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Synthesis and Molecular Structure of the Niobocenecarbonylhydride Adduct to Bis(tetrahydroborate)zinc

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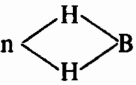
The combination of a transition metal heterobinuclear grouping with a wedge-like sandwich dicyclopentadienyl system which encloses the coordination sphere as *e.g.* in $Cp_2V\text{-}Cr(CO)_3Cp$ where Cp is $\pi\text{-}C_5H_5$ [1], is of interest for constructing selective catalysts. The possible route to such systems is the preparation of adducts of metal-containing Lewis acids to electron saturated sandwich complexes of the type Cp_2ML_n. The addition may occur via bridge ligands, with the formation of a direct metal-to-metal bond or by both mechanisms simultaneously. Depending on the type of coordination, the properties of the initial Cp_2ML_n complex are modified to different extents upon adduct formation. Thus, the coordination of $AlEt_3$ with $Cp_2Nb(CO)H$ (I) in an 1:1 adduct probably occurs via the hydride H atom, because the corresponding ^1H NMR signal shifts strongly from the parent compound whereas the IR ν_{CO} frequency changes only insignificantly. A similar type of coordination is supposed to occur in AlR_3 adducts to the coordination-saturated molecules Cp_2NbH_3, $Cp_2NbH(C_2H_4)$ and $[Cp(C_5H_4)NbH]_2$ [2]. In the structure of $Cp_2MoH_2\cdot ZnBr_2\cdot DMF$, the molecular fragments are, however, bound not only through the bridge H atoms but also by a direct Mo–Zn bond of 2.739 Å length [3].

We deemed it interesting to determine the type of coordination of an unusual Lewis acid, bis(tetrahydroborate)zinc, $Zn(BH_4)_2$, and changes in the structure and properties of the molecular fragment $Cp_2Nb(CO)H$ [4] caused by coordination, in the adduct $Cp_2Nb(CO)H\cdot Zn(BH_4)_2$ prepared by us.

Adduct $Cp_2Nb(CO)H\cdot Zn(BH_4)_2$ (II) was made by reduction of $NbCl_5$ with sodium cyclopentadienyl and zinc metal powder in THF under CO at room temperature followed by treatment with $NaBH_4$. Rapid recrystallization from benzene gave nonsolvated adduct II as yellow prisms (found/calc., %: C, 37.44/38.04; H, 5.40/5.47; B, 6.10/6.35). The IR spectrum of the product contained the bands at (cm^{-1}): 1960 vs (ν_{CO}); 2445 s, 2320 sh, 2100 s (ν_{B-H}); 1130 vs, 1400 mb ($\nu_{B-H\ bridge}$ and ν_{Nb-H}, respectively). The mass spectrum contained the molecular fragment ions I^+ (m/e 252, 9.4%) and $Zn(BH_4)_2^+$ (m/e 95, 5.4%) and their fragmentation products. X-ray diffraction was studied with red-orange crystals (obtained from a benzene–THF mixture by slow crystallization in an evacuated sealed ampoule) which contained 0.5 mol of benzene per mol of II.

The diffraction patterns were taken with a Syntex $P2\bar{1}$ diffractometer, λ Mo-K_α. The crystals are triclynic and have the dimensions $a = 8.105(2)$, $b = 9.350(2)$, $c = 11.252(2)$ Å, $\alpha = 89.65(1)$, $\beta = 95.49(1)$, $\gamma = 94.33(2)^\circ$, $Z = 2$, space group $P\bar{1}$. The structure was solved from 3333 nonzero reflections, the coordinates of non-hydrogen atoms were determined from the Patterson and Fourier syntheses. The structure was refined in the anisotropic approximation by the block-diagonal LSM to $R = 0.036$.

