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STRUCTURE, SPECTRAL PROPERTIES AND INTERCONVERSIONS OF BIS-NIOBOCENES AND THEIR DIANIONS. THE CRYSTAL AND MOLECULAR STRUCTURE OF $[(\eta^5\text{-}C_5H_4SiMe_2OSiMe_2\text{-}\eta^5 : \eta^1\text{-}C_5H_3)_2Nb_2H_2]$ $[Na(OEt_2)_2]_2$ *

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Summary

Electron-acceptor properties of bis-niobocenes $(\eta^5\text{-}C_5H_4Y)(H)\overline{Nb(\eta^5 : \eta^1\text{-}C_5H_3X)_2Nb}(H)(\eta^5\text{-}C_5H_4Y)$ with X = Y = H and XY = —SiMe$_2$OSiMe$_2$— have been investigated. Bis-niobocenes are shown to readily add two electrons forming stable salts of the corresponding dianions $[(\eta^5\text{-}C_5H_4Y)(H)Nb(\eta^5 : \eta^1\text{-}C_5H_3X)_2Nb(H)(\eta^5\text{-}C_5H_4Y)]^{2-}$. The surplus electrons can be removed to give quantitative regeneration of initial neutral bis-niobocenes. The crystal and molecular structure of the title compound has been determined; $R = 0.044$, interatomic distance are Nb...Nb 3.93, Nb—H 1.62, average Nb—C(π) 2.36, Nb—C(σ) 2.31 Å, other distances correspond to the usually observed values. Unlike the neutral bis-niobocenes, there is no direct metal—metal bond in the dianionic structures. This conclusion is supported by electronic spectra of neutral and dianionic species.

Discussion

Bis-cyclopentadienyl compounds of elements of the early transition series (Groups IV—VI) exist mostly as dimers. Recently it was shown that, although the molecular structures of these dimers had some common features, they often differed considerably from one another. Among all the variety of known complexes one can rather easily distinguish two essentially differest classes:

A. Compounds containing a spontaneously formed fulvalene ligand, i.e. complexes with the $(\eta^5 : \eta^5\text{-}C_{10}H_8)M_2$ moiety [1—5]. Usually they are final prod-

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* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

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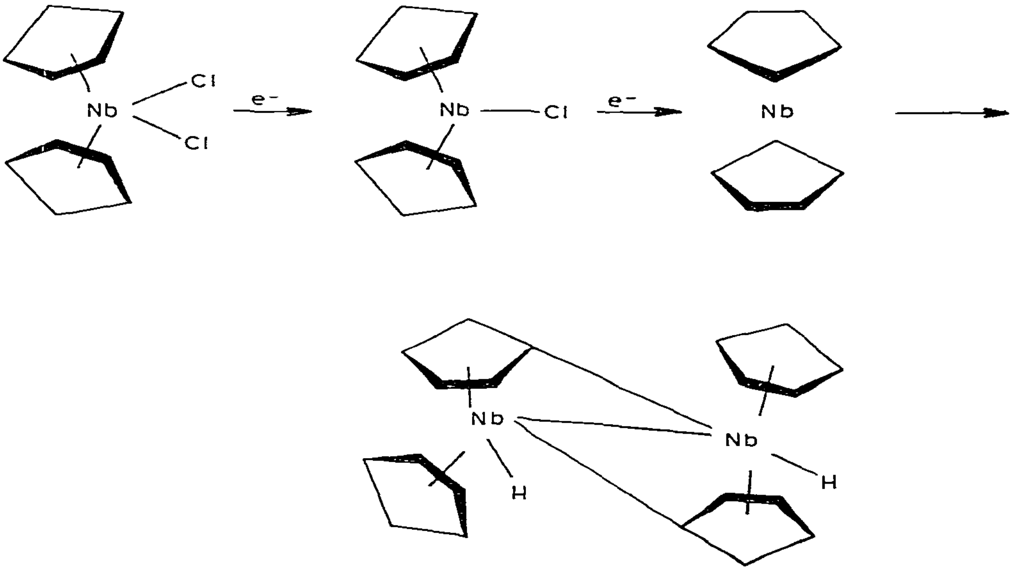
ucts of a sandwich system rearrangement and so are the most stable thermodynamically.

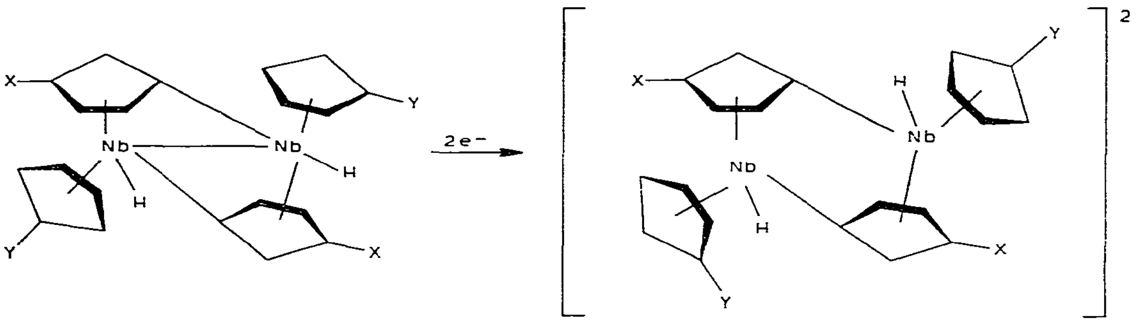
B. Compounds containing the bridging $\eta^5:\eta^5$-C_5H_4 ligand bonded to two metal atoms [4,6—8]. At present only five complexes of this type are structurally investigated, one of Ti [6], one of Nb [7] and three of W [8], the latter are very similar.

