Journal of Organometallic Chemistry, 482 (1994) 187–190

Is electrophilic substitution possible in the coordinated cyclopentadienyl ligand of early transition metal metallocene complexes? Molecular structure of binuclear nitrene niobocene complex $[(C_5H_4C(COOEt){=}N\text{-}\mu\text{-}N)\text{-}(C_5H_5)Nb]_2$

G.I. Nikonov, M. Putala [1], N.B. Kazennova, D.A. Lemenovskii
Chemical Department, Moscow State University, Moscow 119899 (Russian Federation)

A.S. Batsanov and Yu. T. Struchkov
Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow 117813 (Russian Federation)

(Received February 4, 1994)

Abstract

Diazoacetates $N_2CHCOOR$ (**a**: R = Et; **b**: R = *t*-Bu) readily react with Cp_2NbH_3 to give $Cp_2NbH(\eta^1\text{-}N_2CHCOOR)$ (**1**) as the first identifiable product, characterized by means of ^1H NMR spectroscopy. Complex **1a** converts stepwise into a unique binuclear nitrene niobocene complex $[(C_5H_4\text{-}C(COOEt){=}N\text{-}\mu\text{-}N)(C_5H_5)Nb]_2$ (**2a**). The latter is in fact a product of the Cp-ligand functionalized by the diazoacetate group. Mechanistic aspects of the formation of **2a** are discussed with the results of an X-ray diffraction study.

Key words: Niobium; Crystal structure; Cyclopentadienyl; Group 5

1. Introduction

Substituted diazoalkanes are recognized as versatile ligands demonstrating a number of coordinating modes [1–7] in early transition metal complexes. In spite of increasing understanding of simple diazo ligand derivatives, the chemistry of functionalized diazoalkane complexes is comparatively undeveloped. However, one would expect a functional group attached to the coordinated diazomethane to provide additional reactivity thus transforming the whole diazo moiety.

We have recently found clear confirmation of this prediction in the thermal reaction of $Cp_2NbH(\eta^1\text{-}NNC(Ph)\text{-}o\text{-}C_6H_4Br)$ affording a bis indazoline complex $Cp_2Nb(\text{-}N\text{-}N{=}C(Ph)\text{-}C_6H_4\text{-}o)_2$ [8]. Our attempts to obtain an analogous ethyl diazoacetate complex $Cp_2NbH(\eta^1\text{-}NNCHCOOEt)$ (**1a**) resulted in the formation of the unprecedented binuclear complex **2a** with the Cp-ligand functionalized by the diazo group. Here we report the molecular structure of **2a** and a possible mechanism for its formation.

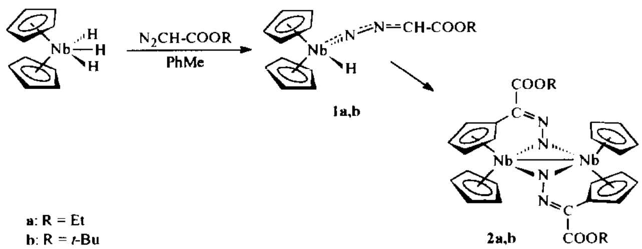
2. Results and discussion

We have recently shown [8,9] that diazoalkanes react with Cp_2MH_3 (M = Nb, Ta) affording $Cp_2MH(NNCR'R'')$ as the first isolatable product. In the case of alkyl diazoacetate, a complex of this type has also been observed in the ^1H NMR spectra, showing it to be the major component in the reaction mixture at the first reaction step.

Correspondence to Prof. D.A. Lemenovskii.

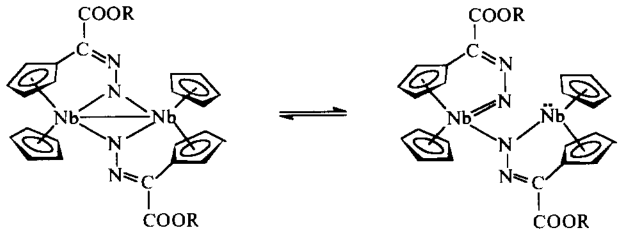
[1] Present address: Faculty of Natural Sciences, Comenius University, Bratislava 842 15, Slovak Republic.

