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Binuclear and mononuclear di-η^5-cyclopentadienylniobium chemistry: a new insight. Crystal and molecular structure of $[Cp_2NbH_2]^-[Na \cdot benzo\text{-}15\text{-}crown\text{-}5]^+$

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Abstract

A mononuclear di-η^5-cyclopentadienylniobium complex Cp_2NbH_2Na (I) has been found to be a by-product of the reaction of Cp_2NbCl_2 with NaH, the principal products being $(\eta^5:\eta^1\text{-}C_5H_4)_2Cp_2Nb_2H_2$ (II) in THF and $(\eta^5:\eta^5\text{-}C_5H_4C_5H_4)Cp_2Nb_2(\mu\text{-}H)_2$ (III) in DME. Cp_2NbH_2Na was also obtained by reaction of Cp_2NbH_3 or the mixture $Cp_2NbBH_4 + Et_3N$ with NaH.

Crystal and molecular structure of $[Cp_2NbH_2]^-[Na \cdot B15C5]^+$ (Ia) (B15C5 = benzo-15-crown-5) was established by an X-ray diffraction study (4208 reflections, $R = 0.022$; monoclinic, at $-120\,°C$, a 17.345(3), b 11.742(3), c 22.965(5) Å, β 98.52(1)°, $Z = 8$, space group $C2/c$). The structural data indicate substantial ionic character of the $(Cp_2NbH_2)^- \cdots (Na \cdot B15C5)^+$ interaction in the solid.

Introduction

Recently it has been found that some di-η^5-cyclopentadienyl derivatives of early transition metals are smoothly converted into binuclear compounds, both homo- and hetero-metallic. This conversion is most typical of coordinatively unsaturated low-valence metallocene compounds and their hydride and alkyl derivatives. Two principal types of bimetallocenes were found to have formed: with bridging $\eta^5:\eta^1$-C_5H_4 ligands (type **A**) and with bridging fulvalene $\eta^5:\eta^5$-$C_5H_4C_5H_4$ ligands (type **B**).

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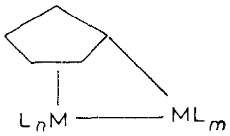
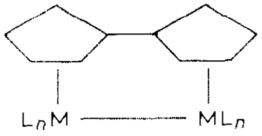


(**A**)



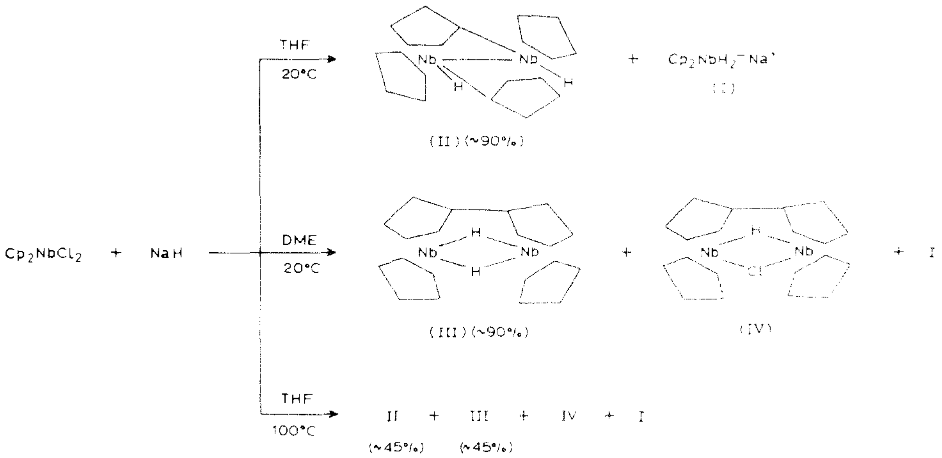
(**B**)

Peculiarities of the chemical properties of the types **A** and **B** (bimetallocene) molecules are due mainly to the spatial proximity of the two metal atoms, the structure and properties of these compounds being directly dependent on electronic configuration of the metal atoms [1]. To our knowledge no systematic study on the mechanism of formation of bimetallocenes has ever been undertaken. However the formation of the type **A** bimetallocenes is usually associated with generation and subsequent dimerization of mononuclear Cp_2M species (M = Nb [2], W [3]).

Here we attempt to sum up the data on the routes of formation of both types (**A** and **B**) of isomeric biniobocenes and suggest more detailed and generalized notions as to the routes to bimetallocene.

Results and discussion

We recently reported the synthesis of two isomeric biniobocenes by reduction of Cp_2NbCl_2 with NaH [4].



We were keen to find out the crucial role played by the solvent in this apparently simple reaction, which yields the two different binuclear complexes, **A** and **B**. It was also of interest to elucidate the routes of formation of binuclear metallocene species from the mononuclear ones.

Two principles seem to be the most adequate. The first is that various mononuclear niobocene derivatives easily transform into each other in the reaction mixtures. The second is that all coordinatively unsaturated mononuclear metallocene complexes can produce bimetallocene species. This meant that further, more detailed study of the reaction of Cp_2NbCl_2 and NaH under different conditions was necessary.

While studying the above-mentioned reactions, it was found, that in all cases small amounts of a deep red oily substance, insoluble in aromatic solvents, were obtained. After addition of benzo-15-crown-5 (B15C5) in THF, the deep red solution of the by-product yielded red crystals of $[Cp_2NbH_2]^-[Na\cdot B15C5]^+$ (Ia), the structure of which will be discussed further on. Complex I is an analog of Cp_2NbH_2Li, reported in our previous publication [5].

It is noteworthy that in all experiments where III is formed as a main product small amounts of $(\eta:\eta^5\text{-}C_5H_4C_5H_4)Cp_2Nb_2(\mu\text{-}H)(\mu\text{-}Cl)$ (IV) are obtained as a by-product [4].

