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Studies on the reactivity of alkoxo-niobium(V) compounds towards *O*,*O*- or *S*,*S*-enolate ligands. Synthesis and structural characterisation of (alkoxo)(β-diketonato)- and (alkoxo)[dialkyl(aryl)dithiocarbamato] complexes of niobium(V)

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Abstract

Reaction of the alkoxo-containing niobium complexes $[NbCl_3(OR)_2]_2$ (R = Me, Et, ^{i}Pr) with β-diketones $R'COCH_2COR'$ [R′ = Me (Hacac); R′ = ^{t}Bu (Hdpm); R′ = Ph (Hdbm)] in a 1:2 molar ratio, afforded the corresponding (alkoxo)(β-diketonato) complexes $[NbCl_2(OR)_2$(*O*,*O*′-R′COCHCOR′)] (R = Me, R′ = Me **1**; R = Et, R′ = Me **2**; R = ^{i}Pr, R′ = Me **3**; R = Me, R′ = ^{t}Bu **4**; R = Et, R′ = ^{t}Bu **5**; R = ^{i}Pr, R′ = ^{t}Bu **6**; R = Me, R′ = Ph **7**; R = Et, R′ = Ph **8**; R = ^{i}Pr, R′ = Ph **9**). The molecular structure of **8** was elucidated by an X-ray diffraction study. The kinetics of the displacement reaction of **5** and **8** with Hacac to give complex **2** and the corresponding β-diketone Hdpm or Hdbm have also been studied by ^{1}H-NMR spectroscopy. Finally, the complexes $[NbCl_3(OR)_2]_2$ reacted with reagents of the type $Na(S_2CNR'_2)$, in a 1:4 molar ratio, to give the corresponding (alkoxo)[dialkyl(aryl)dithiocarbamato] complexes $[NbCl(OR)_2$(*S*,*S*′-S_2CNR')$_2]$ (R = Me, R′ = Me **10**; R = Me, R′ = Et **11**; R = Me, R′ = Bz **12**; R = Et, R′ = Me **13**; R = Et, R′ = Et **14**; R = Et, R′ = Bz **15**; R = ^{i}Pr, R′ = Me **16**; R = ^{i}Pr, R′ = Et **17**; R = ^{i}Pr, R′ = Bz **18**). All complexes were characterised spectroscopically. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkoxy; Niobium; Enolate ligands; Dithiocarbamate

1. Introduction

Alkoxide compounds of a wide variety of elements have been extensively investigated [1] often because they can be used as precursor compounds for solving technical materials-related problems [2]. With respect to the Group 5 metals, this class of complex especially those of the elements Nb and Ta, have been known for many years [1,3]. Ten years ago, some of us reported [4] a general method for the preparation of alkoxoniobium(V) derivatives of the type $NbCl_{5-x}(OR)_x$ by reaction of $NbCl_5$ with the appropriate Me_3SiOR reagents. At present we are interested in the study of the reactivity of these complexes towards *O*,*O*′- or *S*,*S*′-chelate ligands, namely β-diketonate or dialkyl(aryl)dithiocarbamato anions, in order to prepare new families of alkoxo-containing niobium(V) derivatives. Several β-diketonato-containing niobium complexes have been previously described [5], and in some cases one alkoxide is also present as an ancillary ligand in the coordination sphere of the niobium centre. Examples of such complexes include $[Nb(OR)_{5-x}(acac)_x]$ [6] and $[Nb(OR)_{5-x}(dbm)_x]$ [7], although few X-ray crystal structures have been determined. Furthermore, alkyl(aryl)-dithiocarbamato-containing metal complexes are well known [8]. For Group 5 metals, the most important family of this class of complex corresponds to the compounds of stoichiometry $ML(S_2CNR_2)_3$ (M = Nb or Ta; L = O, S, NR, S_2, N_2R_2 or RC≡CR′) [9]. The aim of this work was to investigate the synthesis and

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structural characterisation of new β-diketonato $[NbCl_2(OR)_2(O,O'\text{-}R'COCHCOR')]$ and dialkyl(aryl)dithiocarbamato $[NbCl(OR)_2(S,S'\text{-}S_2CNR'_2)_2]$ niobium complexes containing alkoxides as ancillary ligands.

2. Results and discussion

2.1. Preparation of the β-diketonato-containing niobium complexes

Firstly, we considered the reactivity of alkoxo-containing niobium complexes $[NbCl_3(OR)_2]_2$ towards some β-diketones, namely $MeCOCH_2COMe$ (Hacac), $^tBuCOCH_2CO^tBu$ (Hdpm), $PhCOCH_2COPh$ (Hdbm). The different complexes react at room temperature (r.t.) with the appropriate β-diketones in CH_2Cl_2 in a 1:2 molar ratio to give, after the appropriate work-up, the complexes $[NbCl_2(OR)_2(O,O'\text{-}R'COCHCOR')]$ (Eq. (1)). The different complexes were isolated in high yields as yellow moisture-sensitive solids (Section 3).

$$1/2[NbCl_3(OR)_2]_2 + R'COCH_2COR' \xrightarrow{-HCl} [NbCl_2(OR)_2(O,O'\text{-}R'COCHCOR')] \qquad (1)$$

1 R = Me, R′ = Me; **2** R = Et, R′ = Me;

3 R = ^{i}Pr, R′ = Me;

4 R = Me, R′ = ^{t}Bu; **5** R = Et, R′ = ^{t}Bu;

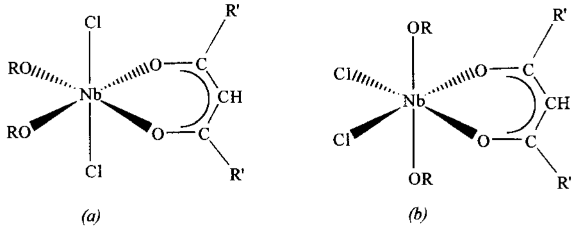
6 R = ^{i}Pr, R′ = ^{t}Bu;

7 R = Me, R′ = Ph; **8** R = Et, R′ = Ph;

9 R = ^{i}Pr, R′ = Ph.

The complexes are soluble in polar solvents such as dichloromethane, chloroform and acetone, but insoluble in alkanes.

Complexes **1**–**9** were characterised by standard spectroscopic techniques. Their IR spectra exhibit characteristic bands at ca. 1575 and 1520 cm^{-1}, corresponding to the $\nu(C\overset{\cdots}{-}C)$ and $\nu(C\overset{\cdots}{-}O)$ of a β-diketonate unit coordinated in a bidentate fashion. In addition, the bands corresponding to ν(Nb–Cl) appear at ca. 340 cm^{-1} (see Section 3). However, the NMR spectroscopy data are valuable in establishing the structure of the complexes. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra at r.t. show only one set of highly resolved resonances for the alkoxide groups, indicating that the units are equivalent. In addition, one set of resonances is also present for the alkyl (aryl) groups of the β-diketonate ligand (see Section 3). The spectroscopic results are in accordance with two symmetrical octahedral structures, as shown in Fig. 1, in which two chloride or, alternatively, two alkoxide ligands occupy two axial positions (Fig. 1(a) and (b), respectively).



