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Synthesis and structure of η^1-N-diphenyldiazomethane complexes of niobo- and tantalocene monohydrides

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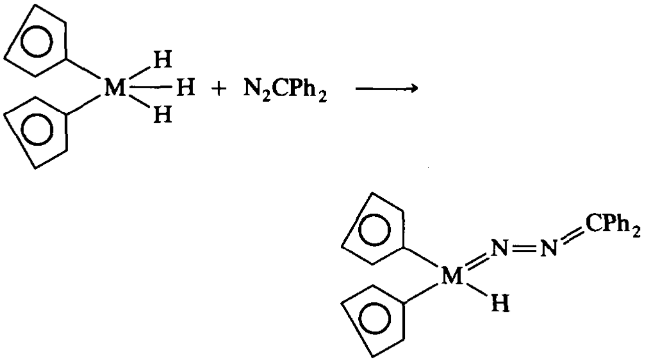
Abstract

Interaction of niobo- and tantalocene trihydrides (Cp_2MH_3; M = Nb, Ta) with diphenyldiazomethane under mild conditions leads to monohydride complexes of a new type, $Cp_2M(H)(\eta^1\text{-}NNCPh_2)$, where M = Nb **I** and Ta **II**. **I** and **II** have been characterized by a ^1H NMR study, and **I** also by an X-ray single crystal diffraction study at 183 K ($R = 0.029$ for 1510 reflections). The molecule of **I** is of a bent sandwich type with the distances Nb–Cp(plane) of 2.13 Å, Nb–N 1.850 Å (multiple bond), Nb–H 1.65 Å and H–Nb–N angle of 94°.

1. Results and discussion

Dicyclopentadienyl trihydride complexes of Nb and Ta, Cp_2MH_3, are of interest as new specific reagents for the partial reduction of organic substrates with several unsaturated fragments. However though reactions with simple alkenes and acetylenes were studied some time ago, there is no systematic information on other types of reagent. They are therefore of some definite interest from the synthetic point of view. As a matter of fact the trihydrides Cp_2MH_3 are also of theoretical interest as they may be used in the study of detailed mechanisms of hydrometallation reactions. This is due to the evident ease with which the valency and co-ordination of the central metal atom may be changed, which is the subject of current discussion in the literature about the eventual dynamic processes $M(H)_3 \rightleftharpoons M(H)(\eta^2\text{-}H_2) \rightleftharpoons M(\eta^3\text{-}_3)$ [1–3].

In this paper we present results relating to the first distinct step in the transformation of niobo- and tantalocene trihydrides when treated with diphenyldiazomethane. In following publications we will discuss data on the subsequent intermolecular transformations of the complexes described below.



Reaction between niobo- and tantalocene trihydrides and diphenyldiazomethane takes several minutes at room temperature. Even at moderate negative temperatures (to −30°C) the reaction rate is significant. During the reaction free hydrogen is released. It is noteworthy that the process proceeds via the addition-elimination step and not via formation of intermediate free Cp_2MH, which might have been regarded as the simplest route. This conclusion is reached on the basis of experience, that in the absence of N_2CPh_2 the tantalocene complex Cp_2TaH_3 is quite stable thermally

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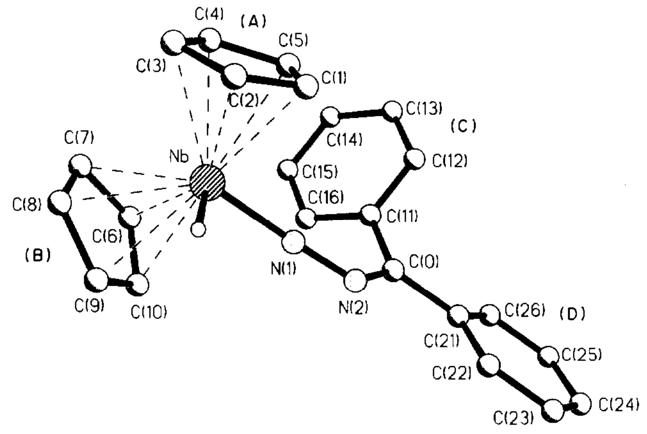


Fig. 1.