We thus suggest that, the most reasonable scheme of complex I formation is:

$$Cp_2NbCl_2 \xrightarrow{+NaH} Cp_2NbCl^* \xrightarrow{+NaH} Cp_2NbH^* \xrightarrow{+NaH} \underset{\text{(I)}}{Cp_2NbH_2{}^-Na^+}$$

The reaction between Cp_2NbCl_2 and NaH is slow because of heterogeneity of the reaction mixture, but when greater amounts of NaH are used the yields of I are generally higher.

In search of additional information we studied the reactions of NaH with Cp_2NbH_3, and of Et_3N with Cp_2NbBH_4. Cp_2NbH_3 was reported to give Cp_2NbH on heating [6] and a mixture of $Cp_2NbBH_4 + Et_3N$ was also believed to generate Cp_2NbH at room temperature [7]. Pure Cp_2NbH, however, was proved never to exist in solutions or in solid state but was generally taken to be an intermediate species. Both reactions give Ia in satisfactory yields. In addition we found that

$$Cp_2NbH_3 \xrightarrow[50\,^\circ C]{(1)\ NaH;\ (2)\ B15C5} \underset{\text{(Ia)}}{[Cp_2NbH_2]^-[Na\cdot B15C5]^+}$$

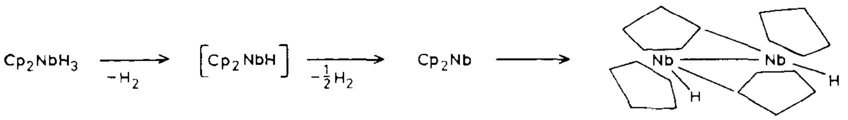
$$Cp_2NbBH_4 \xrightarrow{Et_3N} [Cp_2NbH] \xrightarrow[50\,^\circ C]{(1)\ NaH;\ (2)\ B15C5} \underset{\text{(Ia)}}{[Cp_2NbH_2]^-[Na\cdot B15C5]^+}$$

biniobocene $(\eta^5:\eta^1\text{-}C_5H_4)_2Cp_2Nb_2H_2$ (II) was not cleaved by NaH in THF even at 100 ° C.

Thus NaH reacts in these mixtures with highly reactive and thermally unstable Cp_2NbH through sui generis "oxidative-addition" mechanism.

$$Cp_2NbH + NaH \rightarrow Cp_2NbH_2Na$$

In the absence of NaH, Cp_2NbH generated from Cp_2NbH_3 converts smoothly into biniobocene II releasing H_2 [6]. On monitoring this thermolysis reaction with ESR intermediate formation of monomeric Cp_2Nb was observed ($g = 1.9894$; A_{Nb} 103 G) (lit. data for Cp_2Nb [8]).



(II)

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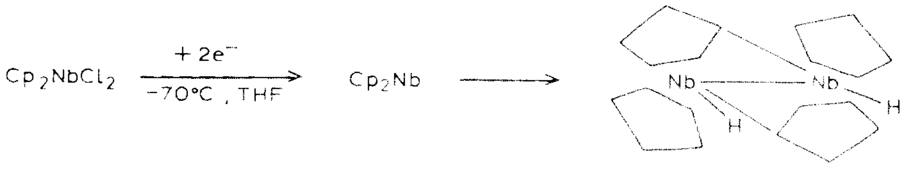
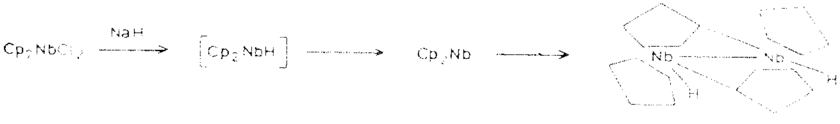
* It is possible that these complexes are stabilized in solutions by coordination of at least one molecule of solvent, i.e. $Cp_2NbX(Solv.)$ (Solv. = THF or DME).

So the final step of this process is identical with that of the reaction between Cp_2NbCl_2 and 2 equivalents of Na · naphthalene at $-70\,^\circ$C [2].



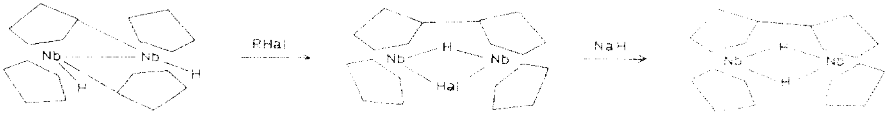
(II)

Thus biniobocene II is a product of direct Cp_2Nb dimerization. On the basis of the two latter reactions we assume that interaction of Cp_2NbCl_2 with NaH in THF, yielding biniobocene II, proceeds along the same line.



(II)

The route to fulvalenic biniobocene III is more complicated. We had previously discovered that the rearrangement reaction of II which leads to fulvalene compounds IV is an associative substitution [4]. The chloro derivative IV gives III quantitatively. So the hydride-halogenide complex IV is today the only definite precursor of biniobocene III.



(II) (IV) (III)

In the reaction between Cp_2NbCl_2 and NaH the hydride-halogenide complex IV may arise as a regular kinetic product. We have already mentioned that IV is present in many reaction mixtures, with niobocene chlorides being the halogenating agents in these cases.

