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Unexpected results of the reactions of manganese and vanadium β-diketiminate halide complexes with Na[HBEt$_3$]*

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The reaction of [(^{Me}nacnac^{Dipp})Mn(μ-Cl)]$_2$ (**2**) (^{Me}nacnac^{Dipp} = HC(C(Me)NDipp)$_2$; Dipp = 2,6-Pr$^i_2$C$_6$H$_3$) with sodium triethylborohydride in a toluene—THF mixture afforded the complex [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$(THF)] (**3**). The reaction of **2** with Na[HBEt$_3$] in toluene under THF-free conditions gave a mixture of products. The set and the ratio of these products in the resulting crystalline mixture were established by quantitative powder X-ray diffraction analysis: [(^{Me}nacnac^{Dipp})Mn(μ-H)]$_2$ (**1**), [(^{Me}nacnac^{Dipp})-Mn(μ-H)$_2$BEt$_2$] (**4**), and unreacted compound **2** in the ratio of 15 : 4 : 1 and traces of an unknown crystalline phase. The reaction of [(^{Me}nacnac^{Dipp})VCl$_2$] (**5**) with Na[HBEt$_3$] yielded the compound [(^{Me}nacnac^{Dipp})V(μ-H)(μ,κ$^{1:1}$-C:C'-C$_2$H$_4$)BEt$_2$] (**6**) containing the unusual ligand [HBEt$_2$(CH$_2$CH$_2$)]$^{2-}$. The vanadium analog of compound **3**, [(^{Me}nacnac^{Dipp})V(μ-H)$_2$BEt$_2$(THF)] (**7**), was isolated in one experiment. Besides. a small amount of the complex [(^{Me}nacnac^{Dipp})V(μ-H)BEt$_3$(THF)] (**8**) was detected in the mixture of crystalline products. The structures of compounds **3**, **4**, **6**, **7**, and **8** were determined by single-crystal X-ray diffraction.

Key words: hydride, manganese, vanadium, boron, crystal structure, agostic interaction.

Metal hydrides take an important place in modern inorganic and organometallic chemistry and are widely used in a number of key sectors of the chemical industry as highly selective and efficient catalysts for homogeneous processes and as new energy storage materials.[1—3] Besides, these compounds have attracted great attention due to their involvement in important biochemical processes in metal enzymes.[4]

In recent years, hydride β-diketiminate complexes received particular interest. This is associated with the fact that these complexes were found to exhibit catalytic properties in oxidative cross-coupling,[5] dehydrofluorination,[6] alkene hydrosilylation,[7] and nitrile dihydroboration.[8] Most of the known hydride β-diketiminate complexes exist as the dimers [($^{R^1}$nacnac$^{R^2}$)M(μ-H)$_2$M($^{R^1}$nacnac$^{R^2}$)] ($^{R^1}$nacnac$^{R^2}$ = [HC(C(R^1)NR^2]$_2$; M = Mn,[7,9] Fe,[10,11] Cd,[12] Co,[13] Ni[14]), although there are a few examples of monomolecular complexes, in which hydride ions are coordinated to the metal in a terminal mode.[12,15,16]

The most commonly used approach to the synthesis of hydride β-diketiminate complexes is based on the hydrogenation of [($^{R^1}$nacnac$^{R^2}$)MCl] with alkali metal triethylborohydrides, which are well-known as convenient reducing and hydrogenating agents in organic and organometallic synthesis. The most popular agent is Li[HBEt$_3$], trivially named superhydride. Alkali metal triethylborohydrides have become popular due to good solubility in aprotic organic solvents and the commercial availability as solutions in THF or toluene.

In this study, we made an attempt to slightly modify the procedure of the synthesis of the known complex [(^{Me}nacnac^{Dipp})Mn(μ-H)]$_2$ (**1**, ^{Me}nacnac^{Dipp} = = HC(C(Me)NDipp)$_2$, Dipp = 2,6-Pr$^i_2$C$_6$H$_3$) based on the reaction of [(^{Me}nacnac^{Dipp})Mn(μ-Cl)]$_2$ (**2**) with Na[HBEt$_3$] in toluene.[7] We added the commercially available solution of Na[HBEt$_3$] in THF to a solution of **2** in toluene. Surprisingly, the reaction afforded the new complex [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$(THF)] (**3**) containing the [H$_2$BEt$_2$]$^-$ ligand instead of the expected complex [(^{Me}nacnac^{Dipp})Mn(μ-H)]$_2$ (**1**). This result was consistently reproduced. Moreover, when we prepared a solution of Na[HBEt$_3$] in toluene from

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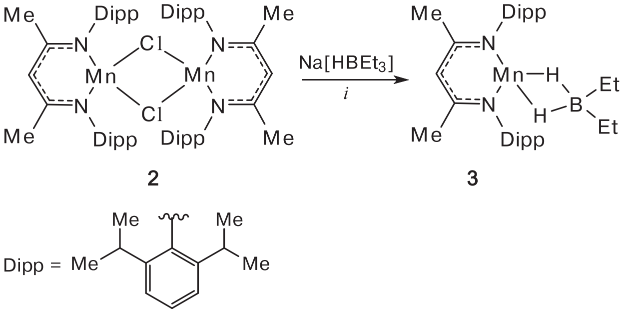
the residue, which was obtained by concentrating the commercially available solution of Na[$HBEt_3$] in THF. After the reaction of **2** with this solution, we also obtained compound **1** along with significant amounts of the complex [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$] (**4**), the coordination sphere which does not contain THF, in contrast to **3**.

The reaction of the V^{III} complex [(^{Me}nacnac^{Dipp})-VCl$_2$] (**5**) with Na[$HBEt_3$] also gave an unexpected result. In this case, we obtained a mixture of products, from which we reproducibly isolated the pure compound [(^{Me}nacnac^{Dipp})V(μ-H)(μ,κ$^{1:1}$-C:C'-C$_2$H$_4$)BEt$_2$] (**6**) in a yield of up to 38%. This compound contains the unusual [H(C$_2$H$_4$)BEt$_2$]$^{2-}$ ligand as the deprotonated form of [HBEt$_3$]$^-$. In a single experiment, we obtained the crystalline phase of the compound [(^{Me}nacnac^{Dipp}) V(μ-H)$_2$BEt$_2$(THF)] (**7**); besides, we isolated several crystals of the V^{II} complex [(^{Me}nacnac^{Dipp})V(μ-H)-BEt$_3$(THF)] (**8**).

