Inorganica Chimica Acta, 71 (1983) 119–124

Synthesis and Reactivity of Ta(III) Halide γ-Picoline Adducts. Formation of Ta(IV) β-Diketonate and Carboxylate, and Ta(III) Alkoxide

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Received September 27, 1982

Molecular tantalum(III) adducts $Ta_2X_6(\gamma\text{-}pic)_4$ *(X = Cl or Br) have been obtained in high yields by reducing* Ta_2X_{10} *by magnesium in the presence of the ligand. Preliminary results of their reactivity are given. Ta(IV) β-diketonates or carboxylates,* $Ta_2Cl_4(dpm)_4$ *and* $Ta_2Cl_4(^tBuCO_2)_4$, 2^tBuCO_2H *or oxo derivatives were obtained by treating* $Ta_2Cl_6(\gamma\text{-}pic)_4$ *with the weak protonic acids: dipivaloylmethane (dpmH), pivalic acid and acetic acid respectively. Reactions between* $Ta_2Cl_6(\gamma\text{-}pic)_4$ *and* LiO^tBu *led to the formation of the first tantalum(III) alkoxide* $Ta_2Cl_2(O^tBu)_4$.

All new derivatives, which are diamagnetic, were characterised by elemental analysis, IR and ^1H *NMR spectroscopy.*

Introduction

We are currently investigating the access to and the reactivity of molecular low-valent niobium and tantalum derivatives [1]. The recent account of Brown *et al.* [2], who mentioned the obtaining of $NbCl_3L_3$ (L = pyridine (py), 4-methylpyridine (γ-pic) and 3,5-dimethylpyridine) and of $Ta_2Cl_6(py)_4$ by a ligand exchange reaction from $M_2Cl_6(SC_4H_8)_3$ (M = Nb or Ta), prompted us to publish the synthesis of $Ta_2X_6(\gamma\text{-pic})_4$ (X = Cl or Br) by reduction of the corresponding pentahalides by magnesium in the presence of the nitrogen donor ligand. Preliminary results concerning the reactivity of $Ta_2Cl_6(\gamma\text{-pic})_4$ are also given.

In order to obtain metal derivatives which may provide a useful entry into the synthesis of other complexes of low-valent tantalum, and thereby facilitate the investigation of its chemistry, we explored the interactions of the new tantalum(III) adduct with weak protonic acids such as β-diketones or carboxylic acids. Indeed, the tantalum low-valent β-diketonates are limited to $Ta(dbm)_4$ [3] (dbmH = dibenzoylmethane), while only tantalum(V) carboxylates – generally oxo derivatives [4] – are known. The reactants wery selected in the hope that their crowding would hinder the formation of insoluble inert clusters [5] or oxo derivatives [3, 4]. Highly soluble tantalum(IV) derivatives such as $Ta_2Cl_4(dpm)_4$ (dpmH = dipivaloylmethane, 2,2,6,6-tetramethyl-3,5-heptadione) and $Ta_2Cl_4(O_2C^tBu)_4$, 2^tBuCO_2H are obtained by this method. On the contrary, oxidation state 3 was retained by reaction with lithium derivatives, and $Ta_2Cl_2(O^tBu)_4$ was isolated. All the new derivatives were characterized by elemental analysis, infra-red and NMR spectroscopy. Some indications concerning the molecular constitutions of their solutions are also given.

Results and Discussion

Synthesis and Characterisation of $Ta_2X_6(\gamma\text{-}pic)_4$

$Ta_2X_6(\gamma\text{-pic})_4$ (X = Cl or Br) were obtained directly from the pentahalides Ta_2X_{10} in reaction conditions similar to those applied for the synthesis of $Nb_2Cl_6(PhPMe_2)_4$: excess of magnesium turnings, ligand to metal ratio of about 4, and dichloromethane as the solvent. After a 24 h reaction time the tantalum adduct was separated from the magnesium derivatives and isolated in good yield. Attempts to recrystallise $Ta_2Cl_6(\gamma\text{-pic})_4$ led to a partial loss of γ-picoline, as illustrated by the evolution of the microanalytical data, which was accompanied by a

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TABLE I. Analytical and Spectroscopic Data.[a]

