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# Synthesis and Characterisation of Niobium and Tantalum Crown Ether Complexes

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*The ability of various crown-ethers L (dibenzo-18-crown-6, 18-crown-6 and 15-crown-5) to coordinate and reduce niobium and tantalum pentachlorides has been explored. Compounds of different stoichiometries, such as* $(NbCl_5)_2 \cdot L$ *(L = DBC, 18-CRW-6, 15-CRW-5),* $NbCl_5 \cdot L$ *(L = DBC, 18-CRW-6),* $(NbCl_4)_2$*(15-CRW-5),* $(NbCl_4)_3 \cdot L_2$ *(L = 18-CRW-6, 15-CRW-5) and* $(TaCl_5)_2$*(DBC);* $TaCl_5$*(15-CRW-5),* $(TaCl_4)_2$*(18-CRW-6), were isolated and characterized by elemental analysis, magnetic susceptibility measurements, infra-red and nmr spectroscopy. The proton nmr data were tentatively interpreted to mean that disproportionation reactions, leading to mono and polynuclear species having various ligand to metal ratios, occur in solution.*

## Introduction

Macrocyclic polyethers have been used primarily for selective complexation of alkali metal and alkaline earth-metal cations [1], but little attention has been given to their ability to complex transition metal derivatives [2, 3]. Although the main available structural X-ray data are those obtained for alkali, alkaline earth-metal [4] or uranyl [5] complexes, these macrocyclic ethers seem to be able to form complexes displaying a large structural variety depending on the ligand conformation, $D_{3d}$ [4] or $C_2$ [6], exo or endo, the number and the nature of the donor sites, oxygen atoms or $\pi$-system [7] for benzenic derivatives, and the stoechiometry (molar ratio R = L/M) of the complex. 'Sandwich' (R = 2) or 'club sandwich' (R = 3/2) complexes or compounds in which the ligand is bridging (R = 0.5) have been described.

As a part of a project concerning the obtention of reduced, but still molecular, niobium and tantalum adducts [8], we have investigated the ability of crown ethers to coordinate and reduce niobium and tantalum pentachlorides. Complexes between niobium and tantalum penta or tetrachlorides and aliphatic ethers are known [9], and it was anticipated that upon complexation, the crown ethers would impose unusual coordination properties and help avoid extensive metal–metal bond formation, thus reducing the formation of insoluble clusters for these metals in the low oxidation states. Crown ethers having varying cavity size and flexibility, such as 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene ($C_{20}H_{24}O_6$: dibenzo-18-crown-6, DBC (≅2.9 Å), 1,4,7,10,13,16-hexaoxacyclooctadecane ($C_{12}H_{24}O_6$ = 18-CRW-6 (≅2.6 Å) and 1,4,7,10,13-pentaoxacyclopentadecane ($C_{10}H_{20}O_5$ = 15-CRW-5) (2.2 to 1.7 Å) were tested for this purpose. Compounds of different stoichiometries (R = L/M = 0.5, 1 or 2/3) such as $Nb_2Cl_{10} \cdot L$ (L = DBC, 18-CRW-6, 15-CRW-5); $NbCl_5 \cdot L$ (L = DBC, 18-CRW-6); $Nb_2Cl_8 \cdot$(15-CRW-5); $(NbCl_4)_3 \cdot L_2$ (L = 18-CRW-6, 15-CRW-5) and $Ta_2Cl_{10}$(DBC), $TaCl_5$(15-CRW-5), $Ta_2Cl_8$(18-CRW-6) were isolated and characterized by elemental analysis, infra-red and n.m.r. spectroscopy and magnetic susceptibility measurements.

## Results and Discussion

The reactions between niobium and tantalum pentachlorides and the macrocyclic crown ethers: dibenzo 18-crown-6, 18-crown-6 and 15-crown-5 were carried out in non-complexing solvents such as methylene chloride or carbon tetrachloride, the molar R = L/M ratio being 0.5 or 1. An immediate reaction was evidenced by the obtention of highly coloured solutions (probably due to transfer absorptions around 300 nm), from which crystalline compounds of various stoichiometries were isolated in good yields (70–98%). Scheme 1 summarizes the various synthetic routes used for the niobium derivatives.

