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Metallocene derivatives of early transition metals. Synthesis and characterization of new halo hydridobis(silylated cyclopentadienyl)niobium complexes

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Abstract

The reduction of the niobocene complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2$ (I: X = Br, II: X = I) with one equivalent of sodium amalgam gives the Nb^{III} solids $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$ (III: X = Br, IV: X = I). These complexes can also be obtained by treatment of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ (V) with one equivalent of EtBr or MeI. Reactions of III and IV with CO, PhC≡CPh, $P(OMe)_3$ and $CN(2,6\text{-}Me_2C_6H_3)$ give the solid 1/1 adducts $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL$ (VI: X = Br, L = CO; VII: X = Br, L = PhC≡CPh; VIII: X = Br, L = $P(OMe)_3$; IX: X = Br, L = $CN(2,6\text{-}Me_2C_6H_3)$; X: X = I, L = CO; XI: X = I, L = PhC≡CPh; XII: X = I, L = $P(OMe)_3$; XIII: X = I, L = $CN(2,6\text{-}Me_2C_6H_3)$. The carbenoid-like III reacts with cumulenes to give the complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(XCY)$ (XIV: X = Y = S; XV: X = PhN, Y = O; XVI: X = PhN, Y = S). The hydride complexes $Nb(\eta^5\text{-}C_5H_3RR')_2HL$ (XVII: R = H, R′ = $SiMe_3$; XVIII: R = R′ = $SiMe_3$) have been prepared by treating the trihydride complexes $Nb(\eta^5\text{-}C_5H_3RR')_2H_3$ in the presence of CO. The related complexes $Nb(\eta^5\text{-}C_5H_3RR')_2HL$ (XIX: R = H, R′ = $SiMe_3$, L = PhC≡CPh; XX: R = H, R′ = $SiMe_3$, L = $P(OMe)_3$) were made by reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL$ with an excess of $NaAlH_2(OCH_2CH_2OMe)_2$.

Introduction

The chemistry of metallocene derivatives of the early transition metals involving substituted cyclopentadienyl ligands has attracted increasing interest in recent years. Several niobocene complexes have been reported [1] and the properties of those containing the $\eta^5\text{-}C_5H_5$ ligand, such as $Nb(\eta^5\text{-}C_5H_5)_2(H)_3$, are of much interest in respect, for example, of C–H activation [2a,2b], olefin insertion and β-H elimination processes [2c]. As part of a study of the electronic and steric influence of trimethylsilyl-substituted cyclopentadienyl ligands on the properties of niobocene

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complexes [3] we have prepared a series of new halide and hydrido bis-silylated cyclopentadienyl complexes in which the steric demands and electron-withdrawing effects of the ligands considerably modify the reactivity at the metal centers. The chemistry of some new complexes has been studied and structural information obtained by IR and ^{1}H and ^{13}C NMR spectroscopy.

Results and discussion

Synthetic studies

We have prepared the niobocene sixteen electron complexes III and IV by two alternative methods. Complexes III and IV were made by reducing a THF solution of I or II with a 1/1 molar proportion of sodium amalgam (eq. 1(i)) and by treatment of V with one equivalent of EtBr or MeI (eq. 1(ii)).

$$\left.\begin{array}{l} \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X}_2 + \mathrm{Na/Hg} \xrightarrow[\text{(i)}]{-\mathrm{NaX}} \\ \quad (\mathrm{I: X = Br,} \\ \quad \ \mathrm{II: X = I}) \\ \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{H})_3 + \mathrm{RX} \xrightarrow[-\mathrm{H_2};\ -\mathrm{RH}]{\text{(ii)}} \\ \quad (\mathrm{V}) \qquad (\mathrm{R = Et, X = Br;} \\ \qquad\qquad\quad \mathrm{R = Me, X = I}) \end{array}\right] \rightarrow \begin{array}{l} \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X} \\ (\mathrm{III: X = Br,} \\ \ \mathrm{IV: X = I}) \end{array} \qquad (1)$$

Complexes III and IV are very air sensitive solids, brown and red respectively, and great care must be taken during their handling to avoid decomposition. Their solubilities are similar to that of the previously described $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl}$ complex [4], and they are very soluble in THF, diethyl ether and toluene, and soluble in alkanes.

