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Investigation into the reactivity of oxoniobocene complexes [Cp$^*_2$Nb(=O)R] (Cp* = η^5-C_5Me_5; R = H, OH, OMe) towards heterocumulenes: formation of carbamato and thiocarbamato complexes and catalytic cyclization of PhNCO

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Abstract

The reaction of [Cp$^*_2$NbCl$_2$] (Cp* = η^5-C_5Me_5) with KOH or $Ba(OH)_2\cdot 8H_2O$ in THF was investigated under slightly modified conditions. In addition to the known complex [Cp$^*_2$Nb(=O)H] (**1**), the new compound [Cp$^*_2$Nb(=O)OH] (**2**) was formed. The reaction of **2** with PhNCS gave yellow [Cp$^*_2$Nb(=O){SC(O)NHPh}] (**3**), while PhNCO formed yellow [Cp$^*_2$Nb(=O){OC(O)NHPh}] (**4**). Complexes **3** and **4** were analytically and spectroscopically characterized. X-ray diffraction analyses of both compounds show that they contain either η^1-*S*-thiocarbamato (**3**) or η^1-*O*-carbamato ligand (**4**) along with a terminal Nb=O group. The reaction of **1** with one equivalent of PhNCO mainly gave orange [Cp$^*_2$NbH{OC(O)NPh}] (**5**) along with some **4**. The molecular structure of **5** contains a niobocene unit comprising η^2-*N*,*O*-carbamato chelate, which formally is a [2 + 2] cycloaddition product of the Nb=O group and the heterocumulene. A hydride ligand completes the coordination sphere around Nb. Reaction of **1** with excess PhNCO gave a mixture of heterocycles $(PhNCO)_2$ (**6**) and $(PhNCO)_3$ (**7**) in the approximate ratio 3:2. By contrast, the reaction of [Cp$^*_2$Nb(=O)OMe] with PhNCO in molar ratios from 1:3 to 1:100 gave nearly pure triphenylisocyanurate **7**. © 2001 Published by Elsevier Science B.V.

Keywords: Niobocene; Oxo ligands; Heterocumulenes; Cyclization

1. Introduction

The transfer of an oxygen atom from a metal to an organic molecule is a key step in many catalytic oxidation reactions [1,2]. Metal oxo complexes play an important role in these reactions and sometimes intermediate products may be isolated from such reactions [3]. In this regard, metallacycles arising from [2 + 2] cycloaddition reactions of M=O bonds with unsaturated organic substrates are of continued interest [1,4,5]. Recently, we have described oxo niobocene complexes of the type [Cp$^*_2$Nb(=O)R] (Cp* = η^5-C_5Me_5; R=H, OCH_3), which have two different reaction sites [6]. In order to study the reactivity of the Nb=O and Nb–X units towards heterocumulenes we investigated the reaction of [Cp$^*_2$Nb(=O)H] (**1**) with PhNCS and PhNCO, respectively. During this study it turned out that the preparation of **1** as described in Ref. [6] needed to be revisited. Therefore, the reaction of [Cp$^*_2$NbCl$_2$] with KOH and $Ba(OH)_2\cdot 8H_2O$ was reinvestigated, which led to the discovery of [Cp$^*_2$Nb(=O)OH] (**2**) as a further participant in the reaction system. The results obtained from the reaction of **1** and **2** with PhNCX (X = S, O) finally contribute to the investigation of the catalytic cyclization of PhNCO via a formal [2 + 2] cycloaddition.

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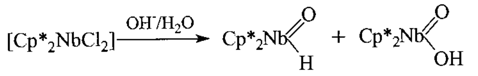
2. Results

2.1. Reinvestigation of the reaction of [$Cp^*_2NbCl_2$] with metal hydroxides

We have reported [6] that the reaction of [$Cp^*_2NbCl_2$] with two equivalents of $Ba(OH)_2{\cdot}8H_2O$ in THF gives [$Cp^*_2Nb(O)H$] (**1**), while in the analogous reaction with KOH [$Cp^*_2Nb(O)Cl$] is formed. Attempts to reproduce the results obtained with $Ba(OH)_2{\cdot}8H_2O$ showed that **1** obviously contained a bright yellow compound **2**. Then we found that the formation of **2** is favored if the reaction is carried out at 40 °C in a mixture of THF–water 10:1 (Eq. (1)). After 20 h the ratio **2**/**1** is about 90:10. If, however, the reaction was stopped after the green color of the starting material has disappeared (after 1–2 h), [$Cp^*_2Nb(O)Cl$] was found.



$$[Cp^*_2NbCl_2] \xrightarrow{OH^-/H_2O} Cp^*_2Nb(=O)H + Cp^*_2Nb(=O)OH \qquad (1)$$

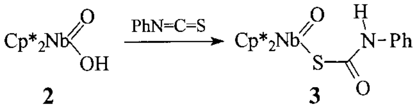
1 **2**

Complex **2** was characterized by means of its FD mass spectrum and elemental analyses. Its IR spectrum shows a strong $\nu_{Nb=O}$ absorption at 843 cm^{-1} along with a weak and sharp ν_{OH} absorption at 3470 cm^{-1}. The ^1H-NMR spectrum in C_6D_6 exhibits one intense singlet at $\delta = 1.77$ and a weak resonance at $\delta = 2.11$. The latter is tentatively assigned to the Nb–OH unit. It is important to note that the ^1H-NMR spectra alone are not able to distinguish between **2** and [$Cp^*_2Nb(O)Cl$], for both compounds exhibit identical chemical shifts for the Cp* ligand.