Results and Discussion

Reaction of [(^{Me}nacnac^{Dipp})Mn(μ-Cl)]$_2$ (2) with Na[HBEt$_3$], the structures of complexes 3 and 4. The complex [(^{Me}nacnac^{Dipp})Mn(μ-H)]$_2$ (**1**) was previously prepared by the treatment of a solution of [(^{Me}nacnac^{Dipp}) Mn(μ-Cl)]$_2$ (**2**) in toluene with a solution of Na[HBEt$_3$] in the same solvent at −35 °C. The related hydride complex [(^{Me}nacnac^{Dep})Mn(μ-H)]$_2$ (**9**) (^{Me}nacnac^{Dep} = HC(C(Me)NDep)$_2$; Dep = 2,6-Et$_2$C$_6$H$_3$) was synthesized by the reaction of a toluene solution of [(^{Me}nacnac^{Dep})Mn(μ-Br)]$_2$ with a solution of K[HBEt$_3$] in THF at room temperature.[9] Compounds **1** and **9** are structurally very similar and differ only by two methyl groups in the aryl substituents of the ligand. The fact that compounds **1** and **9** were synthesized using different solvents and at different temperatures suggests that these factors are not really important and compound **1** can be synthesized using the commercially available solution of Na[HBEt$_3$] in THF. However, in the latter case, the reaction of **2** with Na[HBEt$_3$] was found to afford the complex [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$-(THF)] (**3**), which was isolated in the crystalline state in 42% yield (Scheme 1).

Scheme 1



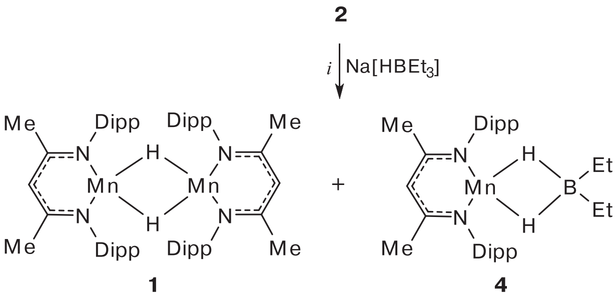
i. THF—toluene.

In compound **3**, the [H$_2$BEt$_2$]$^-$ ligand is coordinated to the manganese atom through two hydride hydrogen atoms serving as bridges between the manganese and boron atoms (Fig. 1, *a*). The boron atom is in a tetrahedral environment. The coordination sphere of the manganese atom involves, apart from the β-diketiminate ligand, one tetrahydrofuran molecule coordinated to the metal through an oxygen atom. The Mn—H bond lengths are in the range of 1.94—1.97 Å and are similar to those in complex **1** (1.79—1.94 Å).[7] The Mn—B distance (2.40 Å) is somewhat larger than the Mn—B bond lengths in the known manganese organoboron complexes (1.95—2.19 Å).[17—19]

Attempting to reproduce as close as possible the procedure for the synthesis of compound **1** described in the literature,[7] we performed the following experiment. The available solution of Na[HBEt$_3$] in THF was concentrated to remove the solvent as completely as possible and then the residue was dissolved in toluene. The treatment of a solution of complex **2** in toluene with this solution on cooling also gave a mixture of products, which were isolated from the reaction mixture in the crystalline state. According to the powder X-ray diffraction, this mixture contained a small amount of unreacted compound **2**, significant amounts of **1**, and also unknown crystalline phases. One phase was identified by single-crystal X-ray diffraction. We found a single crystal of the compound [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$] (**4**) (Scheme 2, Fig. 1, *b*). The quantitative powder X-ray diffraction analysis of the mixture of crystalline products by the Rietveld method using the GSAS-II software[20] demonstrated that this mixture contained compounds **1**, **4**, and **2** in a ratio of 15 : 4 : 1 and also traces of an unknown crystalline phase. The latter phase showed three low-intensity peaks in the 2θ angle range from 5.7 to 14.7°.

Therefore, the reactions of **2** with Na[HBEt$_3$] in toluene and in a toluene—THF mixture actually gave different results. Apparently, hydride complex **1** was isolated in the pure form because it was the major component in the mixture of the reaction products in toluene. The reaction in a toluene—THF mixture afforded complex **3** as the major product. The above procedure allows the reproducible synthesis of this complex.

Scheme 2



i. Toluene.

In contrast to complex **3**, compound **4** does not contain THF coordinated to manganese. Consequently, the coordination number of Mn in compound **4** is 4 and its coordination polyhedron can be described as a distorted tetrahedron. The C(1), C(2), C(3), N(1), N(2) atoms and the Mn, B, and C(4), C(6) atoms lie in a single plane. This plane is perpendicular to the H(1)H(2)Mn plane. The B atom slightly deviates from the H(1)H(2)Mn plane because of the unsymmetric arrangement of the Et groups of the diethylborate ligand. This leads to a slight asymmetry in the Mn—H bond lengths (1.87 and 1.97 Å) and a decrease in the Mn—B distance to 2.33 Å compared to those in **3**. The other bond lengths in compounds **3** and **4** are slightly different (Table 1).

Table 1. Selected bond lengths (*d*) of compounds **3** and **4**

Bond	*d*/Å	
	3	**4**
Mn(1)—N(1)	2.080(3)	2.042(7)
Mn(1)—N(2)	2.080(3)	2.029(7)
Mn(1)—H(1A)	1.97(4)	1.87
Mn(1)—H(1B)	1.93(4)	1.97
Mn(1)—O(1)	2.208(2)	—
C(30)—C(31)	1.530(6)	1.447(14)
C(30)—B(1)	1.614(6)	1.733(13)
C(32)—C(33)	1.525(5)	1.505(13)
C(32)—B(1)	1.615(5)	1.616(10)
B(1)—H(1A)	1.19(4)	1.15
B(1)—H(1B)	1.16(4)	1.15

Reaction of [(^{Me}nacnac^{Dipp})VCl$_2$] (5) with Na[HBEt$_3$]. Complexes of vanadium in low oxidation states or/and complexes containing reducing ligands in the coordination sphere are of interest as convenient multifunctional starting compounds for the synthesis of various derivatives. For example, we have recently demonstrated that the reduction of chalcogens with V^{I} β-diiminate complexes provides a facile method for the synthesis of the binuclear complexes [{(^{Me}nacnac^{Dipp})VQ}$_2$(μ,η^2-Q$_2$)]