	Microanalysis % Found (Calc.)				IR (main absorptions) (cm^{-1})		^1H NMR (δ in ppm) (CD_2Cl_2, 25 °C)
	C	H	Cl	N	Ligand	ν M–Cl or M–Br	
$Ta_2Cl_6(\gamma\text{-pic})_4$	30.28 (30.40)	3.12 (2.96)	22.10 (22.48)	5.29 (5.91)	νC=N: 1620	335sh, 310vs, 290sh	2.42, 7.30, 8.61d(6.1)
$Ta_2Br_6(\gamma\text{-pic})_4$	23.65 (23.72)	2.50 (2.31)		4.20 (4.62)	νC=N: 1610	330sh, 310vs, 300s, 280s, 270m, 245vs	2.65, 2.87, 2.34; 7.82, 8.58d(6.5) NH (10.7)*
$Ta_2Cl_4(dpm)_4$	43.46 (42.69)	6.34 (6.14)	12.35 (11.41)		νC=O 1580vs, 1560sh νC=C 1535s, 1508vs	320m, 295s, 285s, 245w	^{t}Bu: 1.17 Hγ: 6.20
$Ta_2Cl_4(O_2C^tBu)_4, 2^tBuCO_2H$	33.42 (32.36)	4.78 (5.03)	12.05 (12.74)		νCO_2: 1705s $\nu asCO_2$: 1660s, 1640s 1630s νsCO_2: 1560m, 1550w	315sh, 295vs, 285sh, 260sh, 245m	^{t}Bu: 1.30, 1.25(1:1), 1.22, 1.16 OH (12.8)
$TaOCl(OAc)_2\ \gamma\text{-pic}$	27.10 (27.05)	3.10 (2.95)	8.50 (8.00)	3.03 (3.15)	νC=N: 1640m $\nu asCO_2$: 1575s, 1535s νsCO_2: 1355vs νTa=O: 860s	320m, 305m, 295vs, 275s, 250m	OAc: 2.10 γ-pic: 2.65, 7.64, 8.64d (7.0)
$Ta_2Cl_2(O^tBu)_4$	26.10 (26.48)	4.68 (4.96)	10.43 (9.78)		νTa–O: 545s	350w, 285s	O^{t}Bu: 1.22

[a] d = doublet; ( ) = J in Hz; * in MeCN. s = strong; sh = shoulder; m = medium; w = weak.

decrease in the solubility properties. A similar variation of the solubility was observed after storing the solid for some weeks, even at –30 °C. A more stable product was obtained if the new tantalum adduct was isolated as a solvate $Ta_2Cl_6(\gamma\text{-pic})_4$, x$\gamma$-pic (x varying from 0 to 3 as a function of the isolation conditions).

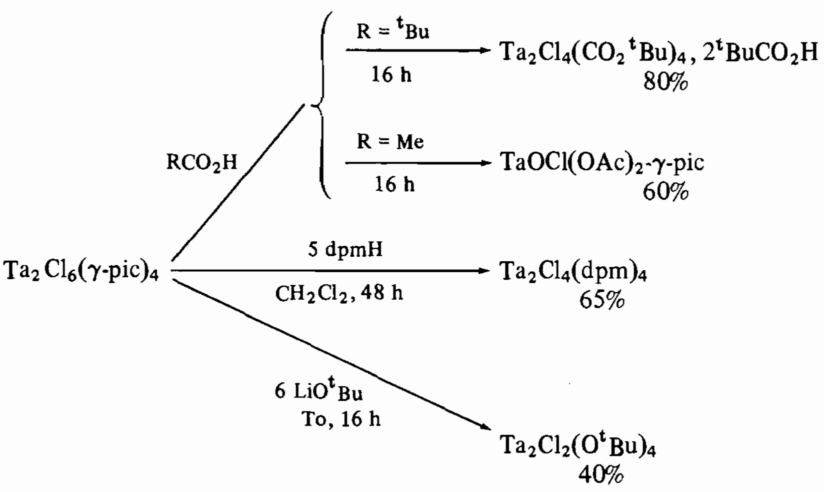
$Ta_2X_6(\gamma\text{-pic})_4$ and all other new derivatives reported here were characterized by microanalytical data, magnetic susceptibility measurements and spectroscopic data (IR and ^1H NMR) (Table I). $Ta_2Cl_6(\gamma\text{-pic})_4$ was found to be diamagnetic in the solid and in solution, as was compound $Ta_2Cl_6(py)_4$, for which magnetic data only were reported by Brown [2]. The new adducts, especially the chloride derivative, were found to be very soluble in common solvents and, despite the lability of the γ-picoline, $Ta_2Cl_6(\gamma\text{-pic})_4$ appear to be relatively stable in MeCN; no evolution to the known Ta(V) diimidoethene derivative $Ta_2Cl_6(C_4H_6N_2)(MeCN)_4$ [6] was observed after 24 h at 25 °C.

