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Preparation and structural characterization of chloro- and alkyl-isocyanidoniobocene compounds. Synthesis of the first dicyclopentadienylniobium species containing iminoacyl groups

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Abstract

The reduction of the niobocene complexes $Nb(\eta^5\text{-}C_5H_3RR')_2Cl_2$ ($R = H$, $R' = SiMe_3$ (I); $R = R' = SiMe_3$ (II)) with one equivalent of (1%) sodium amalgam in the presence of an isocyanide ligand $R''NC$ yields $Nb(\eta^5\text{-}C_5H_3RR')_2Cl(CNR'')$ ($R = H$, $R' = SiMe_3$, $R'' = Cy =$ cyclohexyl (III); ${}^tBu$ (IV); Ph (V); $2,6\text{-}Me_2C_6H_3$ (VI), and $R = R' = SiMe_3$, $R'' = Cy$ (VII), ${}^tBu$ (VIII)). Reactions of III and V with LiMe and $LiCH_2SiMe_3$ give the thermally stable iminoacyl compounds $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CRNR')]_n$ ($R = Me$, $R' = Cy$ (IX); $R = CH_2SiMe_3$, $R' = Cy$ (X) and $R = Me$, $R' = Ph$ (XII)), through spontaneous insertion of the isocyanide ligand into the alkyl–niobium bond. Insertion of t-BuNC into the metal–alkyl bond in IV was not observed, and only the alkyl isocyanide derivative $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Me)(CN{}^tBu)$ (XI) was isolated. The compounds were characterized by IR and NMR spectroscopy.

Introduction

Isocyanide complexes of a wide variety of transition metals have been prepared [1] and $(\eta^5\text{-}C_5H_5)$ niobocene isocyanide complexes [2,3] in particular have received much attention. Insertions of isocyanides into metal–alkyl or metal–aryl bonds are well known but no iminoacyl niobocene complexes have been previously described. We describe the isolation and characterization of new chloronioboceneisocyanide derivatives containing substituted cyclopentadienyl rings $\eta^5\text{-}C_5H_3RR'$, and their alkylation reactions which in some cases lead to the isolation of the iminoacyl derivatives.

Results and discussion

Synthetic studies

Reduction of I and II [4,5] with one equivalent of Na–Hg (1%) has been carried out in the presence of the isocyanide ligands; according to eq. 1.

$$\mathrm{Nb(\eta^5\text{-}C_5H_3RR')_2Cl_2 + Na\text{–}Hg + CNR'' \rightarrow Nb(\eta^5\text{-}C_5H_3RR')_2Cl(CNR'')} \qquad (1)$$

(I: $R = H, R' = SiMe_3$;
II: $R = R' = SiMe_3$)

(III: $R = H, R' = SiMe_3, R'' = Cy$;
IV: $R = H, R' = SiMe_3, R'' = {}^tBu$;
V: $R = H, R' = SiMe_3, R'' = Ph$;
VI: $R = H, R' = SiMe_3$,
$R'' = 2,6\text{-}Me_2C_6H_3$;
VII: $R = R' = SiMe_3, R'' = Cy$;
VIII: $R = R' = SiMe_3, R'' = {}^tBu$)

Complexes III–VIII were isolated as air sensitive crystalline solids. They are soluble in chloroform or dichloromethane (with decomposition), THF, diethyl ether, and aromatic and aliphatic hydrocarbons. The complexes with the η^5-$C_5H_3(SiMe_3)_2$ ring are more soluble than those with η^5-$C_5H_4SiMe_3$. The reactions of III and V with alkyllithiums (1/1 molar ratio) yield the corresponding iminoacyl compounds, according to eq. 2:

$$\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(CNR') + LiR \rightarrow Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CRNR')} \qquad (2)$$

(III: $R' = Cy$;
V: $R' = Ph$)

(IX: $R = Me, R' = Cy$;
X: $R = CH_2SiMe_3$; $R' = Cy$;
XII: $R = Me, R' = Ph$)