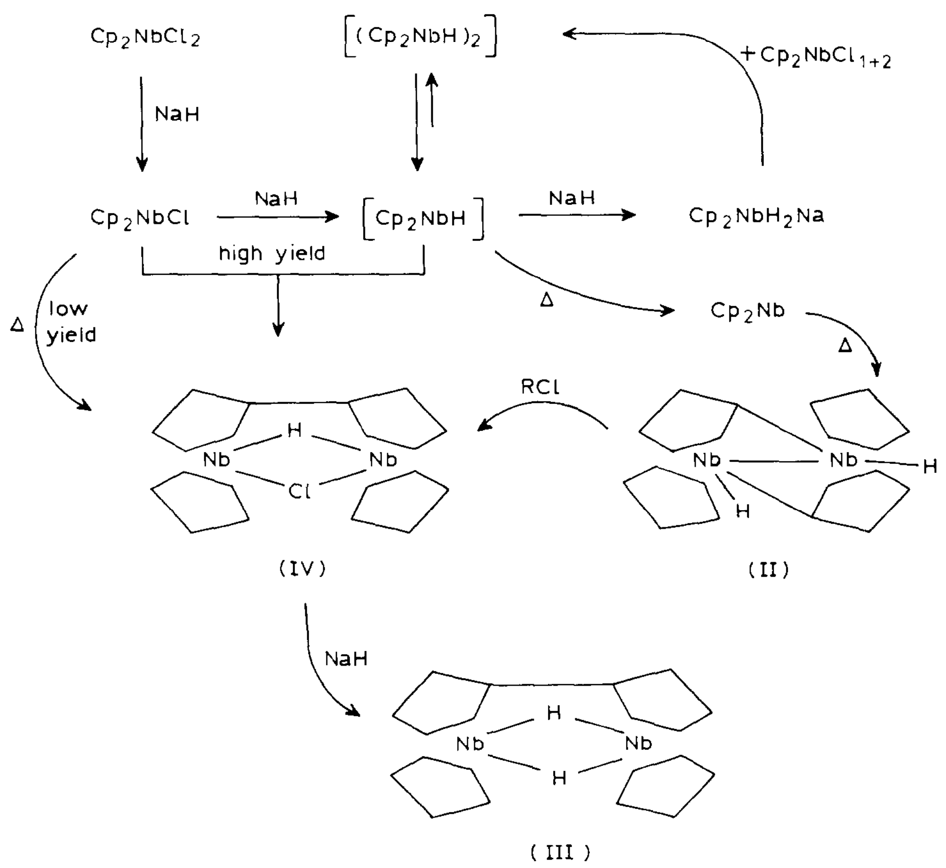
Thus Scheme 1 is proposed showing in general the interaction processes between Cp_2NbCl_2 and NaH.

In THF Cp_2NbH is relatively unreactive towards Cp_2NbCl and is most probably the result of the strong solvation of both these molecules by THF. So Cp_2NbH accumulates, which then gives Cp_2Nb and finally biniobocene II. Only traces of Cp_2NbH_2Na are obtained, provided there is no very large excess of NaH.

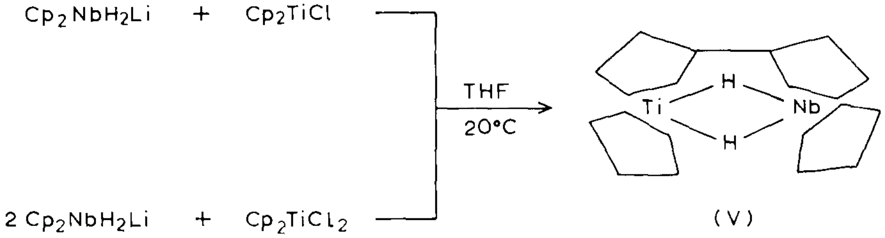
In DME both Cp_2NbCl and Cp_2NbH are highly reactive owing to weak solvation, and the mixture yields $(\eta^5:\eta^5\text{-}C_5H_4C_5H_4)Cp_2Nb_2(\mu\text{-}H)(\mu\text{-}Cl)$ (IV) effectively to give finally dihydride complex III.

Reaction between Cp_2NbCl_2 and NaH in both solvents, at room temperature is very slow, but selective. When heated the selectivity of the process is lost and a wide variety of complexes results.

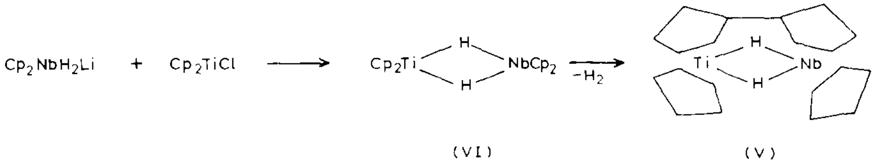
We recently obtained first mixed-metal Nb–Ti complex V with fulvalene ligand [5].



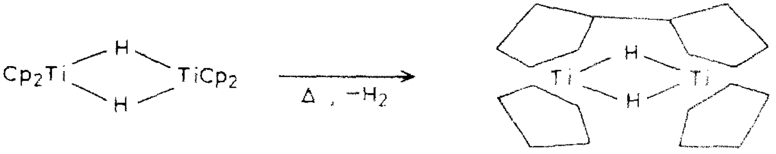
Scheme 1



It is quite possible that the fulvalene binuclear complexes of type **B**, e.g. III, IV and V, may be obtained directly from mononuclear species without intermediate formation of stable binuclear complexes of type **A**. The most probable intermediate in formation of a Nb–Ti mixed-metal complex is a hydride bridged dimer VI.

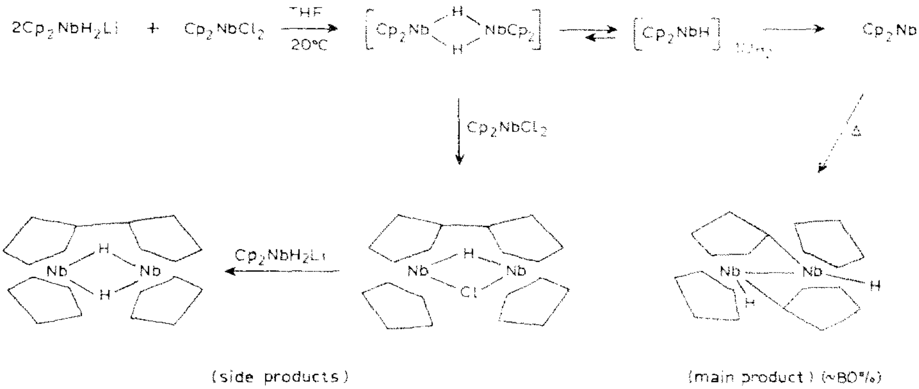


It is essential to remind one of the known transformation of dimeric titanocene monohydride into fulvalene bititanocene VII. A close contact between Cp rings in the initial dimer may promote elimination of two hydrogen atoms * [9].