Compounds $Nb_2Cl_{10} \cdot L$ (L = DBC, 18-CRW-6, 15-CRW-5); $NbCl_5 \cdot L$ (L = DBC, 18-CRW-6), $(NbCl_4)_2$(15-CRW-5); $(NbCl_4)_3 \cdot L_2$ (L = 18-CRW-6, 15-CRW-5) and $Ta_2Cl_{10}$(DBC), $TaCl_5$(15-CRW-5), $(TaCl_4)_2$(18-CRW-6), the composition of which was attested by elemental analysis (Table I), were isolated.

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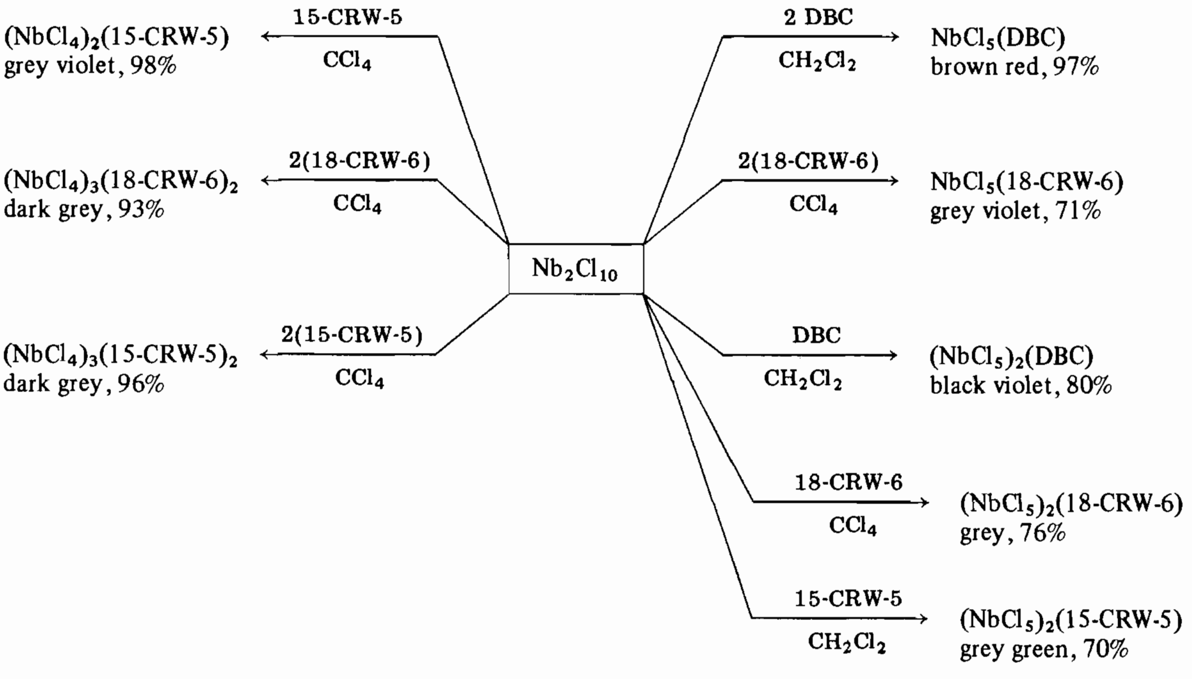
TABLE I. Analytical Data for Niobium and Tantalum Crown-ether Complexes.

| Compound | Color | Melting Point (°C) | Found (Calcd) % | | |
|---|---|---|---|---|---|
| | | | C | H | Cl |
| $Nb_2Cl_{10}$(DBC) | black-brown | 127 | 26.85(26.67) | 2.85(2.68) | 39.45(39.36) |
| $NbCl_5$(DBC) | dark red | 84 | 37.94(38.09) | 4.03(3.84) | 28.14(28.11) |
| $Nb_2Cl_{10}$(18-CRW-6) | light grey | – | 17.30(17.96) | 3.03(3.00) | 42.77(44.06) |
| $NbCl_5$(18-CRW-6) | light grey | 132 | 26.08(26.97) | 4.54(4.53) | 33.12(33.16) |
| $(NbCl_4)_3$(18-CRW-6)$_2$ | dark grey | 177 | 23.51(23.38) | 3.67(3.27) | 33.56(34.51) |
| $Nb_2Cl_{10}$(15-CRW-5) | grey-green | 164 | 15.92(15.79) | 2.62(2.65) | 46.67(46.61) |
| $(NbCl_4)_2$(15-CRW-5) | grey-brown | 127 | 17.64(17.16) | 2.98(2.92) | 40.70(41.12) |
| $(NbCl_4)_3$(15-CRW-5)$_2$ | dark grey | 100 dec. | 20.13(20.99) | 3.23(3.52) | 36.85(37.17) |
| $Ta_2Cl_{10}$(DBC) | dark red | 230 dec. | 22.16(22.31) | 2.31(2.25) | 32.63(32.93) |
| $TaCl_5$(15-CRW-5) | grey violet | 117 dec. | 20.87(20.76) | 3.36(3.48) | 29.28(30.64) |
| $(TaCl_4)_2$(18-CRW-6) | brown | 131 | 16.23(15.84) | 2.77(2.65) | 31.76(31.17) |