The intermediate alkyl isocyanide complexes which presumably are formed in the alkylation are spontaneously transformed at 0 °C into the corresponding iminoacyl

Table 1

Analyses and physical properties of niobocene complexes

Complex [a]	Analysis (Found (Calcd.) (%))			Colour	Yield (%)
	C	H	N		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)CNCy$	54.2	7.9	2.7	Red	80
(III)	(53.9)	(7.3)	(2.7)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CN{}^tBu)$	52.2	7.6	3.2	Red	80
(IV)	(51.9)	(7.3)	(2.9)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CNPh)$	54.5	6.1	2.8	Brown	75
(V)	(54.5)	(6.2)	(2.8)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CNXy)$	57.0	6.9	2.9	Green	80
(VI)	(56.2)	(6.6)	(2.6)		
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2(Cl)(CNCy)$	53.6	8.5	2.2	Red	70
(VII)	(53.1)	(8.1)	(2.1)		
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2(Cl)(CN{}^tBu)$	51.9	8.6	2.5	Red	70
(VIII)	(51.4)	(8.1)	(2.2)		

[a] Cy = cyclohexyl; Xy = $2,6\text{-}Me_2C_6H_3$.

complexes. However, the corresponding reaction of IV with LiMe (1/1 molar ratio) gives the alkyl compound XI, according to eq. 3.

$$\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl}(\mathrm{CN^tBu}) + \mathrm{LiMe} \rightarrow \underset{\text{(XI)}}{\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{Me})(\mathrm{CN^tBu})} \qquad (3)$$

In this case the insertion does not take place. Complexes VII and VIII do not react with the alkylating agents mentioned. Complexes IX, X, XI and XII could not be isolated as solids, but they were characterized spectroscopically in the green or red oils obtained upon evaporation of the solvents. They are very air sensitive and soluble in most common solvents.

All the solid compounds were characterized by analysis (see Table 1).

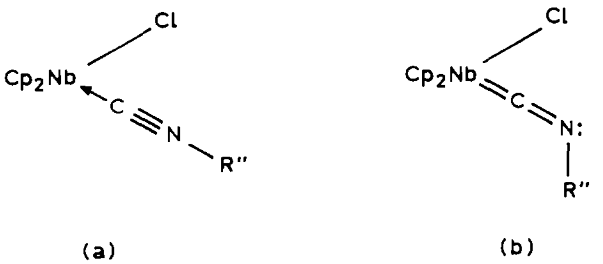
IR spectroscopy

The IR spectra of the niobocene derivatives show the absorptions expected for the η^5-cyclopentadienyl ligand and the $SiMe_3$ group [6,7]. All the IR spectra for $Nb(\eta^5\text{-}C_5H_3RR')_2Cl(CNR'')$ show bands between 247 and 260 cm^{-1} due to the (Nb–Cl) stretching vibration (Table 2). A single absorption at ca. 2100 cm^{-1} (Table 2) is observed for complexes III–VIII and XI, suggesting a linear C–N–R structure (a) (Scheme 1). However we cannot account for the presence of an unexpected additional absorption observed for complexes III, IV and XI, since the presence of species containing a bent structure (b) is extremely unlikely, especially since the same samples give the simple NMR spectra discussed below.

Table 2

Selected IR data for niobocene derivatives $\nu(cm^{-1})$

Complex	$\nu(C\equiv N)$	$\nu(C=N)$	$\nu(Nb-Cl)$
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CNCy)$ (III)	2080(m);1855(m)		255(m)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CN^tBu)$ (IV)	2080(s);1870(m)		252(w)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CNPh)$ (V)	1797(s)		260(m)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CN)Xy$ (VI)	2075(s)		255(w)
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2(Cl)(CNCy)$ (VII)	2110(s)		247(w)
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2(Cl)(CN^tBu)$ (VIII)	2090(s)		247(w)
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CMeNCy)]_n$ (IX)		1640(m)	
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{C(CH_2SiMe_3)NCy\}]_n$ (X)		1608(m)	
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Me)(CN^tBu)$ (XI)	2095(s);1863(m)		
$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(CMeNPh)]_n$ (XII)		1620(m)	



