Synthesis of bis(cyclopentadienyl)diazadiene complexes of ytterbium. An X-ray structural study of the $Cp_2Yb(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bu^t\text{—}N\text{=}CH\text{—}CH\text{=}N\text{—}Bu^t)Li(DME)$ complex

A. A. Trifonov,[a] L. N. Zakharov,[a] M. N. Bochkarev,[a] and Yu. T. Struchkov[b]*

[a] *Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.*
Fax: +7 (095) 135 5085

Ytterbium complexes, $Cp_2Yb(\mu\text{-}\eta^2\text{:}\eta^2\text{-DAB})Li(DME)$ (**1**) and $CpYb(DAB)K(THF)_2$ (**2**), containing a bridging diazadiene ligand were prepared by the reaction of $CpYbCl_2(THF)_3$ with $(DAB)Li_2$ (1:1) and $(DAB)^-K^+$ (1:2) (DAB = $Bu^t\text{—}N\text{=}CH\text{—}CH\text{=}N\text{—}Bu^t$). The structure of complex **1** was established by X-ray diffraction analysis. The complex is binuclear: the Yb atom of the Cp_2Yb fragment and the Li atom, which is bonded as well with the chelating DME molecule, are linked by the DAB ligand.

Key words: ytterbium, complexes; X-ray diffraction analysis.

The diazadiene ligand is known to exert a stabilizing effect on the complexes of d-transition metals.[1] The chemistry of these compounds, which are distinguished by the great diversity of the types of ligand—metal coordination, has been comprehensively studied. On the other hand, diazadiene complexes of lanthanides are scantily known; only their homoleptic derivatives, $(DAB)_3Ln$,[2,3] and the recently synthesized complex of trivalent samarium, $(Me_5C_5)_2Sm(DAB)$,[4] have been described.

The structure of $(DAB)_3Yb$, established by an X-ray structural study in the combination with magnetochemical data, attests to the transformation of the diimine structure of the ligand to the enediamide structure as a result of complexation of the DAB molecule with the Yb atom. However, the data obtained do not allow the electronic state of the diazabutadiene ligand to be unambiguously characterized. The nature of the metal—ligand interaction is also not entirely clear: the presence of an Yb^{3+} cation and three equivalent DAB ligands in the complex molecule corresponds to the radical-anion state of the ligand; nevertheless, the compound does not exhibit an ESR signal.

Therefore, it was of interest to us to prepare and study novel heteroleptic lanthanide derivatives which would contain DAB ligands with various degrees of reduction and various types of coordination. In the present paper we report the synthesis and structure of mixed Cp/DAB complexes of ytterbium.

Results and Discussion

We found that the reaction of $CpYbCl_2(THF)_3$ with an equimolar amount of $(DAB)Li_2$ affords bimetallic compound $Cp_2Yb(\mu\text{-DAB})Li(DME)$ (**1**), rather than the expected CpYb—DAB complex.

$$CpYbCl_2(THF)_3 + (DAB)Li_2 \rightarrow \underset{\mathbf{1}}{Cp_2Yb(\mu\text{-DAB})Li(DME)}$$

A similar complex (**2**) with the bridging DAB ligand was obtained, along with $(DAB)_3Yb$, by the reaction of $CpYbCl_2(THF)_3$ with two equivalents of the radical-anion salt $(DAB)^-K^+$.

$$CpYbCl_2(THF)_3 + 2(DAB)K \rightarrow \underset{\mathbf{2}}{Cp_2Yb(DAB)K(THF)_2} + (DAB)_3Yb$$

Complexes **1** and **2** are light-green crystalline solids. The μ_{eff} values for compounds **1** and **2**, equal to 4.1 and 4.25 MB, respectively, are characteristic of the derivatives of trivalent ytterbium.[5] The IR spectra of these complexes exhibit bands of the coordination-bonded THF and DME molecules, in addition to the absorption bands of the cyclopentadienyl and DAB ligands. The absorption band at 1630 cm^{-1}, associated with the vibrations of the imine group of the free DAB molecule, is missing from the spectrum.

Compound **1** is soluble in THF, DME, and toluene and slightly soluble in diethyl ether, while compound **2**

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 148—151, January, 1994.

1066-5285/94/4301-0145 $12.50

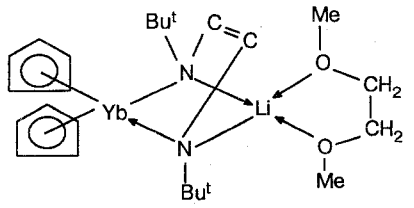
is only soluble in THF; decomposition temperatures for complexes **1** and **2** are 294 °C and 185 °C, respectively. An X-ray structural investigation showed that complex **1** is binuclear: DAB is the bridging ligand that binds the Yb atom of the Cp_2Yb moiety with the Li atom bound with the chelating DME molecule (Fig. 1). (Crystals of **1** also contain a solvating toluene molecule.)

