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Metallocene derivatives of early transition metals. Reactions of bis(silylated cyclopentadienyl)niobium complexes with organic halides

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Abstract

The reactions of the complexes $Nb(\eta^5\text{-}C_5H_3RR')_2H_3$ and $Nb(\eta^5\text{-}C_5H_3\text{-}RR')_2X$ ($X = Br$, I; $R = H$, $R' = SiMe_3$; $R = R' = SiMe_3$) with ethyl bromide and methyl iodide afford the new niobium(IV) complexes, $Nb(\eta^5\text{-}C_5H_3RR')_2X_2$ ($X = Br$, $R = H$, $R' = SiMe_3$ (I); $R = R' = SiMe_3$ (II); $X = I$, $R = H$, $R' = SiMe_3$ (III); $R = R' = SiMe_3$ (IV)) in high yields. The formation of these complexes is explained in terms of an initial oxidative addition of the organic halide. The reaction of complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ with benzyl chloride has also been investigated.

Introduction

The reactions of aliphatic and aromatic halides with low valent transition metal complexes are of synthetic interest, since they are useful in the formation of new carbon–metal bonds [1]. Several metallocene derivatives of early transition metals seem to be particularly suited for those reactions; for example, vanadocene has been reported to react with aliphatic and aromatic halides [2], and also the niobocene (III) dichloride anion has been shown [3] to be a catalyst for the electrochemical reduction of benzyl chloride. As part of our study on the properties of bis(silylated-cyclopentadienyl)niobium complexes we describe below a study of the reactions of niobocene complexes with some organic halides.

Results and discussion

We have previously shown [4] that treatment of the complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ with one equivalent of EtBr or MeI provides a convenient route to

Table 1

Some physical and spectroscopical (ESR) data for bis-silylated cyclopentadienylniobium(IV) complexes

Complex	Analysis (found (calcd.)(%))		Colour	Yield [a]	$a(^{93}Nb$ /mT)	$g_{av.}$
	C	H				
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br_2$	36.5	4.8	Brown-green	85	10.5	2.02
(I)	(36.4)	(4.9)				
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Br_2$	39.3	6.3	Brown-green	87	10.1	2.02
(II)	(39.7)	(6.6)				
$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I_2$	30.9	4.1	Red	90	9.0	2.08
(III)	(30.3)	(3.9)				
$Nb(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2I_2$	34.5	6.1	Red	85	8.8	2.01
(IV)	(33.8)	(6.3)				

[a] Related at both preparative methods.

sixteen electron species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$. An extension of these studies we have examined the reactions of the complexes $Nb(\eta^5\text{-}C_5H_3RR')_2H_3$, $R = H$, $R' = SiMe_3$; $R = R' = SiMe_3$, and $Nb(\eta^5\text{-}C_5H_3RR')_2X$, $X = Br$, I, $R = H$, $R' = SiMe_3$, $R = R' = SiMe_3$, with alkyl halides and of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ with benzyl chloride.

In all cases the reactions take place with the formation in high yield of the bis(halogens)niobocene(IV) (eq. 1).

$$Nb(\eta^5\text{-}C_5H_3RR')_2X + R''\text{-}X \rightarrow Nb(\eta^5\text{-}C_5H_3RR')_2X_2 + \text{“organic products”} \quad (1)$$

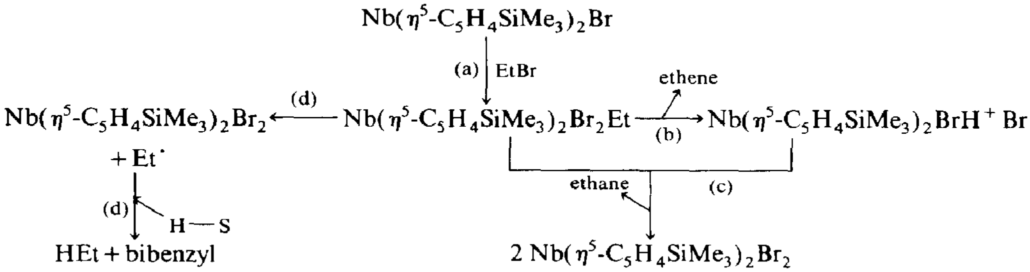
$$\begin{aligned}(&\text{I}: X = Br,\ R = H,\ R' = SiMe_3;\\ &\text{II}: X = Br,\ R = R' = SiMe_3;\\ &\text{III}: X = I,\ R = H,\ R' = SiMe_3;\\ &\text{IV}: X = I,\ R = R' = SiMe_3)\end{aligned}$$

With $Nb(\eta^5\text{-}C_5H_3RR')_2H_3$ the reactions give initially H_2 and $Nb(\eta^5\text{-}C_5H_3RR')_2X$ (see ref. 4).