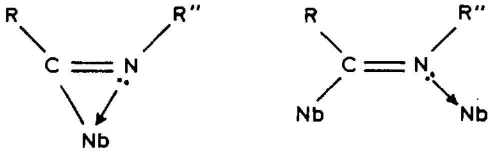
Scheme 1

The IR data agree well with the results of electrochemical studies for complexes $Nb(\eta^5-C_5H_3RR')_2ClL$, ($L = \pi$-acid ligand) [8]. Thus the presence of the $SiMe_3$ groups in the cyclopentadienyl ring produces a higher electronic delocalization on the ring due to the significant $-M$ effect of the $SiMe_3$ group and this reduces the π-donor ability of the $Nb(\eta^5-C_5H_3RR')_2Cl$ moiety with respect to $Nb(\eta^5-C_5H_5)_2Cl$. Probably this electronic influence accounts for the spontaneous insertion of the isocyanide ligand (with $R'' =$ Cy and Ph) into the niobium–alkyl bond to yield the corresponding iminoacyl complex. Teuben and his colleagues [3] have suggested that the strong metal–isocyanide interaction arising from the extensive back donation into the isocyanide π^*-system prevents the formation of the iminoacyl product in niobocene and tantalocene complexes containing the $\eta^5-C_5H_5$ ring.

The IR spectra of the iminoacyl complexes IX, X and XII show the ν(N=C) at ca. 1600 cm^{-1} (Table 2). The values agree well with those previously reported for many iminoacyl complexes [1]. It is difficult to account for the differing effects of the isocyanide ligands on the insertion reaction, but probably the insertion of the bulky CN^tBu into the metal–carbon bond is sterically hindered.

NMR spectroscopy

All the complexes exhibit ^1H NMR spectra showing the expected singlet for the $SiMe_3$ group and several broad peaks due to the non-equivalent $\eta^5-C_5H_3RR'$ protons [9] (Table 3). In addition, complexes III–VIII show the ^1H signals characteristic of the isocyanide ligands (Table 3). The chemical shifts for the methyl group in complexes IX and XII and CH_2 in complex X indicate that they are attached to a carbon atom, whereas that shift for the methyl group in complex XI is characteristic of a Me directly attached to the niobium(III) atom (see Table 3). In addition the low values for the mean shifts for the cyclopentadienyl protons, mean values $\overline{H}(C_5H_4)$, in complexes IX, X and XII confirm the extensive back donation into the cyclopentadienyl ring, enhanced by the coordination of the nitrogen atom. These data and also the ^{13}C NMR spectra (see below) are in agreement with structure (a), depicted in Scheme 2, containing a terminal η^2-iminoacyl ligand, and not with the unlikely bridged structure (b).



Scheme 2

Table 3

^{1}H NMR spectra for niobocene complexes; δ(ppm) (multiplicity; rel. int.) [a]

Complex	H_{SiMe_3}	$H_{C_5H_3RR'}$	$\bar{H}_{C_5H_3RR'}$	CNR″	R‴
III	0.19(s;18)	5.50(m;4);4.92(m;2); 4.81(m;2)	5.18	3.34(br;1)CH(Cy) 1.51,1.41,1.11(m;10) CH_2(Cy)	
IV	0.18(s;18)	5.58(m;2);5.40(m;2); 4.98(m;2);4.84(m;2)	5.20	1.16(s;9)^{t}Bu	
V	0.22(s;18)	5.39(m;4);5.22(m;2); 5.08(m;2)	5.27	7.34–6.93(m;5)Ph	
VI	0.16(s;18)	5.45(m;4);4.92(m;4)	5.19	6.70(s;3)Ph;2.26(s;6)Me	
VII	0.38(s;18) 0.23(s;18)	5.67(m;2);4.86(m;2); 4.78(m;2)	5.10	3.42(br;1)CH(Cy) 1.82–0.89(m;10)CH_2(Cy)	
VIII	0.38(s;18) 0.22(s;18)	5.62(m;2);4.86(m;2); 4.75(m;2)	5.08	1.15(s;9)^{t}Bu	
IX	0.33(s;18)	5.27(m;4);3.60(m;2); 3.35(m;2)	4.37	2.97(br;1);CH(Cy) 1.57–0.92(m;10)CH_2(Cy)	1.98(s;3)Me
X	0.32(s;18)	5.30(m;4);3.71(m;2); 3.56(m;2)	4.47	3.16(br;1)CH(Cy) 1.60–0.88(m;10)CH_2(Cy)	2.31(s;2)CH_2 −0.02(s;9)$SiMe_3$
XI	0.20(s;18)	5.10(m;4);4.66(m;4)	4.88	1.26(s;9)^{t}Bu	−0.46(s;3)Me
XII	0.27(s;18)	5.37(m;2);5.28(m;2); 3.60(m;4)	4.46	6.96,6.68,6.58(m;5)Ph	2.26(s;3)Me