The convenient solubility and the diamagnetic nature of the products allowed us to obtain the ^1H NMR data. The spectra of $Ta_2Cl_6(\gamma\text{-pic})_4$ depend on the dilution, on the temperature and on the presence of additional ligand. For instance, only one signal at 2.42 ppm is observed for the methyl region at 25 °C for a 0.003 *M* solution of $Ta_2Cl_6(\gamma\text{-pic})_4$ in CD_2Cl_2. At –90 °C three signals (2.60, 2.57 and 2.34 ppm) whose relative areas are a function of the dilution, are detected. The resonance of free γ-picoline is never observed, but the addition of γ-picoline shows that the ligand is rapidly exchanging on the NMR time scale, even at –90 °C. These observations suggest the presence of several molecular species – geometrical isomers or complexes of different ligand to metal stoichiometries – in dynamic equilibrium.

The ^1H NMR spectra of the less soluble $Ta_2Br_6(\gamma\text{-pic})_4$ adduct are also indicative of the presence of several molecular species. The striking difference from the chloro analog is the presence of picolinium bromide (δNH: 10.72 ppm, δMe: 2.65 ppm in MeCN, 60% of the total area), thus involving electron transfer reactions in solutions, with formation again of diamagnetic species. A similar difference in the behaviour in solution of tantalum(III) chloride and bromide adducts has already been reported [1].

Reactivity

The high air-sensitivity and the low stability of the Ta(III)–γ-picoline adducts encouraged us to obtain other derivatives by investigating their substitution reactions. The reactants were chosen in order to attempt to avoid the undesirable formation of clusters or oxo compounds, but also in the hope of leading to other soluble and useful – for synthesis and potential applications [7] – low-



Scheme 1. Reactivity of $Ta_2Cl_6(\gamma\text{-pic})_4$ (all reactions were effected at room temperature).

valent tantalum derivatives. Chelating and/or crowded substituents, which would also contribute a convenient probe for gaining structural information by ^{1}H NMR, were therefore retained. The various reactions are summarized in Scheme 1.

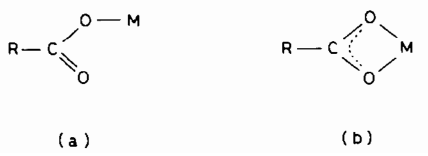
The reactions, in various stoichiometries, between $Ta_2Cl_6(\gamma\text{-pic})_4$ in toluene or dichloromethane and weak protonic acids – dipivaloylmethane, pivalic acid, glacial acetic acid – proceed at room temperature by a slow liberation of hydrochloric acid (trapped by the γ-picoline ligand) giving the hydrochloride salt which could be removed by sublimation under high vacuum. Thus the reaction between $Ta_2Cl_6(\gamma\text{-pic})_4$ in CH_2Cl_2 and a slight excess of dipivaloylmethane (ligand to metal molar ratio R = 5) led to $Ta_2Cl_4(dpm)_4$ isolated in a 65% yield. It is noteworthy that no oxo derivatives are formed (see below). Indeed, a similar reaction starting from $Ta_2Cl_6(PhPMe_2)_4$ gives $[TaOCl_2(dpm)]_2$ (νTa–O–Ta = 800 cm^{-1}) as the only isolable, pure product [8]. The high oxophilic character of tantalum, as compared to niobium, is also illustrated by the fact that $Ta(dbm)_4$ (dmbH = dibenzoylmethane) is the only non-pentavalent Ta β-diketonate reported so far. All other attempts starting from $TaCl_4$ invariably gave oxo compounds, while niobium(IV) β-diketonates are numerous [3, 9].

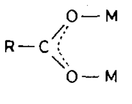
$Ta_2Cl_4(CO_2^tBu)_4$ 2^{t}BuCO$_2$H (80)% and TaOCl(OAc)$_2$·γ-pic (52%) were respectively obtained by substitution reactions with pivalic acid (R = 5 to 6) and glacial acetic acid (R ≅ 20). It should be noted that $Ta_2Cl_4(CO_2{}^tBu)_4$, 2^{t}BuCO$_2$H is the first Ta(IV) carboxylate derivative to be reported. The formation of oxo acetates could not be avoided: high molar ratios of acid are required for the substitution of the chlorine of $Ta_2Cl_6(\gamma\text{-pic})_4$. On the other hand, the use of thallium acetate as a reactant favoured the formation of polymeric oxo derivatives, TaOCl(OAc)$_2$·γ-pic then being isolated in a 15% yield.

