The chemistry of hydride, halide and alkyl niobocene complexes with coordinated diazoalkanes

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Abstract

The complexes $Cp_2Nb(H)(\eta^1$-NNCPhAr$)$ (Ar$\equiv$Ph (**1**) or o-C_6H_4Br (**2**)) were found to undergo easy substitution of a hydride ligand for a halogen atom by the reaction of **1** with various alkylhalides with high yields of $Cp_2Nb(X)(\eta^1$-NNCPh$_2)$ (X$\equiv$Cl (**4**), Br (**5**) or I (**6**)), $Cp_2Nb(Br)(\eta^1$-NNC(Ph)$-o$-C_6H_4Br$)$ (**7**) and **5** were found to be formed in a halogen exchange reaction, and also by the thermolysis of **2**.

Halide diazoalkane niobocene complexes clearly exhibit marked polarity of the metal centre. Nucleophilic substitution of bromine in **5** yielded $Cp_2Nb(Me)(\eta^1$-NNCPh$_2)$ (**8**). The results of X-ray analysis of **7** are provided.

Keywords: Niobium

1. Introduction

Reactions of transition metal complexes with diazoalkanes have become an object of wide investigation in recent 20 years. They give a wide palette of products, such as hydrazide, carbene and many other types of complex [1–5]. The structure of the product depends on the character of transition metal, its coordination and oxidation state and, of course, on the character of the diazoalkane.

Diazoalkane complexes are the most common products of the reactions of diazoalkanes with early transition metal complexes. Some other methods of preparation of early transition metal diazoalkane complexes were also found [6,7]. Transformation of these complexes were generalized in [5].

2. Results and discussion

Recently we have reported [8,9] the synthesis of hydride–diazoalkane niobocene complexes $Cp_2Nb(H)$-

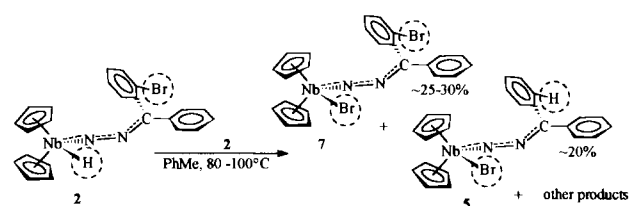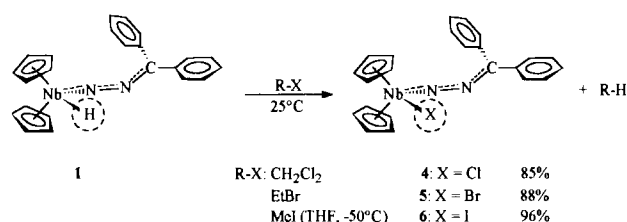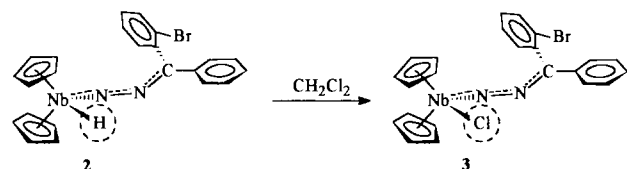(η^1-NNCPhAr$)$ (Ar = Ph (**1**) or o-C_6H_4Br (**2**)) from niobocene trihydride and corresponding diazoalkanes:

We have found [9] that the hydride complex **2** undergoes a quantitative exchange of hydride ligand for chloride under the action of CH_2Cl_2 at room temperature, and we have reported the crystal structure data of product **3**:

Now we report that the hydride–diphenyldiazomethane complex **1**, analogously to the formation of **3** from **2**, easily exchanges the hydride atom for halogen (Cl, Br or I) in the presence of various halide derivatives. The reactions of **1** with CH_2Cl_2, EtBr or MeI seem to be the most convenient synthetic route to the corresponding halide diphenyldiazomethane niobocene complexes **4–6**. These reactions run in mild conditions and they are finished within a few hours, when the reaction mixtures are kept at room temperature. For instance, the reaction of **1** with MeI in tetrahydrofuran (THF) proceeds even at $-50°C$. Corresponding alkyl halides can be added to the reaction mixture either in a stoichiometric amount or in a large excess, using them simply as a solvent. However, no halogen exchange reaction occurs when **1** is reacted with KHF_2.