[a] In C_6D_6 as solvent. Internal standard TMS.

Table 4

^{13}C NMR spectra for niobocene complexes; δ(ppm) [a]

Complex	$SiMe_3$	η^5-C_5H_3RR'	$\bar{C}$	CNR″	R‴
III	0.5	92.8(^{1}C);109.4; 103.1;100.0;95.5	100.1	201.9 *C*NCy;57.7 ^{1}C(Cy); 34.2 ^{2,6}C(Cy);26.0 ^{4}C(Cy); 23.9 ^{3,5}C(Cy)	
IV	0.5	94.3(^{1}C);110.1; 103.8;99.6;95.9	100.7	214.6 *C*N^{t}Bu;61.3 ^{1}C(^{t}Bu); 31.5 Me(^{t}Bu)	
V	0.4	99.1(^{1}C);110.2; 104.4;104.4;97.2	103.0	247.6 *C*NPh;137.4 ^{1}C(Ph); 130.2 ^{3,5}C(Ph) 127.5 ^{4}C(Ph);125.2 ^{2,6}C(Ph)	
VI	0.4	95.0(^{1}C);110.2; 104.3;100.3;96.1	101.2	214.2 *C*NPh;19.5(Me); 130.7 ^{1}C(Ph); 128.6 ^{3,5}C(Ph′);127.4 ^{4}C(Ph′); 133.7 ^{2,6}C(Ph′)	
VII	0.5	98.2(^{1}C);117.4(^{3}C); 124.2;93.2;91.6	104.9	195.4 *C*NCy;57.4 ^{1}C(Cy);34.2 ^{2,6}C(Cy);25.8 ^{4}C(Cy);24.6 ^{3,5}C(Cy)	
VIII	0.6;0.4	98.3(^{1}C);117.3(^{3}C); 123.9;93.4;91.4	104.9	184.0 *C*N^{t}Bu;59.5 ^{1}C(^{t}Bu); 31.2 Me(^{t}Bu)	
IX	1.3	84.7(^{1}C);97.8; 94.4;93.7;93.5	92.8	56.8 ^{1}C(Cy);32.7 ^{2,6}C(Cy); 26.3 ^{4}C(Cy);25.5 ^{3,5}C(Cy)	21.4 Me
X	1.4	84.0(^{1}C);98.3; 95.1;93.6;92.7	92.7	56.7 ^{1}C(Cy);32.6 ^{2,6}C(Cy); 26.1 ^{4}C(Cy);25.5 ^{3,5}C(Cy)	30.3 CH_2 −0.3 $SiMe_3$
XI	0.5	95.2(^{1}C);105.0; 103.1;95.6;93.8	98.5	62.9 ^{1}C(^{t}Bu);32.1 Me(^{t}Bu)	−14.8(br)Me
XII	1.4	85.3(^{1}C);98.7; 97.1;95.0;94.3	94.1	146.3 ^{1}C(Ph);129.2 ^{3,5}C(Ph); 126.2 ^{4}C(Ph);123.7 ^{2,6}C(Ph)	24.1Me

[a] In THF.