Complexes I–IV were isolated as air-stable solids, either brown-green (I, II) or red (III, IV). Their solubilities are similar to that previously described for $Nb(\eta^5\text{-}C_5H_3RR')_2Cl_2$ complexes. All the compounds gave satisfactory analyses (see Table 1). We have carried out a detailed study of these reactions, and we present below results obtained by GLC analysis of the gaseous and liquid phases.

Reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$ with EtBr

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$ reacted quickly with an equimolecular amount of EtBr in toluene or hexane to give a brown-green precipitate in high yield that was identified as complex I. GLC analysis of the gaseous phase showed ethane and ethene to be present in a ratio dependent on the temperature used, and a GLC analysis of the liquid phase, revealed the presence of bibenzyl. For example (see Experimental) in toluene as solvent at low temperature (0 °C) the ethane/ethene ratio was 1/3 and at room temperature it was 6/1 after 2 min. $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ reacted similarly to give complex I. GLC analysis of the gaseous phase showed ethane and ethene to be present in a 17/1 ratio (at room temperature) and molecular hydrogen was also detected.



Scheme 1

In all cases C–C bond formation attributable to radical coupling can be excluded because no butane was ever detected.

We show in Scheme 1 the mechanisms proposed for these processes. Step (a) may be regarded as involving an oxidative addition to give a niobium(V) intermediate Nb(η^5-$C_5H_4SiMe_3$)$_2Br_2$Et. The proposed oxidative addition process has been previously described as the first step in the reaction of an alkyl or aryl halide with a low valent transition metal [2b], [2c]. An outer-sphere electron transfer between the niobium(III) complex and EtBr, such as is well established for platinum(0) complexes [1b], probably cannot account for the formation of both ethane and ethene; also the difference between the reduction potentials [5] of the reagents is more than 1V. Step (b) corresponds to a β-hydrogen elimination to give ethene and an unstable hydrido intermediate from which ethane and complex I are formed by reaction with the primary product of oxidative addition (step c). This process has been previously reported for the reaction of vanadocene with alkyl groups having a hydrogen atom in a β-position.

An alternative mechanism involves homolytic cleavage of niobium–carbon bond in the initially niobium(V) intermediate (step d) to give complex I and ethyl radical, which could then abstract hydrogen atoms from the solvent. Both mechanisms are consistent with the isolation in high yield of complex I. We suggest that the first mechanism is favoured at low temperature because the niobium(V) intermediate may be more stable and the formation of ethane thus slowed down. However the second mechanism is probably favoured at room temperature because the proportion of ethane is greater. An important conclusion is that both mechanisms probably are involved in the product-forming steps, because ethane, ethene, and bibenzyl are detected by the GLC analysis of gaseous and liquid phases, It is also possible, however, that binuclear complexes are intermediates and further investigation of this question is needed.

For Nb(η^5-$C_5H_4SiMe_3$)$_2H_3$ similar mechanisms can be proposed. The larger yield of ethane may be the result of some hydrogenation of ethene.

Reaction of Nb(η^5-$C_5H_4SiMe_3$)$_2$I with MeI

We examined the oxidative addition of MeI to niobocene complexes because the niobium(V) intermediate could be expected to be stable since there are no hydrogen atoms on a β-carbon atom.

Nb(η^5-$C_5H_4SiMe_3$)$_2$I reacts quickly with an equimolecular amount of MeI in toluene to give a red precipitate in high yield which was identified as complex III. GLC analysis of the gaseous phase showed that one equivalent of methane was present along with a small amount of ethane (see Experimental), and GLC analysis of the liquid phase showed bibenzyl to be present.

$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3$ reacts similarly to give complex III.