In the work discussed below, electron addition and elimination of bis-metallocenes of the type B was investigated for the first time using Nb derivatives. This work is a continuation of our investigation of bis-niobocenes.

We have previously described a very simple method for the synthesis of a bis-niobocene by a mild reduction of Cp_2NbCl_2 with various electron donors [9]. This complex was obtained by Parshall and Tebbe in 1971 by thermal decomposition of Cp_2NbH_3 [10]. In this work we extended our method of bis-niobocene synthesis to the preparation of bis-niobocenophanes with the three-membered bridge —$SiMe_2OSiMe_2$— and investigated electron acceptor properties of two bis-niobocenes, ordinary $(C_5H_5)_2(C_5H_4)_2Nb_2H_2$ and a phanic type $(C_5H_4SiMe_2OSiMe_2C_5H_3)_2Nb_2H_2$ prepared from $(C_5H_5)_2NbCl_2$ and $(C_5H_4SiMe_2OSiMe_2C_5H_4)NbCl_2$, respectively. In the first case a THF solution of sodium naphthalene was used as a reducing agent and in the second case, for experimental convenience, we employed an excess of finely powdered sodium in toluene. In the course of the reduction, metastable paramagnetic monomeric niobocenes were initially formed. These then underwent fast irreversible dimerization, which in fact represents an oxidative addition reaction.



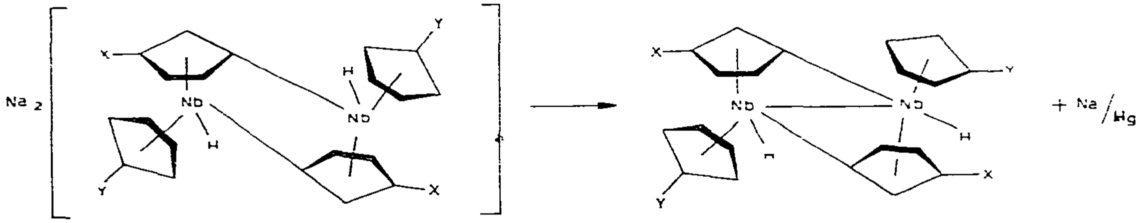
We found that the bis-niobocenes formed through dimerization were in their turn very strong electron acceptors. The electron transfer was easily accomplished with the same reducing agents which were used in the synthesis of bis-niobocenes. The reaction proceeded smoothly without formation of by-products.



(A) (B)

I, X = Y = H, II, XY = $SiMe_2OSiMe_2$

The addition of two electrons gave rise to the formation of stable diamagnetic anionic complexes. The process is completely reversible as elimination of additional electrons and regeneration of initial neutral bis-niobocenes was effected even by traces of oxidants (O_2) or proton donors (H_2O) in the solvent used *. The most convenient preparative method of regeneration is the action of metallic mercury on a dianionic complex giving a quantitative yield of neutral bisniobocene and sodium in the form of amalgam.



B A

This reaction is in itself a good chemical proof of the structure of the dianionic complexes, a relatively rare occurrence in modern organometallic chemistry.

The easily effected electron addition to bis-niobocenes and the complete reversibility of this process indicate the existence of a low-lying vacant electronic level in bis-niobocenes. This level most likely represents an antibonding σ^*(Nb—Nb) molecular orbital. This assumption is consistent with quantum chemical calculations of a large number of various bimetallic complexes [11]. One of the results of these calculations is an indication of a relatively small energy gain by the formation of an ordinary metal—metal bond. In fact it indicates a small energy gap between the bonding σ(M—M) and antibonding σ^*(M—M) molecular orbitals as well as a similarity in energy of both the nonbonding orbitals of the mononuclear fragments from which these two first orbitals are formed. In neutral bis-niobocenes consisting of two 17-electron mononuclear Cp_2Nb(-H)(σ-Cp) fragments the only occupied MO is the σ(M—M) MO, but in the dianions the σ^*(M—M) MO is also filled.

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* Neutral bis-niobocenes also react readily with larger amounts of these reagents, but the process is irreversible.