Reactions between $Ta_2Cl_6(\gamma\text{-pic})_4$ and lithium reagents appeared to be a more successful route to other Ta(III) derivatives, and $Ta_2Cl_2(O^tBu)_4$ was isolated in a 40% yield using LiO^{t}Bu at room temperature. The substitution of all chlorine atoms was not observed even by working at the toluene reflux temperature. $Ta_2Cl_2(O^tBu)_4$ is the first tantalum(III) alkoxide reported so far and further studies on its reactivity are in progress. We are also currently investigating the nature of the other derivatives formed in this reaction as the reactivity of $Ta_2Cl_6(\gamma\text{-pic})_4$ towards other lithium alkoxides.

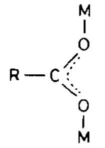
The IR spectra of $Ta_2Cl_4(dpm)_4$ on the solid state exhibit the usual bands of the chelating O-bonded pivaloylmethanato ligand. The $\nu C \simeq O$ absorptions appear at *ca.* 1580 and 1560 cm^{-1}, while the $\nu C \simeq C$ absorptions are located as expected in the 1535–1510 cm^{-1} region. Ring deformation was found at 628 cm^{-1}. The presence of oxo derivatives is excluded by the absence of a strong, sharp absorption at *ca.* 920–860 cm^{-1} or of a broad one in the 800–720 region, which could be attributed respectively to terminal or metal-oxo bonds.

The carboxylate moieties are known to display an interesting structural diversity and can exhibit monodentate (a), bidentate-chelating (b) or bridging (c,e)-ligating behaviour (Scheme 2):

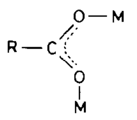




(c) syn-syn



(d) anti-anti



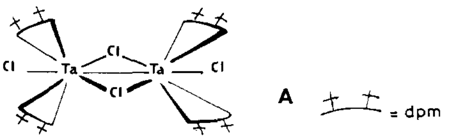
(e) syn-anti

It is apparent that as the coordination mode changes from monodentate to bidentate there is a decrease in the double bond character of the C=O bond and consequently changes in the IR stretching frequencies of the CO_2 moieties are expected. The difference between the asymmetric and symmetric O–C–O stretching frequencies $\Delta\nu(CO_2)$ has been used as a guide to the ligation of the carboxylate group. It was noted that if this value was approximately 100 cm^{-1} or less, there was a strong possibility of chelating coordination; bridging being likely when $\Delta\nu(CO_2)$ was between 100 and 200 cm^{-1} and values greater than 200 cm^{-1} were indicative of a monodentate behaviour [10]. The IR on the solid state of $Ta_2Cl_4(O_2C^tBu)_4$, 2^tBuCO_2H shows a strong νCO_2 absorption at 1700 cm^{-1} corresponding to free pivalic acid, which solvates the tantalum(IV) compound. The $\nu_{as}CO_2$ stretching of the pivalato groups appear as broad and intense absorptions at 1640 cm^{-1}, while the ν_sCO_2 bands are located in the region 1560 to 1400 cm^{-1}. These data, like those obtained from the spectrum of $TaOCl(OAc)_2\cdot\gamma$-pic (Table I), are in agreement with bridging or chelating behaviour of the carboxylato ligand, but exclude monodentate coordination. Moreover, the presence in the spectra of the acetato derivative of a strong, sharp absorption at 860 cm^{-1} can be attributed to a terminal metal–oxo bond.

The IR of $Ta_2Cl_2(O^tBu)_4$ presents a νTa–OR stretching at 545 cm^{-1}. The metal–chlorine absorptions are located as expected below 400 cm^{-1} for all compounds [11].

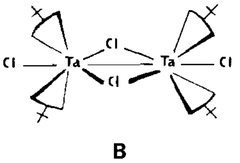
We were able to gain structural information by ^1H NMR as a result of the good solubility of all compounds, as of their diamagnetic character in the solid and in solution. This diamagnetism suggests the existence of at least dinuclear units for the tantalum(IV) and tantalum(III) derivatives.