0022-328X/94/$7.00
SSDI 0022-328X(94)24625-S



The Cp-ring protons of **1a** give rise to a singlet at δ 5.095 ppm very close to the corresponding signal of $Cp_2NbH(\eta^1\text{-}NNCPh_2)$ (5.165 ppm). The ethyl group exhibits resonances at δ 0.295 ppm (t, $^3J_{H-H} = 7.2$ Hz) and δ 2.414 ppm (q, $^3J_{H-H} = 7.2$ Hz). However, the hydride signal (Nb–H) expected at about 1.25 ppm has not been found, probably due to its breadth. Analogously, the ^1H NMR spectrum of **1b** in d_8-toluene exhibits the Cp-ring proton resonance at 5.035 ppm and the t-Bu group signal at 1.658 ppm.

We failed to isolate **1** in analytically pure form, as the reaction proceeds to form **2** as the main product. The ^1H NMR spectrum of **2a** contains very broad unresolved signals at 5.7 ppm (4.6–6.7 ppm, 18H, C_5H_5, C_5H_4), 4.2 ppm (3.7–4.6 ppm, 4H, OCH_2), 1.3 ppm. (0.9–1.6 ppm, 6H, CH_3). The breadth of the proton resonance signals did not change markedly while recording the spectrum at 200 K. Moreover, the sample of **2a** shows only an unresolved low intensity signal in the EPR spectrum, probably due either to a paramagnetic admixture of low concentration or to the presence of **2a**, also in a biradical form. On the basis of spectral data, we suggest that **2a** undergoes some dynamic exchange process (equilibrium), which could be expressed by the following scheme:



A small amount of complex **2a** was obtained in crystalline form after standing the reaction mixture for 6 months at room temperature. The molecular structure of **2a** was elucidated by X-ray diffraction.

The molecular structure of **2a** is depicted in Fig. 1, and selected bond distances and angles are given in Tables 1 and 2. **2a** possesses two-fold symmetry and belongs to the binuclear homometallic metallocene type. Both metallocene moieties are bonded via the end-on nitrogen atom of bridging nitrene group.

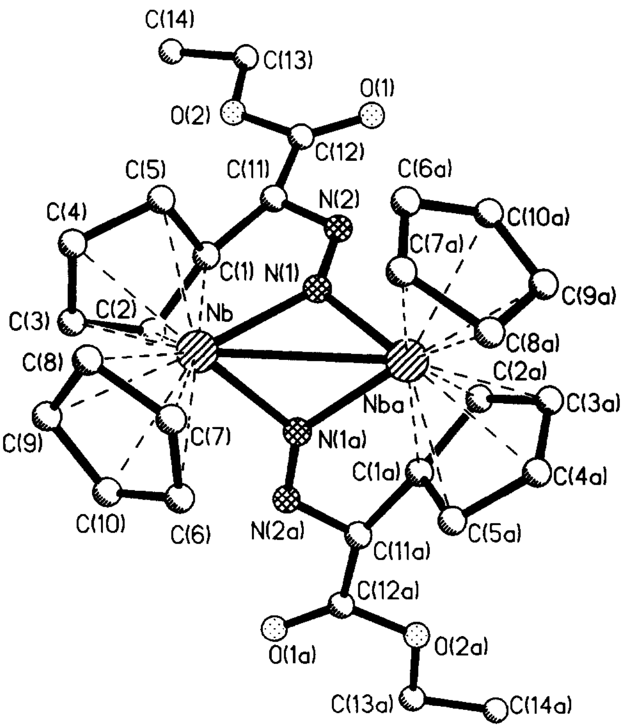


Fig. 1.

TABLE 1. Bond lengths (Å) in structure **2a**

Nb–N(1)	2.14(2)	Nb–Nb(a)	3.001(3)	C(7)–C(8)	1.42(3)
Nb–C(6)	2.54(3)	Nb–N(1a)	2.01(1)	C(8)–C(9)	1.38(4)
Nb–C(7)	2.59(3)	N(1)–N(2)	1.34(3)	C(9)–C(10)	1.40(3)
Nb–C(8)	2.51(2)	N(1)–Nb(a)	2.01(1)	C(11)–C(12)	1.50(3)
Nb–C(9)	2.50(2)	N(2)–C(11)	1.31(2)	C(11)–C(1)	1.51(4)
Nb–C(10)	2.43(3)	O(1)–C(12)	1.22(3)	C(13)–C(14)	1.46(3)
Nb–C(1)	2.36(2)	O(2)–C(12)	1.36(2)	C(1)–C(5)	1.48(3)
Nb–C(2)	2.42(3)	O(2)–C(13)	1.37(4)	C(2)–C(3)	1.47(4)
Nb-C(3)	2.38(2)	C(6)–C(7)	1.40(4)	C(3)–C(4)	1.48(4)
Nb–C(4)	2.43(2)	C(6)–C(10)	1.33(3)	C(4)–C(5)	1.47(3)
Nb–C(5)	2.42(2)				