TABLE 1

FINAL ATOMIC POSITION PARAMETERS (X 10^4, FOR Nb X 10^5) AND ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$ (X 10)

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nb	3269(6)	12020(5)	5710(3)	12.0(2)	9.8(3)	15.0(3)	−0.6(2)	2.0(2)	−0.9(2)
Na	−657(3)	−654(2)	1489(1)	18(1)	18(1)	20(1)	1(1)	2(1)	2(1)
Si(1)	−203(2)	3452(2)	1504(1)	19.6(7)	15.0(9)	21.9(9)	−0.2(6)	1.9(7)	−5.0(7)
Si(2)	−2206(2)	3339(2)	312(1)	21.0(8)	15.2(8)	21.1(9)	4.9(6)	0.8(7)	−1.5(7)
O(1)	−1270(5)	3863(4)	916(2)	25(2)	20(2)	27(2)	7(2)	−4(2)	−9(2)
O(2)	−3006(5)	−1375(4)	1476(2)	18(2)	21(2)	32(2)	−1(2)	5(2)	4(2)
O(3)	718(5)	−1375(4)	2333(2)	25(2)	21(2)	23(2)	1(2)	−4(2)	8(2)
C(1)	1048(7)	2394(5)	1352(3)	20(3)	13(3)	14(3)	−3(2)	3(2)	−5(2)
C(2)	1213(7)	1332(6)	1617(3)	19(3)	16(3)	15(3)	−6(2)	−5(2)	−5(3)
C(3)	2238(7)	742(6)	1382(3)	20(3)	17(3)	19(3)	−1(2)	−8(2)	−4(3)
C(4)	2771(7)	1377(6)	944(3)	15(3)	19(3)	28(3)	0(2)	−4(2)	−5(3)
C(5)	2059(7)	2410(6)	934(3)	17(3)	17(3)	21(3)	−1(2)	0(2)	−2(3)
C(6)	−1219(7)	2312(6)	−47(3)	17(3)	18(3)	14(3)	0(2)	0(2)	1(3)
C(7)	−1606(6)	1200(6)	−210(3)	17(2)	14(3)	13(3)	0(2)	−1(2)	1(3)
C(8)	−503(6)	647(5)	−449(3)	17(3)	11(3)	16(3)	2(2)	1(2)	3(2)
C(9)	616(7)	1403(6)	−425(3)	19(3)	18(3)	18(3)	−3(2)	8(2)	−2(3)
C(10)	200(7)	2422(5)	−192(3)	19(3)	14(3)	21(4)	0(2)	1(3)	3(3)
C(11)	−1248(8)	2933(7)	2084(4)	30(3)	33(4)	33(4)	−1(3)	12(3)	−2(3)
C(12)	801(8)	4709(6)	1790(4)	28(3)	14(3)	42(4)	−3(3)	−1(3)	−18(3)
C(13)	−3884(7)	2716(7)	506(4)	19(3)	28(4)	44(4)	5(3)	7(3)	−6(3)
C(14)	−2629(9)	4529(6)	−198(4)	45(4)	19(4)	41(5)	18(3)	8(4)	9(3)
C(15)	−3391(8)	−2430(7)	1219(4)	26(3)	29(4)	41(4)	−5(3)	3(3)	2(3)
C(16)	−2209(8)	−3214(7)	1438(4)	32(4)	28(4)	44(5)	−2(3)	15(3)	8(3)
C(17)	−4147(8)	−615(7)	1355(4)	19(3)	35(4)	61(5)	7(3)	−5(3)	3(4)
C(18)	−3798(8)	365(6)	1739(4)	26(3)	25(4)	44(5)	6(3)	3(3)	7(3)
C(19)	261(8)	−1296(7)	2907(3)	27(3)	36(4)	24(3)	2(3)	−1(3)	11(3)
C(20)	−242(9)	−168(8)	3012(4)	33(4)	46(5)	32(4)	4(3)	−1(3)	6(4)
C(21)	1407(9)	−2397(6)	2272(4)	40(4)	18(4)	36(4)	1(3)	−10(3)	0(3)
C(22)	2119(9)	−2398(7)	1738(4)	32(4)	26(4)	53(5)	6(3)	5(4)	5(4)
H(Nb) [a]	1008	9152	9104	4.8 [b]					

[a] Localized in the difference Fourier synthesis. [b] B_{iso}.