*Scheme 1: Synthesis of niobium crown-ether complexes (all reactions at room temperature)*



In the absence of well-formed single crystals suited for X-ray studies, structural information was obtained on the solid state by IR spectroscopy and magnetic susceptibility measurements, and in solution using proton n.m.r., molecular weight and conductivity data. However, the poor solubility of the various products limited the study to their behaviour in polar solvents (acetonitrile or nitromethane).

To start with, evidence for an interaction between the metal and the crown ether was obtained from the infra-red spectra measured on the solid state. With respect to the free ligand, the $\nu_a$(C–O–C) bands are shifted to lower frequency by a maximum of 60 cm$^{-1}$ (Table II), but these shifts vary with the ligand and increase from dibenzo-18-crown-6 to the 15-crown-5. The relatively small shift (20 cm$^{-1}$ max.)

TABLE II. Ir Data for Niobium and Tantalum Crown-ether Complexes (Nujol mulls).[a]

| Compound | $\nu_{as}$ C–O Stretching | $\nu$ M–Cl Stretching |
|---|---|---|
| $Nb_2Cl_{10}$(DBC) | 1135 sh, 1125 m, 1105 m | 360 s, 380 sh |
| $NbCl_5$(DBC) | 1130 m, 1105 m | 355 sh, 330 s |
| $Nb_2Cl_{10}$(18-CRW-6) | 1105 sh, 1090 m, 1070 sh | 350 sh, 325 s, 300 sh |
| $NbCl_5$(18-CRW-6) | 1110 sh, 1090 s, 1075 sh | 330 s |
| $(NbCl_4)_3$(18-CRW-6)$_2$ | 1115 sh, 1090 s, 1075 sh | 350 sh, 330 s, 275 sh |
| $Nb_2Cl_{10}$(15-CRW-5) | 1120 m, 1095 s, 1080 sh | 355 sh, 335 s |
| $(NbCl_4)_2$(15-CRW-5) | 1115 sh, 1100 m, 1085 s, 1065 w | 325 s, 275 sh |
| $(NbCl_4)_3$(15-CRW-5)$_2$ | 1105 sh, 1087 m, 1075 sh | 330 s, 275 w |
| $Ta_2Cl_{10}$(DBC) | 1135 sh, 1125 m | 340 s, 365 sh, 295 m |
| $(TaCl_4)_2$(18-CRW-6) | 1105 sh, 1095 s, 1075 sh | 380 sh, 320 s |
| $TaCl_5$(15-CRW-5) | 1100 s, 1095 s, 1075 sh | 330 sh, 315 s, 290 sh |

[a] The $\nu_{as}$C–O absorptions for the free ligands are observed respectively at 1130 cm$^{-1}$ (DBC), 1105 cm$^{-1}$ (18-CRW-6) and 1125 (15-CRW-5) (s = strong, m = medium, w = weak, sh = shoulder).

measured for the dibenzo-crown complexes suggests weak metal–oxygen interaction. The presence, in all the compounds, of a shoulder near the $\nu$CO stretch of the free ligand is consistent with the hypothesis that the metal interacts strongly with only a few oxygen atoms of the polyether, leaving the others essentially unaffected. The spectra of the 18-CRW-6 and 15-CRW-5 complexes show numerous sharp bands in the 1000–800 cm$^{-1}$ region ($CH_2$ modes), suggesting that several types of $OCH_2CH_2$ monomer units are present [10], but the ligand conformation could not be further elucidated. Metal–chlorine stretching absorptions [11] are found as expected between 380 and 275 cm$^{-1}$.