The room temperature spectra of $Ta_2Cl_4(dpm)_4$ in CD_2Cl_2 (10^{-3} *M*) exhibit a single signal for the ^{t}Bu protons at 1.17 ppm and for the Hγ proton at 6.20 ppm. They are independent of the dilution (10^{-2} to 10^{-3} *M*) and of the temperature to –90 °C. These data are compatible with the presence of a single molecular species, in which the butyl groups are equivalent; structure A (the metal being at least heptacoordinated – depending on the presence or not of metal–metal bonding) seems the most likely.

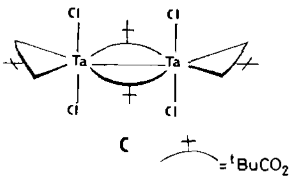


A

The spectra of $Ta_2Cl_4(O_2C^tBu)_4$, 2^tBuCO_2H (10^{-3} *M* in $CDCl_3$) show several peaks (δ = 1.30, 1.25, 1.22 and 1.16 ppm) for the butyl groups, even at room temperature. The presence of free pivalic acid (δ^tBu = 1.16 ppm) is pointed out by the presence of a hydroxyl group at 12.8 ppm (–65 °C). The integration ratios of the ^{t}Bu groups corresponding to free and coordinated carboxylic acid confirmed the proposed formula. Dilution experiments show that the resonances at 1.30 and 1.25 ppm always remain of comparable area, while the peak at 1.22 ppm varies independently. These data suggest that two tantalum molecular species are present in solution. The IR data are in favour of bidentate pivalato groups, and two geometrical isomers (B or C) are possible for $Ta_2Cl_4(O_2C^tBu)_4$.



B



C

It seems likely that the single peak at 1.22 ppm (about 80% of the total area of the pivalato groups) would correspond to isomer B (same basic skeleton as for $Ta_2Cl_4(dpm)_4$), having magnetically equivalent butyl groups; the two other singlets can probably be attributed to isomer C. The spectra are a function of the temperature, and coalescence of all ^{t}Bu signals is observed at temperatures above 60 °C.

The spectra of $Ta_2Cl_2(O^tBu)_4$ in CD_2Cl_2 are independent of the dilution and of the temperature, and only one sharp signal (located at 1.22 ppm) was detected down to –90 °C. This suggests that the butoxo groups have magnetically equivalent environments, or are rapidly exchanging their positions. Dinuclear units (eclipsed or staggered) [12] or tetranuclear units are compatible with the diamagnetism and the NMR data. The highest peak observed in the mass spectrum corresponds to $Ta_2Cl_2(O^tBu)_3(OMe)$, and no information about the degree of association in solution could be obtained by osmometry or cryometry.

Metal alkoxides tend to undergo oligomerisation consistent with the attainment of the favoured coordination number of the metal [13]. Tetranuclear alkoxides, as illustrated for instance by $W_4(OEt)_{16}$ [14] $Mo_4F_4(O^tBu)_8$ [15] or $V_4Cl_4(OMe)_8$ [16], are commonly found among metals in low oxidation states. Thus we favour a tetranuclear structure of the tantalum(III) alkoxide, which would result in the pentacoordination of the metallic center. X-ray studies are required to determine its structure more precisely. Indeed, various cluster arrangements [18] with extended metal–metal bonding or structures, resulting from the association of two doubly metal bonded dimers through bridging ligands [15] can be considered.

Experimental

All the manipulations were carried out under dry argon using Schlenk tubes or vacuum line techniques. The solvents were purified by standard methods and carefully deoxygenated. The γ-picoline and glacial acetic acid were distilled over CaH_2 and P_2O_5 respectively. LiO^tBu was synthesized as reported [19] and the other reactants were commercial products. Infra-red spectra were recorded as Nujol mulls on a Perkin Elmer 577 spectrometer. NMR spectra were recorded on a Bruker WH-90 spectrometer operating in the Fourier transform mode. The elemental analyses were performed by the Centre de Microanalyses of the C.N.R.S.

Synthesis of $Ta_2Cl_6(\gamma\text{-pic})_4$

A solution of 0.61 ml (6.2 mmol) of γ-picoline in 10 ml CH_2Cl_2 was added to a suspension of 640 mg (1.78 mmol) $TaCl_5$ and 172 mg (26.6 mmol) of magnesium turnings in 15 ml CH_2Cl_2 at room temperature. After 24 h a brown-red suspension was obtained. The magnesium derivatives were removed by filtration and carefully discarded with about 60 ml of a solution of CH_2Cl_2 with 1% γ-picoline. The filtrate was concentrated to about 10 ml and crystallisation was induced by adding ligroin. After storing at −30 °C for 3 days, 465 mg (0.49 mmol) of $Ta_2Cl_6(\gamma\text{-pic})_4$ in the form of a brown-red powder were isolated by filtration and vacuum dried.