The reaction of [$Cp^*_2NbCl_2$] with excess KOH in boiling THF was described to form **1** in yields between 0 and 50% [6]. We now found that addition of H_2O and decrease of the reaction temperature to 20 °C gave **1** in better reproducible yields around 40%. However, the product still contains small amounts of **2** (< 8%). The difficulties in controlling the formation of **1** may be due to the proposed reduction–protonation-mechanism of the reaction of [$Cp^*_2NbCl_2$] with OH^- [6]. The observed influence of the cations may be explained by different stabilization of intermediate products.

2.2. The reaction of [$Cp^*_2Nb(=O)OH$] (2) with PhNCS and PhNCO

The reaction of **2** with an equimolar amount of phenylisothiocyanate gave the yellow complex **3**, which turned out due to FD mass spectrum and elemental analyses to have the composition [$Cp^*_2Nb(=O)\{SC(O)NHPh\}$] (Eq. (2)). Although **2** still contained minor amounts of **1** no by-products were isolated. The IR spectrum of **3** shows characteristic absorptions at 3220 (ν_{NH}), 1635 and 1520 (ν_{NHCO}), and 860 ($\nu_{Nb=O}$) cm^{-1}. The ^1H-NMR spectrum exhibits one singlet at $\delta = 1.93$ for the C_5Me_5 groups, three multiplets for the C_6H_5 group, and one singlet at $\delta = 9.00$ for the NH proton. The integration of the signals is in agreement with the proposed structure.



$$Cp^*_2Nb(=O)OH \xrightarrow{PhN=C=S} Cp^*_2Nb(=O)SC(=O)N(H)Ph \qquad (2)$$

2 **3**

Although only twinned single crystals of complex **3** were available for an X-ray crystallographic study, the molecular structure could be resolved unambiguously. As a central feature **3** contains an oxo niobocene unit to which a thiocarbamato ligand is coordinated via its sulfur atom (Fig. 1). This ligand, including the phenyl group, nearly forms a plane. The hydrogen atom fixed at nitrogen was located directly from difference Fourier synthesis. It is oriented towards the oxo ligand at Nb and the order of the corresponding O–H distance of 2.084 Å may indicate an intramolecular hydrogen bond [7]. The distance C(21)–N (1.358(4) Å) is typical for carbamato and thiocarbamato complexes (Table 1).

N-Monosubstituted thiocarbamato complexes seem to be rare in the literature and the only structurally characterized example is [$Co(NH_3)_5$-{η^1-*S*-C(O)-NHPh}][ClO_4]$_2$ [8] due to a Cambridge Data File research. This compound is the result of a reaction of [$Co(NH_3)_5(OH)]^{2+}$ with PhNCO, for which a nucleophilic attack of the Co(OH) oxygen at the electrophilic carbon atom of PhNCS has been established, followed by hydrogen migration to the N atom. The resulting O-bonded complex rapidly isomerizes to the stable S-bonded species.

The reaction of **2** with phenylisocyanate in THF at room temperature gave the yellow complex [$Cp^*_2Nb(=O)\{OC(O)NHPh\}$] (**4**) (Eq. (3)). The composition was confirmed by means of FD mass spectrum and elemental analyses. The IR spectrum of **4** shows

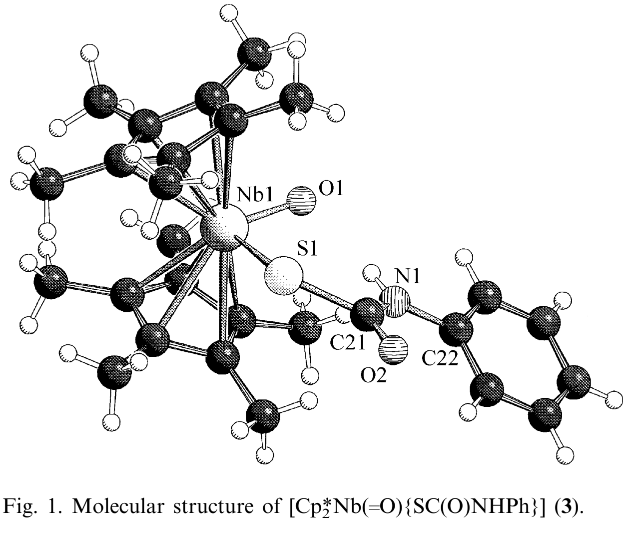
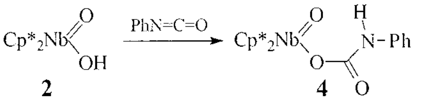


Fig. 1. Molecular structure of [$Cp^*_2Nb(=O)\{SC(O)NHPh\}$] (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for [$Cp^*_2Nb(O)$-{SC(O)NHPh}] (**3**), [$Cp^*_2Nb(O)${OC(O)NHPh}] (**4**) and [Cp^*_2NbH-{OC(O)NPh}] (**5**)