(a) (b)

Fig. 1. Proposed structural dispositions for complexes **1**–**9**.

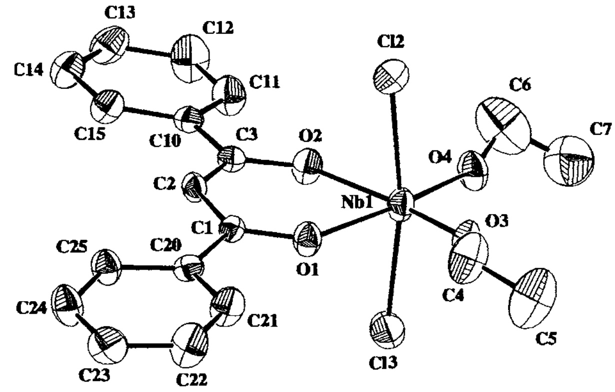


Fig. 2. ORTEP drawing of complex **8**.

It is noteworthy that at r.t. a static structure is present in complexes **1**–**9** with highly resolved resonances for the alkoxide groups. This is in contrast with the situation for the starting complexes $[NbCl_3(OR)_2]_2$ where fluxionality was observed, as indicated by the presence of broad and weak resonances, which renders the alkoxide groups equivalent [4]. The X-ray crystal structure determination for **8**, which is described in more detail below, indicates that Fig. 1(a), with the chloride ligands occupying axial positions, is most probably present in our complexes in the solid state. An ORTEP drawing of complex **8** is presented in Fig. 2 and selected bond lengths and angles are listed in Table 1.

Complex **8** crystallises in the monoclinic space group $P2_1/n$, with one molecule in the asymmetric unit cell, and can be described as a pseudooctahedral Nb(V) complex containing two *trans*-chloride ligands in the axial positions; in the equatorial plane are placed two *cis*-ethoxide ligands and a β-diketonate ligand.

The terminal alkoxides form a very strong bond to the metal [Nb–O distances are 1.804(5) and 1.809(5) Å] due to considerable π-interactions, evidence of which is provided by Nb–O–C angles [143.0(5) and 157.2(10)°]. The β-diketonate group is coordinated to the Nb centre through both oxygen atoms, forming a six-membered metallacycle. The metallacycle ring is reasonably planar [distances of the atoms from the plane defined by Nb(1), O(1), C(1), C(2), C(3) and O(2) are Nb(1), −0.0016(7); O(1), 0.051(4); C(1), 0.008(5); C(2), −0.082(6); C(3), −0.027(6); O(2), 0.077(5) Å] and the parameters within this ring suggest significant delocalization. As a result, both C–O distances [1.282(6) and 1.298(7) Å] [10] are intermediate between the single- and double-bonded extremes (1.43 and 1.23 Å, respectively [10]). Similarly, the C(1)–C(2) and C(2)–C(3) distances [1.386(8) and 1.378(8) Å] are intermediate between single and double bond distances involving sp^2 carbons (1.44 and 1.34 Å). Rings C(10)–C(15) and C(20)–C(25) are displaced slightly on opposite sides of the metallacycle plane, thereby minimising contacts between each other.

Table 1
Selected bonds lengths (Å) and angles (°) for **8**

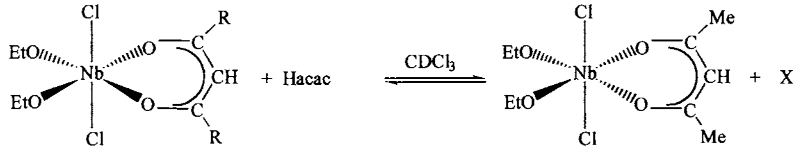
Nb(1)–O(4)	1.804(5)	O(2)–C(3)	1.298(7)
Nb(1)–O(3)	1.809(5)	C(1)–C(2)	1.386(8)
Nb(1)–O(2)	2.045(4)	C(2)–C(3)	1.378(8)
Nb(1)–O(1)	2.085(4)	O(3)–C(4)	1.465(10)
Nb(1)–Cl(3)	2.392(2)	C(4)–C(5)	1.335(14)
Nb(1)–Cl(2)	2.403(2)	O(4)–C(6)	1.462(18)
O(1)–C(1)	1.282(6)	C(6)–C(7)	1.34(3)
O(4)–Nb(1)–O(3)	100.7(2)	Cl(3)–Nb(1)–Cl(2)	170.23(8)
O(4)–Nb(1)–O(2)	92.9(2)	C(1)–O(1)–Nb(1)	134.8(4)
O(3)–Nb(1)–O(2)	165.67(19)	C(3)–O(2)–Nb(1)	135.7(4)
O(4)–Nb(1)–O(1)	172.6(2)	O(1)–C(1)–C(2)	122.5(5)
O(3)–Nb(1)–O(1)	86.66(18)	C(3)–C(2)–C(1)	124.3(5)
O(2)–Nb(1)–O(1)	79.72(16)	O(2)–C(3)–C(2)	122.1(5)
O(4)–Nb(1)–Cl(3)	92.20(18)	C(15)–C(10)–C(11)	118.2(6)
O(3)–Nb(1)–Cl(3)	96.39(17)	C(10)–C(15)–C(14)	120.8(6)
O(2)–Nb(1)–Cl(3)	87.39(15)	C(4)–O(3)–Nb(1)	143.0(5)
O(1)–Nb(1)–Cl(3)	87.09(14)	C(5)–C(4)–O(3)	115.2(9)
O(4)–Nb(1)–Cl(2)	92.80(18)	C(6)–O(4)–Nb(1)	157.2(10)
O(3)–Nb(1)–Cl(2)	90.92(16)	C(71)–C(6)–C(7)	46(3)
O(2)–Nb(1)–Cl(2)	83.98(15)	C(71)–C(6)–O(4)	118(3)
O(1)–Nb(1)–Cl(2)	86.88(14)	C(7)–C(6)–O(4)	109(2)

Table 2
Values of rate constant at 313 K, for different molar ratios [Hacac]/[**5**], in experiment 1

[Complex **5**] (M)	[Hacac] (M)	[Hacac]/[complex **5**]	$k_{app} \times 10^3$
0.09	0.09	1:1	0.7 ± 0.2
0.09	0.18	2:1	2.0 ± 0.2
0.09	0.36	4:1	3.1 ± 0.2
0.09	0.45	5:1	3.1 ± 0.2
0.09	0.63	7:1	3.1 ± 0.2

*2.2. Kinetic studies on the displacement reactions of **5** and **8** with Hacac*

The reactivity of complexes **5** and **8**, which bear the dpm and dbm β-diketonates respectively, towards the β-diketone Hacac in the corresponding exchange reactions has been studied. The reactions were monitored by ^{1}H-NMR spectroscopy. In fact, complexes **5** and **8** react with Hacac in $CDCl_3$ to afford the exchange product **2**, along with the free diketones Hdpm and Hdbm, respectively (Eq. (2)).