The structure is made up of dinuclear complexes $Cp_2Nb(CO)(\mu\text{-}H)\cdot Zn(BH_4)_2$ packed together with solvate benzene molecules. The geometry of the complex molecule is shown in Fig. 1. It has an approximately C_s symmetry with the mirror plane containing the Nb, Zn, H, and C(CO) atoms. The plane relates the two C_5H_5 rings and two BH_4 groups to each other. The Nb–Zn axis practically coincides both with the ZnH_4 pyramid axis and with the bissector axis of the dihedral angle between the C_5H_5 planes. This angle (39.3°) is widened somewhat from free I (37.0°) [4]; in both I and II, the cyclopentadienyl rings are in the eclipsed conformation. Most structure parameters of I change only insignificantly on adduct formation (Table I). The angle between the Nb–H and Nb–CO bonds lying in the bissector plane of the dihedral angle between the rings, however, increases to 102.8°, which is noticeably larger than 90°, the value assumed from geometrical considerations for I [4], or 92°, the value found for $Cp_2Nb(CO)SH$ [5]. The zinc atom in the $Zn(BH_4)_2$ fragment is linked with BH_4 through pairs of hydrogen atoms; it occupies a vertex of a pyramid having a square-planar base (the deviations from the H(13)–H(16) plane are within ±0.05 Å). The four-membered metallocycles  $Zn\langle{}^{H}_{H}\rangle B$ are nearly planar. Both B atoms are displaced out of the ZnH_4 pyramids, the deflection angles about the H...H axes being equal to *ca.* 6.5 and 2°.

The principal structural chemistry problem arising in the analysis of the geometry of complex II is the type of bonding between I and $Zn(BH_4)_2$. The large

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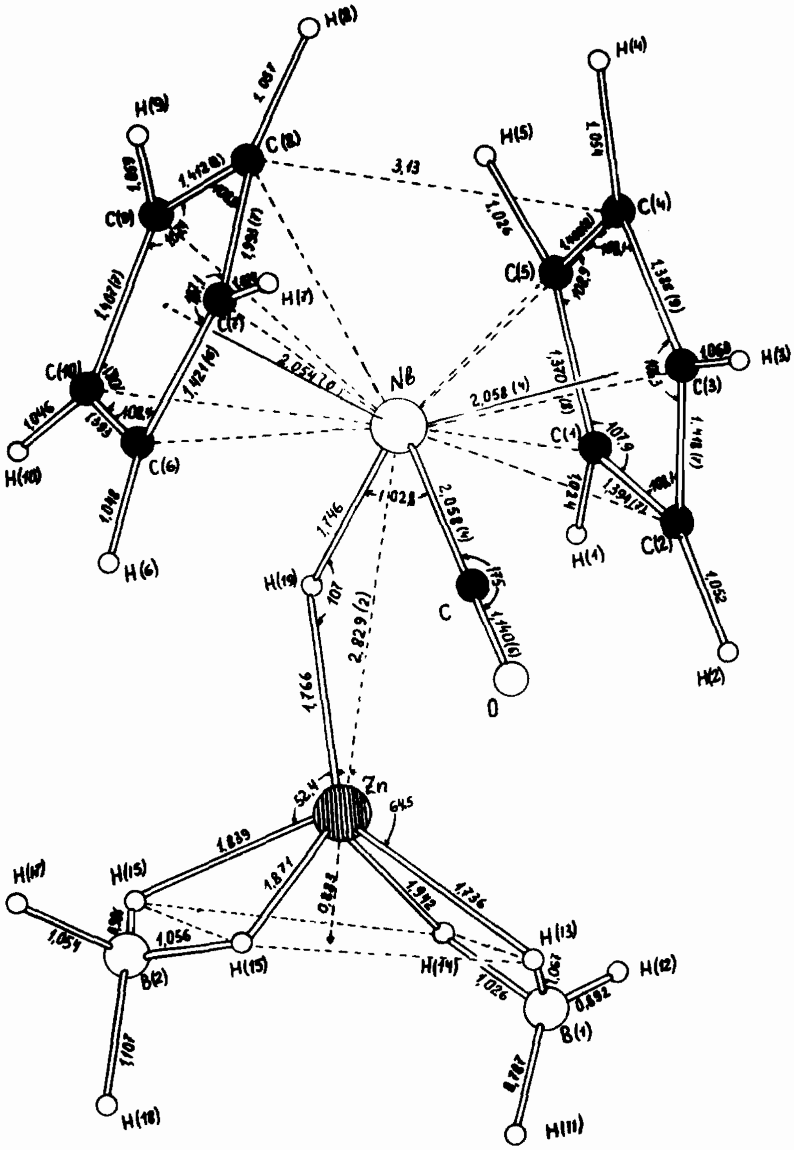

Fig. 1. The structure, principal interatomic distances and valence angles in the complex $(\pi\text{-}C_5H_5)_2Nb(CO)(\mu\text{-}H)Zn(BH_4)_2$.