	3	4	5
Bond lengths			
Nb(1)–S(1)	2.525(1)		
Nb(1)–O(1)	1.752(2)	2.042(1)	2.121(2)
Nb(1)–O(3)		1.757(2)	
Nb(1)–N(1)			2.162(2)
Nb(1)–C(1–5)$_{mean}$	2.514(4)	2.503(3)	2.456(4)
Nb(1)–C(11–15)$_{mean}$	2.518(4)	2.540(3)	2.441(4)
S(1)–C(21)	1.802(3)		
O(1)–C(21)		1.318(4)	1.318(4)
O(2)–C(21)	1.187(4)	1.231(3)	1.206(4)
N(1)–C(21)	1.358(4)	1.371(3)	1.391(4)
N(1)–C(22)	1.414(4)	1.425(3)	1.412(4)
Bond distances			
S(1)–Nb(1)–O(1)	94.8(1)		
O(1)–Nb–O(3)		97.9(1)	
Nb(1)–S(1)–C(21)	113.7(1)		
O(1)–Nb–N(1)			60.0(1)
C(21)–N(1)–C(22)	127.4(2)	125.7(2)	122.6(2)
S(1)–C21)–O(2)	118.9(3)		
S(1)–C(21)–N(1)	116.2(2)		
O(2)–C(21)–N(1)	124.9(3)	123.9(2)	129.3(3)

characteristic absorptions at 3290 (ν_{NH}), 1684 (ν_{NHCO}), and 825 ($\nu_{Nb=O}$ cm^{-1}. Further strong absorptions at 1590, 1525, and 1495 cm^{-1} may be typical of the carbamate skeleton. The ^{1}H-NMR spectrum exhibits one singlet at $\delta = 1.94$ for the C_5Me_5 groups, three multiplets for the C_6H_5 group, and one singlet at $\delta = 7.23$ for the NH proton. As in **3** the ratio of C_5Me_5–C_6H_5 groups is equal to 2:1.



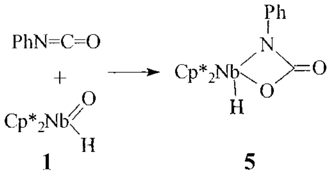
(3)

An X-ray crystallographic study of **4** reveals that its molecular structure contains an oxo niobocene unit to which a carbamato ligand is coordinated via its oxygen atom (Fig. 2). Two types of Nb–O distances are found as expected for Nb=O double and Nb–O single bonds [6] (Table 1). The other bonding parameters are close to those in the related compound **3**. Like the thiocarbamato ligand in **3** the carbamato ligand is roughly coplanar with the Nb=O moiety. The same orientation towards the oxo ligand as in **3** is found for the NH group. This means that both complexes **3** and **4** possess similar conformations of the heteroatom chain.

As already mentioned for the reaction of **2** with PhNCS (Eq. (2)), one may consider as a first step, a nucleophilic attack of the OH ligand at the electrophilic C atom of the heterocumulene (Scheme 1a), followed by proton migration. The final step for the formation of **3** would be a rapid isomerization. Alternatively, one may envisage an attack of the oxo ligand at the heterocumulene carbon atom according to Scheme 1b. Such an enhanced nucleophilicity of metallocene oxo ligands has been proposed for $Cp^*_2Zr(=O)$pyr [9] due to a negative polarization of the oxygen atom within the Zr=O bond.

2.3. The reaction of [$Cp^*_2Nb(=O)R$] (R=H, OMe) with PhNCO

The reaction of **1** with 1 equivalent of PhNCO gave a mixture of several compounds, which could not be separated by chromatographic methods. However, after recrystallization orange prisms were obtained, contaminated by fine yellow and white needles. The orange material was shown by means of FD mass spectroscopy, elemental analyses and X-ray crystallography to have the composition [Cp^*_2NbH{OC(O)NPh}] (**5**) (Eq. (4)). The yellow needles are assigned to complex **4** by means of FD mass and ^{1}H-NMR spectra. Complex **4** may arise from reaction of PhNCO with impurities of **2** in the starting material (see Eq. (1) and the related discussion there). The white material is attributed to triphenylisocyanurate **7** (see below). The content of both side products in the reaction mixture is estimated by means of ^{1}H-NMR spectra to 10–20%.



(4)

The IR spectrum of **5** exhibits a weak absorption at 1800 cm^{-1}, which may be assigned to a ν_{NbH} frequency, and strong absorptions at 1650, 1600 and 1500 cm^{-1}, characteristic of a carbamato ligand. The ^{1}H-NMR spectrum contains besides aromatic multiplets and a singlet for the C_5Me_5 group a slightly broadened