(VII)

On the basis of these data we took an interest in a similar diniobium situation. The interaction of two niobium complexes Cp_2NbCl_2 and Cp_2NbH_2Li was studied. This reaction gives mainly non-fulvalene biniobocene II, which is in contrast to those of dititanium and mixed-metal Ti–Nb complexes.



The assumption that the dimer $(Cp_2Nb)_2(\mu\text{-}H)_2$ dissociates in solution to give highly reactive Cp_2NbH monomer may account for the peculiar direction taken to produce a mixture of two isomeric niobocenes, mainly of type **A**, while Ti–Ti and mixed Ti–Nb complexes yield single products, only type **B**.

So here the question of what causes the formation of the intermediate compounds $Cp_2M(\mu\text{-}X)\mu\text{-}Y)M'Cp_2$ (**C**) arises and what is their rôle in the formation of the fulvalene complexes?

The stability of these binuclear species should depend on the number of valence electrons and the nature of the bridging atoms. Thus we suggest that the 30- and 31-electron dimers **C** (X = Y = H) are more stable than initial Cp_2MH and $Cp_2M'H$ species, and ≥ 32-electron dimers **C** (X = Y = H) are relatively unstable. All monomeric and dimeric hydride complexes are thermally unstable, but their transformations are different. Monomeric Cp_2MH species lead to type **A** bimetallocenes and the dimeric ones give the fulvalene, type **B** bimetallocenes.

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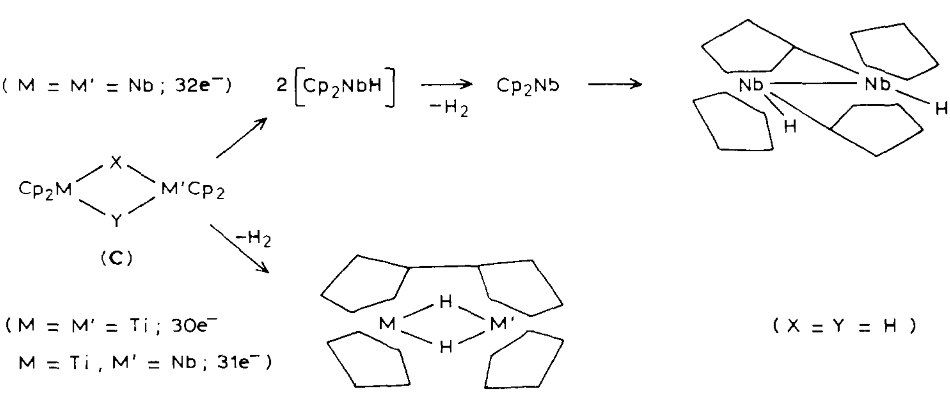
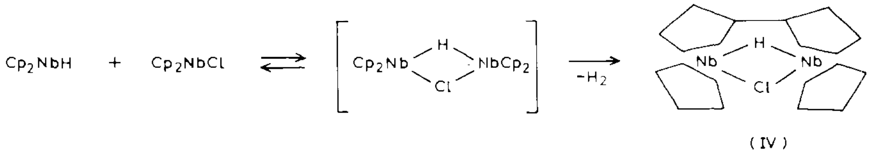
* In $(Cp_2TiCl)_2$ the closest contact of the carbon atoms of the Cp rings is 3.65 Å [10].



The dimers C, in which X and/or Y are *n*-donating atoms, e.g. Cl, give only fulvalene complexes (on heating) due to presumably higher stability of the latter.



Thus we found that the very different reaction mixtures obtained on reduction of Cp_2NbCl_2, contain complex IV as the only isolable product.

It is apparent, however, that much more detailed and sophisticated experiments must be carried out in order to elucidate the mechanism of the formation of complexes with the general formula $(\eta^5:\eta^5\text{-}C_{10}H_8)Cp_2MM'(\mu\text{-}X)(\mu\text{-}Y)$ from mononuclear species.

Crystal and molecular structure of $[Cp_2NbH_2]^-[Na \cdot B15C5]^+$ (Ia)

Crystals of Ia consist of $[Cp_2NbH_2]^-$ anions and $[Na \cdot B15C5]^+$ cations associated in pairs, with the hydride ligands of the anions being weakly bridging (Fig. 1). The bond lengths and main bond angles are listed in Table 1. The geometrical parameters of the Cp_2Nb moiety with average distances Nb–C 2.370, Nb–Cp 2.035, C–C 1.418 Å are quite typical of bent-sandwich niobocene derivatives [11]. Hydride H′ and H″ atoms are situated near the bisecting plane of the Cp_2Nb moiety, the dihedral angles between the NbH′H″ plane and the least squares planes of the two Cp rings, C(1)–C(5) and C(6)–C(10), being 21.3 and 19.3°, respectively. The angle θ between the normals to the least squares planes of the Cp rings is 139.4° (Fig. 2). The Nb–H distances of 1.70 Å, are equal to the average Nb–H bond length calculated by Teller and Bau from available structural data [12] and are very close to analogous distances in Cp_2NbH_3 (1.69 Å [13]), Cp_2NbH_2ZnCp (1.69 Å [14]) and biniobocene (II) (1.70 Å [15]). Somewhat shorter Nb–H bond distances, 1.62 Å, were found previously in the structure of the disodium salt of siloxabis(niobocenophane) $\{[(\eta^5:\eta^1\text{-}C_5H_3)SiMe_2OSiMe_2(\eta^5\text{-}C_5H_4)]_2Nb_2H_2\}^{2-}$ $[Na(OEt_2)_2]_2{}^+$ (IIa), wherein hydride ligand was located in the difference Fourier synthesis but not