Route (ii) provides a new method for preparation of sixteen electron species $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X}$. We have previously described [5] the preparation in high yield of a series of niobium and tantalum hydrides containing silylated cyclopentadienyl groups and have established that the niobium trihydrides have non-classical structures as indicated by the anomalous ^{1}H NMR properties (short relaxation times T_1, large temperature-dependent couplings, $^1J(\mathrm{H,H})$), because the steric demands and the electron-withdrawing effects of the silylated cyclopentadienyl groups promote H–H bonding interactions. In accord with this, we found that complex V reacts readily with EtBr and MeI to give initially $\mathrm{H_2}$ and the intermediate $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{H}$, which is then transformed into the corresponding $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X}$ (eq. 2).

$$\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{H})_3 \xrightarrow[-\mathrm{H_2}]{\text{(a)}} \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{H} \xrightarrow[+\mathrm{RX};\ -\mathrm{RH}]{\text{(b)}} \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X} \qquad (2)$$

Analogous intermediate species $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{H}$ have been proposed previously [6] in other reactions of $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{H})_3$. In the case of our complex step (a) may be specially favoured because of the non-classical character of the trihydride. Step (b) may be regarded as involving an oxidative addition to give a niobium(V) intermediate $\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{H})\mathrm{RX}$, which is spontaneously transformed into the niobium(III) complex and RH, and the latter was detected by GLC. The proposed oxidative addition process has been previously observed as the first step in the interaction of an alkyl or aryl halide with a low valent transition metal [7].

Furthermore Labinger et al. [8] observed the formation of $\mathrm{Ta(\eta^5\text{-}C_5H_4Me)_2I}$(dialkylacetylene) in the reaction of $\mathrm{Ta(\eta^5\text{-}C_5H_4Me)_2(H)_3}$ with iodobenzene in the presence of the corresponding π-acetylene ligand.

Complexes III and IV behave as coordinatively unsaturated species, and react with π-acid ligands to give the corresponding 18-electron species $\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL}$ (see eq. 3).

$$\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X + L \longrightarrow \underset{(VI\text{-}XIII)}{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL}} \qquad (3)$$

(VI: $\mathrm{X = Br, L = CO}$; VII: $\mathrm{X = Br, L = PhC{\equiv}CPh}$; VIII: $\mathrm{X = Br, L = P(OMe)_3}$;
IX: $\mathrm{X = Br, L = CN(2,6\text{-}Me_2C_6H_3)}$; X: $\mathrm{X = I, L = CO}$; XI: $\mathrm{X = I, L = PhC{\equiv}CPh}$;
XII: $\mathrm{X = I, L = P(OMe)_3}$; XIII: $\mathrm{X = I, L = CN(2,6\text{-}Me_2C_6H_3)}$)

The 18 neutral electron-niobocene complexes were isolated as air-sensitive microcrystalline solids. They are soluble in THF, diethyl ether, and aromatic and aliphatic hydrocarbons.

We also studied the metal-promoted activations of several cumulenes with complex III, and found that this complex behaves like $\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl}$ [4]. Thus, complex III reacts with a molar propertion of a cumulenes X=C=Y to give the corresponding complex with the cumulene attached to the niobium atom, as shown in eq. 4.

$$\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br + X{=}C{=}Y \longrightarrow \underset{(XIV\text{-}XVI)}{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(XCY)}} \qquad (4)$$

(XIV: $\mathrm{X = Y = S}$, XV: $\mathrm{X = PhN, Y = O}$; XVI: $\mathrm{X = PhN, Y = S}$)

All these complexes were isolated as non air-sensitive microcrystalline solids, very soluble in THF, diethyl ether, and aromatic hydrocarbons.