Niobium and tantalum(V) adducts present an overall stoichiometry of $MCl_5 \cdot L_{0.5}$ or $MCl_5 \cdot L$ (L = crown-ether). Molecular weight data in acetonitrile establish a dimeric structure for the species $(MCl_5 \cdot L_{0.5})_2$ and the monomeric nature of the $NbCl_5 \cdot L$ adducts, while the low conductivity of these solutions excludes ionic formulations such as $[NbCl_4 \cdot L]^+$ $[NbCl_6^-]$ or $[NbCl_4 \cdot L]^+ \cdot Cl^-$. Thus, contrary to previously described transition metal crown-ether derivatives [$(CoCl_2)_2$(dicyclohexyl-18-crown-6) [3] which were found to be ionic, the adducts $M_2Cl_{10} \cdot L$ and $MCl_5 \cdot L$ correspond to neutral molecular species.

On the other hand, reduced compounds having stoichiometries $MCl_4 \cdot L_{0.5}$ and $(NbCl_4)_3L_2$ were also isolated. The reducing ability of the crown-ethers with respect to the niobium and tantalum pentachlorides generally shows up when the molar ratio R is higher than 0.5, and with the flexible crown-ether 18-CRW-6 and 15-CRW-5, but no influence of the solvent was observed. It must be noted that an adduct $(UCl_4)_3 \cdot$(18-CRW-6)$_2$ has recently been obtained by allowing $UCl_4$ to react with various amounts of the crown ether [6]. Magnetic susceptibility measurements on the solid state established the diamagnetic character for all formally niobium(IV) or tantalum(IV) adducts, suggesting strong metal–metal interactions [12] and thus at least dimeric structures. The instability of the compounds $(MCl_4)_2 \cdot L$ and $(NbCl_4)_3 \cdot L_2$ in acetonitrile solutions, however, prevented the measurement of the molecular weight data by vapour pressure osmometry.

Although O-desalkylation of aliphatic ethers (isopropylether, trioxane, dimethoxyethane) by early transition metal halogenides [13], and especially by $TaCl_5$ [14], have been reported, no side products such as methylchloride or hydrochloric acid could be detected in our case during the monitoring by n.m.r. of the various reactions between the niobium and tantalum pentachlorides and the crown ethers. Moreover, no absorptions which could be assigned to metal–alkoxo vibrations [15] were found in the infra-red of the isolated complexes. The high yields in which the various compounds have been isolated also show that the degradation of the ligand is limited, if it occurs at all.

Table III summarises the proton n.m.r. data. The poor solubility of the isolated DBC complexes in non-polar media and the decomposition reactions occurring in complexing solvents (THF, $Me_2CO$) as a result of a lesser basicity of the oxygen attached to an aryl group, prevented their characterisation by n.m.r. However, spectra recorded after mixing the

TABLE III. Nmr Data on Crown-ether Complexes.[a]

| Compound | $CH_2$–O Resonances (δ in ppm) |
|---|---|
| 18-CRW-6 | 3.51 |
| $(NbCl_5)_2$(18-CRW-6) | 5.24*, 4.51*, 3.71, 3.60 |
| $NbCl_5$(18-CRW-6) | – – 3.70, 3.61, 3.58 |
| $(NbCl_4)_3$(18-CRW-6)$_2$ | 5.25*, 4.60*, 3.71, 3.60, 3.57 |
| $(TaCl_4)_2$(18-CRW-6) | 5.34*, 4.58*, 3.70, 3.60 |
| | |
| 15-CRW-5 | 3.57 |
| $(NbCl_5)_2$(15-CRW-5) | 5.24*, 4.52*, 3.71, 3.66, 3.64 |
| $(NbCl_4)_2$(15-CRW-5) | 5.25*, 4.53*, 3.72, 3.61, 3.60 |
| $(NbCl_4)_3$(15-CRW-5)$_2$ | 5.24*, 4.51*, 3.68, 3.60 |
| $TaCl_5$(15-CRW-5) | 5.24*, 4.62*, 3.64 |

[a] All spectra have been registered in $CD_3CN$ ($\cong 10^{-2}$ molar) at room temperature. *multiplets (A and B) centered at approximately.