TABLE 1. Bond lengths (Å) in structure I

Nb–N(1)	1.850(5)	N(2)–C(0)	1.309(7)	C(11)–C(12)	1.40(1)
Nb–H(0)	1.65(6)	C(1)–C(2)	1.40(1)	C(11)–C(16)	1.38(1)
Nb–C(1)	2.429(8)	C(1)–C(5)	1.35(1)	C(12)–C(13)	1.38(1)
Nb–C(2)	2.453(8)	C(2)–C(3)	1.41(1)	C(13)–C(14)	1.37(1)
Nb–C(3)	2.473(8)	C(3)–C(4)	1.39(1)	C(14)–C(15)	1.39(1)
Nb–C(4)	2.415(7)	C(4)–C(5)	1.39(1)	C(15)–C(16)	1.38(1)
Nb–C(5)	2.420(7)	C(6)–C(7)	1.44(1)	C(21)–C(22)	1.41(1)
Nb–C(6)	2.419(7)	C(6)–C(10)	1.38(1)	C(21)–C(26)	1.39(1)
Nb–C(7)	2.469(7)	C(7)–C(8)	1.38(1)	C(22)–C(23)	1.40(1)
Nb–C(8)	2.464(7)	C(8)–C(9)	1.40(1)	C(23)–C(24)	1.38(1)
Nb–C(9)	2.441(7)	C(9)–C(10)	1.41(1)	C(24)–C(25)	1.38(1)
Nb–C(10)	2.422(8)	C(0)–C(11)	1.496(8)	C(25)–C(26)	1.39(1)
N(1)–N(2)	1.293(7)	C(0)–C(21)	1.466(9)		

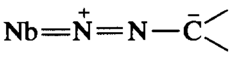
and Cp_2NbH_3 is practically stable under the reaction conditions, *i.e.* it is degraded very slowly. Moreover, the products and the rate of thermolysis of Cp_2NbH_3 in different solvents, and of Cp_2TaH_3 under stronger heating, are well studied. Thermolysis of Cp_2NbH_3 proceeds via Cp_2NbH and leads to a dimer, $Cp_2Nb_2(H)_2(\eta^5:\eta^1\text{-}C_5H_4)_2$ [4].

^1H NMR spectra of **I** and **II** contain the singlets of the Cp and hydride protons in the ratio 10:1; 5.165 (Cp) and 1.27 (NbH), widened, and 5.139 (Cp) and 1.22 (TaH), widened (δ, toluene-d_8) for **I** and **II** respectively, and Ph multiplets in the range 6.90–7.25 ppm for both complexes.

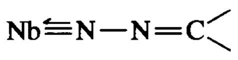
In IR spectrum of **I** the vibrational frequencies of multiple bonds, characteristic of the Nb–N–N–C fragment are 1597 and 1785 cm^{-1}.

An X-ray structural study was performed for complex **I**. The Nb atom in this molecule (Fig. 1, Tables 1 and 2), has a bent sandwich coordination with two cyclopentadienyl ligands (A and B), forming a dihedral angle of 134.9°. In the bisector plane of this angle two other ligands (diphenyldiazomethane and hydride) are coordinated. The distances between the Nb atom and both cyclopentadienyl ring planes are 2.13 Å. The N(1)–N(2)–C(0)–C(11)–C(21) moiety is planar, with the C and D phenyl rings being unequally inclined to its plane (by 60.7° and 8.9°) and the Nb atom being tilted out of this plane by 0.21 Å. With respect to the N(1)–N(2) bond the Nb and C(0) atoms are in the *cis*-position.

