

Synthesis and reactivity of bis(trimethylsilylcyclopentadienyl)-niobium compounds with cumulene ligands

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(Received April 14th, 1987)

Abstract

The reduction of $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2$ (I) with Na/Hg in a 1/1 molar ratio gives $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}$ (II). Reactions of II with some cumulenes give the corresponding niobocene derivatives with the functional groups anchored to the bis(trimethylsilylcyclopentadienyl)niobium unit, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{CS}_2)$, $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{PhNCX})$ ($\text{X} = \text{O}$ or S) and $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{CyCN-Cy})$. The imido compound $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{NPh})$ has been prepared. The chemical properties and structural features of the compounds are described.

Introduction

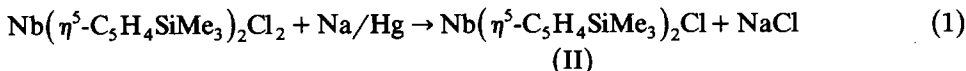
Metal-promoted activations on some cumulenes can simulate the metal-induced transformations on carbon dioxide, the activation of which is a matter of great interest [1]. The activation of cumulenes, like $\text{X}=\text{C}=\text{Y}$, by metallocene derivatives of the early transition metals have been described previously [2–4]. We now report the results of the interactions of the carbenoid-like $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}$ (II) with cumulenes to give new niobocene compounds $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{XCy})$ (III–VI). The chemistry of the new complexes has been studied and structural information obtained from IR and ^1H and ^{13}C NMR spectroscopy. The oxidation-reduction potentials of the $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{PhNCO})$ (IV) have been determined by cyclic voltammetry.

Results and discussion

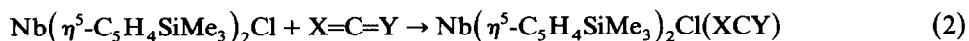
Synthetic studies

Complex I was prepared as previously described [5]. Complex II was obtained as brown crystals by reducing a THF solution of I with a 1/1 molar proportion of

sodium amalgam according to eq. 1:



Complex II is very air sensitive, and great care must be taken during its handling to avoid decomposition. It is very soluble in toluene, diethyl ether, and THF, and soluble in alkanes. It decomposes in halogenated solvents to give complex I. Similar compounds containing the $\eta^5\text{-C}_5\text{H}_5$ ligand have been described previously [6,7]. Complex II reacts with π -acid ligands to give the 18-electrons species $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl(L)}$, where L is a π -acid ligand [8]. We thus decided to study the metal-promoted, reactions of several cumulenes with the carbenoid-like complex II, and found that with a molar proportion of cumulenes $\text{X}=\text{C}=\text{Y}$ in hexane as solvent they gave the corresponding complexes with the cumulene coordinated to the metal centre, according to eq. 2.



(III: X = Y = S;

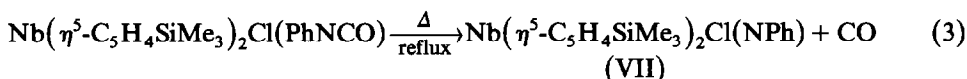
IV: X = PhN, Y = O;

V: X = PhN, Y = S;

VI: X = Y = CyN)

All the complexes were isolated as microcrystalline solids, insoluble in hexane. They are soluble in THF, diethyl ether, dichloromethane and chloroform. Complex VI is very air-sensitive and decomposes readily in solution even under nitrogen, whereas complexes III, IV, and V are indefinitely stable under nitrogen.

We also examined the reactions of complex IV, because it is known that the coordination of a cumulene to metal centre changes its reactivity [9] and found that complex VII could be isolated as an orange crystalline solid when a toluene solution of IV was refluxed for several hours, according to eq. 3.



Complex VII is air-sensitive but can be stored unchanged under nitrogen and is soluble in the common organic solvents. As far as we know it is the first complex having an imido group bonded to a niobocene unit. The preparation of imido derivatives by interaction of an oxo compound with the corresponding organic isocyanate has been described previously [10].

When the reaction is carried out in the presence of an excess of PhNCO, a mixture of complex VII and the triphenyl isocyanurate trimer $(\text{PhNCO})_3$, was isolated. The trimerization of phenylisocyanate may be the result of multiple insertion processes previously observed for niobium alkoxides [11].

We finally examined the reaction of complex II with species containing only one double bond, namely $\text{PhCH}=\text{NPh}$, $\text{PhCH}=\text{O}$, and $\text{PhN}=\text{NPh}$. In all cases complex I was obtained along with intractable products.