In all cases the yields are almost quantitative, and minor losses are connected with the special experimen-

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1: Ar = Ph; 2: Ar = o-C$_6$H$_4$Br

2   PhMe, 80 -100°C   7   ~25-30%   +   ~20%   5   + other products

R-X: CH$_2$Cl$_2$
EtBr
MeI (THF, -50°C)

4: X = Cl	85%
5: X = Br	88%
6: X = I	96%

tal technique essential for the work with such air and moisture sensitive compounds. Products **4–6** are characterized by ^{1}H NMR, IR spectra and elemental analysis.

In ^{1}H NMR spectra of the hydride (**1**), halides (**4–6**) and other diphenyldiazomethane niobocene complexes Cp$_2$Nb(X)(η^1-NNCPh$_2$) (Table 1), we observed that Cp hydrogen atom signals were shifted to the low field proportionally to the increasing electron withdrawal character of ligand X. Ph hydrogen atom signals in the diphenyldiazomethane ligand were found in a wider region (about 1.0 ppm) in comparison with the free diphenyldiazomethane owing to magnetic nonequivalency of Ph rings in coordinated diazoalkane.

Table 1
^{1}H NMR spectra of Cp$_2$Nb(X)(η^1-NNCPh$_2$)(C$_6$D$_6$, 80 MHz)

Complex	X	δ(Cp) (10H) (ppm)	δ(Ph) (10H) [a] (ppm)	δ(Nb–X) (ppm)
8 [b]	Me	5.24 (s)	6.80–7.90	0.51 (s, 3H)
1 [c]	H	5.17 (s)	6.95–7.75	1.27 (s, 1H) [d]
1	H	5.20 (s)	6.90–7.85	1.25 (s, 1H) [d]
6	I	5.45 (s)	6.90–7.53	
5 [d]	Br	5.47 (s)	6.78–7.60	
5	Br	5.50 (s)	6.85–7.70	
4	Cl	5.53 (s)	6.85–7.85	

[a] Complex multiplets.
[b] Spectrum also contains signals of Et$_2$O: 1.13 (t, 6H, CH$_3$); 3.33 (q, 4H, CH$_2$).
[c] (C$_6$D$_5$CD$_3$, 400 MHz).
[d] Broad signals.

IR spectra of the hydride (**1**) and halide (**4–6**) diphenyldiazomethane niobocene complexes recorded in the 4000–400 cm^{-1} region differ from each other only within the resolution limit of the measurement ($\pm$5–10 cm^{-1}).

The bromide niobocene complex Cp$_2$Nb(Br)(η^1-NNC(Ph)–o-C$_6$H$_4$Br) (**7**) was also prepared in a different manner, but the nature of the process of its formation is apparently relative to the reaction described above. We discovered that the complex Cp$_2$Nb(H)(η^1-NNC(Ph)–o-C$_6$H$_4$Br) (**2**) had limited thermal stability. It is fully transformed to other niobocene derivatives when its solution is heated to 80–100 °C for 1 week. The complicated reaction mixture contains products of substitution of the Nb hydrogen atom for bromine, namely Cp$_2$Nb(Br)(η^1-NNC(Ph)–o-C$_6$H$_4$Br) (**7**) and Cp$_2$Nb(Br)(η^1-NNCPh$_2$) (**5**):In the case of the formation of **7** the hydrogen for bromine substitution in **2** is performed by the o-C$_6$H$_4$Br group of the second molecule of the initial complex **2**. On the contrary, the formation of **5** from **2** can proceed as an intramolecular process.

We think that the possible mechanism of the formation of **5** could be a common radical aromatic substitution in the C$_6$H$_4$Br ring, the Nb–H bond acting as a nucleophilic agent.