TABLE 2. Bond angles (deg.) in structure **2a**

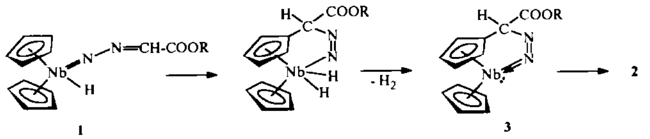
N(1)–Nb–N(1a)	61.3(9)	C(12)–C(11)–C(1)	152.7(16)
Nb–N(1)–N(2)	140.2(10)	O(1)–C(12)–O(2)	119.2(22)
Nb–N(1)–Nb(a)	92.6(7)	O(1)–C(12)–C(11)	130.0(17)
N(2)–N(1)–Nb(a)	127.2(11)	O(2)–C(12)–C(11)	110.4(18)
N(1)–N(2)–C(11)	117.9(18)	O(2)–C(13)–C(14)	107.6(23)
C(12)–O(2)–C(13)	118.4(17)	C(11)–C(1)–C(2)	136.8(23)
C(7)–C(6)–C(10)	108.7(19)	C(11)–C(1)–C(5)	106.9(20)
C(6)–C(7)–C(8)	109.2(21)	C(2)–C(1)–C(5)	111.6(20)
C(7)–C(8)–C(9)	102.6(22)	C(2)–C(3)–C(4)	115.3(26)
C(8)–C(9)–C(10)	111.6(18)	C(3)–C(4)–C(5)	103.1(24)
C(6)–C(10)–C(9)	106.8(23)	C(1)–C(2)–C(3)	101.4(25)
N(2)–C(11)–C(12)	115.7(18)	C(1)–C(5)–C(4)	108.5(22)
N(2)–C(11)–C(1)	91.5(17)		

The Nb–Nb(a) distance (3.001(3) Å) indicates the presence of a direct metal–metal bond. It is rather less than that found in other binuclear niobocenes also believed to have a direct Nb–Nb bond (for instance 3.105(6) Å in "bis-niobocene" [10]), but it is longer than the Nb–Nb distance in the fulvalene nitrene niobocene complexes (2.884(1) and 2.921(1) Å) [11]. Electron counting rules indicate the attainment of an 18 electron valency shell on each metal atom in **2a**. This corresponds to the involvement of all three non-bonding orbitals of the niobocene moiety [12] in the formation of the other bonds. The mean Nb–X (X — centroid of Cp ligands) distances (2.143 Å) are close to the corresponding values in other niobocene complexes [13]. However, Nb lies noticeably closer to the substituted Cp-ring (2.066 *versus* 2.220 Å).

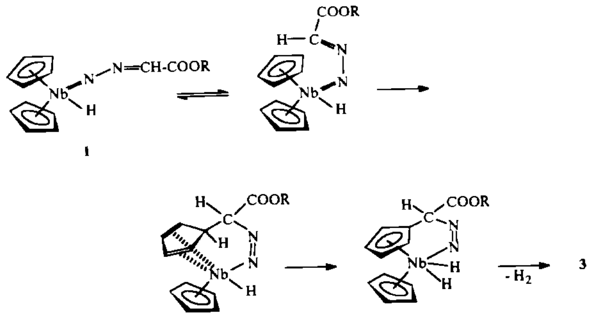
The dihedral angle between Cp-rings (121°), is one of the smallest recorded for niobocenes, comparable only with that in the electron deficient complexes $(Cp_2NbCl)_2O^{2+}$ (129.7°) [14] and Cp_2NbClO_2 (127.3°) [15]. However, this angle is remarkably close to the corresponding angle in the short-bridged ansa-metallocenes of the IV group (121–125.4°) [16,17]. In the case of **2a**, this is surely caused by the presence of a very strained C(11)–N(2)–N(1) bridge.