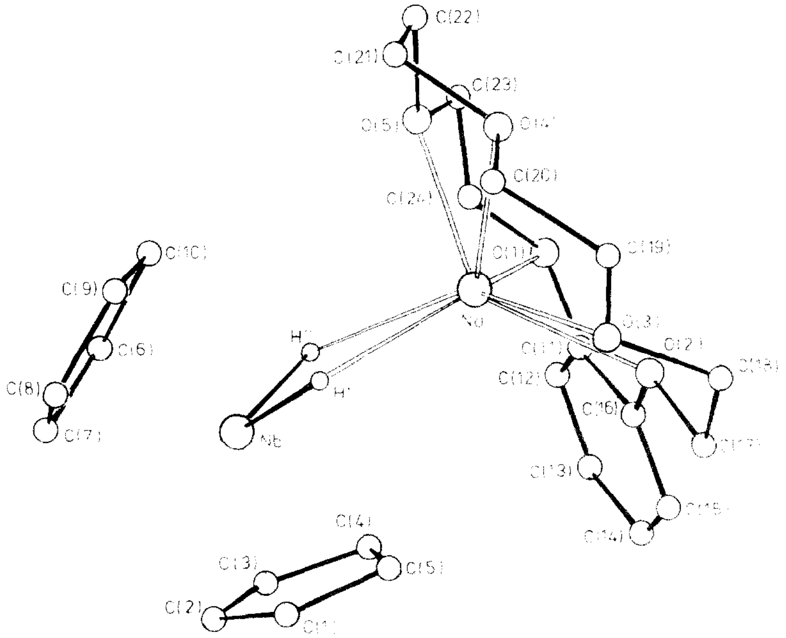


Fig. 1. Molecular structure of $[Cp_2NbH_2]^-[Na(benzo\text{-}15\text{-}crown\text{-}5)]^+$ (Ia). Hydrogen atoms are omitted.

refined [16]. Neutral Cp_2MoH_2, which is isoelectronic to $Cp_2NbH_2^-$, has a similar structure with the Mo–H distance (1.685 Å by neutron diffraction study [17]) close to the Nb–H distance in the Nb analog. However in the Mo compound the dihedral angle θ in the sandwich (145.8°) is somewhat wider and the bond angle H′–Mo–H″ of 75.5° is significantly smaller than the angle H′–Nb–H″ of 86(1)° in $Cp_2NbH_2^-$ (ϕ value in Fig. 2).

In Ia the Na^+ cation is coordinated by five oxygen atoms of the macrocyclic benzo-15-crown-5 ligand, the Na–O distances of 2.406 to 2.547 Å being typical of such complexes [18]. The cation also forms Na...H′ and Na...H″ contacts of 2.35(3) Å with the hydride ligands, deviating towards the anion from the least squares plane of the macrocycle oxygen atoms by 0.97 Å, with the maximum displacement of the oxygen atoms from this plane being 0.30 Å. The Nb...Na distance of 3.337(1) Å is 0.4 Å greater than the sum of their metal ground state radii 2.91 Å according to Pauling [19] and is very close to the corresponding value of 3.319 Å in IIa. In the latter the Na...H and the two Na–O distances are 2.29 Å and 2.338, 2.405 Å, respectively [16].

The bridging or semi-bridging character of hydrogen ligands in mixed transition/non-transition metal complexes has previously been observed in a series of compounds related to Ia, e.g. $[Cp_2MoH]^-[K \cdot 18\text{-crown-}6]^+$ [20], Cp_2MoH_2-$ZnBr_2(OCHNMe_2)$ [21] and Cp_2NbH_2ZnCp [14]. In the last case, however, the value of the Zn–H distance, 1.97 Å, indicates μ_2-bridging character of the H ligands, the Nb–Zn distance of 2.541 Å, which is close to the sum of the ground state radii of 2.59 Å [19], and the H–Nb–H angle value of 102°, both indicate direct Nb–Zn bonding.

The increase by 10° of the ϕ angle in $[Cp_2NbH_2]^-$, as compared with its analog Cp_2MoH_2, places it beyond the usual limits for ϕ of 76–82° for bent sandwiches Cp_2MX_2 with d^2 configuration of the central atom [22]. At first sight this points to the existence of weak Nb...Na bonding in Ia. However results of the calculations of π-complex geometry by the molecular mechanics technique [23] have reinforced the analysis of steric factors as grounds for the bent sandwich geometry of Cp_2ML_n molecules. Our calculations which model them as Cp_2MH_2 moieties with rigid ligands, fixed at distances found experimentally, and able to rotate freely around the central M atom to give θ and ϕ angle values which are consistent with the dominating influence of non-valent inter-ligand repulsion on the geometry of such complexes. Calculated θ and ϕ angles for $[Cp_2NbH_2]^-$ are 137° (139.4°) and 84° (86°), for Cp_2MoH_2 they are 139° (145.8°) and 81° (75.5°), respectively. Observed values are in parentheses. Values for Cp_2MoH_2 were taken from ref. 17.