reactants (R = 0.5 or 1) show that niobium and tantalum dibenzo-18-crown-6 complexes have a pattern similar to those of the free ligand, but with their resonances shifted downfield. The fact that all the $OCH_2$ resonances are shifted by the same amount (about 0.15 ppm) suggests that the $MCl_5$ moieties (M = Nb or Ta) undergo rapid exchange among the various available oxygen coordination sites of the polyether, as was also noted for the $Nb_2Cl_{10}(S_4\text{-Et-pr})$ ($S_4$-Et-pr [14] = 1,4,8,11-tetrathiocyclotetradecane $C_{10}H_{20}S_4$) adduct [16].

The spectra of the 18-CRW-6 and 15-CRW-5 niobium complexes in acetonitrile solutions ($\sim 10^{-2}$ molar) generally present two sets of resonances. Already at room temperature, a complex pattern, consisting in two multiplets A and B (see for instance Fig. 1) is detected at low field (maximum shift of 1.9 ppm from the free ligand), in addition to several singlets, which are only slightly shifted downfield. The relative areas of the various resonances depend to a small extent on the temperature (between –40 and 80°) and on the addition of an excess of ligand, which means that several molecular species are present. No free ligand was ever detected. It is striking that the spectra obtained for the various isolated complexes were so similar in their chemical shifts, despite their different stoichiometries and oxidation states.

N.m.r. data on metal complexes with 18-CRW-6 and 15-CRW-5 are rather scarce [17], and information on the ligand conformation is only available for benzocrown-ethers [18]. The 18-CRW-6 and 15-CRW-5 ligands are sufficiently flexible to adopt several easily interconvertible conformations and only one resonance was detected down to –130° [19]. Among the possible conformations, those having all $OCH_2CH_2$ units gauche have been calculated to be more stable by *ca.* 1.7 kJ mol$^{-1}$ [20]. The well-known alkali metal crown complexes [4] all display $D_{3d}$ symmetry for the ligand in the solid, but a $C_2$ symmetry has been established recently for the 18-CRW-6 crown coordinated to the $UCl_3^+$ ion [6]. The occurrence of this new conformation for the coordinated 18-CRW-6 demonstrates once more the versatility of this ligand in adopting various shapes, and thus the ligand conformation may change from one complex to the other and be different from that in the free state.

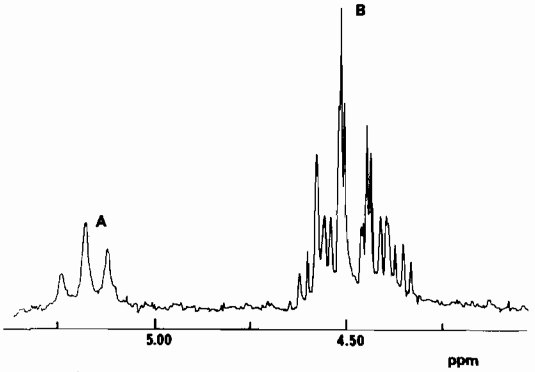
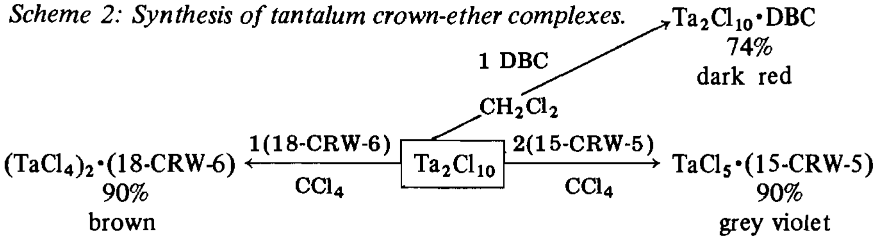


Fig. 1. $^1H$ n.m.r. spectra of a 0.01 molar solution of $(NbCl_5)_2$18-CRW-6 in $CD_3CN$ at room temperature (multiplets A and B only are presented).