Experiment 1, R = ^{t}Bu, X =Hdpm

Experiment 2, R = Ph, X = Hdbm (2)

Kinetic studies on these exchange processes have been carried out by following the reactions as a function of time and temperature by ^{1}H-NMR spectroscopy. Several values of rate constant (Table 2), were obtained for different [Hacac]/[**5**] molar ratios at 20°C (see Section 3, experiment 1). A plot of these values versus the [Hacac]/[**5**] values is shown in Fig. 3.

We can observe in the Fig. 3 that, for molar ratios higher than 4:1, [Hacac]/[Nb complex], respectively, a negligible dependence on the rate constant can be considered. A possible mechanism for these processes, for these conditions of high [Hacac]/[Nb complex] molar ratios, is shown in Scheme 1 and this corresponds to a consecutive reaction with reversible step. The 'saturation' behaviour observed for the rate constant is typical of a pseudo-first-order dissociative process [11] and, as such, the formation of a pentacoordinated and electronically unsaturated species can be proposed as the rate-limiting step in these experimental conditions for the commented processes.

This observation agrees with the intermediate proposed in the isotopic interchange processes for tris-β

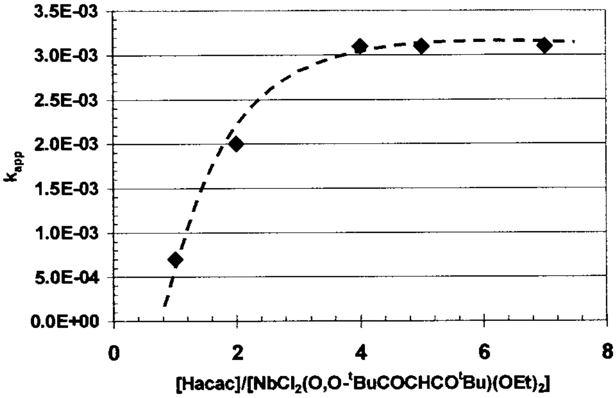
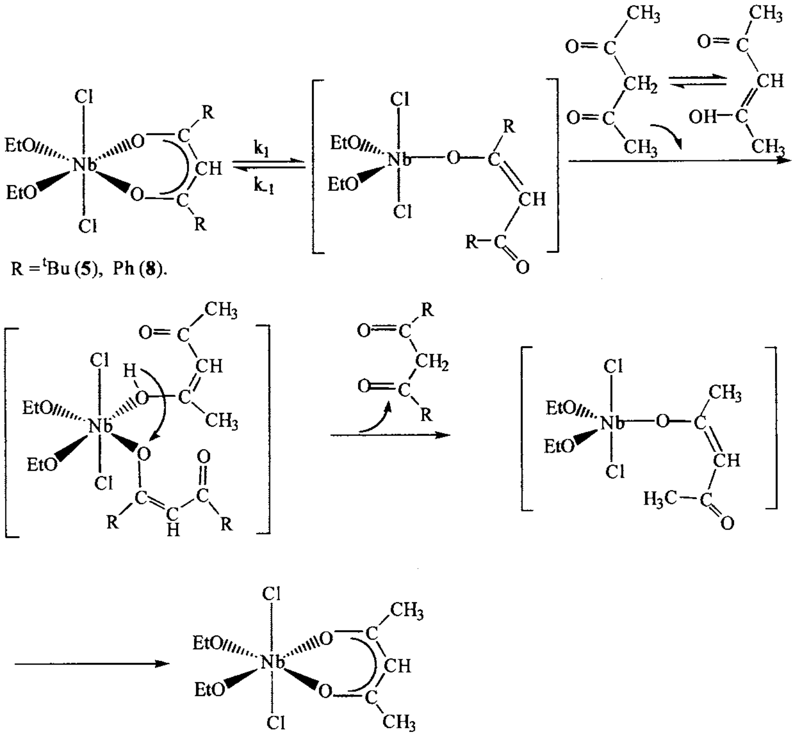


Fig. 3. Plot of k_{app} (s^{-1}) vs. [Hacac]/[**5**], in experiment 1.

diketonato derivatives of Group 13 elements [12]. Several irreversible steps, which correspond to the coordination of the Hacac, probably throughout the enol tautomer, which enhances its acidic character, and the de-coordination of the appropriate β-diketone (Hdpm or Hdbm) on the metal centre, can be considered in the proposed mechanism.

Activation parameters have been estimated from these studies. In order to optimise and simplify the experiments, they were carried out under the commented pseudo-first-order conditions with respect to the species **5** and **8**, using a high initial concentration of Hacac (see Section 3, experiments 1 and 2). Values of the apparent pseudo-first-order rate constants, k_{app}, at five temperature values were obtained for the two studied processes (Table 3).

The k_{app} values give a satisfactory fit to the Arrhenius plot, $k_{\mathrm{app}} = A\ \exp(-E_a/RT)$, and the E_a values for the different processes were calculated (Table 3). The Eyring plot, $\ln(k_{\mathrm{app}}/T)$ against $1/T$, $k_{\mathrm{app}} = (kT/h)\exp(-\Delta H^{\#}/RT)\exp(\Delta S^{\#}/R)$, gives the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ for the two processes (Table 3). The calculated E_a and $\Delta H^{\#}$ values are comparable to those previously described in the isotopic exchange processes for tris-β-diketonato derivatives of Group 13 elements [12]. The difference observed in the activation energy calculated in the two processes could be explained in terms of a more stable bonding between the dbm ligand and the niobium atom in complex **8**, throughout a delocalized π system implying the phenyl rings of the ligand, than in complex **5** with the dpm ligand.



Scheme 1. A possible mechanism on the displacement reactions of **5** and **8** with Hacac.

Table 3
Kinetic and thermodynamic parameters on the displacement reactions of **5** and **8** with Hacac

Experiment	$k_{\mathrm{app}} \times 10^3$ (s^{-1})	T (K)	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
1	0.3 ± 0.2	293	90.3 ± 0.1	87.8 ± 0.1	−11 ± 4
	0.6 ± 0.2	298			
	1.2 ± 0.2	303			
	2.1 ± 0.2	308			
	3.1 ± 0.2	313			
2	0.1 ± 0.2	293	105.5 ± 0.1	102.9 ± 0.1	31 ± 4
	0.2 ± 0.2	298			
	0.5 ± 0.2	303			
	0.9 ± 0.2	308			
	1.5 ± 0.2	313			

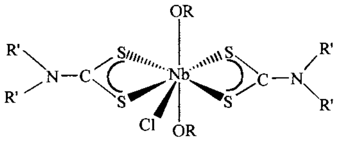


Fig. 4. Proposed structural disposition for complexes **10**–**18**.