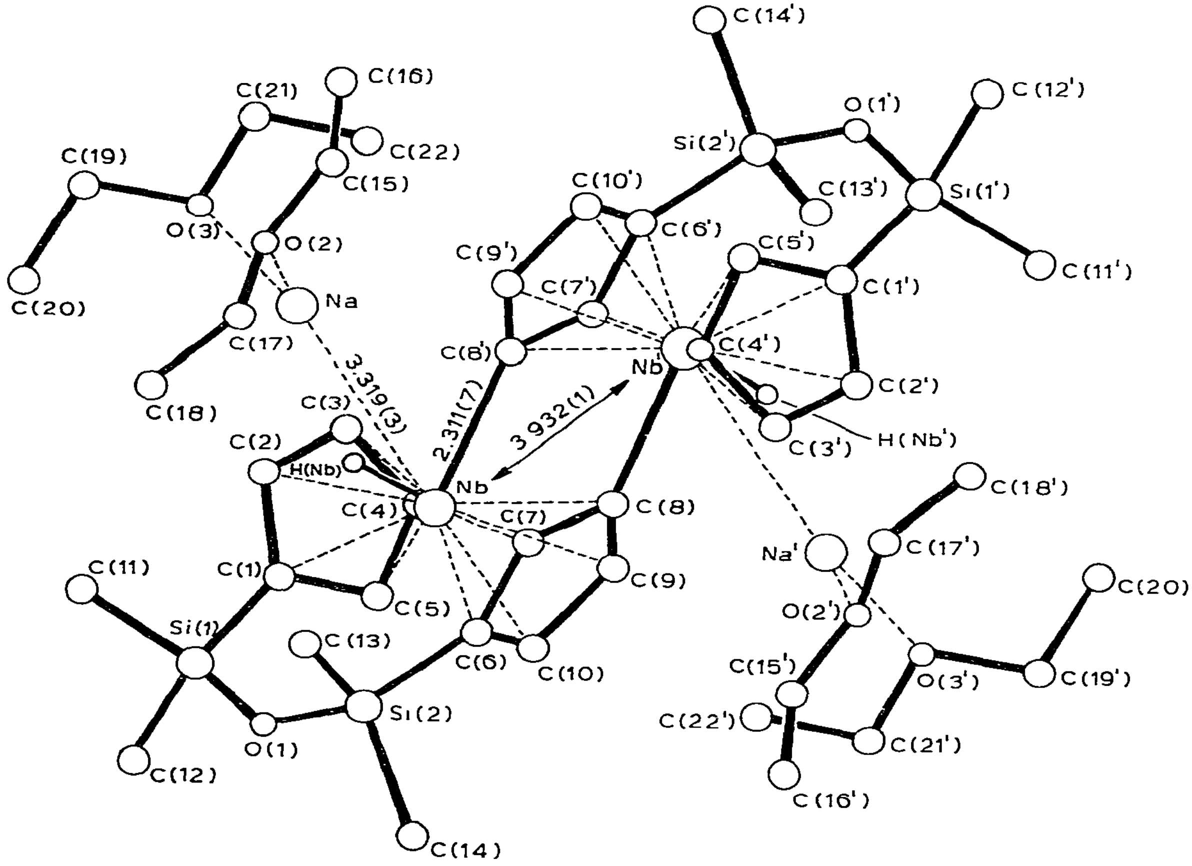

Fig. 1. Structure of complex IIB.

According to our X-ray crystal structure investigation the complex IIB turned out to be the sodium salt of the dianion $[(\eta^5\text{-}C_5H_4\text{-}SiMe_2OSiMe_2\text{-}\eta^5 : \eta^1\text{-}C_5H_3)_2Nb_2H_2]^{2-}$ wherein each Na^+ cation was solvated by two Et_2O molecules (Fig. 1). The binuclear centrosymmetric dianion consists of niobocenophane sandwiches with three-membered $\text{—}SiMe_2\text{—}O\text{—}SiMe_2\text{—}$ bridges linking two Cp-rings as well as bridging $\eta^5 : \eta^1$-Cp ligands and hydride H atoms, located by a difference electron density map. The presence of hydride atoms in the dianionic complexes is in agreement with their IR spectra. The vibrational frequency ν(Nb—H) for IB and IIB occurs at 1720 and 1705 cm^{-1}, respectively, in neutral niobocene, IA, it occurs at 1680 cm^{-1} [10].

Binuclear metallocene derivatives with $\eta^5 : \eta^1$-Cp ligands and hydride atoms have been structurally studied for Nb ($[(\eta^5\text{-}C_5H_5)_2(\eta^5 : \eta^1\text{-}C_5H_4)_2Nb_2H_2]$, IA [7]) and W ($[(\eta^5\text{-}C_5H_5)_2(\eta^5 : \eta^1\text{-}C_5H_4)_2W_2HR]$ R = H (III) and R = CH_2SiMe_3 (IV) [8]). *Cis-* and *trans-* isomers of dimeric tungstenocene, III, differing in the arrangement of the bridging Cp ligands are known (the *trans*-isomer molecule is centrosymmetric). Hydride atoms were located in the difference electron density map of IA but were not found by an X-ray study of III and IV, although hydride ligands are present according to NMR data.

It is of interest that the dianion of IIB has two more electrons than the neutral IA molecule and is isoelectronic with the complexes III and IV, with the similar general structure of the binuclear $M_2(\eta^5 : \eta^1\text{-Cp})_2$ fragment in all four compounds. This allows some conclusions about the metal—metal bond and its influence on the molecular geometry to be drawn.

The centrosymmetric dianion IIB has a *trans*-configuration of bridging Cp ligands relative to the line correcting the Nb atoms whereas the neutral bis-niobocene molecule is close to the non-crystallographic C_2 symmetry [7] and therefore represents a *cis*-isomer. The two π-cyclopentadienyl rings at each Nb atom in IIB are in eclipsed conformation, being rotated by 4.5° relative to one another in the bisector plane projection. Mononuclear bent Cp_2Nb fragments of the molecule have approximate C_s symmetry. Interatomic Nb-C(π) distances (Table 2) of 2.285(7)—2.463(7) Å (average 2.361 Å), the average C—C bond length in Cp rings of 1.43(1) Å and the dihedral angle of 46.3° between best planes of Cp ligands in sandwiches are close to the corresponding values in IA (2.398 Å, 1.418 Å and 39.6° [7]) and fall within the range common for bis-cyclopentadienyl Nb complexes [12]. Although intra-ring angles (Table 3) at the Cp carbon atoms linked to Si atoms (104.0(6) and 104.1(6)°) and at the carbon atom σ-bonded to the Nb atom (105.2(6)°) are reduced as compared with the ideal pentagon value of 108°, the deviations of carbon atoms in Cp ligands from their best least-squares planes do not exceed 0.012 Å and the bonds C(1)—Si(1) and C(6)—Si(2) to the bridging Si atoms lie practically in the corresponding Cp planes (angles with C(1)—C(5) and C(6)—C(10) planes are of 1.8 and 3.2° respectively). Thus addition of two electrons to the dimeric niobocene molecule has no significant influence on the metal—cyclopentadienyl π-bonding and on the C—C bonds of the Cp rings. Also, the three-membered