When heated in the presence of carbon monoxide in toluene, complexes $\mathrm{Nb(\eta^5\text{-}C_5H_3RR')_2(H)_3}$ give the corresponding hydridocarbonyls $\mathrm{Nb(\eta^5\text{-}C_5H_3RR')_2(H)CO}$, XVII and XVIII (eq. 5(i)) in quantitative yield. The ease of elimination of $\mathrm{H_2}$ and the consequent formation of the hydridocarbonyl complex increases with increase in the number of $\mathrm{SiMe_3}$ group in the cyclopentadienyl ring, because a decrease in the electron density at the metal centre favours H–H interactions. Thus we have previously noted [5] that the extent of the H–H bonding interaction increases on going from $\mathrm{Nb(\eta^5\text{-}C_5H_4(SiMe_3)_2)_2(H)_3}$ to $\mathrm{Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2(H)_3}$.

We also tried to prepare analogous complexes from $\mathrm{PhC{\equiv}CPh}$ and $\mathrm{C_2H_4}$, but obtained only intractable products, probably of because of insertion of the acetylene or olefin into the Nb–H bond [2a] under the conditions used.

$$\left.\begin{array}{l}\mathrm{Nb(\eta^5\text{-}C_5H_3RR')_2(H)_3 + L \xrightarrow{(i)}} \\ \mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL + NaAlH_2(OCH_2CH_2OMe)_2 \xrightarrow{(ii)}}\end{array}\right] \rightarrow \mathrm{\underset{(XVII\text{-}XX)}{Nb(\eta^5\text{-}C_5H_3RR')_2HL}} \qquad (5)$$

(XVII: $\mathrm{R = H; R' = SiMe_3; L = CO}$; XVIII: $\mathrm{R = R' = SiMe_3; L = CO}$;
XIX: $\mathrm{R = H; R' = SiMe_3; L = PhC{\equiv}CPh}$; XX: $\mathrm{R = H; R' = SiMe_3;}$
$\mathrm{L = P(OMe)_3}$)

Other $\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2HL}$ complexes have been made (eq. 5(ii)) by treatment of $\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL}$ with an excess of $\mathrm{NaAlH_2(OCH_2CH_2OMe)_2}$. This

Table 1

Analyses (found(calcd.) (%)) and colours of the trimethylsilylcyclopentadienylniobium complexes

Complex	C	H	N	Colour	Yield (%)
Nb(η^5-$C_5H_4SiMe_3$)$_2$Br	42.6	5.9		Brown	87
(II)	(42.9)	(5.8)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$I	39.0	5.4		Red	80
(IV)	(38.8)	(5.3)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$Br(CO)	41.9	5.5		Grey-violet	80
(VI)	(42.9)	(5.4)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$Br(PhC≡CPh)	52.9	5.3		Yellow	64
(VII)	(53.7)	(5.4)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$BrP(OMe)$_3$	39.7	6.6		Green	80
(VIII)	(39.9)	(6.1)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$BrNC(2,6-$Me_2C_6H_3$)	51.3	6.2	2.5	Green	82
(IX)	(51.9)	(6.0)	(2.4)		
Nb(η^5-$C_5H_4SiMe_3$)$_2$I(CO)	39.9	5.6		Grey-violet	80
(X)	(39.1)	(5.0)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$I(PhC≡CPh)	53.7	5.3		Yellow	60
(XI)	(53.6)	(5.4)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$IP(OMe)$_3$	38.6	6.6		Green	80
(XII)	(38.9)	(6.0)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$ICN(2,6-$Me_2C_6H_3$)	48.8	5.8	2.4	Green	85
(XIII)	(48.0)	(5.6)	(2.2)		
Nb(η^5-$C_5H_4SiMe_3$)$_2$Br(CS_2)	38.6	5.0		Orange	86
(XIV)	(39.0)	(4.9)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$Br(PhNCO)	48.0	5.0	2.4	Pale-yellow	83
(XV)	(48.7)	(5.4)	(2.4)		
Nb(η^5-$C_5H_4SiMe_3$)$_2$Br(PhNCS)	46.8	5.5	2.2	Yellow-greenish	80
(XVI)	(47.1)	(5.3)	(2.3)		
Nb(η^5-$C_5H_4SiMe_3$)$_2$H(CO)	51.3	6.7		Red	70
(XVII)	(51.5)	(6.8)			
Nb(η^5-$C_5H_3(SiMe_3)_2$)$_2$H(CO)	50.8	7.4		Red	70
(XVIII)	(51.1)	(7.9)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$H(PhC≡CPh)	66.0	7.0		Red-brown	65
(XIX)	(65.9)	(6.8)			
Nb(η^5-$C_5H_4SiMe_3$)$_2$H(P(OMe)$_3$)	49.9	7.5		Red-brown	60
(XX)	(49.6)	(7.8)			