The N(1) atom has nearly linear (*quasi* sp) bond geometry while for the N(2) atom this is bent, corresponding to sp^2 configuration, as in previously studied transition metal complexes with diazoalkane ligands, *viz.* $[(dppe)_2BrWNNCMe_2]^+$ (**III**), $[(dppe)_2BrWNNCH(CH_2)_3OH]^+$/(**IV**) [5], $Cp(OC)_3MoMoCp({=}CTol)(NNCTol_2)$ (**V**) [6] and $[(iso\text{-}PrO)_2MoNNCPh_2]_2(\mu\text{-}OPr\text{-}iso)_3$ (**VI**) [7]. The N(1)–N(2) (1.293(7) Å) and N(2)–C(0) (1.309(7) Å) bonds in **I** are somewhat longer than the standard double bonds (1.22 and 1.38 Å respectively) [8] and close to those found in **III**–**V**. The Nb–N(1) bond distance of 1.85 Å is significantly shorter than the sum of the niobium and nitrogen covalent radii. Therefore the electronic structure of the ligand can be interpreted as a superposition of the following structures:


$Nb{=}\overset{+}{N}{=}N{-}\overset{-}{C}<$

(a)


$Nb{\equiv}N{-}N{=}C<$

(b)

The ligand acts as a donor of two electrons in structure (a) and of four electrons in structure (b). In the cations **III** and **IV** the diazoalkane ligands have

TABLE 2. Bond angles in molecule I

Cp(A)NbCp(B) [a]	133.2(3)	C(1)C(2)C(3)	106.0(7)	N(2)C(0)C(11)	121.5(6)
Cp(A)NbN(1)	111.2(3)	C(2)C(3)C(4)	107.2(7)	N(2)C(0)C(21)	116.8(5)
Cp(A)NbH(0)	100(2)	C(3)C(4)C(5)	109.0(7)	C(11)C(0)C(21)	121.6(5)
Cp(B)NbN(1)	112.3(3)	C(1)C(5)C(4)	107.1(7)	C(0)C(11)C(12)	119.9(6)
Cp(B)NbH(0)	94(2)	C(7)C(6)C(10)	106.6(6)	C(0)C(11)C(16)	121.5(5)
N(1)NbH(0)	94(2)	C(6)C(7)C(8)	107.3(6)	C(12)C(11)C(16)	118.5(6)
NbN(1)N(2)	171.4(5)	C(7)C(8)C(9)	110.2(7)	C(0)C(21)C(22)	120.2(5)
N(1)N(2)C(0)	124.2(5)	C(8)C(9)C(10)	105.6(6)	C(0)C(21)C(26)	121.3(5)
C(2)C(1)C(5)	110.6(8)	C(6)C(10)C(9)	110.2(7)	C(22)C(21)C(26)	118.6(6)

[a] Cp(A) and Cp(B): centroids of the cyclopentadienyl rings A and B.

been considered [5] as four-electron donors, as only this hypothesis agrees with the EAN rule for the W atom. Concerning the electronic structure of **I** and **II** a relative low-field position of Nb–H and Ta–H signals in NMR ^1H spectra is noteworthy. In our opinion, the most probable explanation of this effect is that the hydride hydrogen atoms are situated in the deshielding area of the acetylene-like N(1)–N(2) moiety.

2. Experimental section

2.1. Synthesis of $Cp_2MH(NNCPh_2)$, I and II

To a solution of 0.84 g (4.32 mmol) $NNCPh_2$ in 30 ml of anhydrous toluene at 0°C 0.93 g (4.11 mmol) pure Cp_2NbH_3 was added. All the process was carried out in a sealed Schlenk-type vessel *in vacuo*. The colour of the reaction mixture rapidly turned from red to orange and gaseous hydrogen was released. The mixture was kept at room temperature for 12 h. Once the reaction was complete, the solvent was removed *in vacuo*, and the dry residue was subsequently washed with hexane and ether to remove an excess of N_2CPh_2. The product was recrystallized from toluene. Yield 1.20 g (69% of the theoretical quantity) of **I**. Decomposition above 70°C.

Anal. Found: C, 65.95; H, 5.15; N, 6.23; Nb, 21.86. Calc. for $C_{23}H_{21}N_2Nb$: C, 66.01; H, 5.06; N, 6.70; Nb, 22.21%.

Complex II was obtained analogously. Yield 75% of theoretical. Decomposition without melting above 80°C.

Anal. Found: C, 54.03; H, 4.04; N, 5.22; Ta, 36.13. Calc. for $C_{23}H_{21}N_2Ta$: C, 54.56; H, 4.18; N, 5.53; Ta, 35.73%.