TABLE 2

BOND LENGTHS *d* (Å)

Bond	*d*	Bond	*d*
C(1)—C(2)	1.442(9)	Nb—C(8')	2.311(7)
C(2)—C(3)	1.384(9)	Nb—H	1.62
C(3)—C(4)	1.415(10)	Si(1)—C(1)	1.835(7)
C(4)—C(5)	1.444(10)	Si(1)—C(11)	1.872(8)
C(5)—C(1)	1.444(9)	Si(1)—C(12)	1.890(8)
C(6)—C(7)	1.456(10)	Si(2)—C(6)	1.836(7)
C(7)—C(8)	1.423(9)	Si(2)—C(13)	1.881(8)
C(8)—C(9)	1.413(9)	Si(2)—C(14)	1.879(8)
C(9)—C(10)	1.442(10)	Si(1)—O(1)	1.638(5)
C(10)—C(6)	1.442(9)	Si(2)—O(1)	1.657(5)
Nb—C(1)	2.331(7)	C(15)—C(16)	1.515(11)
Nb—C(2)	2.407(6)	C(17)—C(18)	1.501(12)
Nb—C(3)	2.463(7)	C(19)—C(20)	1.504(13)
Nb—C(4)	2.371(6)	C(21)—C(22)	1.469(13)
Nb—C(5)	2.290(7)	C(15)—O(2)	1.454(10)
Nb—C(6)	2.331(7)	C(17)—O(2)	1.433(10)
Nb—C(7)	2.368(6)	C(19)—O(3)	1.432(9)
Nb—C(8)	2.433(6)	C(21)—O(3)	1.439(9)
Nb—C(9)	2.326(7)	Na—O(2)	2.405(5)
Nb—C(10)	2.285(7)	Na—O(3)	2.338(5)

TABLE 3

BOND ANGLES ω (°)

Angle	ω	Angle	ω
C(5)C(1)C(2)	104.6(6)	C(1)Si(1)O(1)	114.4(3)
C(1)C(2)C(3)	111.1(6)	C(11)Si(1)C(12)	109.5(4)
C(2)C(3)C(4)	108.7(6)	C(11)Si(1)O(1)	110.3(3)
C(3)C(4)C(5)	106.7(6)	C(12)Si(1)O(1)	104.5(3)
C(4)C(5)C(1)	109.5(6)	Si(1)O(1)Si(2)	138.7(3)
C(10)C(6)C(7)	104.1(6)	O(1)Si(2)C(13)	110.0(3)
C(6)C(7)C(8)	112.0(6)	O(1)Si(2)C(14)	104.3(3)
C(7)C(8)C(9)	105.2(6)	C(13)Si(2)C(14)	110.4(4)
C(8)C(9)C(10)	110.2(6)	O(1)Si(2)C(6)	112.8(3)
C(9)C(10)C(6)	108.5(6)	C(13)Si(2)C(6)	109.0(3)
C(5)C(1)Si(1)	128.7(5)	C(14)Si(2)C(6)	110.3(3)
C(2)C(1)Si(1)	127.3(5)	O(2)C(15)C(16)	108.0(6)
C(7)C(6)Si(2)	129.6(5)	C(15)O(2)C(17)	111.7(6)
C(10)C(6)Si(2)	126.2(5)	O(2)C(17)C(18)	108.5(7)
C(9)C(8)Nb′	126.3(5)	O(3)C(19)C(20)	110.5(6)
C(7)C(8)Nb′	126.2(5)	O(3)C(21)C(22)	110.5(7)
C(1)Si(1)C(11)	108.1(3)	C(19)O(3)C(21)	110.3(6)
C(1)Si(1)C(12)	109.8(3)	C(8′)NbH	82

—Si—O—Si— bridge linking two Cp ligands in the sandwich does not noticeably distort the sandwich geometry. It is to be noted that in IIB the distance (2.032 Å) from the Nb atom to the plane of η^5-Cp ligand not bonded to the other Nb atom is somewhat longer than the distance (2.003 Å) to the bridging ligand plane. A similar difference was also found in the structures of III and IV, the corresponding distances in the *trans*-isomer of III being 1.95 and 1.93 Å [8].