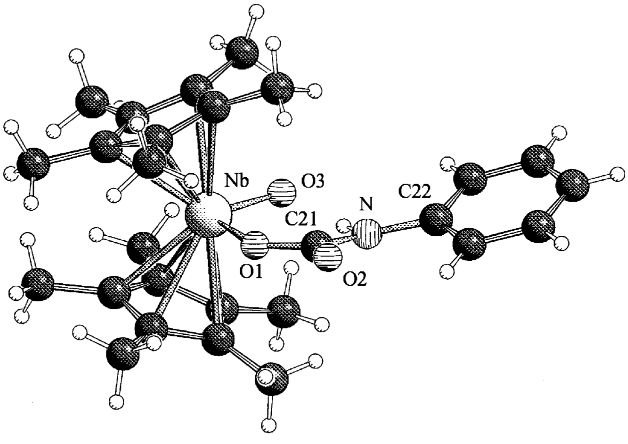
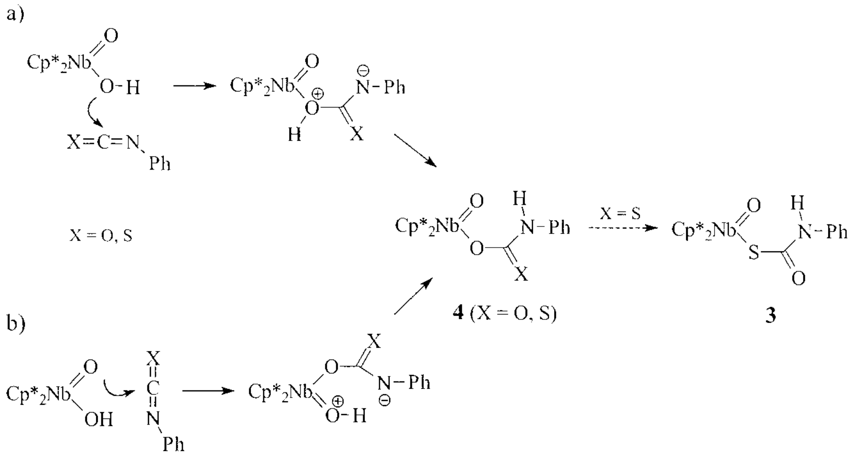


Fig. 2. Molecular structure of [$Cp^*_2Nb(=O)${OC(O)NHPh}] (**4**). One of the Cp* rings is disordered and occupies positions rotated by 21.5°. The disorder degree is 50%.



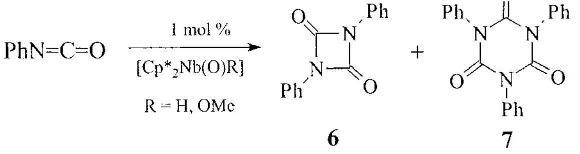
Scheme 1.

singlet at $\delta = 4.89$, which may arise from the Nb bonded hydride. The molecular structure of **5** shows a niobocene unit comprising an *N*,*O*-coordinated carbamate ligand (Fig. 3). The coordination sphere of the Nb center is completed by a hydride ligand. The oxygen atom of the metallacycle occupies the central position of the frontier plane bisecting the Cp* rings. Bond distances and angles within the four-membered ring are typical of a chelated η^2-*N*,*O*-carbamato chelate [1,5,10]. A comparison of bond parameters of complexes **3**–**5** shows only small differences. The only striking trend is a decrease of the C–N bond from 1.391(4) (**5**) to 1.371(3) (**4**) and 1.358(4) (**3**) Å (Table 1). This distance has been ascribed to possess partial double bond character [1].

Formally, one may describe the formation of **5** as a [2 + 2] cycloaddition. In fact, if one follows the ideas given in Scheme 1, the absence of an acidic proton provokes attack of the nucleophilic nitrogen at the positively polarized metal center. Similar coupling reactions are those of PhNCO with the Mo=O bond of [$(C_5H_5)_2MoO$] [1] or with one of the Re=O bonds in [$Cp^*_2Re_2O_4$] [5] and [$Re(O)_2I(PPh_3)_2$] [10]. An analogous cycloaddition at the Ta=S bond of [$(t\text{-}BuC_5H_4)_2Ta(S)H$] has been reported for PhNCS [11].

If, in the reaction of [$Cp^*_2Nb(O)H$] (**1**) an excess of PhNCO (molar ratio 1:100) was employed, a white crystalline material formed, which contains due to IR, ^{13}C-NMR and mass spectra a mixture of $(PhNCO)_2$ (**6**) and triphenylisocyanurate $(PhNCO)_3$ (**7**) (Eq. (5)). A distinction between both heterocycles is possible by means of IR and ^{13}C-NMR spectra. Thus, the ν_{CO} frequency at 1760 cm^{-1} is typical for the dimer [12], whereas that of **7** appears at 1710 cm^{-1} [12,13]. No ^{13}C-NMR spectrum has been reported thus far for $(PhNCO)_2$, the chemical shifts of **6** are quite close to those of **7**. An integration of the *C*=O resonances of the recrystallized material allows to estimate the ratio $(PhNCO)_2$–$(PhNCO)_3$ to ca. 60:40.

The reaction of [$Cp^*_2Nb(O)OMe$] [6] with three equivalents of PhNCO gave a white precipitate, which was identified as triphenylisocyanurate **7**·THF (Eq. (5)). After careful drying the solvent free compound gave correct elemental analyses and a weak parent ion in the EI mass spectrum. ^{1}H-NMR and IR spectra are identical with those of known samples [12]. The crude material only contains a small amount of $(PhNCO)_2$, for in the IR spectrum the intensity of its ν_{CO} frequency at 1760 cm^{-1} is very weak. The reaction also works with catalytical amounts of [$Cp^*_2Nb(O)OMe$]. Thus, in a typical experiment 1 mol% of this complex is sufficient to trimerize PhNCO in yields between 41 and 68% even after 5 min at room temperature.