The "irregular" increase of the ϕ angle in Ia as compared with Cp_2MoH_2 is reproduced, at least qualitatively, in our molecular mechanics calculations and may be accounted for and so include the companying decrease of the θ angle value, by the significant lengthening (0.10 Å) of Nb–Cp distances in $[Cp_2NbH_2]^-$ compared with the Mo–Cp distances in its isoelectronic analog with the same M–H bond distances (Table 2). As a result the Cp_2Nb moiety becomes "more opened", owing to non-valent repulsion of the Cp rings by the hydride ligands in the bent sandwich, so that Cp ring separation is increased. Only the larger differences between experimental and calculated values of $\Delta\theta$ and of $\Delta\phi$ for Cp_2MoH_2, -6.8 and -5.5°, as compared with those for $[Cp_2NbH_2]^-$, -2.4 and -2°, respectively, may point to some contribution by the anion–cation bonding interaction in $[Cp_2NbH_2]^-[Na \cdot B15C5]^+$. However, this difference is probably due to weak additional "repulsion" of hydride ligands in Ia, which may be of a purely electrostatic nature. Our molecular mechanics calculations are thus important evidence that there is only very weak cation–anion covalent bonding in Ia.

The good fit of the molecular mechanics model to organo-transition metal compounds presupposes the absence of rigid geometrical localization of non-bonding electrons of the central atom. In other words, this means quite a uniform distribution of the non-bonding electron density around the transition metal atom. However all three ion complexes discussed here, Ia, IIa and $[Cp_2MoH]^-[K \cdot 18C6]^+$ consist of contact ion pairs in the solid with apparent localization of the alkali metal cation at hydride ligands of the organometallic anion. This is very simply accounted for, by the fact that the hydrogen atom bonded to the transition metal atom is actually drawn into the electron shell of the latter, thus localizing the electron density of the metal atom and rendering it accessible to polar interaction with cation species. The structures of a series of other organo-transition metal complexes with bridging hydrogen atoms are consistent with the above formulated idea [12]. In a sense a transition metal-hydrogen fragment is an analog of a non-bonding electron pair at the atom of non-transition elements.

Experimental

All syntheses and analytical operations were carried out in standard Schlenk-type apparatus. All solvents were purified by use of conventional techniques. NMR samples sealed into 5 mm tubes were run on a JEOL FX-100 spectrometer with benzene-d_6 and THF-d_8 used as the solvents. EPR spectra were studied with a Varian E3 instrument.

X-ray diffraction study of $[Cp_2NbH_2]^-[Na \cdot B15C5]^+$ *(Ia)*

Crystals are monoclinic, a 17.345(3), b 11.742(3), c 22.965(5) Å, β 98.52(1)°, space group $C2/c$, $Z = 8$. Unit cell parameters and intensities of 4297 independent reflections were measured at −120 °C with a Syntex $P2_1$ diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max}$ 60°). 4254 observed reflections with $I > 2\sigma(I)$ were used in the calculations. The structure was solved by direct methods using the MULTAN program and refined by the block-diagonal least-squares technique to an anisotropic approximation. The difference Fourier synthesis revealed all hydrogen atoms which were refined in isotropic approximation. Finally $R = 0.022$, $R_w = 0.028$ with 4208 reflections with $I > 4\sigma(I)$. Atomic coordinates and equivalent isotropic thermal parameters (for H atom isotropic parameters) are listed in Table 2. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [24].

Preparation of complexes

Reactions of Cp_2NbCl_2 with NaH at room temperature in THF and DME see ref. 4.

Reaction of Cp_2NbCl_2 *with NaH in THF with heating.* A mixture of 1.50 g (5.1 mmol) of Cp_2NbCl_2 and 0.60 g (25 mmol) of NaH in 20 ml of THF was heated at 100 °C in a sealed tube for 36 h. After cooling and separation of insoluble residue, the brown solution was decanted, THF removed, and the residue was extracted with 200 ml of toluene. Evaporation of toluene gave 0.5 g of a mixture of two biniobocenes II and III, the total yield 45%. The ^1H NMR spectrum proved the mixture to consist of equal quantities of II and III.

The residue which is unsoluble in toluene was dissolved in 20 ml THF. 2.68 g (10 mmol) of benzo-15-crown-5 was added to this solution. After a few minutes we observed the deposition of small red crystals which grew in size when the reaction mixture was heated. The crystalline compound was separated, washed with THF, 3 × 20 ml, and dried in vacuum. 0.52 g (20%) of Ia was obtained. Found: C, 54.77; H, 5.72; $C_{24}H_{32}O_5NbNa$ calcd.: C, 55.81; H, 6.20%. ^1H NMR spectrum of $[Cp_2NbH_2]^-$ moiety of Ia in THF-d_8 (δ, ppm): 4.1 (10H); −10.8 (2H).

Synthesis of $[Cp_2NbH_2]^-[Na \cdot B15C5]^+$*, alternative procedures.* (a) To a solution of 1.13 g (0.5 mmol) of Cp_2NbH_3 in 20 ml THF was added (0.60 g, 25 mmol) NaH. Then the mixture was heated to 50 °C and stirred for 4 h. After cooling and decantation the resulting deep-red solution was mixed with 2.68 g (10 mmol) of B15C5. The crystalline residue was separated off, washed with THF, and dried, yield 0.78 g (~30%) of Ia.

(b) A mixture of 1.50 g (5.1 mmol) of Cp_2NbCl_2 and 0.76 g (20 mmol) of $NaBH_4$ in 20 ml THF was stirred vigorously during 10 min. The resulting deep-green solution of Cp_2NbBH_4 was filtered, and then Et_3N (1.0 g) was added to the solution. Within a minute the solution had turned dark brown, whereupon 0.60 g (25 mmol) of NaH was added. The suspension was heated to 50 °C and stirred for 2 h. After cooling and removal of the residue, the deep-red solution was decanted off and 2.68 g (10 mmol) of B15C5 was added. Ia separated off and was washed with THF, and dried, yield 1.55 g (~50%).