We suggest for these reactions the mechanism involving homolytic cleavage of a niobium–carbon bond in an initial undetected niobium(V) intermediate $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I_2Me$, to give complex III, methane, and bibenzyl. Any significant degree of C–C bond formation attributable to radical coupling can be excluded since ethane was detected only in small amounts.

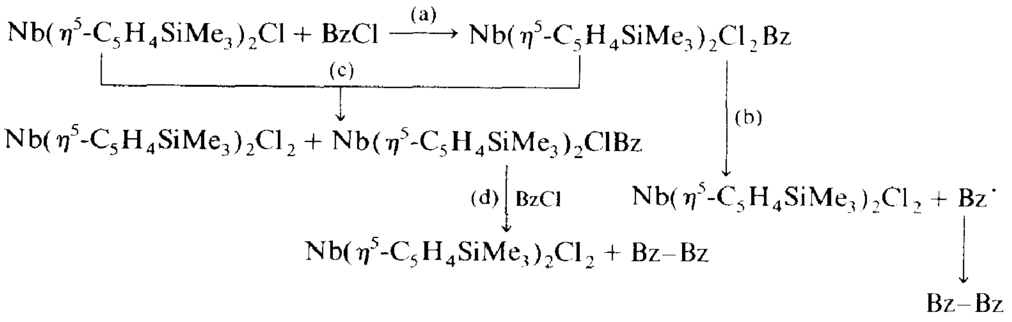
Reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ with BzCl

To provide a comparison with the results above we examined the reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ with an equimolecular amount of benzyl chloride. The niobium(III) complex reacted quickly with BzCl in hexane to give a green precipitate of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ in high yield. Removal of the mother liquor give bibenzyl, which was characterized after recrystallization by analysis and ^1H NMR spectroscopy. The GLC analysis of the gaseous phase did not show the presence of any volatile organic products.

We show in Scheme 2 the two mechanisms considered for this process. In both mechanisms the first step (step a) could be oxidative addition to give an niobium(V) intermediate, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2Bz$, which could not be detected. Step (b) involves homolytic cleavage of the niobium–carbon bond in the niobium(V) intermediate to give complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ and benzyl radicals, and dimerization of the latter would give bibenzyl. In accord with this mechanism, the only products isolated were the niobium(IV) complex and bibenzyl.

An alternative mechanism would involve the reaction of niobium(V) intermediate (step c) with an excess of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ to give the both niobium(IV) complexes, $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ and $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ClBz$. We have previously observed [6] that several niobium(III) complexes react with niobium(V) complexes to give niobium(IV) complexes as the result of a redox processes. The chloro(benzyl) intermediate complex could react with the remaining BzCl (step d) to give bibenzyl and complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$. This last mechanism has been suggested [2b] for the reaction of vanadocene with BzBr. An accord with this mechanism, the only products would be the niobium(IV) complex and bibenzyl.

In order to gain more insight into the mechanism we tried to detect the two niobium(IV) species proposed for the second mechanism by injecting into an



Scheme 2

equimolar amount of BzCl an equimolar solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ in hexane in an ESR tube in the cavity of the ESR spectrometer. We could not detect the expected $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ClBz$ species, only the signal corresponding to $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ was observed. Either the intermediate was a highly unstable species or it was not formed at all, or in too low a concentration. Lappert et al. have previously described [7] the preparation of several bis(cyclopentadienyl)niobium(IV) dialkyl and chloro(alkyl) complexes by alkylation processes, and they have pointed out that the use of Grignard reagents such as MgBzCl induced dialkylation, since the chloro(alkyl) complex appears to be unstable with respect to disproportionation to give dialkyl and dichloro complexes.

In the light of this report the second mechanism might seem unlikely, since no $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ClBz$ was detected in the ESR experiment, but this could be due to the instability of the complex under the reaction conditions.

From our results we favour a mechanism which involves homolytic cleavage of niobium–carbon bond in the niobium(V) intermediate (first mechanism), but the second mechanism, involving a redox process between niobium(V) and niobium(III) cannot be definitively excluded. Further investigations are needed.

In conclusion, the reaction of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl$ with BzCl affords bibenzyl as the result of C–C coupling. However, with EtBr and MeI, C–C bond formation attributed to radical coupling was never observed. In all cases $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2$ (X = halogen) was the only organometallic species isolated.