On the basis of the ^{1}H NMR spectrum of reaction mixture after the thermolysis of **2**, we discovered that only one stereoisomer of **7** was formed. The stereoselectivity of the formation of **7** we believe, is due to the steric demands of molecule **2** while attacking the Nb–H bond by the second molecule **2** acting as a brominating agent. The formation of **5** was confirmed by comparison with an authentic sample.

In ^{1}H NMR spectra of the series of complexes Cp$_2$Nb(X)(η^1-NNC(Ph)–o-C$_6$H$_4$Br) (**2**, **3** and **7**) (Table 2) we observed a down–field shift of the Cp hydrogen signal with increasing electron withdrawal character of the X ligand, analogous to that observed in the series of complexes with unsubstituted Ph ring Cp$_2$Nb(Y)(η^1-NNCPh$_2$) (**1** and **4–6**) (Table 1).

The molecular structure of **7** was confirmed by an X-ray diffraction study. There are two independent molecules **7A** and **7B** with significantly diverse structural features and two solvate molecules of toluene in the independent part of the primitive unit. The structure

Table 2
^{1}H NMR spectra of $Cp_2Nb(X)(\eta^1$-NNC(Ph)– o-$C_6H_4Br)(C_6D_5CD_3$, 400 MHz)

Complex	X	δ(Cp) (10H) (ppm)	δ(Ar) (9H) [a] (ppm)
2'	H	5.166 (s); 5.167 (s) (1:1) [b]	6.76–7.60
2"	H	5.232 (s); 5.233 (s) (1:1) [b]	6.76–7.60
7	Br	5.58 (s)	6.78–7.60
3' [c]	Cl	5.58 (s) [b]	6.75–7.72
3" [c]	Cl	5.60 (s) [b]	6.75–7.72

[a] Complex multiplets.
[b] Ratio of isomers 2':2", and also for 3':3" ≈ 1:5.
[c] C_6D_6, 300 MHz.

of **7A** is depicted in Fig. 1, and the bond lengths and angles are listed in Tables 3 and 4.

The structure of **7** resembles in its main features those reported for $Cp_2Nb(H)N_2CPh_2$ (**1**) and $Cp_2Nb(Cl)N_2C(Ph)$–o-C_6H_4Br (**3**) [9]. The Nb atom has pseudotetrahedral surroundings formed by the centroids of Cp rings, bromine and nitrogen. We observed that in the Cp_2NbX (X≡H, Cl or Br) moiety of **1**, **3** and **7B** (Table 5) the distance between the Nb and Cp ring planes increases and the dihedral angle between the Cp planes decreases on increase in the radius of X.

A marked difference between **7A** and **7B** was found in the coordinated diazo moiety. The Nb–N(1)–N(2) angle of **7A** is significantly smaller than those of **1**, **3** and **7B**, and the N(1)–N(2) bond in **7A** is insignificantly shorter (1.20(3) Å) than the mean values for the N=N double bond (1.22–1.25 Å [10]). The Nb(1)–N(1) bond length in **7A** (1.86(2) Å) is very similar to the Nb–N distance in **1** and **3** and it is noticeably longer than in **7B** (1.79(2) Å), indicating a smaller bonding
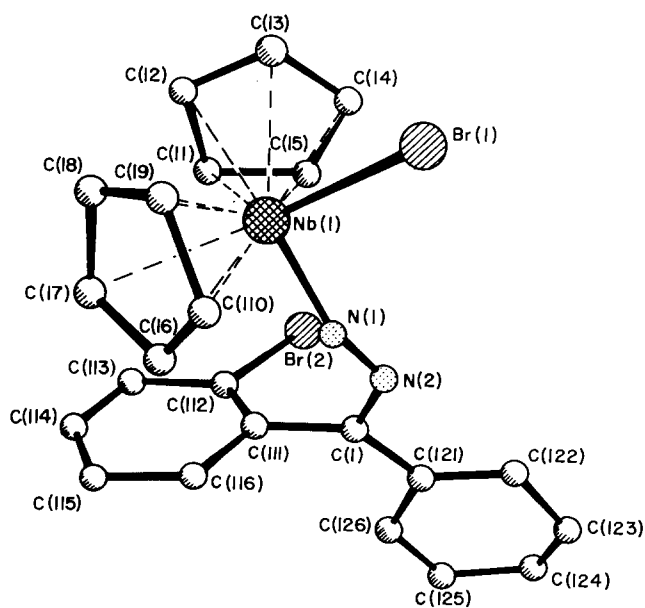

