and organometallic chemistry of niobium in this oxidation state. As β-diketonates also are good starting materials [3] and sometimes present catalytic activity [4], we have attempted the synthesis of such derivatives for niobium(III), particularly with 2,2,6,6-tetramethyl-3,5-heptadione (dipivaloylmethane = dpmH) in the hope that its crowding would hinder the formation of insoluble inert clusters [5].

We now wish to report the synthesis in high yields of $Nb_2Cl_5(dpm)(PhPMe_2)_2$, $Nb_2Cl_3(dpm)_3$ and $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ (acacH = acetylacetone), which are very soluble niobium(III) derivatives, and their characterization by elemental analysis, infra-red, NMR, mass spectroscopy and magnetic susceptibility measurement, as well as some aspects of the molecular constitution of their solutions.

Results and Discussion

Synthesis

The reaction, in various stoechiometries (ligand/metal from 1 to 3), of dmpH with a solution of $Nb_2Cl_6(PhPMe_2)_4$ in CH_2Cl_2 or thf proceeds at room temperature with slow liberation of HCl. After 36 h, a soluble product, whose analysis is consistent with the formula $Nb_2Cl_5(dpm)(PhPMe_2)_2$, independently of the ligand/metal stoechiometry, was isolated in 80% yields.

By contrast, the reaction between $Nb_2Cl_6(SMe_2)_3$ and dmpH was found to be dependent on the dpmH/metal ratio, perhaps as a result of the lower coordinating ability of dimethylsulfide towards Nb(III) derivatives. When the reaction was conducted in a ligand/metal molar ratio of 2, a product was isolated whose analytical and spectral data are consistent with the formation of a mixture of $Nb_2Cl_4(dpm)_2$ and $Nb_2Cl_3(dpm)_3$ in comparable amounts. A more selective route to $Nb_2Cl_3(dpm)_3$ was found by reacting the starting materials in a ligand/metal molar ratio of 3 or with an excess of dpmH.

The working out of a procedure for preparing a definite molecular adduct was less straightforward with the less crowded acetylacetone. Thus the compound $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$, which contains both anionic and neutral acetylacetone ligands, was always obtained from $Nb_2Cl_6(PhPMe_2)_4$ and acetylacetone in CH_2Cl_2, independently of the ligand/metal ratio, but it was contaminated by products that resulted from side reactions between the phosphorus ligand and the β-diketone [5], which made its isolation in a pure state difficult. These side reactions could be avoided by using toluene instead of CH_2Cl_2 as solvent, and $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ was then isolated in 95% yield. This may be due to the lower solubility of the product of the reaction in toluene, in which it precipitates. It is noteworthy that the formation of niobium(V) oxo derivatives was not detected during this reaction. When thallium acetylacetonate was used as a reactant instead of acetylacetone, the reaction was very much slower, although the same product formed (from the

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infra-red), but it was difficult to free from thallium salts.

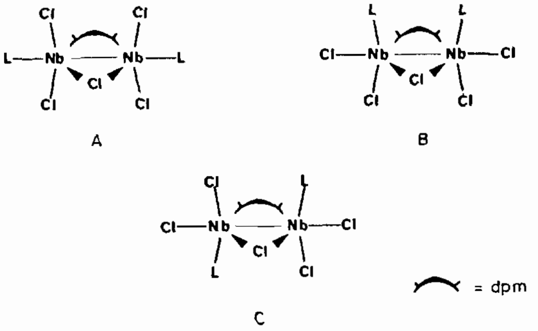
Characterization and Molecular Constitution of the Solutions

The volatility of the new products isolated allowed their characterization by mass spectroscopy, which established the dinuclear nature of all of them in the vapor phase. Magnetic susceptibility measurements showed them to be diamagnetic both in the solid state and in solution, thus establishing the presence of structural units that are at least dinuclear, therefore allowing spin–spin interactions through direct metal–metal interactions or through the bridging ligands.