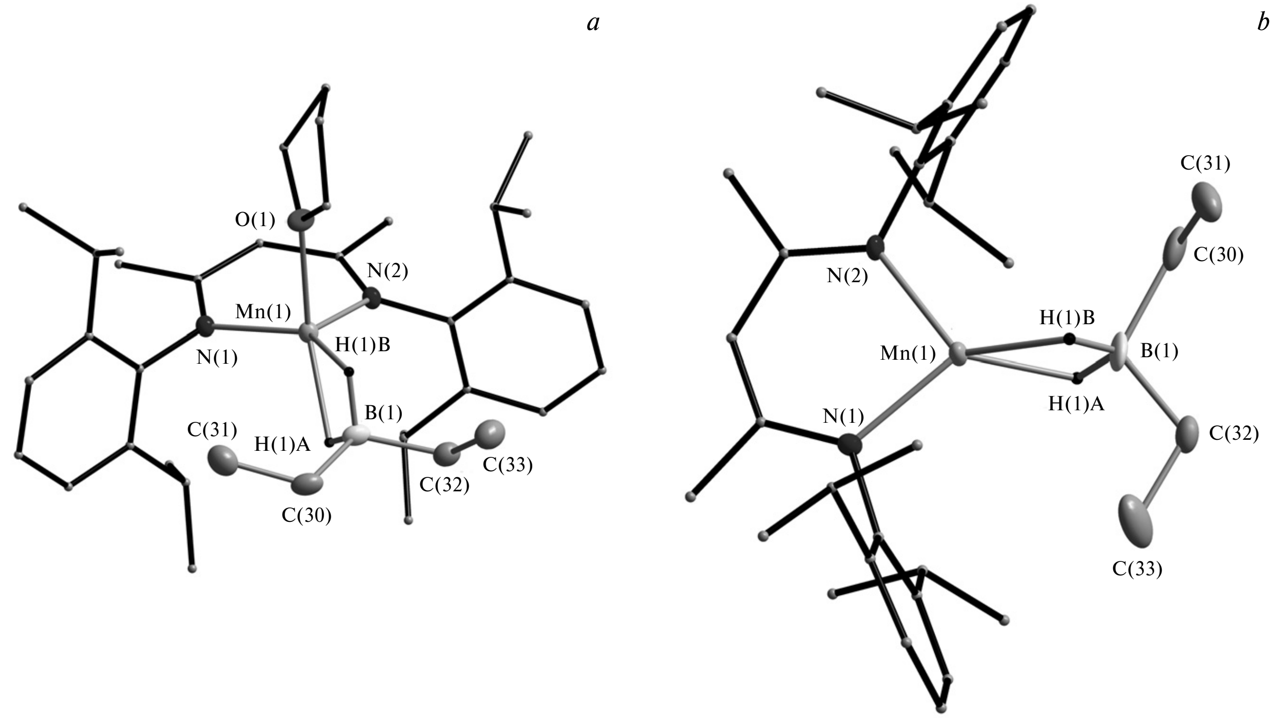


Fig. 1. Molecular structures of the complexes [(nacnac)Mn(μ-H)$_2$BEt$_2$(THF)] (**3**) (*a*) and [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$] (**4**) (*b*) with displacement ellipsoids for the N, Mn, O, and ethyl C atoms drawn at the 30% probability level. Hydrogen atoms, except for the bridging H atoms, are omitted for clarity.

(Q = S, Se) and $[\{(^{Me}nacnac^{Dip})V\}_2(\mu\text{-}Te)_2]$.**21** β-Diiminate ethylborohydride or hydride complexes of V^{II} similar to complexes **1**, **3**, and **4** would be of interest for such synthetic purposes; however, such complexes were unknown. According to the Cambridge Structural Database (CSD), there is only one structurally characterized vanadium complex with the $[H_2BEt_2]^-$ ligand, $[\{(^{Me}nacnac^{Dep})V(H_2BEt_2)\}_2(\mu\text{-}N_2)]$, but there is only a private communication in the CSD for this complex.**22**

It can *a priori* be suggested that compounds similar to **3**, **4**, and/or **1** should be produced in the reaction of $[(^{Me}nacnac^{Dipp})VCl_2]$ (**5**) with $Na[HBEt_3]$ because the latter compound can serve as a reducing agent with respect to V^{III} and as a source of the hydride or alkylborohydride ligand. Actually, the treatment of a solution of **5** in toluene with a solution of $Na[HBEt_3]$ in a toluene—THF mixture and the subsequent synthetic steps described in the Experimental afforded the V^{II} complex $[(^{Me}nacnac^{Dipp})V(\mu\text{-}H)_2BEt_2(THF)]$ (**7**) similar in composition to complex **3** (Scheme 3). However, this result was obtained in a single experiment. All our attempts to reproduce this synthesis failed.