2.2. X-ray diffraction study of I

The experiment was carried out at 183 K with a four-cycle computer-controlled Siemens P3/PC diffractometer, using graphite-monochromated Mo Kα radiation.

Crystal data: $C_{23}H_{21}N_2Nb$, monoclinic, a = 10.308(3); b = 8.596(2); c = 10.603(2) Å; β = 99.90(2)°; V = 925.5(7) Å; space group $P2_1$, $Z = 2$, $D_c = 1.50$ g cm^{-3}, λ(Mo Kα) = 6.3 cm^{-1}. The intensities of 1644 independent reflections with $2\theta \leq 50°$ were measured by $\theta/2\theta$ scan mode, 1510 of which having $I > 2\sigma(I)$ were used in calculations. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares, using SHELXTL PLUS programs. All non-hydrogen atoms were refined with anisotropic thermal factors, all H atoms were located in a difference Fourier synthesis and refined in isotropic approximation. The refinement converged at $R = 0.0281$ (R_w = 0.0259) for one enantiomeric model and at R^i = 0.0286 (R_w = 0.0263) for an inverted one, taking into account the anomalous dispersion by all atoms. Though the absolute difference between R and R^i is small, the R^i/R ratio of 1.017, according to Hamilton's test [9], proves the first absolute structure to be correct with a probability exceeding 99.5%. The final atomic coordinates are listed in Table 3.

TABLE 3. Atom coordinates ($\times 10^4$, for $H \times 10^3$) in structure I

Atom	x	y	z
Nb	2963(1)	5023 [a]	5216(1)
N(1)	3988(5)	4363(6)	4048(5)
N(2)	4755(5)	4120(6)	3223(4)
C(1)	2315(9)	7166(10)	3751(7)
C(2)	2270(8)	7752(9)	4980(7)
C(3)	1236(8)	6961(10)	5411(8)
C(4)	734(7)	5885(10)	4468(8)
C(5)	1405(8)	6040(10)	3439(7)
C(6)	2521(7)	2472(8)	6007(7)
C(7)	1845(7)	3540(9)	6712(6)
C(8)	2789(8)	4437(9)	7456(6)
C(9)	4051(7)	3985(9)	7271(6)
C(10)	3852(8)	2737(10)	6395(7)
C(0)	4432(6)	3287(7)	2183(6)
C(11)	3103(6)	2550(7)	1845(5)
C(12)	2256(7)	2995(10)	727(7)
C(13)	996(7)	2392(9)	450(7)
C(14)	556(7)	1352(10)	1262(8)
C(15)	1395(7)	887(9)	2370(7)
C(16)	2653(6)	1493(8)	2650(6)
C(21)	5422(6)	3144(7)	1349(5)
C(22)	6588(6)	4030(8)	1597(6)
C(23)	7531(6)	3879(8)	799(6)
C(24)	7329(6)	2865(8)	−226(6)
C(25)	6196(7)	1989(8)	−470(6)
C(26)	5250(7)	2119(8)	319(6)
H(0)	413(6)	615(8)	599(5)
H(1)	284(9)	747(12)	350(9)
H(2)	276(7)	860(9)	521(7)
H(3)	122(12)	729(14)	618(11)
H(4)	2(6)	510(13)	463(5)
H(5)	122(6)	554(8)	271(6)
H(6)	216(7)	180(8)	548(7)
H(7)	92(7)	364(8)	649(6)
H(8)	270(7)	529(11)	791(6)
H(9)	488(6)	436(7)	772(6)
H(10)	427(9)	219(11)	620(8)
H(12)	243(6)	362(8)	25(6)
H(13)	44(7)	265(9)	−26(7)
H(14)	−8(7)	93(9)	106(6)
H(15)	117(6)	24(12)	293(5)
H(16)	319(5)	101(7)	341(5)
H(22)	669(5)	474(8)	229(5)
H(23)	841(7)	481(15)	97(6)
H(24)	807(9)	265(11)	−85(8)
H(25)	606(6)	141(8)	−106(6)
H(26)	443(6)	137(9)	8(5)

[a] Fixed to define origin.

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