Fig. 1.

Table 3
Bond lengths in **7**

7A		7B	
Atoms	Bond length (Å)	Atoms	Bond length (Å)
Nb(1)–Br(1)	2.673(5)	Nb(2)–Br(4)	2.589(5)
Nb(1)–C(11)	2.43(3)	Nb(2)–C(21)	2.40(4)
Nb(1)–C(13)	2.42(3)	Nb(2)–C(23)	2.40(3)
Nb(1)–C(15)	2.43(3)	Nb(2)–C(25)	2.40(4)
Nb(1)–C(17)	2.48(3)	Nb(2)–C(27)	2.33(3)
Nb(1)–C(19)	2.47(3)	Nb(2)–C(29)	2.37(3)
Nb(1)–N(1)	1.86(2)	Nb(2)–N(3)	1.79(2)
Nb(1)–C(12)	2.47(3)	Nb(2)–C(22)	2.39(4)
Nb(1)–C(14)	2.46(2)	Nb(2)–C(24)	2.40(3)
Nb(1)–C(16)	2.43(3)	Nb(2)–C(26)	2.40(3)
Nb(1)–C(18)	2.49(3)	Nb(2)–C(28)	2.46(3)
Nb(1)–C(110)	2.46(30)	Nb(2)–C(210)	2.42(3)
Br(2)–C(112)	1.92(4)	Br(3)–C(212)	1.85(4)
N(1)–N(2)	1.20(3)	N(3)–N(4)	1.35(3)
N(2)–C(1)	1.31(4)	C(21)–C(22)	1.39(6)
C(11)–C(12)	1.46(5)	C(22)–C(23)	1.31(6)
C(12)–C(13)	1.38(5)	C(24)–C(25)	1.25(6)
C(14)–C(15)	1.38(4)	C(26)–C(210)	1.37(5)
C(16)–C(110)	1.35(5)	C(28)–C(29)	1.33(5)
C(18)–C(19)	1.37(5)	C(2)–C(211)	1.51(4)
C(1)–C(111)	1.50(4)	N(4)–C(2)	1.34(3)
C(11)–C(15)	1.43(4)	C(21)–C(25)	1.40(7)
C(13)–C(14)	1.39(5)	C(23)–C(24)	1.36(6)
C(16)–C(17)	1.39(5)	C(26)–C(27)	1.31(5)
C(17)–C(18)	1.45(4)	C(27)–C(28)	1.36(5)
C(19)–C(110)	1.45(5)	C(29)–C(210)	1.39(5)
C(1)–C(121)	1.49(4)	C(2)–C(221)	1.45(4)

Table 4
Bond angles (°) in **7**

7A		7B	
Atoms	Bond angle (°)	Atoms	Bond angle (°)
Br(1)–Nb(1)–N(1)	97.0(7)	Br(4)–Nb(2)–N(3)	95.4(7)
Nb(1)–N(1)–N(2)	159(2)	N(3)–N(4)–C(2)	121(2)
N(1)–N(2)–C(1)	126(3)	Nb(2)–N(3)–N(4)	171(2)
N(2)–C(1)–C(111)	118(3)	Nb(4)–C(2)–C(221)	117(2)
N(2)–C(1)–C(121)	120(3)	N(4)–C(2)–C(211)	122(2)
Br(2)–C(112)–C(111)	121(3)	Br(3)–C(212)–C(211)	125(2)
Br(2)–C(112)–C(113)	118(3)	Br(3)–C(212)–C(213)	115(2)