In the course of these studies, we have observed that, for long reaction times, higher than 24 h, equilibrium was reached between reagents and products. Equilibrium constants at 20°C were calculated from the spectra (see Section 3). The obtained values, near 0.45 (Complex **5**: $K_{eq} = 0.44$; complex **8**: $K_{eq} = 0.46$), were similar for both niobium complexes, **5** and **8**, indicating that they exhibit similar stability with regard to complex **2**.

2.3. Preparation of dialkyl(aryl)dithiocarbamato-containing niobium complexes

The reactivity of our starting complexes $[NbCl_3(OR)_2]_2$ towards sodium dialkyl(aryl)dithiocarbamato salts, $Na(S_2CNR'_2)$, was considered. The study involved the addition of $Na(S_2CNR'_2)$ to a THF solution of the complex in a 1:4 molar ratio to give, after stirring for 20 h at 60°C, a solution from which the corresponding products were isolated, after appropriate work-up, as white crystalline air-stable solids $[NbCl(OR)_2(S,S'\text{-}S_2CNR'_2)_2]$ (**10**–**18**) (Eq. (3)). Complexes **10**, **11** and **12** have been described previously [13] and were obtained by reaction of $NbCl_5$ with the appropriate $Na(S_2CNR'_2)$ salt in methanol. The different complexes were isolated in high yields and are soluble in polar solvents, but insoluble in alkanes.

$$1/2[NbCl_3(OR)_2]_2 + 2Na(S_2CNR'_2) \rightarrow [NbCl(OR)_2(S_2CNR'_2)_2] + 2NaCl \qquad (3)$$

10 R = Me, R′ = Me; **11** R = Me, R′ = Et;

12 R = Me, R′ = Bz;

13 R = Et, R′ = Me; **14** R = Et, R′ = Et;

15 R = Et, R′ = Bz;

16 R = ^{i}Pr, R′ = Me; **17** R = ^{i}Pr, R′ = Et;

18 R = ^{i}Pr, R′ = Bz.

Complexes **10**–**18** were characterised spectroscopically. Their IR spectra show a characteristic band at ca. 990 cm^{-1}, corresponding to the ν(C$\underline{\cdots}$S) of a dithiocarbamato unit coordinated in a bidentate fashion [14], and another band at ca. 360 cm^{-1} for ν(Nb–Cl) (see Section 3). The complexes have also been characterised by NMR spectroscopy. ^{1}H- and ^{13}C{^{1}H}-NMR spectra at r.t. show only one set of resonances for the alkoxide groups as well as two sets of resonances for the alkyl(aryl) groups on the dithiocarbamate ligands (see Section 3). These data are in accordance with a pentagonal bipyramidal structure in the solid state, as shown in Fig. 4, where two dithiocarbamate ligands occupy four equatorial coordination sites and the alkoxide ligands two axial sites.

This bipyramidal disposition was previously found in the dialkyldithiocarbamato complexes $[Nb(RC{\equiv}CR')(S_2CNR''_2)_3]$ [15].

In conclusion, this study has revealed that the alkoxo-containing complexes $[NbCl_3OR)_2]_2$ react readily with β-diketones and sodium dialkyl(aryl)dithiocarbamato salts, giving rise to the β-diketonato and dialkyl(aryl)dithiocarbamato-containing niobium species, namely $[NbCl_2(OR)_2(O,O'\text{-}R'COCHCOR')]$ and $[NbCl(OR)_2(S,S'\text{-}S_2CNR'_2)_2]$. In addition, kinetic studies on the exchange processes with β-diketonato complexes have been considered. We believe that the results reported offer an advance in the chemistry of alkoxo-containing niobium complexes and further work in this field is ongoing.

3. Experimental

3.1. General

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin–Elmer 2400 CHN analyser. IR spectra were obtained in the 4000–200 cm^{-1} region, using a Perkin–Elmer 883 spectrophotometer. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Varian Unity FT-300 spectrometer and referenced to the residual deuterated solvent. The NMR probe temperatures were varied using an Oxford Instruments VTC 4 unit, measured by a thermocouple and calibrated with CH_3OH.

The complexes $[NbCl_3(OR)_2]_2$ (R = Me, Et, ^{i}Pr) were prepared as reported previously [4]. The β-diketones and the sodium dialkyldithiocarbamates were purchased from Fluka.

3.2. Preparation of [NbCl$_2$(OMe)$_2$(acac)] (1)

To a CH_2Cl_2 (50 cm^3) solution of $[NbCl_3(OMe)_2]_2$ (0.670 g, 1.28 mmol) was added Hacac (0.26 cm^3, 2.56 mmol). The suspension was stirred for 6 h at r.t. The solvent was removed under reduced pressure and a yellow solid was obtained. Yield 81%. Found: C, 25.87; H, 4.03. Anal. Calc. for $NbCl_2O_4C_7H_{13}$: C, 25.94; H, 4.00%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 5.97 (s, 1H, MeCO*CH*COMe), 2.16 (s, 6H, *Me*COCHCO*Me*), 4.60 (s, 6H, OMe). ^{13}C{^{1}H} ($CDCl_3$), δ 191.4 (Me*C*OCH*C*OMe), 108.0 (MeCO*C*HCOMe), 26.6 (*Me*COCHCO*Me*), 67.6 (O*Me*). IR (Nujol, cm^{-1}) 1590 [ν(C$\underline{\cdots}$C)], 1542 [ν(C$\underline{\cdots}$O)], 334 [ν(Nb–Cl)].

3.3. Preparation of [$NbCl_2(OEt)_2$(acac)] (**2**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(OEt)_2]_2$ (0.226 g, 0.39 mmol) and Hacac (0.08 cm^3, 0.78 mmol), to give complex **2** as a yellow solid. Yield 86%. Found: C, 30.62; H, 4.85. Anal. Calc. for $NbCl_2O_4C_9H_{17}$: C, 29.95; H, 4.44%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 5.93 (s, 1H, MeCO*CH*-COMe), 2.13 (s, 6H, *Me*COCHCO*Me*), 4.87 (q, 4H, $^3J_{HH} = 7.0$, O*CH*$_2$CH$_3$), 1.48 (t, 6H, $^3J_{HH} = 7.0$, OCH$_2$*CH*$_3$). ^{13}C{^{1}H} ($CDCl_3$), δ 191.1 (Me*C*OCH-*C*OMe), 107.7 (MeCO*C*HCOMe), 26.6 (*Me*COCH-CO*Me*), 76.6 (O*C*H$_2$CH$_3$), 16.1 (OCH$_2$*C*H$_3$). IR (Nujol, cm^{-1}) 1583 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1533 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 340 [$\nu$(Nb–Cl)].