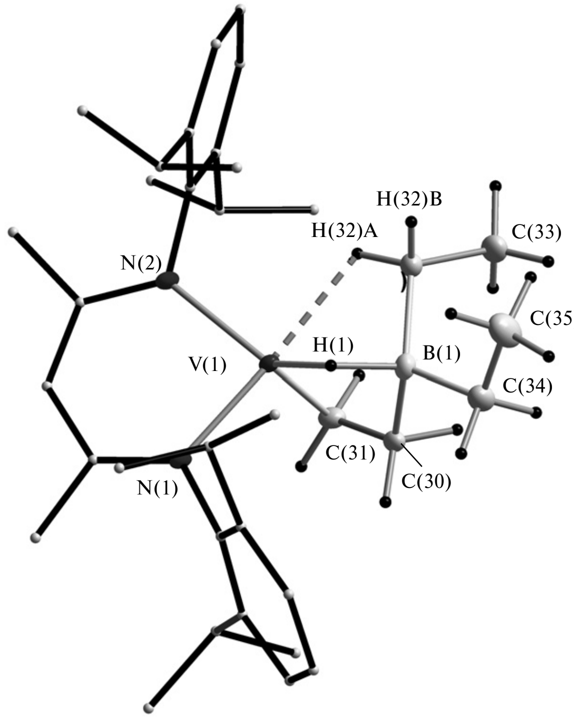
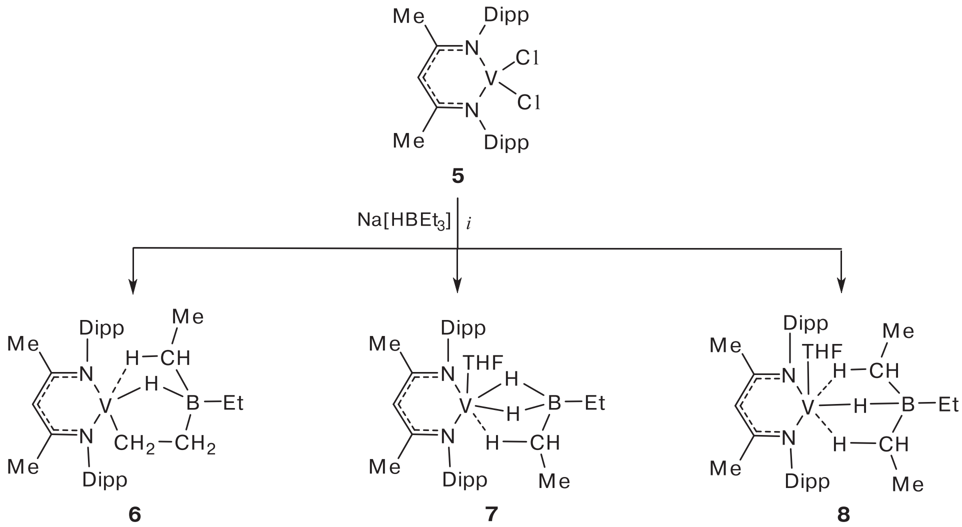


Fig. 2. Molecular structure of the complex $[(^{Me}nacnac^{Dipp})$-$V(\mu\text{-}H)(\mu,\kappa^{1:1}\text{-}C{:}C'\text{-}C_2H_4)BEt_2]$ (**6**) with displacement ellipsoids drawn at the 30% probability level. The H atoms of the ligand $(^{Me}nacnac^{Dipp})^-$ are omitted for clarity.

Assuming that the failure can be due to the very high solubility of complex **7** in THF, from which the crystallization was performed, we changed the final step of the isolation of the product. Thus, the solid residue, obtained by concentrating the reaction solution, was extracted with hexane, and the crystallization was performed from the same solvent. Surprisingly, in this case another compound, *viz.*, the V^{III} complex $[(^{Me}nacnac^{Dipp})V(\mu\text{-}H)(\mu,\kappa^{1:1}\text{-}C{:}C'\text{-}C_2H_4)BEt_2]$ (**6**), was obtained as the crystalline phase (Scheme 3, Fig. 2). In this complex, the $[H(C_2H_4BEt_2)]^{2-}$ anion, the deprotonated form of the triethylborohydride anion, is

Scheme 3



i. Toluene.

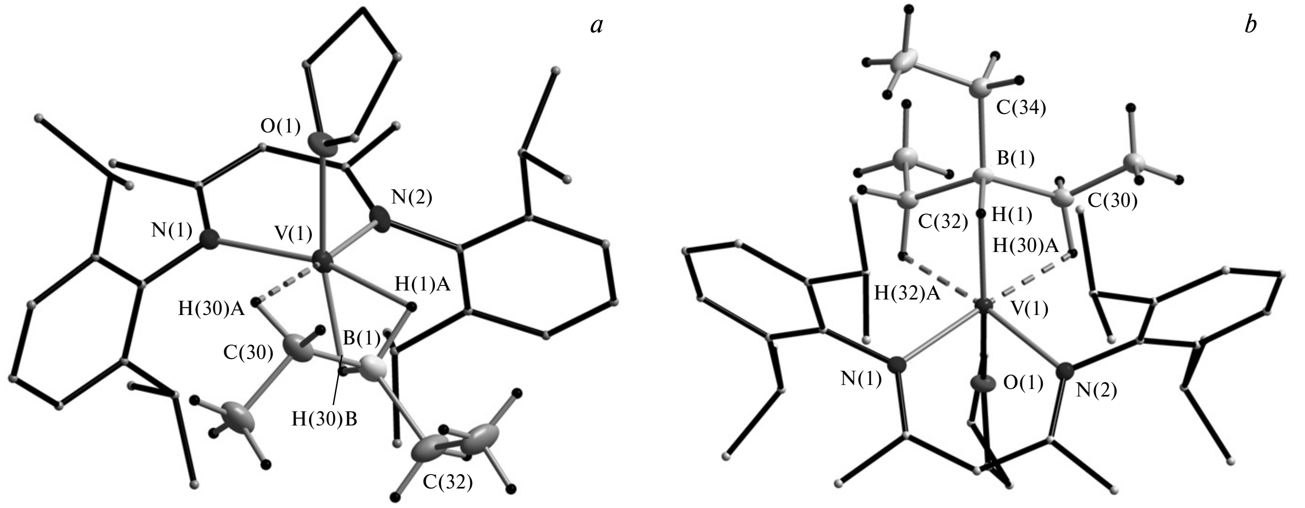


Fig. 3. Molecular structures of the complexes $[(^{Me}nacnac^{Dipp})V(\mu\text{-}H)_2BEt_2(THF)]$ (**7**) (*a*) and $[(^{Me}nacnac^{Dipp})V(\mu\text{-}H)BEt_3(THF)]$ (**8**) (*b*) with displacement ellipsoids drawn at the 30% probability level. The H atoms of the ligands $(^{Me}nacnac^{Dipp})^-$ and THF and the disorder of one ethyl group of **7** are omitted for clarity.

coordinated to the vanadium atom through the bridging hydride hydrogen atom and the carbon atom.

This reaction was repeated several times with small variations in the procedure of the isolation of the crystalline phase. The yield and purity of the isolated product were not well reproduced. Strict adherence to the procedure described in the Experimental allowed us to twice reproduce the results. According to the powder X-ray diffraction, the crystalline phase of **6** does not contain other crystalline impurities, although a somewhat underestimated carbon content and a slightly overestimated hydrogen content do not rule out the presence of a small amount of X-ray amorphous components. In other experiments, compound **6** was isolated as a mixture with other crystalline products. In particular, in one experiment, we found a single crystal of the compound $[(^{Me}nacnac^{Dipp})V(\mu\text{-}H)BEt_3(THF)]$ (**8**) (see Scheme 3, Fig. 3). We failed to isolate this complex in the individual state. However, the structure of this compound deserves consideration in one series with complexes **6** and **7**.