(5)

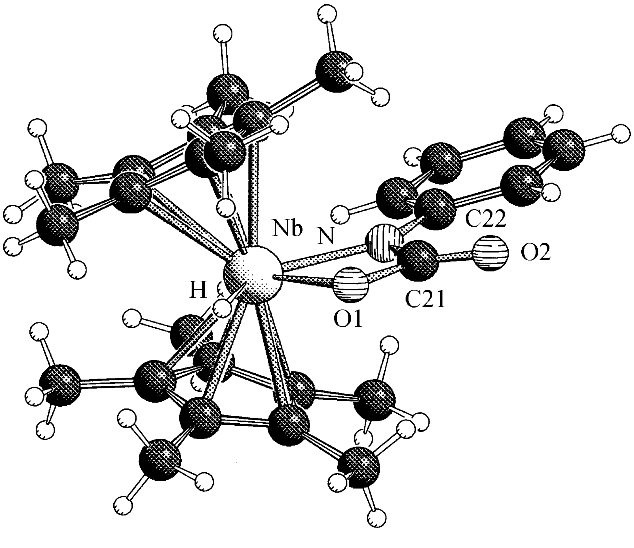


Fig. 3. Molecular structure of [$Cp^*_2NbH\{OC(O)NPh\}$] (**5**).

3. Conclusions

Oxo niobocene complexes of the type [$Cp^*_2Nb(O)R$] (R = H, OH, OMe) are versatile reagents for the transformation of phenylisocyanate and phenylisothiocyanate into carbamato and thiocarbamato complexes and heterocyclic organic products. Inspite of the relatively poor selectivity it is obvious that there is an influence of the functional groups R on nature and distribution of the products. On the other hand, the Nb hydride ligand, which may attack electrophilic carbon atoms in unsaturated organic substrates [15,16], does not participate in the reaction: no hint was detected for the eventual formation of a corresponding *N*,*O*-coordinated formamido complex.

The reaction of transition metal oxo complexes with isocyanates has been intensively investigated in the past with the aim to synthesize imido complexes [1,9,14]. A particular role as intermediates in such reactions was ascribed to the formation of *N*,*O*-carbamato chelates. We have shown in this work that the reaction of equivalent amounts of **1** and PhNCO produces the stable complex **5** in a formal [2 + 2] cycloaddition reaction (Eq. (4)).

With excess PhNCO complexes [$Cp^*_2Nb(O)R$] (R = H, OMe) form the organic heterocycles **6** and **7**: whereas R = H favors the formation of **6**, with R = OMe formation of the six-membered ring **7** is preferred. As probable intermediates one may assume bipolar intermediates the reactivity of which is directed by the different Nb–R functionalities. It may also be noted that the cyclization of PhNCO seems to be a rapid process, whereas complex **5** does not show any reactivity towards excess PhNCO.

4. Experimental

All manipulations were carried out under nitrogen by Schlenk techniques. The preparation of [$Cp^*_2NbCl_2$] is reported in Ref. [17]. [$Cp^*_2Nb(O)OMe$] was prepared from [$Cp^*_2NbCl_2$] and NaOMe in MeOH [6].

*4.1. Synthesis of [$Cp^*_2Nb(O)H$] (**1**)*

A green suspension of 1.12 g (2.58 mmol) of [$Cp^*_2NbCl_2$] and 1.50 g (26.7 mmol) of KOH in a mixture of 180 ml of THF and 15 ml of water was stirred for 20 h at 20 °C. After that time a nearly colorless solution has formed. After evaporation of the solvent the white residue was extracted several times with pentane (100 ml altogether). After evaporation of pentane recrystallization from 20 ml of *n*-hexane at − 20 °C gave 270–420 mg (31–48% yield) of a white crystalline powder of **1**. Spectroscopic and analytical data of **1** are analogous to those reported elsewhere [6]. Due to ^{1}H-NMR spectra, the product contains variable, but small amounts (< 8%) of [$Cp^*_2Nb(O)OH$] (**2**). The percentage of **2** depends on the concentration of [$Cp^*_2NbCl_2$] in the THF–H_2O mixture and the reaction time.

*4.2. Synthesis of [$Cp^*_2Nb(O)OH$] (**2**)*

A green suspension of 170 mg (0.39 mmol) of [$Cp^*_2NbCl_2$] and 220 mg (0.78 mmol) of $Ba(OH)_2\cdot 8H_2O$ in a mixture of 18 ml of THF and 1 ml of water was stirred for 18 h at 40 °C. After evaporation of the solvent the residue was extracted with 80 ml of pentane and then recrystallized at − 20 °C from *n*-hexane to give 83 mg (54%) of bright yellow crystals of [$Cp^*_2Nb(O)OH$] (**2**). The product contains up to 10% of **1** as determined for several experiments by ^{1}H-NMR spectroscopy.