TABLE I. Comparison of Characteristics of $Cp_2Nb(CO)H$ (I) and Its Adduct to $Zn(BH_4)_2$ (II) (Average Values).

Parameter	I	II	Parameter	I	II
$Nb–C_{(C_5H_5)}$, Å	2.36	2.38			
C–C in C_5H_5, Å	1.45	1.40			
	0.09	0.03	Dihedral angle between the C_5H_5 rings (°)	37.0	39.3
Nb–CO, Å	2.04	2.058	H–Nb–CO (°)	90	102.8
C–O, Å	1.10	1.14	ν_{CO}, cm^{-1}	1910	1960
Nb–C–O (°)	172	175.3			

Zn...C(CO) distance (2.90 Å) and a practically linear structure of the Nb–C–O fragment are indicative of the absence of valent interactions between the carbonyl group and Zn. On the other hand, the bridge function of the H atom is doubtless as the Nb–H and Zn–H distances are equal to 1.75 and 1.77 Å, respectively, and the Nb–H–Zn angle is equal to 107°.

Next, the Nb–Zn distance in II (2.829 Å) is comparable with the Mo–Zn distance in the aforementioned molybdenum complex (2.793 Å) [3]. The increase of the H–Nb–CO angle to 102.8° in II from 90° in I is also compatible with the suggestion of the formation of the Nb–Zn bond having an intermediate direction.

As the electron-saturated moiety, I, is a Lewis base and the electron-deficient one, $Zn(BH_4)_2$, is a Lewis acid in II, the dative interaction $Nb \rightarrow Zn$ should play the major role in bonding between the metals. It should be noted that penta-coordinate structures with an electron donor occupying the vertex of a tetragonal pyramid are in general characteristic for Zn. The donor group fills up the zinc outer shell to octet (monohydrates of zinc acetylacetonate [6] and disalicylideneethylenediaminate [7] containing water molecules in pyramid vertices may serve as examples).

The conclusion of direct coordination of the $Zn(BH_4)_2$ fragment in II to Nb agrees with a higher frequency ν_{CO} shift to 1960 cm^{-1} from 1910 cm^{-1} in I (*cf.* $CpNb(CO)_4AlCl_3$ [8]. On the other hand, a far smaller frequency rise has recently been observed [9] in the formation of the adduct $Cp_2Nb(CO)_3Cl \cdot ZnCl_2$ by reduction of Cp_2NbCl_2 by zinc metal in THF under CO (such an adduct of the 1:1 composition with $ZnCl_2$ coordinated to Nb through a bridge chloro atom at niobium is probably formed as intermediate in the synthesis of II; it may give II under the action of $NaBH_4$).

The structure data for II are interesting to compare with the results obtained for $Cp_2Nb(CO)(\mu\text{-}H) \cdot Fe(CO)_4$ (III) published lately [10] and our recent data on $Cp_2NbH(\pi\text{-}C_5H_4) \cdot Fe(CO)_2Cp$ (IV). The authors [10] treat III as an adduct of $Fe(CO)_4$ to I involving both hydrogen bonding and direct Nb–Fe bonding. The Nb–H–Fe angle (141.2°) and Nb...Fe distance (3.318(1) Å) in III are, however, far larger than the Nb–H–Zn angle in II (107.0°) and the Nb–Fe distance in IV (2.968 Å). It thus seems more likely that the formation of III is only due to bridge hydrogen bonding. So II and IV, together with $Cp_2Nb(\mu\text{-}CO) \cdot (\sigma, \pi\text{-}CO)MCp$ (where M is Mo or W) studied by X-ray diffraction recently [11], are the first heteronuclear compounds containing niobium–transition metal bonds whose structure characteristics have been determined.

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