The structures of complexes **6**—**8** were determined by single-crystal X-ray diffraction. Compounds **6**—**8** have molecular structures shown in Figs 2 and 3. Selected interatomic distances in these compounds are given in Tables 2 and 3. In all these compounds, the vanadium atom is coordinated by the $(^{Me}nacnac^{Dipp})^-$ anion and the corresponding borohydride anion. In complexes **7** and **8**, the $[H_2BEt_2]^-$ and $[HBEt_3]^-$ anions are coordinated to the vanadium atom through two (**7**) or one (**8**) hydride hydrogen atoms serving as bridges between the B and V atoms. Besides, the metal coordination sphere in compounds **7** and **8** involves also

Table 2. Selected interatomic distances (*d*) in complex **6**

Distance	*d*/Å
V(1)—N(1)	2.038(2)
V(1)—N(2)	2.002(2)
V(1)—H(1)	1.63(2)
V(1)···H(32A)	2.18(3)
V(1)—C(31)	2.014(3)
C(30)—C(31)	1.503(5)
C(30)—B(1)	1.728(5)
C(32)—C(33)	1.531(4)
C(34)—C(35)	1.500(5)
B(1)—H(1)	1.216(16)

Table 3. Selected interatomic distances (*d*) in compounds **7** and **8**

Distance	*d*/Å	
	7	**8**
V(1)—N(1)	2.091(2)	2.099(2)
V(1)—N(2)	2.079(2)	2.103(2)
V(1)—H(1)	—	1.85(2)
V(1)—H(1A)	1.87(4)	—
V(1)—H(1B)	1.84(4)	—
V(1)···H(30A)	2.18(5)	2.07(3)
V(1)···H(32A)	—	2.05(2)
B(1)—H(1A)	1.20(4)	—
B(1)—H(1B)	1.20(4)	—
V(1)—O(1)	2.176(2)	2.1958(16)
C(30)—B(1)	1.627(6)	1.639(4)
C(32)—B(1)	—	1.653(4)

THF. As opposed to **7** and **8**, the borohydride anion in compound **6** is coordinated to the vanadium atom through the bridging hydrogen atom and also through the carbon atom C(31). The V—C(31) distance is 2.014(3) Å, which corresponds to the average V—C single bond length. Therefore, one ethyl group of the triethylborohydride anion is deprotonated, and the borohydride ligand is the doubly charged $[H(C_2H_4BEt_2)]^{2-}$ anion.

Taking into account the presence of two singly charged anionic ligands in molecules **7** and **8**, the oxidation state of vanadium in these complexes can be assumed to be +2, whereas the oxidation state of vanadium in compound **6** is +3, because the latter molecule contains the singly charged $(^{Me}nacnac^{Dipp})^-$ anion and the doubly charged $[H(C_2H_4BEt_2)]^{2-}$ anion. The conclusion about different oxidation states of vanadium is confirmed by the differences in the bond lengths between vanadium and the nitrogen atoms of $(^{Me}nacnac^{Dipp})^-$ and between vanadium and the bridging hydrogen atoms. Thus, the V—N distances in **7** and **8** are 0.05—0.1 Å longer and the V—H distances are approximately 0.02 Å longer compared to the corresponding distances in **6**. The V—H distances in **7** and **8** are closer to the average V—H bond lengths (1.78—1.93 Å) in vanadium borohydride complexes.[23,24]

Besides, in all three complexes there are agostic interactions between the methylene groups of the ethyl moieties nearest to the metal and the central atom. The V···H distances are 2.18 Å (V(1)···H(32A), **6**), 2.18 Å (V(1)···H(30A), **7**), 2.07 Å (V(1)···H(30A), **8**), and 2.05 Å (V(1)···H(32A), **8**). The V···C distances are 2.60 Å (V(1)...C(32), **6**), 2.49 Å (V(1)···C(30), **7**), 2.50 Å (V(1)···C(30), **8**), and 2.50 Å (V(1)···C(32), **8**), which correspond to the parameters of the classical agostic interaction.

The C—H···V angles centered at the agostic hydrogen atoms are nearly equal in compounds **6** and **8**. Thus, the C(32)—H(32A)···V(1) angle in **6** is 102.9°; the C(30)—H(30A)···V(1) and C(32)—H(32A)···V(1) angles in **8** are 103.8° and 104.0°, respectively. However, the C(30)—H(30A)...V(1) angle in compound **7** is significantly smaller (94.0°). This difference correlates with a decrease in the V(1)···B(1) distance in the case of coordination of the borohydride anion through two bridging hydrogen atoms. Thus, this angle in **7** is 2.18 Å; the corresponding angles in **6** and **8** are 2.20 and 2.28 Å, respectively.

It should be noted that a few vanadium complexes are known, in which the agonstic interaction is observed. For instance, one methyl group of the trimethylsilyl group in the compound $[V(SC_6H_3—2,6-(SiMe_3)_2)_3(THF)]$ is involved in the agostic interaction with the metal; the V···C and V···H distances are 2.61 and 2.20 Å, respectively.[25] In the vanadium(III) pentamethylcyclopentadienyl complex $[VCp^*_2]BPh_4$, the corresponding distances are 2.57 and 2.10 Å, respectively.[26] The agostic interaction is also evidenced by the inclination of the corresponding ethyl substituents toward the vanadium. Thus, in complex **2**, in which an agostic interaction is absent, the Mn(1)—B(1)—C(30) and Mn(1)—B(1)—C(32) angles are close to 120° (117.9° and 125.9°), whereas the corresponding angles in **7** are 80.3° (V(1)—B(1)—C(30)) and 159.3° (V(1)—B(1)—C(32), for the disordered moiety with a higher occupancy factor); in **8**, 77.4° (V(1)—B(1)—C(30)), 76.9° (V(1)—B(1)—C(32)), and 161.0° (V(1)—B(1)—C(34)). In other words, the ethyl groups of the diethylborohydride ligand in the manganese complexes point outward, whereas the ethyl groups in the vanadium complexes tend to point toward the metal.