(Continued on p. 43)

Table 1

Bond distances *d* (Å) and most of the important bond angles *ω* (deg.) in Ia

Bond	*d*	Bond	*d*
Nb...Na	3.3366(8)	Na–O(3)	2.460(2)
Nb–C(1)	2.333(2)	Na–O(4)	2.406(2)
Nb–C(2)	2.289(2)	Na–O(5)	2.408(2)
Nb–C(3)	2.358(2)	Na–H	2.50(2)
Nb–C(4)	2.428(2)	Na–H	2.35(2)
Nb–C(5)	2.409(2)	O(1)–C(11)	1.373(2)
Nb–C(6)	2.324(2)	C(11)–C(12)	1.380(3)
Nb–C(7)	2.314(2)	C(12)–C(13)	1.399(3)
Nb–C(8)	2.403(2)	C(14)–C(15)	1.376(3)
Nb–C(9)	2.446(2)	C(15)–C(16)	1.393(3)
Nb–C(10)	2.389(2)	C(16)–C(11)	1.383(3)
Nb–H	1.70(2)	O(2)–C(16)	1.408(3)
Nb–H	1.70(3)	O(2)–C(17)	1.373(2)
C(1)–C(2)	1.431(3)	C(17)–C(18)	1.438(2)
C(2)–C(3)	1.428(3)	O(3)–C(18)	1.502(3)
C(3)–C(4)	1.408(3)	O(3)–C(19)	1.420(3)
C(4)–C(5)	1.392(3)	C(19)–C(20)	1.432(3)
C(5)–C(1)	1.433(3)	O(4)–C(20)	1.506(3)
C(6)–C(7)	1.428(3)	O(4)–C(21)	1.432(3)
C(7)–C(8)	1.424(3)	C(21)–C(22)	1.431(3)
C(8)–C(9)	1.403(3)	O(5)–C(22)	1.498(3)
C(9)–C(10)	1.406(3)	O(5)–C(23)	1.429(3)
C(10)–C(6)	1.428(3)	C(23)–C(24)	1.419(3)
Na–O(1)	2.547(2)	O(1)–C(24)	1.502(3)
Na–O(2)	2.498(2)	C(13)–C(14)	1.432(2)
C(1)–H(1)	0.92(2)	C(17)–H(17.2)	0.96(2)
C(2)–H(2)	0.92(2)	C(18)–H(18.1)	0.97(2)
C(3)–H(3)	0.92(2)	C(18)–H(18.2)	1.02(2)
C(4)–H(4)	0.89(2)	C(19)–H(19.1)	0.96(2)
C(5)–H(5)	0.94(2)	C(19)–H(19.2)	1.00(2)
C(6)–H(6)	0.95(2)	C(20)–H(20.1)	0.98(2)
C(7)–H(7)	0.90(2)	C(20)–H(20.2)	0.96(2)
C(8)–H(8)	0.89(2)	C(21)–H(21.1)	0.94(2)
C(9)–H(9)	0.91(2)	C(21)–H(21.2)	1.00(2)
C(10)–H(10)	0.94(2)	C(22)–H(22.1)	1.00(2)
C(12)–H(12)	0.89(2)	C(22)–H(22.2)	0.94(2)
C(13)–H(13)	0.95(2)	C(23)–H(23.1)	0.94(2)
C(14)–H(14)	0.93(2)	C(23)–H(23.2)	0.95(2)
C(15)–H(15)	0.91(2)	C(24)–H(24.1)	1.01(2)
C(17)–H(17.1)	1.01(2)	C(24)–H(24.2)	1.00(2)

Angle	*ω*	Angle	*ω*
HNbH′	86(1)	O(2)NaO(5)	121.11(6)
NbHNa	104(1)	O(2)NaH	126.2(5)
NbH′Na	110(1)	O(2)NaH′	119.0(7)
HNaH′	57(1)	O(3)NaO(4)	62.62(5)
O(1)NaO(2)	60.52(6)	O(3)NaO(5)	134.06(6)
O(1)NaO(3)	121.17(6)	O(3)NaH	84.5(5)
O(1)NaO(4)	116.41(6)	O(3)NaH′	136.5(7)
O(1)NaO(5)	66.09(5)	O(4)NaO(5)	69.56(5)
O(1)NaH	147.5(5)	O(4)NaH	90.7(5)
O(1)NaH′	90.9(7)	O(4)NaH′	126.6(7)
O(2)NaO(3)	65.40(5)	O(5)NaH	112.0(5)
O(2)NaO(4)	114.40(6)	O(5)NaH′	83.6(7)

Table 2

Atomic coordinates in Ia ($\times 10^5$, for Nb and Na $\times 10^6$, for H $\times 10^4$) and equivalent isotropic thermal parameters $B_{\mathrm{iso}}^{\mathrm{eq}}$ (for H atoms isotropic thermal parameters B_{iso})

Atom	x	y	z	$B_{\mathrm{iso}}^{\mathrm{eq}}$
Nb	134582(10)	31631(15)	106469(7)	1.01(1)
Na	322777(44)	−31560(70)	145005(33)	1.39(2)
O(1)	37878(8)	−19588(12)	9195(6)	1.48(3)
O(2)	36602(9)	−20867(12)	20070(6)	1.55(3)
O(3)	35824(8)	−481(12)	25187(6)	1.50(3)
O(4)	40708(8)	12983(12)	16880(6)	1.67(3)
O(5)	38057(8)	2594(12)	6052(6)	1.65(3)
C(1)	7766(12)	−2900(12)	18701(9)	1.73(5)
C(2)	2784(12)	−5697(18)	13355(9)	1.64(5)
C(3)	6541(13)	−13170(18)	10307(9)	1.66(5)
C(4)	13740(13)	−16595(18)	13785(10)	1.90(5)
C(5)	14576(13)	−9866(19)	18830(9)	1.96(5)
C(6)	10196(12)	10243(18)	1150(8)	1.48(4)
C(7)	4304(11)	13660(17)	4223(9)	1.40(4)
C(7)	7583(12)	21614(17)	8877(9)	1.55(5)
C(9)	15447(12)	23125(17)	8209(9)	1.56(5)
C(10)	17111(12)	16218(17)	3557(9)	1.47(5)
C(11)	34471(11)	−29469(17)	10755(8)	1.31(4)
C(12)	31745(12)	−38216(18)	7030(9)	1.63(5)
C(13)	28407(13)	−47811(19)	9266(10)	2.03(5)
C(14)	27840(14)	−48510(19)	15170(10)	2.04(5)
C(15)	30516(12)	−39710(18)	19015(9)	1.66(5)
C(16)	33835(11)	−30219(17)	16825(8)	1.30(4)
C(17)	35488(13)	−20562(18)	26151(8)	1.67(5)
C(18)	39273(12)	29736(19)	28604(9)	1.68(5)
C(19)	39429(13)	10224(19)	26893(9)	1.85(5)
C(20)	37800(13)	18273(19)	21751(10)	1.92(5)
C(21)	39428(13)	19575(18)	11583(10)	1.83(5)
C(22)	42554(13)	12811(19)	6918(10)	1.86(5)
C(23)	41228(13)	−5787(19)	2636(9)	1.80(5)
C(24)	36883(13)	−16750(18)	3065(9)	1.69(5)