2: Anal. Found: C, 60.12; H, 7.71. Calc. for $C_{20}H_{31}NbO_2$ (396.0): C, 60.61; H, 7.83%. FD-MS (from toluene): 396.0. ^{1}H-NMR (250 MHz, C_6D_6): δ 1.77 (s, 30H), 2.11 (s, 1H). IR (KBr, cm^{-1}): 3470 (m, ν_{OH}), 843 (vs, $\nu_{Nb=O}$).

*4.3. Preparation of [$Cp^*_2Nb(=O)(SC(O)NHPh)$] (**3**)*

A slight excess of phenylisothiocyanate (18 µl; 0.15 mmol) was added to a solution of 50 mg (0.13 mmol) of [$Cp^*_2Nb(=O)OH$] in 5 ml of THF. After stirring for 16 h at room temperature (r.t.), the solvent was evaporated and the yellow residue was washed with 5 ml of pentane. Recrystallization of the crude material (42 mg) from toluene–pentane gave yellow crystals (21 mg, 31%).

3: Anal. Found: C, 60.82; H, 6.77; N, 2.54. Calc. for $C_{27}H_{36}NNbO_2S$ (531.6): C, 61.01; H, 6.83; N, 2.64%. FD-MS (from toluene): 531.2. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.93 (s, 30H, C_5Me_5), 6.97 (tt, 1H, C_6H_5), 7.23 (t, 2H, C_6H_5), 7.42 (dd, 2H, C_6H_5), 9.00 (s, 1H, NH). {^{1}H} ^{13}C-NMR: (63 MHz, $CDCl_3$): δ 11.3 (C_5Me_5), 118.2 ($\boldsymbol{C}_6H_5$), 121.0 ($\boldsymbol{C}_5Me_5$), 122.6 (C_6H_5), 128.7 (C_6H_5), 139.4 (C_6H_{5ipso}), 167.2 (C=O). IR (KBr, cm^{-1}): 3220 (w, ν_{NH}), 1635 (s, ν_{CO}), 860 (m, $\nu_{Nb=O}$).

*4.4. Preparation of [$Cp^*_2Nb(=O)\{OC(O)NHPh\}$] (**4**)*

The solution of 17 µl (0.16 mmol) of phenylisocyanate and 60 mg (0.15 mmol) of [$Cp^*_2Nb(=O)OH$] (**2**) in 5 ml of THF was stirred for 1 h at r.t. After evaporation of the solvent the yellow residue was washed with 5 ml of pentane. Recrystallization of the crude material from toluene–pentane gave yellow needles of [$Cp^*_2Nb(=O)(OC(O)NHPh)$] (**4**) (20 mg, 26%).

Table 2
Crystallographic data for complexes **3**–**5**

	3	**4**	**5**
Formula	$C_{27}H_{36}NNbO_2S$	$C_{27}H_{36}NNbO_3$	$C_{27}H_{36}NNbO_2$
Molecular weight	531.6	515.2	499.5
Crystal size (mm^3)	$0.18\times0.03\times0.03$	$0.20\times0.10\times0.07$	$0.30\times0.30\times0.20$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
a (Å)	8.666(1)	9.4988(2)	16.352(1)
b (Å)	16.798(1)	9.8109(3)	15.758(1)
c (Å)	17.852(1)	26.383(1)	18.398(1)
β (°)	101.78(1)	97.77(1)	
V (Å^3)	2544(1)	2436.0(1)	4740.6(2)
Space group	$P2_1/n$	$P2_1/c$ (14)	$Pbcn$ (60)
Z	4	4	8
D_{calc} (g cm^{-3})	1.39	1.36	1.40
Instrument	Stoe IPDS	Nonius KappaCCD	Nonius KappaCCD
Temperature (K)	293	110	110
μ (mm^{-1})	0.58	0.517	0.531
Scan range	$2.7<\Theta<25.9.0$	$2.16<\Theta<28.64$	$1.79<\Theta<29.13$
Total reflections	13 580	6208	6348
Observed reflections ($I>2.0\sigma(I)$)	7624	2349	2296
LS parameters	290	280	284
Absorption correction	None	None	None
Residual density (e Å^{-3}) max/min	0.468/−0.319	0.50/−0.63	0.75/−0.54
R_1	0.042	0.038	0.040
wR_2	0.084	0.079	0.106

4: Anal. Found: C, 62.10; H, 7.20; N, 2.80. Calc. for $C_{27}H_{36}NNbO_3$ (515.5): C, 62.91; H, 7.04; N, 2.72%. FD-MS (from THF): 515.2. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.94 (s, 30H, C_5Me_5), 6.93 (t, 2H, C_6H_5), 7.23 (s, 1H, NH), 7.40 (m, 3H, C_6H_5). {^{1}H}^{13}C-NMR (63 MHz, C_6D_6): δ 10.7 ($C_5\mathit{Me}_5$), 117.7 (C_6H_5), 121.8 (C_6H_5), 122.0 (C_5Me_5), 129.2 (C_6H_5), 141.6 (C_6H_{5ipso}), 153.9 (C=O). IR (KBr, cm^{-1}): 3290 (w, ν_{NH}), 1684 (m, ν_{CO}), 825 (m, $\nu_{Nb=O}$).