Possible reaction pathways

In most cases, the salts $M[HBEt_3]$ (M = Li, Na, K) serve as a hydride ion source in the reactions with transition metal halide complexes. More rarely, these reactions are accompanied by the substitution of the halide ion by the anionic ligand $[HBEt_3]^-$. These compounds are scarce. The search in the Cambridge Structural Database gave only 12 compounds with the following metals: Sc,[27] La,[28] Y,[29] Tm,[30] Sm,[31] Ca,[32,33] Fe,[34] V,[35] Cu,[36] and Zr[37] (alkali metals were excluded). Almost all these compounds were synthesized by the reactions of halide complexes with $M[HBEt_3]$, but the lanthanum complex, for example, was prepared by the reaction of the hydride complex $[Cp^*_2LaH]_n$ with BEt_3 ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$).[27]

Interestingly, the compounds with the $[H_2BEt_2]^-$ ligand (only eight refcodes in the CSD) were formally synthesized by just the same reactions: the Ni,[38] Nd,[39] and Re compounds[40] were synthesized by the treatment of halide complexes with the commercial $M[HBEt_3]$ solutions (M = Na, K); Fe compounds,[41,42] by the reaction of iron hydride complexes with BEt_3.

In the cited studies, the formation of diethylborohydride complexes in the reactions of the halide complexes with $M[HBEt_3]$ (M = Na, K) was attributed to the fact that the $[H_2BEt_2]^-$ anion is produced in significant amounts in the commercial $M[HBEt_3]$ solution through the disproportionation of this compound into $M[BEt_4]$ and $M[H_2BEt_2]$. However, the ^{11}B NMR spectrum of the solution of $Na[HBEt_3]$ in THF used in our research is indicative of the presence of only one form, $[HBEt_3]^-$, characterized by a doublet at δ 12.1 ($J_{B,H}$ = 64 Hz) and, with the spin-spin proton decoupling, by a singlet. Therefore, in our case the presence of the $[H_2BEt_2]^-$ anion in the starting reagent can be excluded.

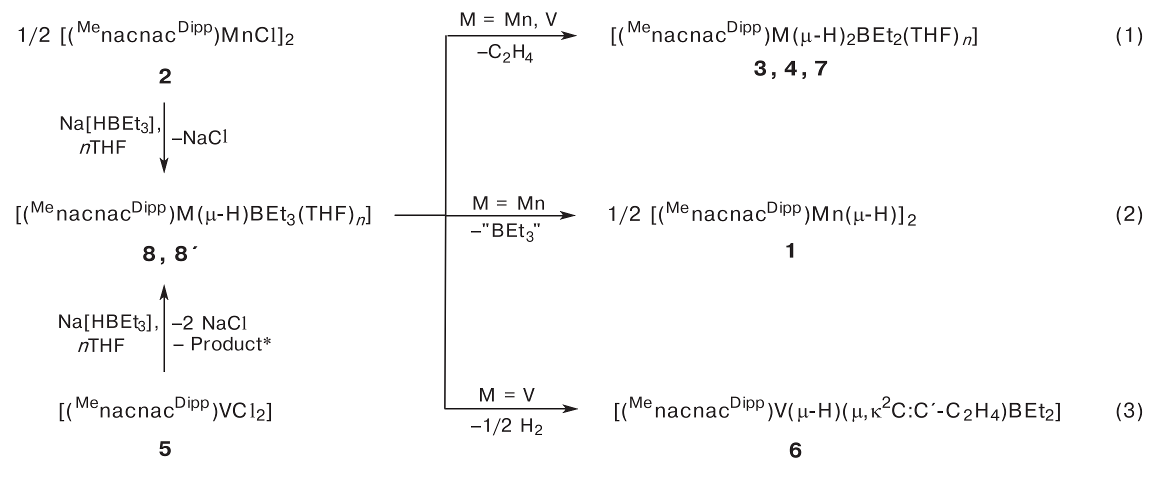
The formation of $[(^{Me}nacnac^{Dipp})Fe(\mu\text{-}H)_2BEt_2]$ in the reaction of $[(^{Me}nacnac^{Dipp})Fe(\mu\text{-}H)]_2$ with BEt_3 occurs at 80 °C and is accompanied by the formation of the complex $[(^{Me}nacnac^{Dipp})FeEt]$, which was not isolated in the pure form, but it was detected in solution by ^1H NMR spectroscopy.**41** Although our experiments were performed at significantly lower temperatures, it cannot be ruled out that our results are due to the reaction of the hydride complexes that formed in the solution with BEt_3. However, we failed to confirm or deny this fact because of the paramagnetism of Mn^{2+}, V^{2+}, and V^{3+} ions, the presence of which leads to a huge broadening of NMR signals.

A comparison of the sets of products isolated in the reactions of the manganese and vanadium complexes with $Na[HBEt_3]$ and the structures of the reaction products suggests that all these compounds fit into a chain assuming that the reactions initially form the ethylborohydride complexes $[(^{Me}nacnac^{Dipp})M(\mu\text{-}H)\text{-}BEt_3(THF)_n]$ (n = 0, 1) followed by their decomposition through different reaction pathways (Scheme 4). In the case of M = V, this is complex **8**, which is produced by the reduction of V^{III} to V^{II} and the replacement of Cl^- by $[HBEt_3]^-$. In the case of M = Mn, the reaction affords the supposed product of the nucleophilic substitution of Cl^- by $[HBEt_3]^-$ (denoted by **8′**), which was not observed in our experiments.

The pathway (1) involves the β-dehydrogenation of the ethyl group of the $[HBEt_3]^-$ anion accompanied by the elimination of C_2H_4. The pathway (2) implies the elimination of the neutral moiety $\{BEt_3\}$, which most likely should leave the reaction zone as a complex with the solvent (in Scheme 4, this complex is denoted as "BEt_3"). The pathway (3) involves the intramolecular redox reaction $V^{2+} + H^+ = V^{3+} + ½H_2$. A comparison of the reducing properties of V^{2+} and Mn^{2+} explains why complex **6** is produced from the vanadium compound but its analog is not formed from the manganese compound. In terms of this scheme, the absence of the hydride analog of **1** in the case of vanadium can be attributed to the fact that the presence of an agostic interaction between the ethyl hydrogen atoms and the vanadium atom makes the pathway (2) the least favorable. Finally, the reactions of the compounds of both metals can proceed through the pathway (1), if this process really occurs, to give compounds **3**, **4**, and **7**. Most likely, this process should also occur more easily in the presence of agostic interactions, which are observed in **8**. Apparently, similar interactions are present in **8′** until the boron atom bears three ethyl moieties. However, there are no arguments in favor of this fact and even the existence of **8′** is only supposed. In general, the proposed scheme can easily be criticized. This scheme is proposed as a hypothesis, which is not contradictory to the experimental data. However, the unusual chemistry encourages us to further investigate the reaction pathways.