The DAB ligand in complex **1** is located in such a way that the central plane of the YbN(1)N(2)C(13)C(17) fragment (the maximum deviation of the atoms from the plane is 0.03 Å) actually coincides with the bisector plane of the wedge-shaped Cp_2Yb sandwich. The central four-membered ring of the molecule, YbN(1)LiN(2), is nonplanar: the dihedral angle between the YbN(1)N(2) and LiN(1)N(2) planes amounts to 138.8°. The interaction of the DAB ligand with Yb and Li atoms results in a noticeable change in the lengths of the C=N and C—C bonds in the central part of the ligand as compared with the bonds in free molecules containing α-diamines. So, for example, the N(1)—C(11) and N(2)—C(12) bonds in complex **1** [1.40(1) and 1.39(1) Å, respectively] are substantially longer, whereas the C(11)—C(12) bond [1.36(1) Å] is, conversely, substantially shorter than the analogous C—N (1.26—1.34 Å) and C—C (1.466—1.51 Å) bonds in free molecules of α-diamines with various substituents.[1]

The lengths of the N(1)—C(17) and N(2)—C(13) bonds in complex **1** [1.51(1) and 1.52(1) Å, respectively] are also somewhat greater than those in the above-mentioned molecules (1.44—1.46 Å).[1] The N(1)—C(11) and N(2)—C(12) distances in the DAB ligand in complex **1** are intermediate between the normal lengths for N···C and N—C bonds (1.34 and 1.47 Å, respectively),[6] and the C(11)—C(12) bond length is close to the standard value for the C=C double bond (1.337 Å).[6]

The lengths of the Yb—N(1) and Yb—N(2) bonds [2.241(7) and 2.243(8) Å] are close to one another, as are the Li—N(1) and Li—N(2) bonds [2.18(2) and 2.19(1) Å, respectively]. It should be noted that the Yb—N distances in complex **1** are somewhat shorter than the Yb—N bonds in the molecules of $\{[(Me_3Si)N]_2CPh\}_2Yb(THF)_2$ (2.468 and 2.478 Å), $\{[(Me_3Si)N]_2CPh\}_2Yb(S_2CNMe_2)_2$ (2.319 and 2.298 Å), and $\{[(Me_3Si)N]_2CPh\}_2Yb(SPh)(THF)$ (2.305 and 2.265 Å).[7]

On the basis of the foregoing, the scheme of the bonding of the atoms in molecule **1** may be represented in the following way:



In view of the rather short Yb—C(11) and Yb—C(12) distances (2.66 and 2.66 Å) as well as the Li—C(11) and Li—C(12) distances (2.30 and 2.31 Å), one cannot rule out the possibility of an additional η^2-interaction of the Yb and Li atoms with the C(11)—C(12) bond whose length, as has been noted, is close to the normal C=C bond length. The size of the Cp_c—Yb—Cp_c angle in complex **1** (122.7°), which indicates a substantial deviation of the Cp rings of the wedge-like Cp_2Yb sandwich from the DAB ligand, is also consistent with this supposition. The normal values of this angle in compounds of trivalent lanthanides of the Cp_2LnR type lie within the range 122—136°; the average value for the Yb—C(η^5) distances in molecule **1** is 2.66 Å. The shortest C...C nonvalent contacts between the Cp rings and the C(11)—C(12) bond within the coordination sphere of the Yb atom in complex **1** are close: C(1)...C(6) is 3.17 Å, C(4)...C(11) is 3.182 Å, *i.e.*, the location of the C(11)—C(12) bond with respect to the Cp ligand observed in complex **1** corresponds to the lengths of the C...C contacts normal for wedge-like Cp_2Ln sandwiches. The Li—O(1) and Li—O(2) distances for the chelating DME molecule, equal to 2.02(2) and 2.05(2) Å, respectively, are close. It is of interest that the C(21) and C(24) atoms are substantially deflected from the central plane of the five-membered ring of the DME molecule towards the *tert*-butyl group of DAB, which is bonded with the N(1) atom; the magnitudes of these deflections are −0.13 and −0.84 Å, respectively. At the same time, disordering of another *tert*-butyl group of the DAB ligand at two positions with equal population multiplicities, differing in the rotation of the *tert*-butyl group around the N(2)—C(13) bond by ~60°, is observed in the crystal. Fig. 1 shows only one of the two positions of this group. The reason for the above-noted deflection is probably the influence of the packing of the molecules in the crystal.