*4.5. Synthesis of [Cp$_2^*$NbH{OC(O)NPh}] (**5**)*

The solution of 18 μl (0.16 mmol) of phenylisocyanate and 50 mg (0.13 mmol) of [Cp$_2^*$Nb(=O)(H)] in 5 ml of THF was stirred for 1 h at r.t. After evaporation of the solvent the residue was washed with pentane and dried to give 55 mg (84% yield) of an orange–yellow powder. Recrystallization from THF–pentane gave orange prisms of **5** which are contaminated by yellow needles. The latter consists of **4** due to mass spectroscopy and ^{1}H-NMR spectra.

5: Anal. Found: C, 64.58;H, 7.18; N, 3.04. Calc. for $C_{27}H_{36}NNbO_2$ (499.5): C, 64.92; H, 7.27; N, 2.80%. FD-MS (from toluene): 499.1. ^{1}H-NMR (250 MHz, C_6D_6): δ 1.57 (s, 30H, C_5Me_5), 4.89 (s, 1H, NbH), 6.97 (m, 1H, C_6H_5), 7.15 (m, 2H, C_6H_5), 7.40 (m, 2H, C_6H_5). IR (KBr, cm^{-1}): 1800 (w, ν_{NbH}), 1650 (vs, ν_{CO}), 1600, 1500 (s, ν_{NCO}).

4.6. Cyclization experiments of phenylisocyanate

A solution of 0.43 ml (3.95 mmol) of phenylisocyanate and 16 mg (0.039 mmol) of [Cp$_2^*$Nb(=O)H] (**1**) in 5 ml of THF was stirred for 1 h. After removal of the solvent the crude material (0.38 g) was washed with 5 ml of pentane and recrystallized from THF–pentane. The resulting white platelets, which contain $(PhNCO)_2$ (**6**) and $(PhNCO)_3$ (**7**) in an approximate ratio of 3:2, were dried for 8 h in high vacuum.

6: Anal. Found: C, 70.30; H, 4.31; N, 11.60. Calc. for $C_{14}H_{10}N_2O_2$ (238.2): C, 70.58; H, 4.23; N, 11.76%. EI-MS: 237.9. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.15–7.57 (m, C_6H_5). {^{1}H}^{13}C-NMR (63 MHz, $CDCl_3$): δ 116.7 (C_6H_5), 125.0 (C_6H_5), 129.5 (C_6H_5), 134.2 (C_6H_{5ipso}), 151.1 (C=O). IR (KBr, cm^{-1}): 1780, 1760 (ν_{CO}).

If [Cp$_2^*$Nb(=O)OMe] was employed instead of **1** under analogous conditions 0.23g (41% yield) of pure $(PhNCO)_3$·THF was obtained. Solvent free **7** was obtained after drying for 8 h in high vacuum. The same result has been obtained after a reaction time of 5 min.

7: Anal. Found: C, 70.37; H, 4.26; N, 11.72. Calc. for $C_{21}H_{15}N_3O_3$ (357.5): C, 70.58; H, 4.23; N, 11.76%. EI-MS: 357.4. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.30–7.55 (m, C_6H_5). {^{1}H}^{13}C-NMR (63 MHz, $CDCl_3$): δ 128.5 (C_6H_5), 129.37 (C_6H_5), 129.68 (C_6H_5), 133.7 (C_6H_{5ipso}), 148.7 (C=O). IR (KBr, cm^{-1}): 1710 (ν_{CO}).

4.7. X-ray structure solution

4.7.1. [Cp$^*_2$Nb(=O)(SC(O)NHPh)] (**3**)

The compound crystallized in thin yellow needles with a size just suitable for X-ray structure analysis on a STOE IPDS diffractometer. For a few crystals the data for at least 180° in φ were collected. The inspection of the reflections in reciprocal space (program part RECIPE of STOE-IPDS software [18]) revealed, that all crystals were twinned following the same law. The crystals belong to the monoclinic crystal system and the twin law is a twofold axis in [100] direction. The matrix to transform one cell into the other is (1 0 0, 0 −1 0, −0.8387 0 −1), the reciprocal lattices coincide almost exactly when $|h| = 0$ or 6 (a similar example is given in Ref. [19]).

It was possible to solve the main part of the structure from a data set of only one twin component. But reliable results of a refinement in this case could only be obtained with the SHELXL97 program [20] and a HKLF 5 instruction thus including all available data and marking the reflections belonging to one of the two components or to both. All reflections with undisturbed intensities were collected by an integration in TWIN modus of the STOE-IPDS software [18] with the two orientation matrices for both components. From a subsequent normal integration with only one orientation matrix we extracted all reflections with intensity contributions from both components. A modified program from Ruck [21] looked with the known transformation matrix for reflections with almost perfect coincidence, added the corresponding $F^2_{(hkl)}$-values of the second component and marked all these reflections to be used with SHELXL97 and HKLF 5. All partially overlapped reflections were discarded because the intensity of such reflections could not be determined correctly.

With this new data set, it was possible to locate the remaining atoms from difference Fourier syntheses and to refine the structure to absolutely reliable final parameters. The refined fractional contribution of twin component two was 0.3048.