method was previously used by Labinger [8] to prepare hydridotantalocene complexes. In some cases Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$ was obtained as a by-product.

The hydridoniobocene complexes were isolated as air-sensitive solids, very soluble in all common organic solvents. They react readily with halogenated solvents to give dihalogenoniobocene species.

All the compounds gave satisfactory analyses (see Table 1).

Spectroscopic data

IR spectra. The IR spectra of all niobocene complexes show the absorptions due to a cyclopentadienyl ring and the $SiMe_3$ group [9,10]. The more significant absorptions are those due to the various coordinated ligands. Thus complexes VI, X,

Table 2

Selected IR data for the trimethylsilylcyclopentadienylniobium complexes (ν in cm^{-1})

Complex	ν(CO)	ν(C≡C)	ν(C≡N)	ν(Nb-H)	ν(C=S)	ν(C=O)	ν(C=N)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(CO)$ (VI)	1930(s)						
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhC{\equiv}CPh)$ (VII)		1760(w)–1735(w)					
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2BrCN(2,6\text{-}Me_2C_6H_3)$ (IX)			2060(s)				
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I(CO)$ (X)	1923(s)						
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I(PhC{\equiv}CPh)$ (XI)		1758(w)–1740(w)					
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ICN(2,6\text{-}Me_2C_6H_3)$ (XIII)			2035(s)				
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(CS_2)$ (XIV)					1155(s)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhNCO)$ (XV)						1726(s)	
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhNCS)$ (XVI)							1643(s)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(CO)$ (XVII)	1900(s)			1680(br)			
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2H(CO)$ (XVIII)	1900(s)			1700(br)			
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(PhC{\equiv}CPh)$ (XIX)		1760(w)–1735(w)		1700(br)			
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(P(OMe)_3)$ (XX)				1730(br)			

Table 3. ^{1}H NMR data for the trimethylsilylcyclopentadienylniobium complexes (δ (ppm) multiplicity, in C_6D_6 as solvent and Me_4Si as internal standard)