The unique peculiarity of complex **2a** is the presence of a C(1)–C(11) single bond (1.51(4) Å) demonstrating the functionalization of the Cp-ligand by the coordinated diazo-ligand. The C(11) atom is sp^2-hybridized, as it forms another single C(11)–C(12) bond (1.50(3) Å) and a double C(11)–N(2) bond (1.31(2) Å). The length of the N(1)–N(2) bond (1.337(25) Å) is close to the single nitrogen–nitrogen bond distance. The whole C(1)–C(11)–N(2)–N(1) moiety is highly strained with C(1)–C(11)–N(2), C(11)–N(2)–N(1) and C(1)–C(11)–C(12) angles, which are equal to 91.5° (17), 115.7° (18), and 152.7° (16) respectively.

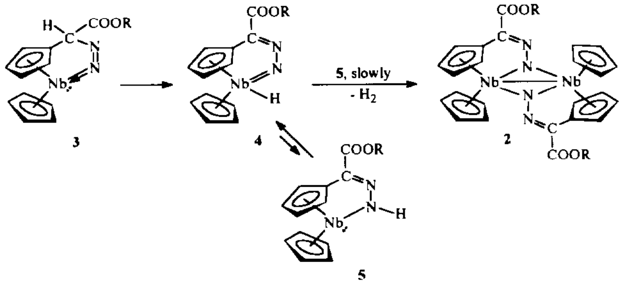
We propose that the formation of complex **2** proceeds via the mechanism shown in the following scheme:



The process starts with complex **1**. Complexes of this type were found to have an almost linear Nb–N(1)–N(2)–C(11) moiety ranging from 159(2)° [18] to 171.4(5)° [8]. However it is quite possible that in solution this angle can vary up to the "normal" value of 120°, typical of the sp^2-hybridized N(1) atom. This means that the N(1)–N(2)–C(11) plane can be orthogonal to the bisector plane of the niobocene moiety because the Nb–N(1) double bond lies in this plane. Based on this assumption, we believe that the electron deficient C(11)-carbon centre can be lifted by the Nb–N(1)–N(2) "hand" to the Cp-ring to attack it directly in a manner resembling the classical arene electrophilic substitution.



Migration of the C(1) proton to the niobium atom followed by elimination of dihydrogen results in formation of the imide intermediate complex **3**. The 16-electron electron-deficient metal centre in **3** can be stabilized by the conjugation of its unoccupied orbital b_2 with the N(1)–N(2) double bond or with the nonbonding electron pair on N(1). The second important step is the migration of acidic proton from C(11) to the basic metal centre giving the hydride-nitrene complex **4**, equilibrating with the amide complex **5** [8,9]. Reaction of **5** with **4** followed by elimination of hydrogen results in the formation of the final product — complex **2**.



3. Experimental section

3.1. Synthesis of 2a

To a solution of 0.57 g (5.00 mmol) N_2CHCO_2Et in 30 ml of anhydrous toluene at 0°C was added 1.01 g (4.46 mmol) pure Cp_2NbH_3. All operations were carried out in a sealed Schlenk-type vessel *in vacuo*. The reaction mixture was allowed to warm to room temperature. The colour turned from bright yellow via orange to dark brown, accompanied by evolution of dihydrogen. After 3 days the mother liquor was removed and a microcrystalline yellowish-brown residue was washed

TABLE 3. Atom coordinates (×10^4) and temperature factors (Å^2 × 10^3) in structure **2a**

Atom	*x*	*y*	*z*	*U*
Nb	1037(1)	0	638(1)	37(1) *
N(1)	−101(10)	−1221(22)	687(12)	45(7) *
N(2)	−267(11)	−2326(20)	1288(10)	42(8) *
O(1)	−532(8)	−4851(53)	2571(9)	75(7) *
O(2)	1006(7)	−5044(43)	3516(8)	56(6) *
C(6)	1075(15)	1803(34)	−825(18)	57(11) *
C(7)	1065(16)	2989(31)	−91(17)	61(12) *
C(8)	1866(14)	2762(29)	936(20)	53(12) *
C(9)	2371(13)	1592(31)	712(18)	63(11) *
C(10)	1850(15)	899(30)	−325(18)	57(11) *
C(11)	443(12)	−3100(29)	2074(14)	52(9) *
C(12)	217(13)	−4337(24)	2718(12)	43(8) *
C(13)	933(16)	−6164(31)	4211(17)	65(11) *
C(14)	1846(17)	−6889(29)	4890(19)	80(14) *
C(24)	3787(18)	5387(47)	3485(21)	106(10)
C(25)	3874(45)	6112(84)	4292(57)	105(18)
C(26)	4448(52)	6336(94)	5185(61)	114(24)
C(22)	5183(28)	4095(56)	4471(31)	45(10)
C(21)	5392(29)	5265(93)	5448(32)	84(15)
C(23)	4461(40)	4242(73)	3535(44)	93(16)
C(1)	1105(13)	−2235(29)	1782(16)	80(12) *
C(2)	1716(17)	−2735(42)	1340(24)	99(18) *
C(3)	2438(15)	−1429(30)	1802(20)	80(13) *
C(4)	2305(11)	−148(50)	2480(14)	83(11) *
C(5)	1463(11)	−727(25)	2489(15)	65(10) *