Spectroscopic properties

The ESR spectra of the d^1 paramagnetic complexes I, II, III, and IV were recorded with dichloromethane solutions. At room temperature a ten-line spectrum was obtained due to hyperfine coupling to ^{93}Nb ($I = 9/2$). The $g_{av.}$ values ranged between 2.01–2.08, in keeping with data for related compounds [7,8]. Electron spin resonance data for the complexes are shown in Table 1.

The IR spectra of all the complexes show the characteristic absorptions due to the cyclopentadienyl ring and the $SiMe_3$ group [9,10].

Experimental

Materials and methods

All reactions were performed by standard Schlenk techniques under dry oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before use.

The complexes $Nb(\eta^5\text{-}C_5H_3RR')_2H_3$, $Nb(\eta^5\text{-}C_5H_3RR')_2X$ and $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ were prepared as previously described [11,4,7].

Elemental analyses were performed with a Perkin–Elmer 240B microanalyser. IR spectra were recorded as Nujol mulls between CsI plates in the region 4000–200 cm^{-1} in a Perkin–Elmer 599 spectrometer. GLC analyses were carried out with a Perkin–Elmer sigma 3B instrument fitted with a flame ionization detector.

Preparation of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br_2$ (I)

To a solution of complex $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Br$ (1.00 g, 2.24 mmol) in hexane or toluene was added ethyl bromide (0.24 g, 2.24 mmol) and the mixture was stirred

Table 2

Variation with time of the composition of the products (gaseous phase) of the reactions of Nb(η^5-$C_5H_4SiMe_3)_2H_3$ and Nb(η^5-$C_5H_4SiMe_3)_2Br$ with EtBr at various temperatures (solvent toluene)

T (°C)	*t* (min)	Ethane (%)	Ethene (%)
(A) Nb(η^5-$C_5H_4SiMe_3)_2H_3$ with EtBr			
0	2	97.3	2.7
	60	94.4	5.6
25	2	94.4	5.6
	60	94.2	5.8
(B) Nb(η^5-$C_5H_4SiMe_3)_2Br$ with EtBr			
0	2	25.7	74.3
	60	39.9	60.1
25	2	86.1	13.9
	60	86.1	13.9

at room temperature. The brown-green precipitate formed was washed with hexane and dried under vacuum to give complex I. Complex II was prepared similarly.

Complexes I and II can be also obtained by reaction of Nb(η^5-$C_5H_3RR')_2H_3$ with an excess of ethyl bromide.

Preparation of Nb(η^5-$C_5H_4SiMe_3)_2I_2$ (III)

MeI (0.29 g, 2.02 mmol) was added to a solution of complex Nb(η^5-$C_5H_4SiMe_3)_2I$ (1.00 g, 2.02 mmol) in hexane or toluene. and the mixture was stirred at room temperature. The red precipitate formed was washed with hexane and dried under vacuum to give complex III. Complex IV was prepared in similarly.

Complexes III and IV can be also obtained by reaction of Nb(η^5-$C_5H_3RR')_2H_3$ with an excess of methyl iodide.

Table 3

Variation with time of the composition of the products (gaseous phase) of the reactions of Nb(η^5-$C_5H_4SiMe_3)_2H_3$ and Nb(η^5-$C_5H_4SiMe_3)_2I$ with MeI at various temperatures (solvent toluene)

T (°C)	*t* (min)	Methane (%)	Ethane (%)
(A) Nb(η^5-$C_5H_4SiMe_3)_2H_3$ with MeI			
0	2	99.0	1.0
	60	99.0	1.0
25	2	99.0	1.0
	60	99.0	1.0
(B) Nb(η^5-$C_5H_4SiMe_3)_2I$ with MeI			
0	2	100	–
	60	100	–
25	2	98.8	1.2
	60	98.8	1.2

GLC analysis of the gaseous phase in the reactions with ethyl bromide and methyl iodide

The reactions were carried out in toluene in a Schlenk vessel which was sealed with a rubber septum. The following procedure was used. Ethyl bromide or methyl iodide was added from a syringe to the $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X$ solution. Samples for GLC analysis were taken from the gaseous phase by syringe and injected directly in the instrument fitted with a Porapak-Q column. Details of the reaction conditions are given in Tables 2 and 3.

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