Along with the molecule of compound **1**, the crystals under study contain solvating molecules of toluene. The latter are located at the second-order crystallographic axes (the C(26) atom is directly on the axis), *i.e.*, they are also disordered at two positions.

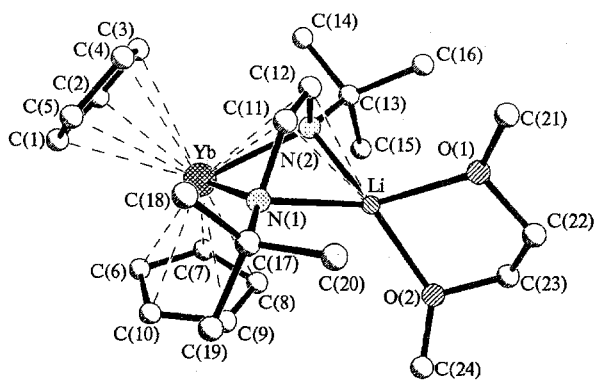


Fig. 1. General view of molecule **1**.

Table 1. Bond lengths (d) in the structure of **1**

Bond	d/Å	Bond	d/Å
Yb—Li	3.19(2)	O(2)—C(24)	1.31(2)
Yb—N(1)	2.241(7)	C(1)—C(2)	1.37(2)
Yb—N(2)	2.243(8)	C(1)—C(5)	1.36(2)
Yb—C(1)	2.66(1)	C(2)—C(3)	1.33(3)
Yb—C(2)	2.66(1)	C(3)—C(4)	1.33(3)
Yb—C(3)	2.64(1)	C(4)—C(5)	1.36(3)
Yb—C(4)	2.66(1)	C(6)—C(7)	1.39(2)
Yb—C(5)	2.67(1)	C(6)—C(10)	1.41(1)
Yb—C(6)	2.67(1)	C(7)—C(8)	1.43(1)
Yb—C(7)	2.636(9)	C(8)—C(9)	1.36(1)
Yb—C(8)	2.656(8)	C(9)—C(10)	1.40(2)
Yb—C(9)	2.658(8)	C(11)—C(12)	1.36(2)
Yb—C(10)	2.66(1)	C(13)—C(14)	1.56(2)
Yb—C(11)	2.66(1)	C(13)—C(15)	1.53(2)
Yb—C(12)	2.66(1)	C(13)—C(16)	1.56(2)
Li—N(1)	2.18(2)	C(13)—C(14a)	1.66(3)
Li—N(2)	2.19(1)	C(13)—C(15a)	1.55(3)
Li—O(1)	2.02(2)	C(13)—C(16a)	1.53(3)
Li—O(2)	2.05(1)	C(17)—C(18)	1.51(2)
Li—C(11)	2.30(2)	C(17)—C(19)	1.50(2)
Li—C(12)	2.31(1)	C(17)—C(20)	1.50(2)
N(1)—C(11)	1.39(1)	C(22)—C(23)	1.29(3)
N(1)—C(17)	1.51(1)	C(25)—C(26)	1.34(2)
N(2)—C(12)	1.40(1)	C(25)—C(30)	1.38(2)
N(2)—C(13)	1.49(1)	C(25)—C(31)	1.44(2)
O(1)—C(21)	1.33(2)	C(26)—C(27)	1.49(2)
O(1)—C(22)	1.46(2)	C(27)—C(28)	1.37(3)
O(2)—C(23)	1.36(3)	C(28)—C(29)	1.33(2)
		C(29)—C(30)	1.35(2)