The most important result of the addition of two electrons to the binuclear dimeric niobocene molecule is the cleavage of the metal—metal bond with a corresponding large increase of the Nb...Nb distance to 3.932(1) Å in the dianion IIB from the usual bond length of 3.105(6) Å in the neutral molecule [7]. In fact, in the neutral diamagnetic bis-niobocene molecule the net number of valent electrons per two Nb atoms is 34 and thus the conditions for formation of a direct metal—metal bond are fulfilled, whereas in the dianion both Nb atoms achieve the rare gas electron configuration due exclusively to their ligand environment. In other words, the two electrons added to the dimeric niobocene molecule to form the dianion IIB occupy the molecular orbital, which is σ^*-antibonding with respect to the two Nb atoms, and this gives rise to elimination of the metal—metal bond. In tungsten complexes III and IV, which are isoelectronic with IIB, the metal—metal bond is absent for the same reason, and the W...W distances are equal to 3.811(1) and 3.816(1) Å in the *trans* and *cis*-isomers of III, respectively, and 3.859(1) Å in IV [8], whereas the usual W—W bond length in various binuclear complexes varies in the range 2.9—3.3 Å (see, e.g. ref. 13).

Elimination of the Nb—Nb bond in the dimeric niobocene structure has a marked influence on the geometry of the bridging $\eta^5 : \eta^1$-Cp ligands. In particular, in molecule IA the Nb—C σ-bond is considerably inclined to the Cp ring mean plane at 35.6° whereas in the dianion IIB the planar coordination of the carbon atom σ-bonded to Nb is much less distorted with the corresponding angle of 12.3°. Distribution of bond lengths in the $\eta^5:\eta^1$-Cp ligands of the dianion shows no regular deviation from a delocalized aromatic system. However, in the case of IA such deviations, though only slightly exceeding experimental errors, are found in the $\eta^5:\eta^1$-Cp ligands of all three molecules of the asymmetric unit. In IIB the Nb—C(8′) σ-bond length is equal to 2.311(7) Å, similar to the known values of 2.32 Å in $[(\eta^5\text{-}C_5H_5)_2Nb(n\text{-}C_4H_9)]_2O$ [12] and 2.316 Å in $(\eta^5\text{-}C_5H_5)_2Nb(\eta^2\text{-}C_2H_4)C_2H_5$ [14], while in the molecule IA this bond is shortened to 2.232(7) Å. On the whole, the binuclear $[Nb(\eta^5:\eta^1\text{-}Cp)]_2$ fragment is less strained sterically in the dianion IIB than in the neutral dimeric niobocene molecule IA. This feature also confirms Guggenberger's conclusion about the existence of the Nb—Nb bond in molecule IA [7] and shows that only the metal—metal bond and not the steric requirement of the bridging ligands defines a number of the geometrical characteristics of this molecule, in particular the degree of the $\eta^5:\eta^1\text{-}C_5H_4$ ligand distortion.

The hydride atom localized in the difference electron density map is situated at 1.62 Å from the Nb atom (1.70(3) Å in IA [7]). The plane through C(8′), Nb and H(Nb) (Fig. 1) is close to the bisector plane of the bent Cp_2Nb fragment, dihedral angles between the C(8′)NbH(Nb) plane and the mean C(1)—C(5) and C(6)—C(10) planes being 26.9 and 20.0° respectively. The bond angle C(8′)—Nb—H(Nb) of 82° in within the range of 76—82° usual for LML′ angles in bis-cyclopentadienyl compounds Cp_2MLL' of transition metals with a formal d^2 electron configuration [15]. All the features mentioned together with the results of the structure refinement (see Experimental part) prove the H(Nb) atom localization.

The siloxane bridge C(1)—Si(1)—O(1)—Si(2)—C(6) has a bent configuration with the O(1) atom lying out of the C(1)Si(1)Si(2)C(6) plane and torsional angle values of 2.9° for C(1)Si(1)Si(2)C(6), 40.6° for C(1)Si(1)O(1)Si(2) and 43.4° for Si(1)O(1)Si(2)C(6). Such configuration gives rise to non-equivalence of the methyl groups at Si atoms. The C(11) and C(13) atoms are approximately in the planes of the Cp ligands C(1)—C(5) and C(6)—C(10), respectively, with deviations from best planes of 0.088 Å for C(11) and 0.341 Å for C(13). At the same time the C(12) and C(14) atoms are displaced out of these planes by 1.473 and 1.457 Å, respectively. The bond angles C(12)Si(1)O(1) of 104.5(3)° and C(14)Si(2)O(1), 104.3(3)°, are significantly decreased as compared with the tetrahedral angle of 109.5°. The bond angles C(11)Si(1)O(1) of 110.3(3)° and C(13)Si(2)O(1) of 110.0(3) are equal to the tetrahedral value within accuracy limits. As a result, non-bonded contacts of the two methyl carbon atoms at each Si atom with the bridging O(1) atom are different, being 2.884 (10), 2.795(9), 2.901(9) and 2.795(10) Å for C(11), C(12), C(13) and C(14), respectively. Bond lengths Si—C(Me) of 1.872—1.890(8) Å Si—O of 1.638(5) and 1.657(5) Å and the bond angle Si—O—Si of 138.7(3)° have values usually found in siloxanes, viz. Si—C(sp^3) 1.88—1.93 Å, Si—O 1.61—1.66 Å, Si—O—Si 130—145°. The bond distances Si—C(1) of 1.835(7) Å and Si—C(6) of 1.836(7) Å are in agreement with the shortening of the Si—C bond on transformation from sp^3- to sp^2-hybridisation of the carbon atom [16].