Complex	H(SiMe$_3$)	H(C$_5$H$_4$ or C$_5$H$_3$)	H(hydride)	L
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$ (III)	−0.13(s;18)	5.79(4); 4.53(4)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I$ (IV)	−0.08(s;18)	5.81(4); 4.59(4)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(CO)$ (VI)	0.09(s;18)	5.22(2); 4.90(4); 4.76(2)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhC{\equiv}CPh)$ (VII)	0.17(s;18)	6.15(2); 5.83(2); 5.37(2); 5.07(2)		7.60–7.20(m;10)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2BrP(OMe)_3$ (VIII)	0.13(s;18)	5.75(2); 5.18(2); 5.08(2); 4.81(2)		3.40(d;9) *J*(P–H)10.16 Hz Me
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2BrCN(2,6\text{-}Me_2C_6H_3)$ (IX)	0.09(s;18)	5.53(4); 5.02(2); 4.80(2)		2.23(s;6)Me; 6.67(m;3)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I(CO)$ (X)	0.08(s;18)	5.34(2); 4.93(4); 4.57(2)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I(PhC{\equiv}CPh)$ (XI)	0.18(s;18)	6.28(2); 5.98(2); 5.29(2); 5.05(2)		7.59–7.21(m;10)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2IP(OMe)_3$ (XII)	0.15(s;18)	5.68(2); 5.26(2); 5.20(2); 4.81(2)		3.38(d;9) *J*(P–H) 10.18 Hz Me
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ICN(2,6\text{-}Me_2C_6H_3)$ (XIII)	0.12(s;18)	5.71(2); 5.35(2); 5.12(2); 4.68(2)		2.26(s;6)Me; 6.68(m;3)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(CS_2)$ (XIV)	0.18(s;18)	5.81(4); 5.03(4)		
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhNCO)$ (XV)	0.12(s;18)	6.13(2); 5.70(2); 5.46(2); 5.24(2)		7.22–8.30(m;5)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhNCS)$ (XVI)	0.19(s;18)	5.93(2); 5.88(2); 5.37(2); 5.26(2)		7.80–7.32(m;5)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(CO)$ (XVII)	0.17(s;18)	4.97(2); 4.67(2); 4.41(2); 4.29(2)	−6.64(s;1)	
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2H(CO)$ (XVIII)	0.19(s;18)	5.04(4); 4.97(2); 4.82(2)	−6.30(s;1)	
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(PhC{\equiv}CPh)$ (XIX)	0.14(s;18)	5.78(2); 5.43(2); 4.96(2); 4.44(2)	−3.88(s;1)	6.99–6.83(m;10)Ph
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2HP(OMe)_3$ (XX)	0.28(s;18)	5.14(2); 4.66(2); 4.30(2); 4.06(2)	−7.57(d;1) *J*(P–H) 34.55 Hz	3.28(d;9) *J*(P–H) 40.88 Hz

Table 4

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

Complex	$SiMe_3$	$C_5H_4SiMe_3$		L
		C(1)	C(2), C(3), C(4), C(5)	
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$ (III)	0.8	89.8	110.0; 103.9	
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I$ (IV)	0.8	90.4	112.0; 105.5	
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(CO)$ (VI)	0.5	93.0	107.8; 103.8; 98.2; 95.6	232.0(*C*O)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhC{\equiv}CPh)$ (VII)	0.4	111.4	122.4; 120.9; 109.2; 103.5	152.8 $\equiv$*C*Ph; 139.1 C(1) (Ph); 130.0 C(2,6) (Ph); 129.3 C(3,5) (Ph); 128.2 C(4) (Ph); 139.6 $\equiv$*C*Ph*; 137.2 C(1) (Ph*); 129.6 C(2,6) (Ph*) 128.8 C(3,5) (Ph*); 126.2C(4) (Ph*).
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2BrP(OMe)_3$ (VIII)	0.8	93.9	112.2; 100.9; 96.7; 96.5	53.4(d; *J*(P–C) 6.4 Hz)Me
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2BrCN(2,6\text{-}Me_2C_6H_3)$ (IX)	0.9	94.6	110.3; 103.9; 100.3; 96,4	136.2(Ph); 129.1(Ph); 129.0(Ph); 128.1(Ph); 19.8(2 Me)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I(CO)$ (X)	0.6	99.3	107.9; 104.0; 99.0; 96.4	
$Nb(\eta^5\text{-}C_5H_4SiM_3)_2I(PhC{\equiv}CPh)$ (XI)	0.9	113.9	121.4; 119.4; 108.2; 102.6	150.5 $\equiv$*C*Ph; 138.3 C(1) (Ph); 130.9 C(2,6) (Ph); 129.6 C(3,5) (Ph); 127.9 C(4) (Ph); 138.5 $\equiv$*C*Ph*; 137.4 C(1) (Ph*); 130.0 C(2,6) (Ph*) 128.9 C(3,5) (Ph*); 127.6 C(4) (Ph*)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2IP(OMe)_3$ (XII)	0.8	91.2	110.4; 100.5; 96.0; 94.5	54.8(d; *J*(P–C) 7.1 Hz)Me
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ICN(2,6\text{-}Me_2C_6H_3)$ (XIII)	0.8	93.4	95.0; 98.9; 102.3; 109.0	130.5(Ph); 129.4(Ph); 129.1(Ph); 128.0(Ph); 19.8(2 Me)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(CS_2)$ (XIV)	0.3	119.8	126.3; 124.3; 112.5; 107.9	300.4(CS_2)
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(PhNCO)$ (XV)	0.4	119.3	123.0; 119.4; 110.4; 108.1	145.0 C(1) (Ph); 128.9(Ph); 125.1(Ph); 124.2(Ph)