3.4. Preparation of [$NbCl_2(O^iPr)_2$(acac)] (**3**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(O^iPr)_2]_2$ (0.529 g, 0.83 mmol) and Hacac (0.17 cm^3, 1.66 mmol), to give complex **3** as a yellow solid. Yield 84%. Found: C, 34.64; H, 5.51. Anal. Calc. for $NbCl_2O_4C_{11}H_{21}$: C, 34.74; H, 5.47%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 5.90 (s, 1H, MeCO*CH*-COMe), 2.10 (s, 6H, *Me*COCHCO*Me*), 5.19 (m, 2H, O*CH*(CH$_3$)$_2$), 1.46 (d, 12H, $^3J_{HH} = 6.4$, OCH(*CH*$_3$)$_2$). ^{13}C{^{1}H} ($CDCl_3$), δ 190.7 (Me*C*OCH*C*OMe), 107.3 (MeCO*C*HCOMe), 26.4 (*Me*COCHCO*Me*), 84.3 [O*C*H(CH$_3$)$_2$], 23.03 [OCH(*C*H$_3$)$_2$]. IR (Nujol, cm^{-1}) 1585 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1532 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 341 [$\nu$(Nb–Cl)].

3.5. Preparation of [$NbCl_2(OMe)_2$(dpm)] (**4**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(OMe)_2]_2$ (0.672 g, 1.28 mmol) and Hdpm (0.54 cm^3, 2.57 mmol), to give complex **4** as a yellow solid. Yield 98%. Found: C, 37.31; H, 6.03. Anal. Calc. for $NbCl_2O_4C_{13}H_{25}$: C, 38.23; H, 6.18%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 6.23 (s, 1H, (Me$_3$CCO*CH*COCMe$_3$), 1.24 (s, 18H, *Me*$_3$CCOCH-COC*Me*$_3$), 4.61 (s, 6H, OMe). ^{13}C{^{1}H} ($CDCl_3$), δ 201.0 (Me$_3$C*C*OCH*C*OCMe$_3$), 98.9 (Me$_3$CCO*C*H-COCMe$_3$), 40.9 (Me$_3$*C*COCHCO*C*Me$_3$), 27.5 (*Me*$_3$CCOCHCOC*Me*$_3$), 66.98 (s, O*Me*). IR (Nujol, cm^{-1}) 1550 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1500 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 332 [$\nu$(Nb–Cl)].

3.6. Preparation of [$NbCl_2(OEt)_2$(dpm)] (**5**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(OEt)_2]_2$ (0.808 g, 1.36 mmol) and Hdpm (0.582 cm^3, 2.72 mmol), to give complex **5** as a yellow solid. Yield 98%. Found: C, 41.03; H, 6.84. Anal. Calc. for $NbCl_2O_4C_{15}H_{29}$: C, 41.28; H, 6.70%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 6.20 (s, 1H, Me$_3$CCO*CH*COCMe$_3$), 1.23 (s, 18H, *Me*$_3$CCOCH-COC*Me*$_3$), 4.90 (q, 4H, $^3J_{HH} = 7.2$, O*CH*$_2$CH$_3$), 1.48 (t, 6H, $^3J_{HH} = 7.2$, OCH$_2$*CH*$_3$). ^{13}C{^{1}H} ($CDCl_3$), δ 201.1 (Me$_3$C*C*OCH*C*OCMe$_3$), 98.5 (Me$_3$CCO*C*H-COCMe$_3$), 40.9 (Me$_3$*C*COCHCO*C*Me$_3$), 27.5 (*Me*$_3$CCOCHCOC*Me*$_3$), 75.9 (O*C*H$_2$CH$_3$), 16.4 (OCH$_2$*C*H$_3$). IR (Nujol, cm^{-1}) 1540 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1507 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 340 [$\nu$(Nb–Cl)].

3.7. Preparation of [$NbCl_2(O^iPr)_2$(dpm)] (**6**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(O^iPr)_2]_2$ (0.727 g, 1.14 mmol) and Hdpm (0.48 cm^3, 2.28 mmol), to give complex **6** as a yellow solid. Yield 90%. Found: C, 41.55; H, 6.79. Anal. Calc. for $NbCl_2O_4C_{17}H_{33}$: C, 41.45; H, 6.71%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 6.16 (s, 1H, Me$_3$CCO*CH*COCMe$_3$), 1.22 (s, 18H, *Me*$_3$CCOCH-COC*Me*$_3$), 5.25 (m, 2H, O*CH*(CH$_3$)$_2$), 1.48 (d, 12H, $^3J_{HH} = 6.3$, OCH(*CH*$_3$)$_2$). ^{13}C{^{1}H} ($CDCl_3$), δ 200.7 (Me$_3$C*C*OCH*C*OCMe$_3$), 98.1 (Me$_3$CCO*C*HCOCMe$_3$), 40.9 (Me$_3$*C*COCHCO*C*Me$_3$), 27.6 (*Me*$_3$CCOCH-COC*Me*$_3$), 84.5 [O*C*H(CH$_3$)$_2$], 23.3 [OCH(*C*H$_3$)$_2$]. IR (Nujol, cm^{-1}) 1553 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1507 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 342 [$\nu$(Nb–Cl)].

3.8. Preparation of [$NbCl_2(OMe)_2$(dbm)] (**7**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(OMe)_2]_2$ (1.10 g, 2.11 mmol) and Hdbm (0.94 g, 4.22 mmol), to give complex **7** as an orange solid. Yield 98%. Found: C, 45.34; H, 3.93. Anal. Calc. for $NbCl_2O_4C_{17}H_{17}$: C, 45.59; H, 3.79%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 7.28 (s, 1H, PhCO*CH*-COPh), 8.08–7.63 (m, 10H, *Ph*COCHCO*Ph*), 4.76 (s, 6H, OMe). ^{13}C{^{1}H} ($CDCl_3$), δ 183.8 (Ph*C*OCH-*C*OPh), 100.7 (PhCO*C*HCOPh), 135.4, 133.7, 128.3, 128.9 (*Ph*COCHCO*Ph*), 67.6 (O*Me*). IR (Nujol, cm^{-1}) 1595 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1531 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 334 [$\nu$(Nb–Cl)].