The Na^+ cation in the IIB structure is situated at a distance of 3.319(3) Å from the Nb atom and is coordinated by two Et_2O molecules. The O(2), O(3) and Nb atoms form a planar trigonal environment of the Na^+ cation and the H(Nb) atom acts as an asymmetric bridge between Nb and Na^+ (Na—H(Nb) 2.29 Å, Na—H(Nb)—Nb 115°). The distances Na...O(2) of 2.405(5) and Na...O(3) of 2.338(5) Å and the angle O(2)—Na—O(3) 106.3(2)° can be compared with corresponding values of 2.33, 2.37 Å and 85.9° in $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{14}H_{10}]_2$ (V) [17] and 2.37, 2.39 Å and 93° in $[Na_2(C_2H_5OC_2H_5)_3C_4H_8O][Cr(C_6H_5)_5]$ (VI) [18], where Na^+ cations are coordinated by two molecules of THF (V) or Et_2O (VI). In the IIB structure there are also short interatomic contacts of Na^+ with C(9′), C(8′) and C(2) of 2.588(7), 2.741(7) and 3.022(7) Å, respectively. In the structures of V and VI the short interatomic Na^+...C distances are equal to 2.94—3.24 and 2.6—2.9 Å. The bond lengths and angles in the solvating Et_2O molecules are equal within accuracy limits to the corresponding values in Et_2O at 128° K (molecular symmetry C_{2v}, C—O 1.428, C—C 1.506 Å, C—O—C 111.83°, O—C—C 108.12° [19], compare with Tables 2 and 3). Unlike the molecular crystal of Et_2O itself the solvating ether molecules in the IIB structure are non-planar.

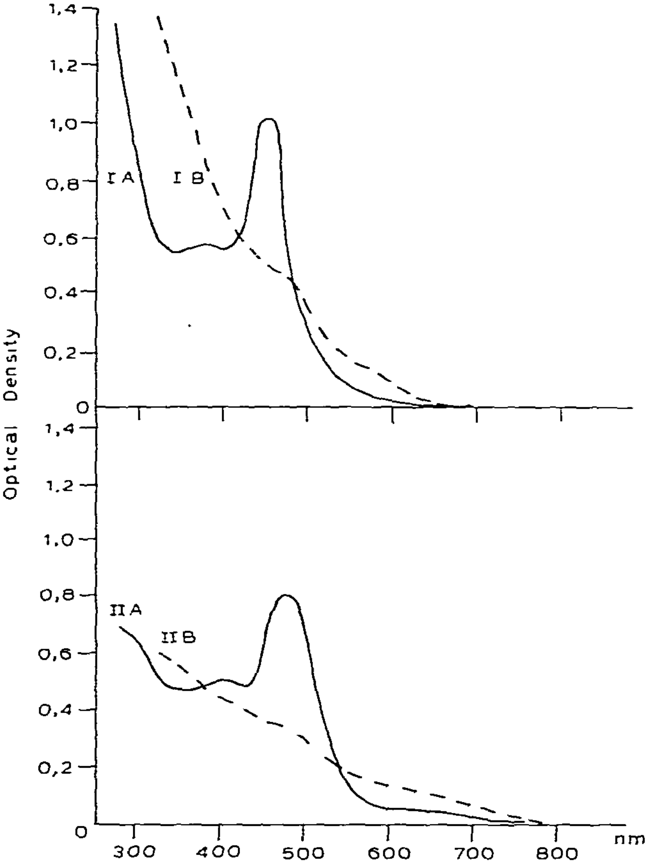

Fig. 2. Electronic spectra of neutral IA, IIA and dianionic IB, IIB bis-niobocenes in THF at 298°K. Equal concentration of both forms (A and B) in each spectrum: C_M(IA) = C_M(IB) and C_M(IIA) = C_M(IIB).

TABLE 4

ELECTRONIC SPECTRA OF IA AND IIA

Complex	ν (cm^{-1} (nm))	ϵ (cm^{-1}/mole) (298°K)
IA	22220 (450)	9000—10000 [a]
IIA	21250 (471)	7000— 8000 [a]

[a] A more accurate determination of ϵ values is difficult due to the above-mentioned high reactivity of the compounds investigated.

Crystals of IIB are built of discrete ionic complexes $\{[Na(O(C_2H_5)_2)_2]_2^+$-$[(C_{14}H_{19}Si_2ONbH)_2]^{2-}\}$. All intercomplex distances are greater than 3.5 Å.

We carried out a comparative investigation of the electronic spectra of neutral (A) and dianionic (B) bis-niobocenes in the 300—800 nm range. These spectra turned out to be distinctly different. Neutral bis-niobocenes are characterized by an intense sharp absorption maximum in the near UV region. This maximum disappears in spectra of the dianions (Fig. 2, Table 4).

The position of the absorption maximum and its high intensity in spectra of IA and IIA make is possible to attribute it to the allowed σ(M—M) → σ^*(M—M) transition. This assignment is in a good agreement with a previous analysis of electronic spectra of other binuclear transition metal complexes, with structures having a two-electron σ-bond [20]. There is no $\sigma \rightarrow \sigma^*$ absorption in the spectra of IB and IIB dianions as both σ- and σ^*-MO's are occupied.