Spectroscopic studies

IR spectra. The IR spectra of the niobocene compounds show the absorptions expected for a η^5 -cyclopentadienyl ligand and the SiMe_3 group [12,13]. Absorption

Table 1

Analyses (found (calcd.)(%)) and physical properties of trimethylsilylcyclopentadienylniobium complexes

Complex	C	H	N	Colour	Yield (%)
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl (II)	47.4 (47.7)	6.8 (6.5)	–	Brown	95
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(CS ₂) (III)	42.2 (42.6)	5.3 (5.9)	–	Orange	90
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(PhNCO) (IV)	52.9 (52.8)	5.9 (5.9)	2.5 (2.7)	Pale yellow	97
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(PhNCS) (V)	51.0 (51.0)	5.9 (5.8)	2.9 (2.9)	Yellow greenish	50
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(CyNCNCy) (VI)	55.6 (57.2)	7.8 (7.9)	4.3 (4.6)	Yellow	60
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(NPh) (VII)	55.9 (56.3)	5.7 (5.9)	2.8 (2.8)	Red orange	80

Table 2

Selected IR data for trimethylsilylcyclopentadienylniobium complexes (ν in cm⁻¹)

Complex	ν (Nb–Cl)	ν (C=O)	ν (C=N)	ν (C=S)
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl (II)	250			
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(CS ₂) (III)	280			1160
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(PhNCO) (IV)	290	1720		
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(PhNCS) (V)	270		1650	
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(CyNCNCy) (VI)	270		1710	
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(NPh) (VII)	290			

bands between 250–290 cm⁻¹ due to the ν (Nb–Cl) stretching vibration are present (see Table 2). The IR spectrum of complex III shows a ν (C=S) band at 1160 cm⁻¹, indicating η^2 -C,S bonding to the metal [14]. In the IR spectrum of complex IV, a strong band at 1720 cm⁻¹ can be assigned to either the ν (N=C) or ν (C=O)

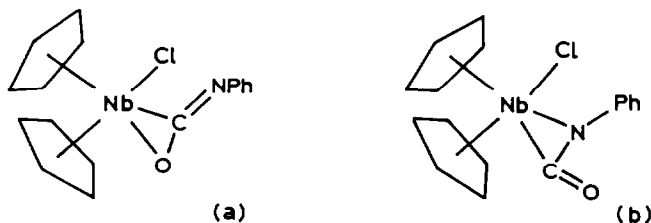


Fig. 1

Table 3

¹H NMR data for trimethylsilylcyclopentadienylniobium complexes (δ ppm multiplicity, in C₆D₆ as solvent with Me₄Si as internal standards)

Complex	H(SiMe ₃)	H(C ₅ H ₄)	L
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl (II)	-0.09(s)	5.72(m); 4.49(m)	
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(CS ₂) (III)	+0.19(s)	5.73(m); 5.61(m); 5.11(m); 5.09(m)	
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(PhNCO) (IV)	+0.17(s)	6.12(m); 5.58(m); 5.36(m); 5.24(m)	8.41(m); 8.29(m); 7.22(m) (Ph)
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(PhNCS) (V)	+0.21(s)	5.93(m); 5.73(m); 5.35(m); 5.22(m)	7.78(m); 7.33(m) (Ph)
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(CyNCNCy) (VI)	+0.30(s)	6.55(m); 6.03(m)	1.57(m) (Cy)
Nb(η^5 -C ₅ H ₄ SiMe ₃) ₂ Cl(NPh) (VII)	+0.20(s)	6.58(m); 6.40(m); 6.09(m); 5.67(m)	7.11(m) (Ph)

stretching vibration depending on whether the coordination of PhNCO occurs through the C=O (a) or the C=N (b) bond (Fig. 1).

There are no examples of an η^2 -C,O-bonded organic isocyanate. The presence of a band at 1650 cm⁻¹ due to the ν (N=C) in the spectrum of complex V suggests η^2 -C,S bonding to metal. This coordination pattern has been observed in many isothiocyanate complexes [15]. The IR spectrum of complex VI shows the expected band due to the ν (N=C) at 1710 cm⁻¹ (see Table 2).

NMR spectra. The ¹H NMR spectra of the complexes show a singlet between δ -0.09–0.30 ppm due to the methyl protons of the SiMe₃ group, and several broad peaks between δ 4.49–6.55 ppm due to the η^5 -C₅H₄ protons, which are not equivalent [16]. The chemical shifts of the methyl protons in complex II are displaced to high field relative to those for the remaining complexes. A complex multiplet is observed for the phenyl protons in complexes IV, V, VII and for the cyclohexyl protons in complex VI (see Table 3).

The ¹³C NMR spectra of the niobocene compounds show the pattern previously observed for the various carbon atoms of the cyclopentadienyl ring for other bis(trimethylsilyl)cyclopentadienylniobium derivatives [8]. The ¹³C NMR spectrum of complex II shows three resonances for the cyclopentadienyl carbon atoms, but the spectra of complexes III, IV, V, VII show five resonances (see Table 4). The weakest of these resonances is due to the carbon bearing the SiMe₃ substituent, probably due to relaxation effects. All the spectra also show a singlet between δ -1.2–0.5 ppm due to the SiMe₃ carbon atoms and the corresponding resonances due to the various carbon atoms of the ligands (see Table 4). The presence of a resonance at δ 188.1 ppm in complex IV can be assigned to the carbon atom of the CO group [17].