Table 5
Structural parameters of Cp_2NbX moiety in $Cp_2Nb(X)(\eta^1$-NNC(Ph)Ar) complexes

Complex	X	Ar	Nb–X (Å)	Nb–Cp [a] (Å)	Cp–Nb–Cp [a] (°)
1	H	Ph	1.65(6)	2.13()	134.9
3	Cl	o-C_6H_4Br	2.496(3)	2.15(2)	129.2
7B	Br	o-C_6H_4Br	2.673(5)		

[a] Centroid of the Cp ligand.

MeLi
Et₂O, 25°C

5   8   + LiBr
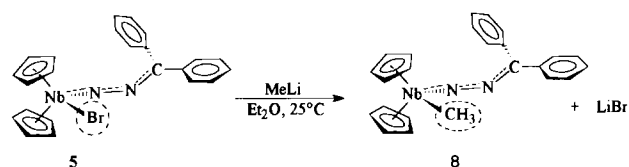
interaction between Cp_2NbBr and diazo fragments in the former. The increase in the Nb–N bond length correlates with the decrease in the N–N distance and with the decrease in the Nb–N–N angle. The structural diversity of η^1-N-coordinated diazoalkanes (N–N bond lengths in crystal structures were found in region from 1.17 Å [11,12] to 1.36 Å [13] and the M–N–N angle from 153° to 177°) confirms the limited non-rigidity of the M–N–N–C fragment. In solution this non-rigidity may be much more essential and it can be responsible for some unprecedented reactions of diazoalkane complexes, such as the formation of **7** from **3**, the formation of $[CpNb-\eta^5-C_5H_4-C(COOEt)=N-\mu-N]_2$ [14] and $Cp_2Nb(-N-N=C(Ph)-C_6H_4-o)_2$ [9] from Cp_2NbH_3 and $N_2CHCOOEt$ or excess of $N_2C(Ph)-o-C_6H_4Br$ respectively.

For instance, the bromine atom of **5** easily undergoes nucleophilic substitution for methyl group when it is treated by MeLi. However, **5** does not react with MeMgI:The methyl diphenyldiazomethane niobocene complex **8** obtained is somewhat more air sensitive than **1** is and its IR spectrum measured immediately after exposure to air exhibits the peak of free diazo group ($\nu = 2040$ cm^{-1}). The ^{1}H NMR spectrum of **8** is given in Table 1. As we expected, the singlet signal of Me protons ($\delta = 0.51$ ppm) is shifted to a lower field compared with that of MeLi ($\delta = 1.74$ ppm [15]).

3. Experimental section

All synthesis, isolation and purification of the products were carried out in sealed evacuated Schlenk-type vessels. All the solvents were thoroughly free from water and oxygen. NMR spectra were recorded on a Tesla BS 587 (80 MHz) and Varian VXR 400 (400 MHz) instruments at 300 K. IR spectra were recorded on Specord 75 IR and Specord M 80 spectrometers.

Complexes **1** and **2** were prepared as described in [8,9], with the exception of improved synthesis Cp_2NbH_3 compared with that described in [16].

3.1. Synthesis of Cp_2NbH_3

To a mixture of 2.00 g (6.81 mmol) of Cp_2NbCl_2 and 1.00 g (26.3 mmol) of $LiAlH_4$, 120 ml of Et_2O was added and it was kept overnight at room temperature. Orange crystals of $Cp_2Nb(\mu-H)_2AlH_2$ were formed.

Then the mixture was cooled to -40 °C and 30 ml of water in portions was carefully added, cooling it in such manner that dihydrogen evolution was kept at a controlled value. The colour of the reaction mixture turned to grey–colourless. The ether layer was decanted off and the water layer was twice extracted with 20 ml of Et_2O. The combined organic layers were dried with anhydrous Na_2SO_4, and the solvent was evaporated. 80–88% of white microcrystalline Cp_2NbH_3 was isolated. ^{1}H NMR (C_6D_6, 80 MHz), δ -3.70 (d, 2H, NbH, $J_{H-H} = 11.7$ Hz), -2.59 (broad s, 1H, NbH); 4.82 (s, 10H C_5H_5) ppm.