In our case, evidence for more than one species, but no free ligand, was found when isolated complexes of any stoichiometry are dissolved in acetonitrile. On the other hand, early transition metals such as niobium or tantalum can easily display coordination numbers greater than six [9]. The fact that the spectra recorded on acetonitrile solutions of complexes of various stoichiometries and oxidation states display numerous resonances having similar chemical shifts, but different relative areas, might mean that disproportionation reactions leading to species having various ligand to metal ratios occur. Such behavior has been recognized to be common in early transition metal adducts in solution [21]. The role of acetonitrile, which is also a ligand for the niobium and tantalum halides [9], could not be defined precisely because of the insolubility of the compounds in non-polar solvents. Although crown ethers can incorporate metal derivatives and not only bare ions, the niobium and tantalum moieties would probably be outside the plane of the macrocycle's cavity. Thus, the sharp singlets (all $CH_2$ equivalents) are tentatively attributed to species in which the ligand adopts a flexible conformation, the metallic moiety scrambling rapidly among the several oxygen atoms. The less shielded singlet was tentatively assigned to a species of $(NbCl_5)_2 \cdot L$ stoichiometry, since its area decreases on addition of an excess of free ligand. The ligand would be bridging in $(NbCl_5)_2 \cdot L$, as it is recognized to be for the sulfur macrocycle in the $(NbCl_5)_2(S_4\text{-Et-Pr})$ [14] adduct in both the solid state and in solution (one singlet in the n.m.r.). A monodentate, bidentate or bridging behavior of the macrocycle would probably account for the equivalence of the $OCH_2$ groups observed in the proton n.m.r.

The two multiplets A and B generally correspond to more than 40% of the overall spectra and their relative area (B:A) is variable (but around 3); they were thus attributed to at least two molecular species but no additional information could so far be gained from their analysis (even by homonuclear decoupling experiments). In these species, the ligand seems to interact strongly with the metal (important downfield shift) and would keep a rigid but nearly symmetrical and apparently gauche conformation ('apparent' coupling constant = 5.4 Hz for multiplet A [18, 2]. A rigid ligand conformation can probably be attained in mononuclear species in which the metal interacts with more than 2 donor atoms or in polynuclear species having sandwich-like structures [2]. Such a structure could for instance account for the $(NbCl_4)_3 \cdot L_2$ stoichiometry. The formation of species in which the crown ether interacts strongly with the metallic centre is also consistent with the fact that the ligand could not be totally recovered by exchange between, for instance, $(NbCl_4)_3(18\text{-CRW-6})_2$ and KCl in acetonitrile solutions at room temperature.

*Scheme 2: Synthesis of tantalum crown-ether complexes.*



In such compounds the exchange between the coordination sites and/or the interconversion among the various species are slow on the n.m.r. time-scale, since no coalescence between the multiplets was observed up to 80 °C.

## Experimental

All the handling was achieved under dry argon using Schlenk tubes or vacuum line techniques. Solvents were purified by standard methods [24] and carefully deoxygenated by purging with argon for several hours. Niobium pentachloride was prepared by chlorination of the metal (gift from Péchiney Ugine Kuhlmann [9]). 15-CRW-5 was prepared as described in the literature [25].

Infra-red spectra were recorded as Nujol mulls on a Perkin-Elmer 577 spectrometer. N.m.r. spectra were recorded on a WH-90 Bruker spectrometer operating in the Fourier transform mode. Molecular weight data were obtained on a Knauer vapour pressure osmometer. The conductivity measurements were performed on a Tacussel CND 6 conductimeter. The UV spectra were obtained on a Cary 118 spectrometer. Magnetic susceptibilities were determined by the Faraday technique using a Cahn RH electrobalance and a Drush magnet calibrated with $HgCo(SCN)_4$. The elemental analyses were obtained from the Centre de Microanalyse of the CNRS, and are reported in Table I.

A typical procedure for the synthesis of the different crown complexes is the following.

### *(18 crown-6)*$Nb_2Cl_{10}$

( 18-crown-6 (0.308 g, 1.16 mmol) in 11 ml of $CCl_4$ was added dropwise to a suspension of $NbCl_5$ (0.605 g, 2.23 mmol) in 20 ml of $CCl_4$ at room temperature. The mixture was stirred for about 120 mn and a precipitate was obtained. The reaction mixture was kept at $-10°$ overnight. The precipitate was removed by filtration. 0.69 g (76%) of a light grey product, slightly soluble in $CH_3NO_2$, $CH_2Cl_2$ and THF, and more soluble in $CH_3CN$, was obtained.

Similar procedures, collected in Scheme 2, were used for the tantalum derivatives.

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