By evaporation to dryness, a more stable adduct, $Ta_2Cl_6(\gamma\text{-pic})_4x\text{pic}$ ($x = 0$ to 3, depending on the drying conditions; $x = 0$ for 1 day at 65 °C and 10^{-5} mm Hg) was obtained.

The products were sometimes contaminated by traces of picolinium hydrochloride, which was eliminated by sublimation (65 °C, 10^{-5} mm Hg). They were slightly soluble in toluene and chlorobenzene, more soluble in dichloromethane or acetonitrile.

Synthesis of $Ta_2Br_6(\gamma\text{-pic})_4$

A similar procedure applied to $TaBr_5$ (1.56 g, 2.70 mmol), γ-picoline (0.92 ml, 9.45 mmol), Mg turnings (262 mg) in 45 ml CH_2Cl_2, and after a 36 h reaction time led to the isolation of 675 mg (41%) of $Ta_2Br_6(\gamma\text{-pic})_4$ as a brown powder, less soluble than the chloride adduct.

Synthesis of $Ta_2Cl_4(dpm)_4$

0.74 ml (3.56 mmol) of dipivaloylmethane were added to a solution of 0.85 g (0.74 mmol) of $Ta_2Cl_6(\gamma\text{-pic})_4$ in 30 ml CH_2Cl_2 at room temperature. Stirring was maintained for 3 days and the dark orange solution was then evaporated to dryness. The residue was washed twice by 60 ml hexane and the picolinium hydrochloride removed by sublimation (65 °C, 10^{-4} mm Hg). Finally 0.59 g (about 65%) of $Ta_2Cl_4(dpm)_4$, as a brown powder, soluble in toluene CH_2Cl_2, MeCN were obtained.

Synthesis of $Ta_2Cl_4(^tBuCO_2)_4$, 2^tBuCO_2H

A solution of pivalic acid (0.21 g, 2.06 mmol) in 10 ml CH_2Cl_2 was added dropwise to a solution of $Ta_2Cl_6(\gamma\text{-pic})_4$ (0.46 g, 0.40 mmol) in 20 ml CH_2Cl_2 at room temperature. After 16 h stirring, the solution was evaporated to dryness and the picolinium hydrochloride removed by high vacuum sublimation. 0.36 g (81%) of a cream powder of $Ta_2Cl_4(^tBuCO_2)_4$, 2^tBuCO_2H, highly soluble in CH_2Cl_2, $CHCl_3$ or CH_3CN, were obtained.

Synthesis of $TaOCl(OAc)_2\cdot\gamma\text{-pic}$

Glacial acetic acid (1 ml, 15.87 mmol) was added dropwise to a solution of $Ta_2Cl_6(\gamma\text{-pic})_4$ (1.16 g, 1.22 mmol) in solution in 50 ml toluene at room temperature. Stirring was maintained for 15 h and a brown precipitate formed. Precipitation was achieved by adding 0.5 ml more glacial acetic acid and by stirring 1 h longer. A microcrystalline brown powder was separated by filtration and vacuum-dried. The picolinium hydrochloride was eliminated by sublimation (about 12 h at 65 °C and 10^{-4} mm Hg). After sublimation, the compound was dissolved in acetonitrile and precipitated by adding toluene. Finally, 565 mg (52%) of a light brown powder, only slightly soluble in the common solvents, were obtained.

Synthesis of $Ta_2Cl_2(O^tBu)_4$

5.8 ml of a solution of LiO^tBu (0.67 *M*) in hexane were added to a suspension of $Ta_2Cl_6(\gamma\text{-pic})_4$ (0.61 g, 0.61 mmol) in 40 ml toluene at room temperature. After 16 h reaction, the reaction mixture was filtered and the filtrate evaporated to dryness. The residue was extracted several times with hexane and the precipitate was dried. 0.175 g (40%) of $Ta_2Cl_2(O^tBu)_4$ in the form of a cream powder, slightly soluble in toluene, more soluble in CH_2Cl_2 or $CHCl_3$, was obtained.

Acknowledgements

Thanks are expressed to Professor J. G. Riess for financial support, and to Mr B. Septe for measuring the NMR spectra.

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