The IR spectra measured on the solid state exhibit the usual absorption of the chelating O-bonded β-diketonato ligands [3], although some are partially obscured by those of $PhPMe_2$ in the case of the phosphane adducts. For the various dipivaloylmethane complexes, the $\nu(\mathrm{C{\cdots}O})$ absorptions appear at *ca.* 1590 cm^{-1}, while the $\nu(\mathrm{C{\cdots}C})$ absorptions are always found in the 1540–1510 cm^{-1} region as expected [6]. The ring deformation vibration was located at *ca.* 630 cm^{-1}. The spectra of $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ exhibit several bands in the carbonyl region between 1710 and 1585 cm^{-1}. The presence of a $\nu(C{=}O)$ vibration at 1710 cm^{-1}, very near to that of free acetylacetone, confirms that the coordination sphere contains – as often observed for early transition metal derivatives [7, 8] – a neutral acetylacetone ligand, in its β-diketone form (absence of $\nu(OH)$ absorption corresponding to the enol form). The metal–chlorine absorptions were found as expected below 400 cm^{-1}. The presence of oxo derivatives is excluded by the absence for all these β-diketonates of broad absorptions in the 800–720 region, or of strong absorptions at *ca.* 940 (other than those corresponding to the ligands), which could be attributed respectively to bridging or terminal metal-oxo bonds [8]. This is noteworthy, since oxygen abstraction has sometimes been observed in the reactions of low valent early transition metal derivatives with β-diketones [10].

We were able to take advantage of the diamagnetic character of the compounds to examine the molecular constitution of their solutions by ^1H and ^{31}P spectroscopy. It is well known that early transition metal derivatives often give complex equilibrated mixtures of isomers, dissociations and disproportionation reactions in solution [11].

The ^{31}P spectra measured at room temperature on a solution of $Nb_2Cl_5(dpm)(PhPMe_2)_2$ in CH_2Cl_2 (8×10^{-2} molar) exhibit a single signal at −2 ppm, although several geometrical isomers (Scheme 1) can be drawn, which have magnetically equivalent phosphorus ligands and bridging dpm anions, assuming a bipyramidal arrangement of the ligands around the metallic center [12].



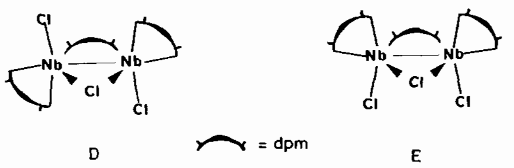
Scheme 1

The ^1H NMR spectra measured on solutions in CD_2Cl_2 at various temperatures (from −50 to +50 °C) and dilutions (from 8×10^{-2} to 8×10^{-3} molar) confirm that one species, displaying tBu groups at 1.09 and 1.07 ppm (1:1 and the γ-proton at 5.99 ppm, is always strongly predominant (95% of the total peak area). The PMe_2 groups of the phenyldimethylphosphane ligand appear as two doublets [δ = 2.55 ppm, J = 13 Hz; δ = 2.24 ppm, J = 13 Hz (1:1)]. Their relative area ratio remains constant under various dilutions. This non-equivalence of the methyl groups is probably due to their being diastereotopic in the complex. The presence in the spectra of two resonances for the t-Bu groups in a constant 1:1 ratio could arise either from coupling with phosphorus or from a species having magnetically non-equivalent groups. The phosphorus coupling is, however, expected to be very small [13], and as the Hγ resonance is sharp, it seems more likely that the t-Bu groups are magnetically non-equivalent, which would point to isomer C.

On the contrary, the ^1H NMR spectra of $Nb_2Cl_3(dpm)_3$ in solvents such as dichloromethane, toluene or acetonitrile show the presence of several molecular species, in equilibrium, since their relative proportions, as given by the relative peak area, depend on the dilution. The equilibria between the various species are slow on the NMR time-scale. The spectra measured on its 2.3×10^{-2} molar solution in $CDCl_3$ show at least 4 signals for the t-Bu group (ranging from 1.30 to 1.17 ppm), while larger shift effects are observed for the γ-proton ring (6.32 to 5.62 ppm). Quantitative analysis at various dilutions (2.3×10^{-2} to 4×10^{-2} molar) shows that two sets of two signals – the latter having consistently 2:1 area ratio – are observed and can therefore be attributed to two distinct molecular species [δt-Bu = 1.17, 1.30; δHγ = 6.14, 6.33 ppm (2.1); δt-Bu = 1.26, 1.18; δHγ = 5.76, 5.62 (2:1)].