3.9. Preparation of [$NbCl_2(OEt)_2$(dbm)] (**8**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(OEt)_2]_2$ (0.612 g, 1.05 mmol) and Hdbm (0.474 g, 2.10 mmol), to give complex **8** as an orange solid. Yield 98%. Crystals for X-ray diffraction were grown from a solution of CH_2Cl_2 by slow evaporation of the solvent. Found: C, 47.30; H, 4.20. Anal. Calc. for $NbCl_2O_4C_{19}H_{21}$: C, 47.81; H, 4.40%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 7.25 (s, 1H, PhCO*CH*-COPh), 8.08–7.63 (m, 10H, *Ph*COCHCO*Ph*), 5.05 (q, 4H, $^3J_{HH} = 7.2$, O*CH*$_2$CH$_3$), 1.59 (t, 6H, $^3J_{HH} = 7.2$, OCH$_2$*CH*$_3$). ^{13}C{^{1}H} ($CDCl_3$), δ 183.7 (Ph*C*OCH-*C*OPh), 100.6 (PhCO*C*HCOPh), 135.7, 133.5, 128.8, 128.2 (*Ph*COCHCO*Ph*), 76.6 (O*C*H$_2$CH$_3$), 16.5 (OCH$_2$*C*H$_3$). IR (Nujol, cm^{-1}) 1602 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$], 1534 [$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$], 342 [$\nu$(Nb–Cl)].

3.10. Preparation of [$NbCl_2(O^iPr)_2(dbm)$] (**9**)

The synthetic procedure was the same as for complex **1**, using [$NbCl_3(O^iPr)_2]_2$ (0.752 g, 1.18 mmol) and Hdpm (0.531 g, 2.36 mmol), to give complex **9** as a yellow solid. Yield 90%. Found: C, 47.33; H, 4.42. Anal. Calc. for $NbCl_2O_4C_{21}H_{25}$: C, 47.21; H, 4.75%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 7.20 (s, 1H, PhCO*CH*-COPh), 8.08–7.63 (m, 10H, *Ph*COCHCO*Ph*), 5.38 (m, 2H, O*CH*($CH_3)_2$), 1.59 (d, 12H, $^3J_{HH} = 6.3$, OCH($CH_3)_2$). $^{13}C\{^1H\}$ ($CDCl_3$), δ 183.7 (Ph*C*OCH-*C*OPh), 100.3 (PhCO*C*HCOPh), 136.1, 133.2, 128.7, 128.1 (*Ph*COCHCO*Ph*), 84.3 [O*C*H($CH_3)_2$], 23.4 [OCH($CH_3)_2$]. IR (Nujol, cm^{-1}) 1585 [$\nu(C\underline{\cdots}C)$], 1532 [$\nu(C\underline{\cdots}O)$], 344 [$\nu$(Nb–Cl)].

3.11. Preparation of [$NbCl(OMe)_2(S_2CNMe_2)_2$] (**10**)

To a THF (50 cm^3) solution of [$NbCl_3(OMe)_2]_2$ (0.470 g, 0.90 mmol) was added $Na(S_2CNMe_2)$ (0.515 g, 3.60 mmol). The suspension was stirred for 20 h at 60°C. The solvent was removed under reduced pressure and, after extraction with CH_2Cl_2 (30 cm^3), a white solid was obtained. Yield 78%. Found: C, 22.35; H, 4.27; N, 6.08. Anal. Calc. for $NbClO_2S_4N_2C_8H_{18}$: C, 22.30; H, 4.21; N, 6.50%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 3.42, 3.40 (all s, 12H, S_2CN*Me*$_2$), 3.94 (s, 6H, OMe). $^{13}C\{^1H\}$ ($CDCl_3$), δ 202.1 (S_2*C*NMe_2), 38.3, 38.2 (S_2CN*Me*$_2$), 68.1 (O*Me*). IR (Nujol, cm^{-1}) 1528 [$\nu(C\underline{\cdots}N)$], 1258 [$\nu(C\underline{\cdots}S)$], 1094 [[$\nu$(O–C)], 274 [$\nu$(Nb–Cl)].

3.12. Preparation of [$NbCl(OMe)_2(S_2CNEt_2)_2$] (**11**)

The synthetic procedure was the same as for complex **10**, using [$NbCl_3(OMe)_2]_2$ (0.632 g, 1.21 mmol) and $Na(S_2CNEt_2)$ (0.828 g, 4.84 mmol), to give complex **11** as a white solid. Yield 82%. Found: C, 29.72; H, 5.21; N, 5.75. Anal. Calc. for $NbClO_2S_4N_2C_{12}H_{26}$: C, 29.60; H, 5.38; N, 5.75%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 3.86 (q, 8H, $^3J_{HH} = 7.4$, S_2CN(*CH*$_2CH_3)_2$), 1.34 (t, 12H, $^3J_{HH} = 7.4$, $S_2CN(CH_2$*CH*$_3)_2$), 3.96 (s, 6H, OMe). $^{13}C\{^1H\}$ ($CDCl_3$), δ 202.9 (S_2*C*NEt_2), 44.4, 43.5 [S_2CN(*C*$H_2CH_3)_2$], 12.5, 12.3 [$S_2CN(CH_2$*C*$H_3)_2$], 62.9 (O*Me*). IR (Nujol, cm^{-1}) 1510 [$\nu(C\underline{\cdots}N)$], 1260 [$\nu(C\underline{\cdots}S)$], 1090 [$\nu$(O–C)], 273 [$\nu$(Nb–Cl)].

3.13. Preparation of [$NbCl(OMe)_2(S_2CNBz_2)_2$] (**12**)

The synthetic procedure was the same as for complex **10**, using [$NbCl_3(OMe)_2]_2$ (0.495 g, 0.95 mmol) and $Na(S_2CNBz_2)$ (1.119 g, 3.79 mmol), to give complex **12** as a white solid. Yield 68%. Found: C, 51.97; H, 4.61; N, 3.78. Anal. Calc. for $NbClO_2S_4N_2C_{32}H_{34}$: C, 52.28; H, 4.66; N, 3.81%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 7.37–7.33 (m, 20H, $S_2CN(CH_2$*Ph*$)_2$), 4.95 (s, 8H, S_2CN(*CH*$_2Ph)_2$), 4.09 (s, 6H, OMe). $^{13}C\{^1H\}$ ($CDCl_3$), δ 203.5 (S_2*C*NBz_2), 51.0, 50.0 [S_2CN(*C*$H_2Ph)_2$], 133.8–127.9 [$S_2CN(CH_2$*Ph*$)_2$], 63.2 (OMe). IR (Nujol, cm^{-1}) 1485 [$\nu(C\underline{\cdots}N)$], 1273 [$\nu(C\underline{\cdots}S)$], 1077 [$\nu$(O–C)], 275 [$\nu$(Nb–Cl)].