3.2. Reactions of 1

3.2.1. With CH_2Cl_2

0.5 g (1.20 mmol) of **1** was dissolved in 10 ml of dry CH_2Cl_2. The solution was stirred at room temperature overnight. During this time the colour changed from orange–red to dark red. The pressure in reaction vessel was somewhat increased, although CH_3Cl formation was not visible. The solvent was removed and the residue was washed with hexane. The product was recrystallized from toluene by very slow diffuse condensation of hexane into the vessel. The yield of red crystalline **4** is 0.46 g (85%). Decomposition occurs above 100°C.

Anal. Found: C, 60.32; H, 4.11; N, 5.39; Cl, 8.02. $C_{23}H_{20}N_2ClNb$, Calc.: C, 61.00; H, 4.45; N, 6.19; Cl, 7.83%.

3.2.2. With EtBr

The complex **5** was obtained analogously to **4** using EtBr instead of CH_2Cl_2 (yield, 88% of red crystalline **5**).

Anal. Found: C, 54.22; H, 3.88; N, 5.06; Br, 16.35. $C_{23}H_{20}N_2BrNb$, Calc.: C, 55.56; H, 4.05; N, 5.63; Br, 16.07%.

3.2.3. With MeI

To a stirred solution of 0.30 g (0.72 mmol) of **1** in 10 ml of dry THF cooled to -50°C, 1.00 g (7.05 mmol) of MeI was added. Reaction was accompanied by stormy methane evolution. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 4 h. Then it was concentrated, and pentane was allowed slowly condense to it. Mother liquor was poured off and red crystals were washed with pentane. The yield was 0.375 g (96%) of **6**.

Anal. Found: C, 49.62; H, 3.66; N, 4.75; I, 23.46. $C_{23}H_{20}N_2INb$, Calc.: C, 50.76; H, 3.70; N, 5.15; I, 23.32%.

3.3. Thermolysis of 2

The solution of 0.30 g (0.63 mmol) of **2** in 15 ml of dry toluene was heated in a boiling-water bath for 1