Table 2. Bond angles (ω) in the structure of **1**

Angle	ω/deg	Angle	ω/deg
N(1)-Yb-N(2)	78.1(3)	N(2)-C(13)-C(14)	108.4(10)
N(1)-Li-N(2)	80.5(5)	N(2)-C(13)-C(15)	110.8(9)
N(1)-Li-O(1)	124.2(8)	C(14)-C(13)-C(15)	108.0(10)
N(2)-Li-O(1)	118.9(8)	N(2)-C(13)-C(16)	111.1(8)
N(1)-Li-O(2)	131.3(9)	C(14)-C(13)-C(16)	110.9(10)
N(2)-Li-O(2)	126.1(8)	C(15)-C(13)-C(16)	107.6(10)
O(1)-Li-O(2)	81.6(6)	N(2)-C(13)-C(14a)	109.3(15)
Yb-N(1)-Li	92.4(5)	C(14)-C(13)-C(14a)	67.7(12)
Yb-N(1)-C(11)	91.2(5)	C(15)-C(13)-C(14a)	43.4(12)
Li-N(1)-C(11)	76.6(7)	C(16)-C(13)-C(14a)	137.3(16)
Yb-N(1)-C(17)	142.1(7)	N(2)-C(13)-C(15a)	112.6(12)
Li-N(1)-C(17)	119.1(7)	C(14)-C(13)-C(15a)	139.0(15)
C(11)-N(1)-C(17)	115.0(7)	C(15)-C(13)-C(15a)	58.9(13)
Yb-N(2)-Li	92.1(5)	C(16)-C(13)-C(15a)	51.4(12)
Yb-N(2)-C(12)	90.9(6)	C(14a)-C(13)-C(15a)	100.0(16)
Li-N(2)-C(12)	76.5(6)	N(2)-C(13)-C(16a)	119.9(16)
Yb-N(2)-C(13)	141.2(5)	C(14)-C(13)-C(16a)	37.3(16)
Li-N(2)-C(13)	118.9(7)	C(15)-C(13)-C(16a)	124.9(16)
C(12)-N(2)-C(13)	117.3(7)	C(16)-C(13)-C(16a)	73.8(16)
Li-O(1)-C(21)	133.5(11)	C(14a)-C(13)-C(16a)	97.5(17)
Li-O(1)-C(22)	108.1(9)	C(15a)-C(13)-C(16a)	114.1(21)
C(21)-O(1)-C(22)	116.2(12)	N(1)-C(17)-C(18)	113.0(7)
Li-O(2)-C(23)	107.0(11)	N(1)-C(17)-C(19)	107.0(8)
Li-O(2)-C(24)	134.3(10)	C(18)-C(17)-C(19)	107.6(11)
C(23)-O(2)-C(24)	113.6(10)	N(1)-C(17)-C(20)	111.1(10)
C(2)-C(1)-C(5)	107.2(13)	C(18)-C(17)-C(20)	109.9(8)
C(1)-C(2)-C(3)	108.9(15)	C(19)-C(17)-C(20)	108.1(8)
C(2)-C(3)-C(4)	107.3(17)	O(1)-C(22)-C(23)	113.4(14)
C(3)-C(4)-C(5)	110.4(17)	O(2)-C(23)-C(22)	117.9(19)
C(1)-C(5)-C(4)	106.0(14)	C(26)-C(25)-C(30)	118.8(12)
C(7)-C(6)-C(10)	107.9(8)	C(26)-C(25)-C(31)	115.4(14)
C(6)-C(7)-C(8)	107.6(8)	C(30)-C(25)-C(31)	125.2(15)
C(7)-C(8)-C(9)	107.8(9)	C(25)-C(26)-C(27)	118.7(13)
C(8)-C(9)-C(10)	109.3(8)	C(26)-C(27)-C(28)	116.2(14)
C(6)-C(10)-C(9)	107.5(9)	C(27)-C(28)-C(29)	121.1(14)
N(1)-C(11)-C(12)	121.7(8)	C(28)-C(29)-C(30)	121.8(16)
N(2)-C(12)-C(11)	121.6(9)	C(25)-C(30)-C(29)	121.0(14)

Thus, reactions of $CpYbCl_2$ with the $(DAB)^{2-}$ dianion and $(DAB)^-$ radical anion are accompanied by disproportionation of the ytterbium complex to give Cp_2Yb^+ particles bonded with the alkaline metal atom by the bridging DAB dianion.

Experimental

Reaction of $CpYbCl_2(THF)_3$ with $(DAB)Li_2$. A solution of $(DAB)Li_2$ prepared by the reaction of DAB (0.94 g, 5.6 mmol) and a fivefold excess of Li (0.196 g, 28 mmol) in 50 mL of THF was slowly added at ~0 °C to a stirred solution of $CpYbCl_2(THF)_3$ (2.94 g, 5.59 mmol) in 60 mL of a 1:1 THF—DME mixture. The reaction mixture turned green, it was stirred for 18 h at ~20 °C and centrifuged. The solution was decanted from the precipitate. The solvents were removed by *in vacuo*, the residue was dried for 1 h at ~20 °C and extracted with 50 mL of toluene, and the solution was concentrated to halve its volume. Cooling the mother liquor to −5 °C gave pale green crystals of compound **1** which were washed three times with toluene and dried *in vacuo* for 30 min at ~20 °C. Yield 1.14 g (36 %). Found (%): C, 49.95; H, 7.12; Yb, 30.38. $C_{24}H_{40}LiN_2O_2Yb$. Calculated (%): C, 50.70; H, 7.08; Yb, 30.43.