The latter set of signals, which corresponds to the minor species in concentrated solutions ≅15% in 2.3

$\times\ 10^{-2}$ molar) was the only one detected in highly diluted solutions ($\cong 8 \times 10^{-5}$ molar in $CDCl_3$). No free dipivaloylmethane was found. The isomer that is predominant in relatively concentrated solutions has dipivaloylmethanato anions which display Hγ resonances at very low field, thus suggesting a notable positive charge on the metal [14]. Conductimetry measurements give, however, conductance values ($\Lambda = 1.15\ \Omega^{-1}\cdot cm^2$ on 10^{-3} molar solution) typical for non-electrolytes [15]. Thus we were left with two molecular species having non-equivalent β-diketonato anions in a 2:1 ratio, consistently with two ligands in a terminal and one in a bridging position. Scheme 2 shows some of the geometrical isomers that are likely to be found for the structure of $Nb_2Cl_3(dpm)_3$, assuming a bipyramidal environment of the metal. Examination of molecular models shows that isomer D is the least sterically hindered.



Scheme 2

Solutions of $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ in CH_2Cl_2 at room temperature show one main signal at −5.3 ppm (95%) as an additional peak at 32 ppm, in the ^{31}P NMR spectra. The equilibria between all species were found to be slow on the NMR time scale. The main feature, as evidenced from the ^1H NMR spectra, is that ≅95% of the neutral acetylacetone molecules of $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ are released in solution. These data suggest that one isomer having equivalent phosphorus ligand is largely predominant. The CH_3 resonances from free acetylacetone in its enol and β-diketone forms were present at 2.03 and 2.20 ppm, respectively. The main additional peaks correspond to the PMe_2 groups (δ = 2.24, J = 13.5 Hz) and to the acetylacetonato ligand (δCH_3 = 2.35 ppm, Hγ = 5.87 ppm). As dissociation reactions were very extensive, the solutions of $Nb_2Cl_4(acac)_2(acacH_2)(PhPMe_2)_2$ contain mainly $Nb_2Cl_4(acac)_2(PhPMe_2)_2$ species. In fact among the six geometrical isomers of $Nb_2Cl_2(\mu^2\text{-}Cl)_2(acac)_2(PhPMe_2)_2$ having equivalent acetylacetonato rings as well as phosphorus ligands, one appears strongly favored. The distribution between the various molecular species is slightly dilution-dependent, but the overlap of the different methyl resonances precludes a more complete analysis.

Experimental

All the manipulations were conducted under dry de-oxygenated argon, using Schlenk tubes and vacuum-line techniques. The solvents were carefully distilled over the standard drying reagents and de-oxygenated. $Nb_2Cl_6(PhPMe_2)_4$ and $Nb_2Cl_6(SMe_2)_3$ were synthesized as previously described [1]. Acetylacetone was distilled immediately before use. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 577 spectrometer, NMR spectra were obtained on a WH-90 BRUKER spectrometer operating in the Fourier transform mode. ^{31}P chemical shifts are given positively towards lower fields relatively to 85% H_3PO_4 as external reference. Conductivity measurements were performed with a Tacussel CD 6NG apparatus on dichloromethane solutions. Mass spectra (VG Micromass 70-70 F spectrometer) and microanalysis data were effected by the Service Central de Microanalyses du C.N.R.S.

Synthesis of $Nb_2Cl_5(dpm)(PhPMe_2)_2$

Dipivaloylmethane (0.285 g, 1.54 mmol) was slowly added to a stirred solution of $Nb_2Cl_6\cdot(PhPMe_2)_4$ (0.737 g, 0.77 mmol) in 35 ml of tetrahydrofuran, freshly distilled. Stirring was maintained for about 36 h. After filtration, the deep blue filtrate was concentrated. Crystallization started and was achieved by adding some toluene and by maintaining at −40 ℃ for some days. 505 mg (80%) of green or yellow* crystals of $Nb_2Cl_5(dpm)(PhPMe_2)_2$ (m.p. 124 ℃), soluble in CH_2Cl_2, insoluble in toluene or diethylether, were isolated after filtration and vacuum drying. *Anal.* Found: C, 39.77; H, 5.20; Cl, 22.50%. Calcd. for $C_{27}H_{41}O_2P_2Cl_5Nb_2$: C, 39.42; H, 5.12; Cl, 21.57%. *IR*: (Nujol): 1590m, 1550m, 1535m, 1510sh, 1500s, 1440vs, 1415m, 1375m, 1320w, 1300s, 1260m, 1220m, 1250sh, 1130vs, 1115vs, 1100sh, 1055sh, 1025m, 960m, 930s, 875s, 800m, 745s, 690s, 620m, 480m, 440m; 400w, 355sh, 310vs, 280vs, 240w. *Mass spectrometry* (70 eV, 200 ℃): (M = $Nb_2Cl_5(dpm)(PhPMe_2)_2$: M 1%, M-dpmH 4%, $Nb_2Cl_3(OC_{11}H_{13})$ 5%, $NbOCl_2(C_{11}H_{19}O_2)$ 5%, Nb(CO)H(dpm) 5%, $NbH(CO)(C_8H_{11}O_2)$ or $NbH(CO)(C_{10}H_{19})$ 23%, $Nb(OC_3H_9)$ 23%, $PhPMe_2$ (100%).