Summarizing the results of this study, it can be stated that the reaction of $[(^{Me}nacnac^{Dipp})Mn(\mu\text{-}Cl)]_2$ **(2)**

Scheme 4



M = V (**8**), Mn (**8′**); n = 0, 1

* Product is the product of the oxidation with $[HBEt_3]^-$.

with Na[HBEt$_3$] affords different products in the presence and in the absence of tetrahydrofuran as the coordinating solvent. In the absence of THF, the crystalline phase contains [(^{Me}nacnac^{Dipp})Mn(μ-H)]$_2$ (**1**) as the major component and also a significant amount of [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$] (**4**). The synthesis in a THF—toluene mixture gives the complex [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$(THF)] (**3**) as the major product.

The reaction of [(^{Me}nacnac^{Dipp})V(μ-H)$_2$BEt$_2$(THF)] (**5**) with Na[HBEt$_3$] is very sensitive to the experimental conditions. We found the conditions for the reproducible synthesis of the V^{III} complex [(^{Me}nacnac^{Dipp}) V(μ-H)(μ,κ$^{1:1}$-C:C′—C$_2$H$_4$)BEt$_2$] (**6**) containing the unique ligand [H(C$_2$H$_4$)BEt$_2$]$^{2-}$, as the deprotonated form of the [HBEt$_3$]$^-$ anion. However, the V^{II} complexes [(^{Me}nacnac^{Dipp})V(μ-H)$_2$BEt$_2$(THF)] (**7**) and [(^{Me}nacnac^{Dipp})V(μ-H)BEt$_3$(THF)] (**8**) were isolated in single experiments.

Complexes **1**, **3**, **4**, **6**, and **7** contain only fragments of [HBEt$_3$]$^-$ anion, whereas this anion in compound **8** remains intact. The vanadium ethylborohydride complexes, as opposed to the related manganese complexes, are characterized by the presence of agostic contacts between the metal ion and the hydrogen atoms of C—H bonds. A comparison of the structures of the complexes and the presence/absence of agostic interactions suggest the hypothesis that there are different pathways of degradation of the [HBEt$_3$]$^-$ anion in the metal coordination sphere through the elimination of C$_2$H$_4$, H$_2$, or "BEt$_3$".

Experimental

The reactions were carried out *in vacuo* or under an argon atmosphere using the Schlenk technique. The compounds were loaded in an argon glove box. Toluene and THF were dried by distillation over the potassium—sodium alloy and potassium benzophenone ketyl, respectively. The starting complexes [(^{Me}nacnac^{Dipp})MnCl]$_2$ (**2**)[43] and [(^{Me}nacnac^{Dipp}) VCl$_2$] (**5**)[44] were prepared by the known procedures. The commercially available 1 *M* Na[HBEt$_3$] solution in THF (Acros) was used as received. The C, H, N elemental analysis was performed in the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences on an Euro EA 3000 analyzer. Infrared spectra were recorded on a Simex FT-801 spectrophotometer as KBr pellets. The single-crystal X-ray diffraction analysis of compounds **3**, **4**, **6**, and **7** and the powder X-ray diffraction analysis of all crystalline mixtures were performed at 150 K on a Bruker D8 Venture diffractometer (at the Center of Shared Use of the Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences) equipped with a CMOS PHOTON III detector and an IμS 3.0 microfocus source (Montel focusing mirrors). The single-crystal X-ray diffraction analysis of compound **8** was carried out at 150 K on a Bruker Apex DUO diffractometer equipped with a CCD detector (Mo-*K*α radiation, graphite monochromator) using the standard procedure for collecting X-ray diffraction data. The X-ray diffraction data were reduced using the APEX3 package.[45] The structures were solved with the SHELXT program package[46] and refined using the SHELX suite of programs[47] *via* the Olex2 interface.[48] The hydrogen atoms were positioned geometrically, except for the bridging H atoms between the B atom and the metal or those, which form agostic contacts with the metals; the latter H atoms were located in residual electron density maps and freely refined. All hydrogen atoms were refined using a riding model. The crystallographic data and the X-ray diffraction data collection and structure refinement statistics for compounds **3**, **4**, and **6** are given in Table 4; for compounds **7** and **8**, in Table 5. The structural data for compounds **3**, **4**, and **6—8** were deposited with the Cambridge Crystallographic Data Centre (CCDC 2129486 (**3**), 2129487 (**4**), 2129489 (**6**), 2129488 (**7**), and 2130114 (**8**)) and are available at deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The crystal structure of **4** has the pseudosymmetry *C*2/*c*, which is violated by atoms of the diethylborohydride ligand. The structure was solved in the lower-symmetry space group *Cc* in order to avoid the disorder of the corresponding atoms; this led to a strong correlation of the atomic displacements for some atoms related by the pseudosymmetry operation and a relatively low accuracy of the bond lengths. In the known structure of the related complex [(nacnac)Fe(μ-H)$_2$BEt$_2$] solved in the space groups *C*2/*c*,[41] the disorder of the diethylborohydride ligand was also observed due to the presence of a twofold axis.

Powder X-ray diffraction patterns were obtained using Cu-*K*α radiation. Powdered samples, which were prepared by grinding the crystalline substance isolated from the reaction mixture, were placed in glass capillaries. Debye diffraction patterns with continuous diffraction rings were measured using the φ-scan technique (360°).[49] To reduce the effect of the predominant orientation, five ω scans were made at different positions of the goniometer in the range from –240 to 0°. The external calibration was carried out with the Si standard and the integration was performed using the Dioptas software.[50] The full-profile analysis of the powder X-ray diffraction patterns was performed using the single-crystal X-ray diffraction data. The background was approximated by the fourth kind Chebyshev polynomial. The unit cell parameters, the peak widths, the sample displacement, and the scale factor were refined for each phase.