Reaction of $CpYbCl_2(THF)_3$ with $(DAB)^-K^+$. A solution of $(DAB)^-K^+$ prepared from the reaction of DAB (1.78 g, 10.58 mmol) and K (0.42 g, 10.58 mmol) in 50 mL of THF was slowly added at ~0 °C to a stirred solution of $CpYbCl_2(THF)_3$ (2.78 g, 5.29 mmol) in 50 mL of THF. When the addition was completed, the reaction mixture turned green. The mixture was stirred for 15 h and centrifuged; the solution was separated from the precipitate, and concentrated to halve its volume. Cooling to −20 °C gave 1.27 g (39 %) of light-yellow crystals of $Cp_2Yb(DAB)K(THF)_2$ (**2**). Found (%): C, 50.47; H, 6.73; Yb 26.54. Calculated (%): C, 51.36; H, 7.07; Yb, 26.42. The mother liquor was separated from the crystals, THF was evaporated, and the dry residue was extracted with 25 mL of toluene. After cooling the toluene solution, 1.18 g (33 %) of red crystals of $(DAB)_3Yb$ was isolated. This compound was identical to the complex described previously,[3] according to its IR spectrum and elemental analysis.

The X-ray structural investigation was carried out on a Siemens P3/PCJ diffractometer at −80 °C (Mo-Kα radiation, $2\theta/\theta$ scanning in the range $2° < \theta \leq 50°$). Crystals of complex **1** are monoclinic, a = 18.312(2) Å, b = 14.120(3) Å, c = 22.609(4) Å, β = 102.94(2)°, d_{calc} = 1.447 g cm^{-3}, Z = 8,

space group $C2/c$. $C_{24}H_{40}N_2O_2Li_1Yb_1 \cdot 0.5(C_6H_5CH_3)$. The structure was solved by a combination of the direct method and the calculation of the Fourier series. The hydrogen atoms could not be objectively revealed, and they were taken into account during the refinement in the positions calculated from geometric conditions, with the isotropic heat parameters B_{iso} = 0.08 Å^2. Absorption in the crystal [μ(Mo-Kα) = 33 cm^{-1}] was taken into account by the DIFABS program.[9] The structure was refined in the full-matrix version of the least-squares method with anisotropic parameters of the thermal vibrations for nonhydrogen atoms with the weight scheme: $W^{-1} = \sigma^2(F) + 0.0003\ F^2$, over 2825 independent reflections having $F^2 > \sigma^2(F)$.

As has already been noted, one of the *tert*-butyl groups in the molecule is disordered at two locations. A crystal of **1** contains a solvating toluene molecule, which is also disordered at two positions (the C(26) atom is located on the second-order crystallographic axis). The disordered atoms were refined with the population multiplicities of the locations equal to 0.5. The final residual values were $R = 0.042$ and $R_w = 0.038$. All the calculations were carried out using the SXELXTL PLUS set of programs. Bond lengths and angles in complex **1** are given in Tables 1 and 2.

References

1. G. Van Koten and K. Vriege, *Adv. Organomet. Chem.*, 1982, **21**, 151.
2. J. Cloke, H. de Lemos, and A. Sameh, *J. Chem. Soc., Chem. Commun.*, 1986, 1344.
3. A. A. Trifonov, M. N. Bochkarev, H. Schumann, and J. Loebel, *J. Organomet. Chem.*, 1993 (in press).
4. A. Recknagel, M. Noltemeyer, and F. Edelmann, *J. Organomet. Chem.*, 1991, **410**, 53.
5. W. J. Evans and M. A. Hogbor, *J. Organomet. Chem.*, 1987, **326**, 299.
6. S. S. Batsanov, in *Eksperimental'nye osnovy strukturnoi khimii* [*Experimental Fundamentals of Structural Chemistry*], Nauka, Moscow, 1986, 66 (in Russian).
7. M. Wedler, M. Noltemeyer, U. Pieper, H. G. Schmidt, D. Stalke, and F. T. Edelmann, *Angew. Chem.*, 1990, **102**, 941.
8. M. N. Bochkarev, G. S. Kalinina, L. N. Zakharov, and S. Ya. Khorshev, in *Organicheskie proizvodnye redkozemel'nykh elementov* [*Organic Derivatives of Rare Earth Elements*], Nauka, Moscow, 1989, 37 (in Russian).
9. N. Walker and D. Stuart, *Acta crystallogr.*, 1983, **A39**, 158.

Received October 19, 1992;
in revised form July 10, 1993