The ^{13}C NMR spectra of all the niobocene complexes show five resonances for the cyclopentadienyl ring carbon atoms, indicating that all these atoms are magnetically different, as was observed for other cyclopentadienyl complexes containing two different substituents in the reflection plane of the rings [8]. Resonances due to the $SiMe_3$ groups and the ligands are also observed (Table 4). The isocyanide atom gives a weak and broad signal for complexes III–VIII (Table 4) owing to the high ^{93}Nb quadrupolar moment [10]. This signal is so weak and broad that it cannot be observed for the isocyanide carbon atom in complex XI and the iminoacyl carbon atom in complexes IX, X and XII. No significant changes of the chemical shift corresponding to carbon atoms of R″ group in the isocyanide ligands are observed with respect the free isocyanides, except for the resonance due to the carbon directly attached to N, which is shifted downfield. The average shift for the five resonances of the cyclopentadienyl ring in complexes IX, X and XII is downfield, in keeping with the extensive back donation considered above.

Experimental

All operations were carried out under vacuum or in an inert atmosphere with Schlenk type glassware. Solvents were dried and distilled under N_2, and degassed before use. Complexes I and II were prepared as reported [4,5].

IR spectra were recorded as Nujol mulls between CsI plates in the region 4000–200 cm^{-1} with a Perkin–Elmer 599 spectrophotometer. Carbon, hydrogen and nitrogen analyses were performed with a Perkin–Elmer 240B microanalyzer. ^1H and ^{13}C NMR spectra were recorded on Varian FT80A or Bruker WP-60-CW spectrometers.

$Nb(\eta^5\text{-}C_5H_3RR')_2Cl(CNR'')$ *(III, IV, V, VI, VII, VIII)*

The procedure was similar in all cases. A THF solution (100 ml) of the CNCy (3.60 mmol) was added to a mixture of sodium amalgam (10%, 3.48 mmol of Na) and $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ (3.42 mmol). The mixture was vigorously stirred 2 h at room temperature, filtered, and evaporated to dryness under vacuum. The residual red oil was extracted, and the extract was concentrated then cooled at −78 °C, to give red crystals of complex III, which were dried under vacuum.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)(CRNR')$ *(IX, X, XII);* $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Me)(CN^tBu)$ *(XI)*

The procedure was similar in all cases. Methyllithium (1.22 ml of a 1.6 *M* solution in diethyl ether) was added to a suspension of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Cl)(CNCy)$ (1.95 mmol) in 100 ml of hexane at −78 °C. The red mixture was allowed to warm up with stirring, and at 0 °C the colour had changed to green. After 2 h, filtration and removal of the solvent in vacuo gave a green oil consisting of the pure complex IX.

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References

1 E. Singleton and H.E. Oosthuizen, Adv. Organomet. Chem., 22 (1984) 209.

2 R. Serrano and P. Royo, J. Organomet. Chem., 247 (1983) 33.

3 A.H. Klazinga and J.H. Teuben, J. Organomet. Chem., 192 (1980) 75.

4 P.B. Hitchcock, M.F. Lappert and C.R.C. Milne, J. Chem. Soc., Dalton Trans., (1981) 180.

5 J.M. Martínez de Ilarduya, private communication.

6 H.P. Fritz, Adv. Organomet. Chem., 1 (1964) 239.

7 H. Burger, Organomet. Chem. Rev. A, 3 (1968) 425.

8 A. Antiñolo, P. Gómez-Sal, J.M. Martínez de Ilarduya, A. Otero, P. Royo, S. Martínez Carrera and S. García Blanco, J. Chem. Soc., Dalton Trans., (1987) 975.

9 M.F. Lappert, C.J. Pickett, P.I. Riley and P.I.W. Yarrow, J. Chem. Soc., Dalton Trans., (1981) 805.

10 N.M. Doherty and J.E. Bercaw, J. Am. Chem. Soc., 107 (1985) 2670.