3.14. Preparation of [$NbCl(OEt)_2(S_2CNMe_2)_2$] (**13**)

The synthetic procedure was the same as for complex **10**, using [$NbCl_3(OEt)_2]_2$ (0.663 g, 1.15 mmol) and $Na(S_2CNMe_2)$ (0.656 g, 4.58 mmol), to give complex **13** as a white solid. Yield 66%. Found: C, 25.77; H, 4.85; N, 5.81. Anal. Calc. for $NbClO_2S_4N_2C_{10}H_{22}$: C, 26.17; H, 4.83; N, 6.10%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 3.40, 3.39 (all s, 12H, S_2CN*Me*$_2$), 4.17 (q, 4H, $^3J_{HH} =$ 7.0, O*CH*$_2CH_3$), 1.09 (t, 6H, $^3J_{HH} = 7.0$, OCH_2*CH*$_3$). $^{13}C\{^1H\}$ ($CDCl_3$), δ 202.8 (S_2*C*NMe_2), 39.5, 39.4 (S_2CN*Me*$_2$), 71.0 (O*C*H_2CH_3), 17.23 (OCH_2*C*H_3). IR (Nujol, cm^{-1}) 1520 [$\nu(C\underline{\cdots}N)$], 1247 [$\nu(C\underline{\cdots}S)$], 1066 [$\nu$(O–C)], 275 [$\nu$(Nb–Cl)].

3.15. Preparation of [$NbCl(OEt)_2(S_2CNEt_2)_2$] (**14**)

The synthetic procedure was the same as for complex **10**, using [$NbCl_3(OEt)_2]_2$ (0.371 g, 0.64 mmol) and $Na(S_2CNEt_2)$ (0.439 g, 2.56 mmol), to give complex **14** as a white solid. Yield 77%. Found: C, 32.58; H, 5.62; N, 5.37. Anal. Calc. for $NbClO_2S_4N_2C_{14}H_{30}$: C, 32.65; H, 5.87; N, 5.42%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 3.84 (q, 8H, $^3J_{HH} = 7.4$, S_2CN(*CH*$_2CH_3)_2$), 1.31 (t, 12H, $^3J_{HH} = 7.4$, $S_2CN(CH_2$*CH*$_3)_2$), 4.20 (q, 4H, $^3J_{HH} = 7.0$, O*CH*$_2CH_3$), 1.12 (t, 6H, $^3J_{HH} = 7.0$, OCH_2*CH*$_3$). $^{13}C\{^1H\}$ ($CDCl_3$), δ 201.3 (S_2*C*NEt_2), 44.8, 44.9 [S_2CN(*C*$H_2CH_3)_2$], 12.9, 13.1 [$S_2CN(CH_2$*C*$H_3)_2$], 71.0 (O*C*H_2CH_3), 17.1 (OCH_2*C*H_3). IR (Nujol, cm^{-1}) 1502 [$\nu(C\underline{\cdots}N)$], 1260 [$\nu(C\underline{\cdots}S)$], 1062 [$\nu$(O–C)], 283 [$\nu$(Nb–Cl)].

3.16. Preparation of [$NbCl(OEt)_2(S_2CNBz_2)_2$] (**15**)

The synthetic procedure was the same as for complex **10**, using [$NbCl_3(OEt)_2]_2$ (0.515 g, 0.89 mmol) and $Na(S_2CNBz_2)$ (1.051 g, 3.56 mmol), to give complex **15** as a white solid. Yield 68%. Found: C, 51.97; H, 4.61; N, 3.78. Anal. Calc. for $NbClO_2S_4N_2C_{34}H_{38}$: C, 52.28; H, 4.66; N, 3.81%. ^{1}H-NMR ($CDCl_3$, 295 K), δ 7.38–7.29 (m, 20H, $S_2CN(CH_2$*Ph*$)_2$), 4.96 (s, 8H, $S_2CN(CH_2Ph)_2$), 4.36 (q, 4H, $^3J_{HH} = 7.0$, O*CH*$_2CH_3$), 1.12 (t, 6H, $^3J_{HH} = 7.0$, OCH_2*CH*$_3$). $^{13}C\{^1H\}$ ($CDCl_3$), δ 204.4 (S_2*C*NBz_2), 51.4, 50.4 [S_2CN(*C*$H_2Ph)_2$], 134.5–128.7 [$S_2CN(CH_2$*Ph*$)_2$], 71.3 (O*C*H_2CH_3), 17.3 (OCH_2*C*H_3). IR (Nujol, cm^{-1}) 1480 [$\nu(C\underline{\cdots}N)$], 1254 [$\nu(C\underline{\cdots}S)$], 1098 [$\nu$(O–C)], 276 [$\nu$(Nb–Cl)].

3.17. Preparation of [NbCl(O^{i}Pr)$_2$(S$_2$CNMe$_2$)$_2$] (**16**)

The synthetic procedure was the same as for complex **10**, using [NbCl$_3$(O^{i}Pr)$_2$]$_2$ (0.535 g, 0.84 mmol) and Na(S$_2$CNMe$_2$) (0.483 g, 3.37 mmol), to give complex **16** as a white solid. Yield 37%. Found: C, 29.48; H, 5.27; N, 5.80. Anal. Calc. for $NbClO_2S_4N_2C_{12}H_{26}$: C, 29.60; H, 5.38; N, 5.75%. ^{1}H-NMR (CDCl$_3$, 295 K), δ 3.40, 3.39 (all s, 12H, S$_2$CN*Me*$_2$), 4.55 (m, 2H, O*CH*(CH$_3$)$_2$), 1.11 (d, 12H, $^3J_{HH} = 6.2$, OCH(*CH*$_3$)$_2$). ^{13}C{^{1}H} (CDCl$_3$), δ 202.9 (S$_2$*C*NMe$_2$), 39.4, 38.6 (S$_2$CN*Me*$_2$), 78.0 [O*C*H(CH$_3$)$_2$], 23.9 [OCH(*C*H$_3$)$_2$]. IR (Nujol, cm^{-1}) 1529 [ν(C$\overset{\cdots}{-}$N)], 1258 [ν(C$\overset{\cdots}{-}$S)], 1121 [ν(O–C)], 260 [ν(Nb–Cl)].

3.18. Preparation of [NbCl(O^{i}Pr)$_2$(S$_2$CNEt$_2$)$_2$] (**17**)

The synthetic procedure was the same as for complex **10**, using [NbCl$_3$(O^{i}Pr)$_2$]$_2$ (0.327 g, 0.52 mmol) and Na(S$_2$CNEt$_2$) (0.353 g, 2.06 mmol), to give complex **17** as a white solid. Yield 35%. Found: C, 33.38; H, 5.73; N, 4.91. Anal. Calc. for $NbClO_2S_4N_2C_{16}H_{34}$: C, 33.65; H, 6.00; N, 4.91%. ^{1}H-NMR (CDCl$_3$, 295 K), δ 3.85 (q, 8H, $^3J_{HH} = 7.4$, S$_2$CN(*CH*$_2$CH$_3$)$_2$), 1.33 (t, 12H, $^3J_{HH} = 7.4$, S$_2$CN(CH$_2$*CH*$_3$)$_2$), 4.72 (m, 2H, O*CH*(CH$_3$)$_2$), 1.12 (d, 12H, $^3J_{HH} = 6.2$, OCH(*CH*$_3$)$_2$). ^{13}C{^{1}H} (CDCl$_3$), δ 202.6 (S$_2$*C*NEt$_2$), 44.8, 44.7 [S$_2$CN(*C*H$_2$CH$_3$)$_2$], 24.6, 24.5 [S$_2$CN(CH$_2$*C*H$_3$)$_2$], 77.4 [O*C*H(CH$_3$)$_2$], 13.1 [OCH(*C*H$_3$)$_2$]. IR (Nujol, cm^{-1}) 1510 [ν(C$\overset{\cdots}{-}$N)], 1262 [ν(C$\overset{\cdots}{-}$S)], 1100 [ν(O–C)], 270 [ν(Nb–Cl)].