Table 6
Atomic parameters in **7**

Atom	x	y	z	B_{iso} ($\times 10$ Å)
Nb(1)	0.0250(2)	0.2168(2)	0.0159(2)	2.6(1)
Nb(2)	0.4772(2)	0.0000(0)	−0.0079(2)	2.2(1)
Br(1)	0.0553(2)	0.0840(3)	−0.1112(2)	4.8(2)
Br(2)	−0.2607(3)	0.2004(4)	0.2535(3)	6.4(2)
Br(3)	0.2183(3)	−0.0082(4)	0.2300(3)	4.8(2)
Br(4)	0.4615(3)	0.1398(3)	−0.1266(3)	10.1(3)
N(1)	0.014(2)	0.127(2)	0.108(1)	2(1)
N(2)	−0.024(2)	0.069(2)	0.156(2)	4(1)
N(3)	0.442(2)	0.076(2)	0.082(1)	5(1)
N(4)	0.427(2)	0.143(2)	0.147(1)	3(1)
C(11)	−0.116(2)	0.318(2)	0.050(2)	3(1)
C(12)	−0.087(2)	0.354(2)	−0.035(3)	4(2)
C(13)	−0.101(2)	0.276(3)	−0.095(2)	0(1)
C(14)	−0.144(2)	0.195(3)	−0.055(2)	0(1)
C(15)	−0.152(2)	0.220(2)	0.033(2)	3(1)
C(16)	0.176(2)	0.258(2)	0.108(2)	4(2)
C(17)	0.129(2)	0.349(2)	0.091(2)	5(2)
C(18)	0.132(2)	0.365(2)	−0.004(2)	2(1)
C(19)	0.177(2)	0.286(3)	−0.040(2)	2(1)
C(110)	0.207(2)	0.219(2)	0.033(2)	1(1)
C(1)	−0.053(2)	0.088(2)	0.235(2)	5(2)
C(111)	−0.049(2)	0.193(2)	0.268(2)	4(1)
C(112)	−0.128(3)	0.251(2)	0.278(2)	9(2)
C(113)	−0.118(4)	0.354(3)	0.307(3)	8(2)
C(114)	−0.027(4)	0.385(4)	0.329(3)	8(2)
C(115)	0.057(3)	0.330(3)	0.327(2)	5(2)
C(116)	0.046(2)	0.227(2)	0.293(2)	5(2)
C(121)	−0.096(2)	0.007(2)	0.289(2)	4(1)
C(122)	−0.109(3)	−0.087(2)	0.254(2)	7(2)
C(123)	−0.138(3)	−0.160(3)	0.313(3)	10(3)
C(124)	−0.169(3)	−0.141(3)	0.390(2)	10(3)
C(125)	−0.154(3)	−0.044(2)	0.429(2)	8(2)
C(126)	−0.119(2)	0.027(2)	0.375(2)	6(2)
C(21)	0.616(3)	−0.083(4)	0.069(3)	5(2)
C(22)	0.634(3)	0.018(2)	0.078(3)	4(2)
C(23)	0.649(2)	0.049(3)	−0.002(3)	2(1)
C(24)	0.637(2)	−0.025(3)	−0.063(3)	2(2)
C(25)	0.620(3)	−0.103(3)	−0.022(4)	4(2)
C(26)	0.317(2)	−0.037(3)	−0.083(2)	1(1)
C(27)	0.384(2)	−0.097(3)	−0.083(2)	1(1)
C(28)	0.405(2)	−0.164(2)	−0.046(3)	5(2)
C(29)	0.371(2)	−0.131(2)	0.029(2)	7(2)
C(210)	0.308(3)	−0.053(2)	0.006(2)	7(2)
C(2)	0.419(2)	0.114(2)	0.232(1)	2(1)
C(211)	0.432(2)	0.007(3)	0.260(2)	4(1)
C(212)	0.347(3)	−0.052(2)	0.259(2)	9(2)
C(213)	0.354(3)	−0.150(3)	0.284(2)	9(2)
C(214)	0.446(4)	−0.188(3)	0.309(3)	12(4)
C(215)	0.533(3)	−0.132(3)	0.309(2)	12(4)
C(216)	0.524(3)	−0.030(3)	0.285(2)	5(2)
C(221)	0.404(2)	0.192(2)	0.295(2)	5(2)
C(222)	0.383(3)	0.169(3)	0.384(2)	9(2)
C(223)	0.369(3)	0.241(3)	0.442(2)	10(3)
C(224)	0.358(4)	0.335(4)	0.422(3)	8(2)
C(225)	0.371(3)	0.359(3)	0.334(3)	10(3)
C(226)	0.390(2)	0.288(2)	0.272(2)	9(2)
C(1′)	−0.209(4)	−0.467(4)	0.469(4)	8(2)
C(2′)	−0.212(5)	−0.418(3)	0.393(3)	8(2)
C(3′)	−0.288(5)	−0.474(6)	0.361(5)	8(3)
C(4′)	−0.376(5)	−0.474(6)	0.361(3)	8(3)
C(5′)	−0.368(7)	−0.535(5)	0.435(5)	8(4)

Table 6 (continued)

Atom	x	y	z	B_{iso} ($\times 10$ Å)
C(6′)	−0.286(5)	−0.524(4)	0.490(5)	8(2)
C(7′)	−0.127(3)	−0.469(3)	0.525(3)	8(2)
C(1″)	0.271(3)	0.667(3)	0.451(3)	7(3)
C(2″)	0.271(6)	0.610(4)	0.370(6)	8(4)
C(3″)	0.180(6)	0.613(4)	0.322(4)	8(3)
C(4″)	0.102(5)	0.671(4)	0.334(3)	8(3)
C(5″)	0.107(4)	0.719(4)	0.409(4)	8(2)
C(6″)	0.191(4)	0.726(3)	0.470(3)	11(3)
C(7″)	0.366(4)	0.659(5)	0.508(4)	8(3)

week. Then the vacuum was restored in the reaction vessel and the solvent was very slowly partially evaporated (during several weeks). Large red crystals were washed with a small amount of toluene, dried and collected. The yield was 0.07 g (20%) of **7**.