[a] * denotes internal $\equiv$CPh.

XVII and XVIII show a strong band at ca. 1900 cm^{-1} (see Table 2) corresponding to $\nu_{\text{stretching}}$ (C≡O), in accord with previously reported data for carbonylniobocene derivatives [2i]. Similarly acetylene VII, XI, XIX and isocyanide IX, XIII complexes show bands at ca. 1760 and 2000 cm^{-1}, respectively, corresponding to ν(C≡C) and ν(C≡N) (see Table 2). The large decrease in the value of ν(C≡C) with respect to that for the corresponding free acetylene has been previously observed in other acetylene niobocene derivatives [1], and reflects the extensive back donation of electronic density into the acetylene $\pi^{\star}_{\shortparallel}$ orbital. The values observed for ν(C≡N) in the isocyanide complexes suggest a linear C–N–R structure for the ligand. The IR spectrum of complex XIV shows a ν(C=S) band at 1155 cm^{-1}, indicating η^2-C,S bonding to the metal. A strong band at 1726 cm^{-1} in the spectrum of complex XV can be assigned to either the ν(C=N) or ν(C=O) depending on whether the coordination of PhNCO occurs through the C=O(η^2-C,O) or the C=N(η^2-C,N) bond [4]. The presence of a band at 1643 cm^{-1} due to the ν(C=N) in the spectrum of complex XVI suggest a η^2-C,S coordination to the metal [4] (see Table 2). The spectra of all the reported hydride complexes show a broad band at ca. 1650 cm^{-1} corresponding to ν(Nb–H) (see Table 2; the data are in agreement with those of previously described hydridoniobocene complexes [2i].

NMR spectra. In the ^{1}H NMR spectra all the complexes exhibit the expected singlet for the SiMe$_3$ group and several broad peaks due to the non-equivalent η^5-C$_5$H$_3$RR′ protons [11] (see Table 3). In addition Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$XL, Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Br(XCY) and Nb(η^5-C$_5$H$_3$RR′)$_2$HL show the signals characteristic of the various coordinated ligands (see Table 3), and the hydride complexes give a signal at high field from the hydride ligand [2a] (see Table 3). The ^{13}C NMR spectra of some of the complexes show the pattern previously observed for the different carbon atoms of the cyclopentadienyl ring in other bis(trimethylsilyl)cyclopentadienylniobium complexes [1]. Thus the ^{13}C NMR spectra of the complexes III and IV show three resonances for the cyclopentadienyl carbon atoms, and the other complexes five resonances and there is also a singlet due to the SiMe$_3$ carbon atoms and resonances due to the various carbon atoms of the other ligands (see Table 4).