Atom	x	y	z	B_{iso}
H	2063(13)	865(20)	1572(10)	1.8(5)
H′	2072(16)	−355(22)	773(18)	3.4(6)
H(1)	653(12)	154(18)	2175(9)	1.3(4)
H(2)	−214(14)	−294(20)	2111(10)	2.1(5)
H(3)	451(12)	−1787(19)	688(9)	1.7(5)
H(4)	1739(13)	−2138(20)	1297(10)	2.0(5)
H(5)	1906(13)	−947(20)	2171(9)	1.8(5)
H(6)	988(12)	590(19)	−235(10)	1.6(5)
H(7)	−69(12)	1127(18)	391(9)	1.5(4)
H(8)	515(12)	2481(19)	1162(9)	1.6(5)
H(9)	1885(12)	2784(19)	1039(9)	1.4(4)
H(10)	2206(12)	1569(19)	240(9)	1.5(5)
H(11)	3220(13)	−3787(20)	323(10)	2.2(5)
H(13)	2639(14)	−5362(21)	661(10)	2.4(5)
H(14)	2564(14)	−5493(20)	1663(11)	2.3(5)
H(15)	2981(13)	−4024(20)	2284(10)	1.8(5)
H(17.1)	2975(12)	−2080(19)	2650(9)	1.5(5)
H(17.2)	3817(12)	−2678(19)	2825(9)	1.4(4)
H(18.1)	3865(12)	−880(18)	3269(9)	1.1(4)

Table 2 (continued)

Atom	x	y	z	B_{iso}
H(18.2)	4514(13)	−1008(20)	287(10)	2.2(5)
H(19.1)	3714(12)	1304(18)	3016(9)	1.4(4)
H(19.2)	4517(13)	934(21)	2804(10)	2.2(5)
H(20.1)	4055(13)	2553(20)	2256(10)	2.3(5)
H(20.2)	3234(13)	1941(20)	2069(10)	2.0(5)
H(21.1)	4178(11)	2678(17)	1211(9)	0.9(4)
H(21.2)	3369(13)	2100(20)	1050(10)	2.1(5)
H(22.1)	4192(13)	1704(20)	309(10)	2.1(5)
H(22.2)	4785(12)	1108(19)	810(9)	1.6(5)
H(23.1)	4650(12)	−694(19)	418(9)	1.3(4)
H(23.2)	4074(13)	−378(20)	−140(10)	2.4(5)
H(24.1)	3941(12)	−2268(19)	79(10)	1.6(5)
H(24.2)	3123(12)	−1597(18)	151(9)	1.3(4)

(c) When $(\eta^5:\eta^1\text{-}C_5H_4)_2Cp_2Nb_2H_2$ (II) (0.5 g; 1.25 mmol) was treated with NaH (0.60 g; 25 mmol) in THF at 100 °C for 10 h, no changes of colour of the solution were observed, and subsequent addition of B15C5 (2.68 g; 10 mmol) did not result in the red crystalline precipitate of Ia.

Reaction of Cp_2NbH_2Li with Cp_2NbCl_2. To a solution of 0.060 g (0.21 mmol) of Cp_2NbH_2Li in 5 ml of THF was added 0.030 g (0.10 mmol) of Cp_2NbCl_2. The mixture was stirred for 10 min to dissolve the Cp_2NbCl_2. The mixture was then heated to 100 °C for 1 h. The solvent was removed and the residue was extracted with 10 ml C_6D_6. After ^1H NMR spectroscopy the resulting solution was found to contain three complexes: biniobocene II, the dominant product, 80%; biniobocene III, only 2%; and 18% of unchanged Cp_2NbH_2Li.

Thermolysis of Cp_2NbCl in THF. The solution of Cp_2NbCl, obtained from 1.50 g (5.1 mmol) of Cp_2NbCl_2 and 5.2 mmol Na · naphthalene [1] at room temperature in 20 ml THF, was heated to 100 °C over 2 h. After slow cooling the reaction solution gave big crystals of complex IV. More IV was obtained on addition of 10 ml of pentane to this solution. The total yield is 0.37 g (~ 30%) of IV. The complex was identified from its ^1H NMR spectrum.

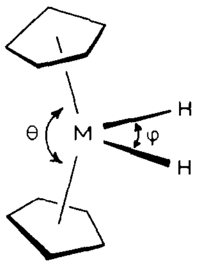


Fig. 2. Angular parameters in dihydride metallocenes by the molecular mechanics calculations (observed parameters are in parentheses): Cp_2MoH_2 θ 139° (145.8°), ϕ 81° (75.5°), [17], $[Cp_2NbH_2]^-$ θ 137° (139.4°), ϕ 84° (86°).

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