An analogous experiment was performed in an NMR ampoule. After prolonged heating (for 1 week) of the reaction mixture it did not contain **2**, but about 25–30 mol.% **7**, 20 mol.% **5** and an unidentifiable mixture of other niobocene derivatives.

3.4. Reactions of 5

3.4.1. With MeLi

To a stirred solution of 2.01 mmol of MeLi in 40 ml of diethyl ether, 1.00 g (2.01 mmol) of **5** was added. The reaction mixture was stirred for 24 h at room temperature. The solution was decanted and the residue was washed with ether. The solution was concentrated, and 40 ml of pentane were very slowly diffusely condensed into the vessel. The brownish-yellow crystals formed were washed with pentane. 1.05 g of **8** containing LiBr–Et$_2$O was isolated. LiBr–Et$_2$O has a solubility similar to that of **8**.

Anal. Found: Sample (A), C, 37.34; H, 4.17; N, 3.03; Br, 10.76; sample (B), C, 30.60; H, 3.59, N, 2.76; Br, 10.33. C$_{24}$H$_{23}$N$_2$Nb–LiBr–C$_4$H$_{10}$O, Calc.: C, 56.68; H, 5.56; N, 4.72; Br, 13.47%. Sample (A), weighed immediately after opening the sample to the air; sample (B), weighed after sample (A).

3.4.2. With MeMgI

To a stirred solution of 3.00 mmol of MeMgI in 40 ml of diethyl ether, 1.00 g (2.01 mmol) of **5** was added. The reaction mixture was stirred for 24 h at room temperature. The colour of the reaction mixture did not change. The solvent was very slowly evaporated from the reaction mixture. Large yellow crystals were separated and identified as MeMgI–Et$_2$O (yield, 82%). ^{1}H NMR C$_6$D$_6$, 80 MHz: δ −0.48 (s, 3H, Mg–CH$_3$); 0.87 (t, 12H, CH$_3$–CH$_2$–O); 3.46 (q, 8H, CH$_3$–CH$_2$–O) ppm.

3.5. X-ray study of 7

The experiment was carried out at 298 K with an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation. The final atom coordinates and temperature factors are given in Table 6.

Crystal data: $C_{60}H_{52}N_4Br_4Nb_2$; monoclinic; $a = 13.498$ (4), $b = 13.474$ (2) and $c = 15.010$ (5) Å; $\beta = 94.73°$ (3); $V = 2720.6$ (3.0) Å^3; space group, $P2_1$; $Z = 2$; $D = 1.856$ g cm^{-3}; $\lambda(MoK\alpha) = 0.71073$ cm; $\mu = 3.74$ cm^{-1}. The intensities of 5176 independent reflections with $2\theta \leqslant 50°$ were measured by the θ–2θ scan mode, 2093 of which having $I > 2\sigma(I)$ were used in the calculations. The structure was solved by direct methods and refined by full-matrix least-squares method, using SHELXL-86 program package. Two independent molecules of **7** were found. All non-hydrogen atoms were refined anysotropically, and all H were imposed in the calculated positions (C–H bond equal to 0.9 Å) and refined isotropically using riding model. The refinement converged at $R = 0.0523$ ($R_w = 0.0523$ and a goodness of fit of 4.31 for 360 parameters) after indentification of two independent toluene solvate molecules, the residual electron density being $\rho_{max} = 0.869$ and $\rho_{min} = -0.807$ electrons.

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