Experimental

All operations were carried out under vacuum or in an inert atmosphere with Schlenk type glassware. Solvents were dried under N$_2$ and degassed before use. IR spectra were recorded as Nujol mulls between CsI plates in the region 4000–200 cm^{-1} with a Perkin–Elmer 599 spectrometer. Carbon, hydrogen and nitrogen analyses were carried out with a Perkin–Elmer 240B microanalyzer. ^{1}H, ^{13}C NMR spectra were recorded on a Varian FT80A instrument. Methane and ethane were determined by GLC using a Perkin–Elmer sigma 3B instrument fitted with a Porapak-Q column and a flame ionization detector. Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$X$_2$ (I,II) and Nb(η^5-C$_5$H$_3$RR′)$_2$(H)$_3$ were prepared as described [12,5].

Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$X (III: X = Br, IV: X = I)

Method A. THF (50 ml) was added to a mixture of Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Br$_2$ (1.000 g, 1.80 mmol) and sodium amalgam (1.80 mmol of Na). The mixture was vigorously stirred under nitrogen for 3 h at room temperature and then evaporated to dryness under vacuum. The residue was extracted with hot hexane, and the extract was concentrated then cooled to give brown crystals of complex III. The crystals were filtered off and dried under vacuum. Complex IV was obtained similarly as a red crystal solid.

Method B. To a solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3$ (V) (0.240 g, 0.64 mmol) in hexane (30 ml) was added methyl iodide (0.04 ml, 0.64 mmol). Immediate gas evolution occurred. After 1 h stirring the red solution formed was worked-up as in (A) to give red crystals of complex IV. The gas was identified as methane by GLC. Complex III was similarly obtained by use of ethyl bromide.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL$ (*VI: X = Br, L = CO; VII: X = Br, L = PhC≡CPh; VIII: X = Br, L = P(OMe)$_3$; IX: X = Br, L = CN(2,6-Me$_2$C$_6$H$_3$); X: X = I, L = CO; XI: X = I, L = PhC≡CPh; XII: X = I, L = P(OMe$_3$); XIII: X = I, L = CN(2,6-Me$_2$C$_6$H$_3$)*)

The same procedure was used in each case and is illustrated by the following example: $CN(2,6\text{-}Me_2C_6H_3)$ (0.080 g, 0.67 mmol) was added to a solution of III (0.300 g, 0.67 mmol) in hexane (25 ml). After 1 h the initially brown solution had become green. Filtration, concentration and cooling (at $-30\,°C$) of this solution gave complex IX as green microcrystals.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br(XCY)$ (*XIV: X = Y = S; XV: X = PhN, Y = O; XVI: X = PhN, Y = S*)

CS_2 (0.080 g, 1.11 mmol) was added to a solution of complex III (0.500 g, 1.11 mmol in pentane (25 ml). The solution was stirred at $0\,°C$ for 0.5 h and the orange microcrystalline solid which separated was filtered off and dried under vacuum. Complexes XV and XVI were obtained similarly.

$Nb(\eta^5\text{-}C_5H_3RR')_2HL$ (*XVII: R = H, R′ = SiMe$_3$, L = CO; XVIII: R = R′ = SiMe$_3$, L = CO; XIX: R = H, R′ = SiMe$_3$, L = PhC≡CPh; XX: R = H, R′ = SiMe$_3$, L = P(OMe)$_3$*)

Method A. A brown solution of complex V in toluene was stirred under reflux under carbon monoxide (1 atm). After 24 h filtration gave a red solution and removal of the toluene in vacuo left the red solid XIV. Complex XV was obtained similarly.

Method B. A solution of complex XI (0.450 g, 0.77 mmol) in toluene was stirred with 0.75 ml of a solution of $NaAlH_2(OCH_2CH_2OMe)_2$ in toluene (40%; 1.2 g/ml; 1.14 mmol). After 4 h the red solution was treated with 2–3 ml of water to give an emulsion. Volatile materials were evaporated off under reduced pressure and the residual red-brown solid was extracted with warm hexane. After filtration, concentration, and cooling (at $-30\,°C$) of the extract complex XIX was obtained as red-brown microcrystals.

Complex XX was obtained similarly from complex XII.

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