4.7.2. [Cp$^*_2$Nb(=O){OC(O)NHPh}] (**4**) *and [Cp$^*_2$NbH{OC(O)NPh}]* (**5**)

A pale yellow crystal of **4** and an orange one of **5** were mounted on a Nonius KappaCCD diffractometer using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 52664 (**4**) and 35711 (**5**) reflections were indexed, integrated and corrected for Lorentz and polarization effects using DENZO-SMN and SCALEPACK [22]. Data reduction yielded 6208 (**4**) and 6348 (**5**) unique reflections of which 2349 (**4**) and 2296 (**5**) had $I > 2\sigma(I)$. The structures were solved by Patterson syntheses and subsequent difference Fourier maps and refined by full-matrix least squares on F^2 using SHELXL [23]. In the case of **4** one of the C$_5$Me$_5$ rings is disordered and occupies two positions rotated by 21.5°. The geometrical centers of C6–C10 and C6*–C10* exhibit a slippage of 0.17 Å. Both cycles were constrained to perfect pentagonal rings and refined with isotropic thermal parameters and a multiplicity of 0.5. Other non-hydrogen atoms in this structure were refined with anisotropic parameters. All non-hydrogen atoms in the structure of **5** were refined with anisotropic thermal parameters. All hydrogen atoms (except the hydride in **5**) in both structures were included in calculated positions and refined in a riding model with isotropic displacement coefficients. The niobium hydride in **5** was located in a difference Fourier map and freely refined with an isotropic temperature factor.

Further details for the structure refinements of complexes **3**–**5** are listed in Table 2.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 161795 (**3**), 161796 (**5**), 161797 (**4**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdccam.ac.uk; deposit@chemcrys. cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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References

[1] R.S. Pilato, C.E. Housmekeridis, P. Jernakoff, D. Rubin, G.L. Geoffroy, A.L. Rheingold, Organometallics 9 (1990) 2333.

[2] R.H. Holm, Chem. Rev. 87 (1987) 1401.

[3] M.J. Carney, P.J. Walsh, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 111 (1989) 8751.

[4] (a) W.A. Herrmann, R. Serrano, U. Küsthardt, M.L. Ziegler, E. Guggolz, T. Zahn, Angew. Chem. 96 (1984) 498;
(b) W.A. Herrmann, R. Serrano, U. Küsthardt, M.L. Ziegler, E. Guggolz, T. Zahn, Angew. Chem. Int. Ed. Engl. 23 (1984) 515.

[5] U. Küsthardt, W.A. Herrmann, M.L. Ziegler, T. Zahn, B. Nuber, J. Organomet. Chem. 311 (1986) 163.

[6] H. Brunner, J.-C. Leblanc, D. Lucas, W. Meier, C. Moise, Y. Mugnier, B. Nuber, S. Rigny, A. Sadorge, J. Wachter, J. Organomet. Chem. 566 (1998) 203.

[7] D. Braga, F. Grepioni, G.R. Desiraju, J. Organomet. Chem. 548 (1997) 33.

[8] R.J. Balahura, G. Ferguson, L. Ecott, P.Y. Siew, J. Chem. Soc. Dalton Trans. (1982) 747.

[9] W.A. Howard, T.M. Truka, M. Waters, G. Parkin, J. Organomet. Chem. 528 (1997) 95 references therein.

[10] S. Schmid, J. Strähle, Z. Naturforsch. B46 (1991) 235.

[11] H. Brunner, M.M. Kubicki, J.-C. Leblanc, C. Moise, F. Volpato, J. Wachter, J. Chem. Soc. Chem. Commun. (1993) 851.

[12] Y. Nambo, T. Endo, J. Org. Chem. 58 (1993) 1932.

[13] S.R. Foley, G.P.A. Yap, D.S. Richeson, Organometallics 18 (1999) 4700 This report on the cyclotrimerization of aryl isocyanates summarizes the actual literature on this subject and contains an X-ray crystal structure of $(PhNCO)_3$.

[14] I.S. Kolomnikov, Yu.D. Koreshkov, T.S. Lobeeva, M.E. Volpin, J. Chem. Soc. Chem. Commun. (1970) 1432.

[15] A. Antiñolo, F. Carillo, M. Fajardo, S. Garcia-Yuste, A. Otero, J. Organomet. Chem. 482 (1994) 93.

[16] J. Amaudrut, J.-C. Leblanc, C. Moise, J. Sala-Pala, J. Organomet. Chem. 295 (1985) 167.

[17] H. Brunner, G. Gehart, W. Meier, J. Wachter, A. Riedel, S. Elkrami, Y. Mugnier, B. Nuber, Organometallics 13 (1994) 134.

[18] STOE IPDS-software, version 2.89, STOE & CIE GmbH, Darmstadt, Germany, 1998.

[19] R. Herbst-Irmer, G.M. Sheldrick, Acta Crystallogr. Sect. B 54 (1998) 443.

[20] G.M. Sheldrick, SHELXL97: Program for crystal structure refinement, University of Göttingen, Germany, 1997.

[21] M. Ruck, Technische Universität Dresden, 1999, private communication.

[22] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.

[23] G.M. Sheldrick, SHELXLS97 and SHELX97, University of Göttingen, 1997.