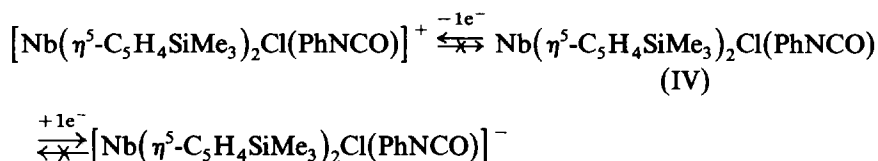
Electrochemical studies. Electrochemical studies have been made on dicyclopentadienylniobium compounds [8,18]. The electrochemistry of complex IV has different features from those known for the Nb(η^5 -C₅H₄SiMe₃)₂Cl(L) (L = π -acid ligand) compounds [8]. One oxidation and one reduction peak, at 0.9 V and -1.85 V, respectively are observed in the cyclovoltamogram, corresponding with the

Table 4

^{13}C NMR data for trimethylsilylcyclopentadienyl niobium complexes (δ (ppm), in THF as solvent, with Me_4Si as internal standard)

Complex	SiMe_3	$\text{C}_5\text{H}_4\text{SiMe}_3$		$\bar{\text{C}}$	L
		C(1)	C(2),C(3),C(4),C(5)		
$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}$ (II)	+0.5	87.7	109.8; 101.1	99.5	
$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{CS}_2)$ (III)	-1.2	120.7	126.5; 123.6; 112.9; 107.7	118.1	
$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{PhNCO})$ (IV)	-0.2	116.9	122.9; 119.1; 110.2; 107.0	115.2	144.6 <i>ipso</i> (Ph); 128.7 (Ph); 124.9 (Ph); 123.6 (Ph); 188.1 (CO)
$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{PhNCS})$ (V)	-0.1	118.9	123.0; 121.7; 111.1; 106.3	116.2	154.1 <i>ipso</i> (Ph); 129.2 (Ph); 124.5 (Ph); 123.3 (Ph)
$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}(\text{NPh})$ (VII)	+0.6	120.3	120.7; 118.6; 112.7; 111.9	116.9	160.7 <i>ipso</i> (Ph); 128.8 (Ph); 127.9 (Ph); 121.8 (Ph)

following irreversible processes:



These values mean that the LUMO and HOMO orbitals of the $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}$ fragment are fully involved in the coordination with the isocyanate ligand.

Experimental

All operations were carried out under vacuum or in an inert atmosphere with Schlenk type glassware. Solvents were dried distilled under N_2 and degassed before use. IR spectra were recorded as Nujol mulls between CsI plates in the region $4000\text{--}200\text{ cm}^{-1}$ with a Perkin-Elmer 599 spectrophotometer. Carbon, hydrogen and nitrogen analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^1H , ^{13}C NMR spectra were recorded on a Varian FT 80A or a Bruker WP-60-CW instruments. Cyclic voltammetry measurements were carried out under dry nitrogen with distilled and dried THF as solvent. Tetrabutylammonium tetrafluoroborate (0.2 M), prepared as previously described [19] was used as electrolyte support, a three platinum electrode cell was used with ferrocene as internal reference.

$\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}$ (II). THF (50 ml) was added to a mixture of $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2$ (1.000 g, 2.28 mmol) and sodium amalgam (2.28 mmol of Na). The mixture was vigorously stirred for 3 h at room temperature, then filtered, and the filtrate was evaporated to dryness under vacuum. The solid residue was extracted with hexane, and the extract was concentrated to give brown crystals of complex II. The crystals were dried under vacuum.

$Nb(\eta^5-C_5H_4SiMe_3)_2Cl(XCY)$ ($X = Y = S$, III; $X = PhN$, $Y = O$, IV; $X = PhN$, $Y = S$, V; $X = Y = CyN$, VI). PhNCO (0.140 g, 1.17 mmol) was added to a solution of complex II (0.460 g, 1.17 mmol) in hexane (50 ml). The solution was stirred at room temperature for 3 h and the pale yellow microcrystalline solid which separated was filtered off, repeatedly washed with cold hexane, and dried under vacuum. It was identified as complex IV. Complexes III, V and VI were prepared similarly.

$Nb(\eta^5-C_5H_4SiMe_3)_2Cl(NPh)$ (VII). A solution of complex IV in toluene was stirred under reflux. After 4 h the initially pale yellow solution became red orange. This solution gave complex VII as red orange crystals after concentration and cooling at $-30^\circ C$.

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