3.19. Preparation of [NbCl(O^{i}Pr)$_2$(S$_2$CNBz$_2$)$_2$] (**18**)

The synthetic procedure was the same as for complex **10**, using [NbCl$_3$(O^{i}Pr)$_2$]$_2$ (0.228 g, 0.36 mmol) and Na(S$_2$CNBz$_2$) (0.424 g, 1.44 mmol), to give complex **18** as a white solid. Yield 20%. Found: C, 54.32; H, 5.26; N, 3.65. Anal. Calc. for $NbClO_2S_4N_2C_{36}H_{42}$: C, 54.64; H, 5.35; N, 3.54%. ^{1}H-NMR (CDCl$_3$, 295 K), δ 7.38–7.30 (m, 20H, S$_2$CN(CH$_2$*Ph*)$_2$), 4.98 (s, 8H, S$_2$CN(*CH*$_2$Ph)$_2$), 4.80 (m, 2H, O*CH*(CH$_3$)$_2$), 1.15 (d, 12H, $^3J_{HH} = 6.2$, OCH(*CH*$_3$)$_2$). ^{13}C{^{1}H} (CDCl$_3$), δ 203.5 (S$_2$*C*NBz$_2$), 51.4, 50.4 [S$_2$CN(*C*H$_2$Ph)$_2$], 134.6–128.9 [S$_2$CN(CH$_2$*Ph*)$_2$], 77.5 [O*C*H(CH$_3$)$_2$], 13.1 [OCH(*C*H$_3$)$_2$]. IR (Nujol, cm^{-1}) 1480 [ν(C$\overset{\cdots}{-}$N)], 1265 [ν(C$\overset{\cdots}{-}$S)], 1099 [ν(O–C)], 272 [ν(Nb–Cl)].

3.20. Kinetics of the reaction of **5** with Hacac — experiment 1

Complex **5** (40 mg) was dissolved in CDCl$_3$ in an NMR tube (5 mm diameter) and Hacac was added. The final volume was 1 ml. The concentration of **5** was 0.09 M and the concentrations of Hacac were systematically varied (see Table 2). The tube was vigorously shaken for about 5 s and then placed into the spectrometer. Each spectrum recorded at 313 K was the result of the coaddition of 16 transients, which required nearly 1 min to acquire. Spectra were automatically recorded every 5 min using the kinetic analysis software from Varian. Variations of the intensity in the singlet signal corresponding to the ^{t}Bu of dpm in **5**, were measured for three $t_{1/2}$. A computer analysis method for intensities gives a straight-line segment in a plot of ln(intensity) against time. The error is given by standard deviation in the regression analysis. For the [Hacac]/[**5**] molar ratio of 7:1, similar experiments were carried out at 293, 298, 303 and 308 K.

3.21. Kinetics of the reaction of **8** with Hacac — experiment 2

Complex **8** (40 mg) was dissolved in CDCl$_3$ in an NMR tube (5 mm diameter) and Hacac (0.060 ml) was added. The final volume was 1 ml. The concentration of **8** was 0.083 M, and the [Hacac]/[**8**] molar ratio was 7:1. The tube was vigorously shaken for about 5 s and then placed into the spectrometer. Each spectrum recorded at 293 K was the result of the coaddition of 16 transients, which required nearly 1 min to acquire. Spectra were automatically recorded every 5 min using the kinetic analysis software from Varian. Variations of the intensity in the singlet signal corresponding to the CH of dbm in **8** were measured for three $t_{1/2}$. A computer analysis method for intensities gives a straight-line segment in a plot of ln(intensity) against time. The error is given by standard deviation in the regression analysis. Similar experiments were carried out at 298, 303, 308 and 313 K.

3.22. Measurements of exchange equilibrium constants

Complex **5** (40 mg) was dissolved in CDCl$_3$ in an NMR tube (5 mm diameter) and Hacac (0.006 ml) was added. The final volume was 1 ml and the [Hacac]/[**5**] molar ratio was 7:1. The mixture was allowed to react for 24 h, at 293 K, in order to reach the equilibrium. Normalized integrals of characteristic peaks of the present species were measured from the ^{1}H-NMR spectra, in order to obtain the equilibrium constant, K_{eq} = [NbCl$_2$(acac)(OEt)$_2$][Hdpm]/[NbCl$_2$(*O*,*O*-^{t}BuCOCHCO^{t}Bu)(OEt)$_2$][Hacac]. An average value (see above) was calculated from five similar experiments.

A similar process was performed for complex **8**, in order to obtain the average equilibrium constant (see above), K_{eq} = [NbCl$_2$(acac)(OEt)$_2$][Hdbm]/[NbCl$_2$(*O*,*O*-PhCOCHCOPh)(OEt)$_2$][Hacac].

3.23. Crystal structure determination of ***8***

Yellow crystal (0.30 × 0.20 × 0.20 mm) of $C_{19}H_{21}Cl_2NbO_4$, which is monoclinic with space group $P2_1/n$ and lattice constants $a = 10.224(2)$, $b = 15.4315(8)$, $c = 14.248(5)$ Å, $\beta = 108.83(2)°$, $V = 2127.6(9)$ $Å^{-3}$, $Z = 4$, $D_{calc} = 1.490$ g cm^{-3}, $M = 477.17$. Reflections were collected at 25°C on a Nonius-MACH3 diffractometer equipped with a graphite-monochromated radiation source ($\lambda = 0.7107$ Å), 5122 reflections collected ($2 < \theta < 28$), 2209 reflections with $I > 2\sigma I$. Data were corrected in the usual fashion for Lorentz and polarisation effects, and empirical absorption correction was not necessary ($\mu = 8.36$ cm^{-1}). Data/restraints/parameters 5122/2/237. The structure was solved by direct methods [16] and refinement on F^2 was carried out by full-matrix least-squares analysis [17]. The C7 is disordered over two positions with different occupation factors (0.722 for C7 and 0.278 for C71). Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions but not refined. Final disagreement indices are $R_1 = 0.0587$, $wR_2 = 0.1578$, Goodness-of-fit = 0.853, largest difference peak and hole 0.602 and −0.731 e $Å^{-3}$.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139411 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: +44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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