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*(*i*,*j*) tensor

with toluene and pentane and dried *in vacuo*. Yield: 1.20 g (76%) of **2a**.

3.2. X-ray diffraction study of 2a

The experiment was carried out at 183 K with a four-cycle computer-control Syntex P2_1 diffractometer, using graphite-monochromated Mo Kα radiation. The final atom coordinates and temperature factors are given in Table 3.

Crystal data; $C_{70}H_{72}N_8O_8Nb_4$, monoclinic, a = 16.516(3); b = 7.930(2); c = 14.106(3) Å; β = 118.94° (3); V = 1618.8 (1.5) Å^3; space group $C2$; $Z = 2$; D = 0.863 g/cm^3; λ(Mo Kα) = 0.71073 cm; μ = 3.60 cm^{-1}. The intensities of 2061 independent reflections with $2\theta \leq 45°$ were measured by the $\theta/2\theta$ scan mode, 902 of which having $I > 2\sigma(I)$ were used in calculations. The structure was solved by the Patterson method and refined by full matrix least squares, using SHELXTL PLUS. All non-hydrogen atoms were refined anisotropically, and all H were imposed in calculated position (C–H bond equal to 0.9 Å) and refined isotropically using riding model. The refinement converged at R = 0.057 (R_w = 0.054, GOF = 1.72 for 196 parameters) after identification of the disordered toluene solvate molecule occupying the vacancy in the crystal lattice.

References

1 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc., 104* (1982) 1918.

2 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc., 105* (1983) 7295.

3 L. Messerle and M.D. Curtis, *J. Am. Chem. Soc., 102* (1980) 7789.

4 G.M. Arvanitis, J. Smegal, I. Meier, A.C.C. Wong, J. Schwartz and D. Van Engen, *Organometallics 8* (1989) 2717.

5 L.B. Kool, M.D. Raush, H.G. Alt, M. Herberhold, A.F. Hill, U. Thewalt and B. Wolf, *J. Chem. Soc. Chem. Commun.*, (1986) 408.

6 S.-I. Murahashi, Y. Kitani, T. Uno, T. Hosokawa, K. Miki, T. Yonezava and N. Kasai, *Organometallics, 5* (1986) 356.

7 J. Clemens, M. Green and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1973) 1620.

8 D.A. Lemenovskii, M. Putala, G.I. Nikonov, N.B. Kazennova, D.S. Yufit and Yu.T. Struchkov, *J. Organomet. Chem., 454* (1993) 123.

9 G.I. Nikonov, M. Putala, A.I. Zinin, N.B. Kazennova, D.A. Lemenovskii, A.S. Batsanov and Yu.T. Struchkov, *J. Organomet. Chem., 452* (1993) 87.

10 L.J. Guggenberger, *Inorg. Chem., 12* (1973) 294.

11 D.A. Lemenovskii, S.A. Konde and E.G. Perevalova, *J. Organomet. Chem., 226* (1982) 223.

12 J.W. Lauher and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 1729.

13 C.E. Holloway and M. Melnik, *J. Organomet. Chem., 330* (1986) 1.

14 K. Prout, S.R. Critchley and G.V. Rees, *Acta Crystallogr., Sect. B, 30* (1974) 2305.

15 I. Bkouche-Waksmann, C. Bois, J. Sala-Pala and J. Guerchais, *J. Organomet. Chem., 195* (1980) 307.

16 A. Smith, J. Seyerl, G. Huttner and H. Brintzinger, *J. Organomet. Chem., 173* (1979) 175.

17 C.S. Bajgur, W.R. Tikkanen and S.L. Patersen, *Inorg. Chem., 24* (1985) 2539.

18 E. Stankovič, M. Putala, G.I. Nikonov, N.B. Kazennova and D.A. Lemenovskii, manuscript in preparation.