Synthesis of $Nb_2Cl_3(dpm)_3$

A solution of dipivaloylmethane (1.40 ml, 6.8 mmol) in 10 ml CH_2Cl_2 was added dropwise into a stirred solution of $Nb_2Cl_6(SMe_2)_3$ (1.22 g, 2.09 mmol) in 40 ml CH_2Cl_2 at room temperature. The dark violet solution veered to dark blue after 15 min.

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*The compounds were isolated as crystals having different colors, the yellow form being the most stable. The analytical and spectral data (^1H NMR, IR) were identical.

Stirring was maintained for 24 h, a small dark brown precipitate was separated out by filtration and the filtrate was evaporated to dryness and dried in high vacuum. 1.70 g (97%) of dark blue crystals of $Nb_2Cl_3(dpm)_3$ (m.p. 51–52 °C) were obtained. This product is slightly soluble in pentane, more soluble in toluene, chloroform, dichloromethane, acetonitrile or tetrahydrofuran. *Anal.* Found: C, 47.35; H, 6.96; Cl, 11.86%. Calcd. for $C_{33}H_{57}O_6Cl_3Nb_2$: C, 47.07; H, 6.82; Cl, 12.63%. *IR* (Nujol): 1590m, 1545s, 1535s, 1500vs, 1330m, 1109m, 1250m, 1225s, 1150s, 1132s, 1030w, 975w, 960m, 940w, 895vs, 880vs, 865m, 810w, 740w, 630s, 530m, 440m; 370vs, 340s, 320sh, 305m, 250w. *Mass spectrometry* (110 °C, 70 eV): $Nb_2Cl_3(dpm)_2(O_2C_{10}H_{12})$ 1%, $Nb_2Cl_3(dpm)(O_2C_{10}H_{16})$ 4%, $Nb_2Cl_3(dpm)(OC_3H_3)$ 11%, $Nb_2Cl_3(O_2C_{14}H_{20})$ 12%, $Nb_2Cl_3(dpm)$ 47%, $Nb_2Cl_3(OC_{11}H_{13})$ 100%, $Nb_2Cl_2(O_2C_{11}H_{17})$ 6%, $NbOCl_2(dpm)$ 51%.

Synthesis of $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$

Freshly distilled acetylacetone (0.2 ml, 2.52 mmol) was added to a dark green suspension of $Nb_2Cl_6(PhPMe_2)_4$ (600 mg, 0.63 mmol) in 25 ml toluene at room temperature. After *ca.* 1 h, the reaction mixture became blue. Stirring was maintained for one week. The blue-grey precipitate was separated by filtration, washed with toluene and vacuum dried. Finally 600 mg (95%) of light blue–grey or pale yellow*, air-sensitive crystals of $Nb_2Cl_4(acac)_2(acacH)_2(PhPMe_2)_2$ were obtained. *Anal.*: Found: C, 43.25; H, 5.28; Cl, 15.30; P, 7.02%. Calcd. for $C_{36}H_{52}O_8P_2Cl_4Nb_2$: C, 43.14; H, 5.23; Cl, 14.17; P, 6.19%. *IR* (Nujol): 1710m, 1675m, 1610m, 1585m, 1300m, 1260w, 1150sh, 1120s, 1095m, 1020w, 935s, 880m, 855sh, 740s, 725sh, 695m, 660w, 540w, 445w, 405m, 340sh, 320s, 250m. *Mass spectrometry* (190 °C, 20 eV): M = $Nb_2Cl_4(acac)_2(PhPMe)_2$; M–OPhPMe$_2$ 2%, M–OPhPMe$_2$–PhPMe$_2$ 1.5%, $Nb_2Cl_3(acac)(C_5H_7O)$ 4%, $Nb_2Cl_2(acac)(C_3H_3O)$ 20%, $Nb_2(O_2CCH_2)_2$ 2%, $Nb_2H(O_2CCH_3)_2$ 12%, PhPMe$_2$ 100%. The solubility properties of the compound are similar to those of $Nb_2Cl_5(dpm)(PhPMe_2)_2$.

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*Note identical to that on p. 83.