In conclusion it is to be noted that in connection with the results given here it would be interesting to investigate electron addition and elimination processes in bis-metallocenes with other transition metals such as Ti, Mo, W.

Experimental

All manipulations during the preparation, extraction and purification of substances were carried out in evacuated Schlenk-type glassware. All solvents were carefully purified, dried and freed of dissolved gases. Samples for spectral and X-ray experiments were prepared either using vacuum techniques or in a dry box under pure argon.

Spectra. IR spectra of Nujol mulls were measured with a UR-20 spectrometer. UV spectra of solutions in THF, ether or toluene were studied with a Specord-UV instrument.

The structure of all complexes obtained was confirmed by their IR spectra. In this paper only Nb—H frequencies are given.

X-ray study. Cell dimensions of IIB and intensities of 2700 unique reflections with $I > 2\sigma$ were measured with a four-circle automatic diffractometer Syntex P2_1 at —120°C (λ Mo—K_α), graphite monochromator, $\theta/2\theta$ scan, $2° \leqslant 2\theta \leqslant 48°$, no absorption correction was applied). A single crystal of IIB was sealed in a glass capillary under argon.

Crystals of IIB are monoclinic, $a = 9.525(5)$, $b = 12.359(9)$, $c = 22.670(16)$ Å, $\beta = 98.11(5)°$, $V = 2642(3)$ Å^3, space group $P2_1/n$, $Z = 2$. The structure was solved by a standard heavy atom technique and refined by full matrix least-squares with an anisotropic approximation to $R = 0.063$. At this stage the difference electron density map revealed almost all hydrogen atoms including one H atom in each methyl group. All H atoms bonded to carbon atoms were included in the refinement with fixed positional and isotropic thermal parameters ($B_{iso} = 6.0$ Å^2). For the above-mentioned H atoms of methyl groups experimental coordinates were used, all other hydrogen atoms were placed in calculated positions. After one more cycle of refinement the hydride atom H(Nb) was located in the difference electron density map and also included in the least-squares calculation with the same $B_{iso} = 6.0$ Å^2. After three refinement cycles the hydride H atom coordinates changed insignificantly; the value of B_{iso} was decreased to 4.8 Å^2. Final residuals are $R = 0.044$, $R_w = 0.054$. In the final difference electron density map (all non-hydrogen atoms and all hydrogen atoms bonded to C atoms were subtracted) the highest peak at the distance of 1.62 Å from the Nb atom corresponds to the hydride atom H(Nb).

All calculations were performed with an Eclipse S/200 mini-computer using Syntes-EXTL programs. Positional and anisotropic thermal parameter of non-hydrogen atoms are listed in Table 1, bond distances in Table 2, and bond angles in Table 3.

Preparation of complexes

Synthesis of IB. A freshly prepared solution of naphthalene-Na, obtained from 1.02 mmol of sodium metal, was added to the greenish-yellow solution of 0.5 mmol of neutral bis-niobocene $Cp_2Nb_2(C_5H_4)_2H_2$ (IA) in 30 ml of THF. The green colour of napthalene-Na instantly disappeared and a bright red powder of $Na_2[Cp_2Nb_2(C_5H_4)_2H_2] \cdot$ THF (IB) precipitated. IB is unsoluble in Et_2O, THF, alkanes and aromatic solvents. After washing and drying, 0.31 g (98%) of IB with decomposition temperature >240° C was obtained. Found: C, 50.87; H, 5.06; $C_{24}H_{28}Nb_2Na_2O$ calcd.: C, 51.06; H, 4.98%.

The THF content in IB was quantiatively determined by integration of the PMR spectrum of the product of decomposition of a weighed sample of IB in air with a admixed standard substance. With 1 : 3 molar ratio of Cp_2NbCl_2 and naphthalene-Na the yield of IB was 55—65%.

Synthesis of IIB. A suspension of 0.5 mmol of $O(SiMe_2)_2(\eta^5\text{-}C_5H_4)_2NbCl_2$ in 30 ml of toluene was vigorously stirred with a large excess of finely powdered Na metal for ca. 50 h. The solution turned slowly red and a bright red voluminous precipitate was formed. The precipitate obtained was repeatedly (15—20 times) extracted with portions of toluene (each about 30 ml) and separated from sodium metal. After removal of toluene the substance obtained was recrystallised from Et_2O. Slow crystallization (for about 2 days) yielded crystals of IIB suitable for an X-ray investigation (0.20 g, 40%, decomposition temperature >190° C).

Reaction of IB and IIB with Hg. A suspension of 0.25 mmol of IB in 40 ml of THF was shaken with 3 ml of mercury metal for 5 min. The red precipitate of IB disappeared and a yellow transparent solution was formed. After removal of the solvent 0.11 g (98%) of crystalline IA was obtained. Its IR spectrum was identical with that of the authentical IA sample. Sodium containing metallic mercury was thoroughly washed with THF and treated with water, which gave rise to H_2 evolution. The NaOH obtained was titrated to give a quantitative yield.

A similar experiment was carried out with IIB.

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