(Diethyldihydroborato-μ-H,μ-H′)[*N*-(2,6-diisopropylphenyl)-*N*-{4-[(2,6-diisopropylphenyl)imino]pent-2-en-2-yl}-amido-κ^2-*N*,*N*′](tetrahydrofuran)manganese(II), [(^{Me}nacnac^{Dipp})Mn(μ-H)$_2$BEt$_2$(THF)] (3). A solution of Na[HBEt$_3$], which was prepared by mixing the commercial 1 *M* Na[HBEt$_3$] solution in THF (1.2 mL, 1.2 mmol) and toluene (5 mL), was added dropwise for 10 min to a solution of complex **2** (0.49 g, 0.5 mmol) in toluene (30 mL) cooled to –40 °C. The reaction mixture was stirred with cooling for 30 min and then heated to room temperature, stirred for 1 h,

Table 4. Crystallographic data and the X-ray diffraction data collection and structure refinement statistics for compounds **3**, **4**, and **6**

Parameter	**3**	**4**	**6**
Molecular formula	$C_{37}H_{61}BMnN_2O$	$C_{33}H_{53}BMnN_2$	$C_{35}H_{56}BN_2V$
M	615.62	543.52	566.56
T/K	150(2)	150(2)	150(2)
Space group	$P2_1$	Cc	$P\bar{1}$
a/Å	9.8134 (2)	14.8070(15)	9.0497(7)
b/Å	16.4052 (4)	10.6562(11)	9.9370(10)
c/Å	11.9123 (3)	20.969(2)	20.2281(11)
α/deg	90	90	95.610(4)
β/deg	109.113 (1)	91.563(4)	90.365(2)
γ/deg	90	90	113.391(2)
V/Å^3	1812.05 (7)	3307.5(6)	1659.5(2)
Z	2	4	2
d_{calc}/g cm^{-3}	1.128	1.092	1.134
μ/mm^{-1}	0.39	0.421	0.323
F(000)	670	1180	616.0
Scan range 2θ/deg	3.6—51.4	3.886—51.414	4.722—50.374
h, k, l Ranges	$-11 \leqslant h \leqslant 10$, $-20 \leqslant k \leqslant 19$, $-14 \leqslant l \leqslant 14$	$-17 \leqslant h \leqslant 18$, $-12 \leqslant k \leqslant 12$, $-25 \leqslant 1 \leqslant 25$	$-10 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 10$, $-21 \leqslant l \leqslant 24$
Number of reflections			
measured	20325	11939	15194
unique	6861	5671	5795
(R_{int})	(0.0401)	(0.0424)	(0.0818)
R_σ	0.0455	0.0564	0.1021
Number of constraints	1	78	5
Number of refined parameters	397	347	380
GOOF on F^2	1.032	1.036	1.024
R factor ($I > 2\sigma(I)$)			
R_1	0.0362	0.0672	0.0601
wR_2	0.0764	0.1774	0.1426
R factor (all reflections)			
R_1	0.0402	0.0773	0.0878
wR_2	0.0801	0.1898	0.1610
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.28/−0.26	1.91/−0.36	0.72/−0.66
Flack parameter	−0.004(8)	0.52(6)	—

and filtered off. The resulting yellow solution was concentrated *in vacuo* to dryness. The residue was dissolved in hexane (~5 mL) and the solution was kept for two days at −30 °C. The yellow crystals of complex **3** that precipitated were separated from the mother liquor by decantation and dried *in vacuo*. The yield was 0.25 g (42%). Found (%): C, 71.9; H, 10.0; N, 4.3. $C_{37}H_{61}BMnN_2O$. Calculated (%): C, 72.2; H, 9.9; N, 4.6. IR, ν/cm^{-1}: 3058 w, 2962 s, 2867 m, 1959 m, 1661 w, 1541 m, 1514 m, 1461 s, 1397 s, 1315 m, 1261 s, 1173 m, 1090 v.s, 1020 v.s, 934 w, 868 m, 798 v.s, 757 m.

Reaction of [(^{Me}nacnac^{Dipp})Mn(μ-Cl)]$_2$ (2) with Na[HBEt$_3$] in toluene. The commercial 1 *M* Na[HBEt$_3$] solution in tetrahydrofuran (0.74 mL, 0.74 mmol) was concentrated *in vacuo*. The resulting white oily residue was dissolved in toluene (5 mL) and cooled to −40 °C. The cold solution was added dropwise for 10 min to a solution of compound **1** (0.3 g, 0.3 mmol) in toluene (20 mL), which was also cooled to −40 °C. The reaction mixture was stirred with cooling for 30 min and then heated to room temperature and stirred for 1 h. The resulting yellow solution was concentrated *in vacuo*. The solid residue was extracted with hexane (~5 mL). The resulting yellow solution was filtered off and kept for 7 days at −30 °C, giving a yellow crystalline mixture. One crystal (compound **4**) was studied by single-crystal X-ray diffraction. The remaining crystalline mixture was studied by powder X-ray diffraction. It was found that this mixture contained compounds **1**, **4**, and **2** in a ratio of 15 : 4 : 1 and traces of an unknown crystalline phase.

[2-Diethylhydroborato)ethyl-μ,κ$^{1:1}$-C:C′,μ-H][*N*-(2,6-diisopropylphenyl)-*N*-{4-[(2,6-diisopropylphenyl)imino]pent-2-en-2-yl}amido-κ^2-*N*,*N*′]vanadium(III), (^{Me}nacnac^{Dipp})V(μ-H)-(μ,κ$^{1:1}$-C:C′-C$_2$H$_4$)BEt$_2$] (6). A solution of Na[HBEt$_3$], which was prepared by mixing the commercial 1 *M* Na[HBEt$_3$] solution in THF (0.74 mL, 0.74 mmol) and toluene (3 mL), was

Table 5. Crystallographic data and the X-ray diffraction data collection and structure refinement statistics for compounds **7** and **8**

Parameter	**7**	**8**
Molecular formula	$C_{37}H_{61}BN_2OV$	$C_{39}H_{65}BN_2OV$
M	611.62	639.68
T/K	150(2)	150(2)
Space group	$P2_1$	$P2_1/n$
a/Å	9.9820(3)	10.2995(6)
b/Å	16.5823(5)	31.907(3)
c/Å	11.7564(3)	12.2548(11)
α/deg	90	90
β/deg	111.668 (1)	108.673(2)
γ/deg	90	90
V/Å^3	1808.47(9)	3815.3(5)
Z	2	4
d_{calc}/g cm^{-3}	1.123	1.114
μ/mm^{-1}	0.30	0.290
F(000)	666	1396.0
Scan range 2θ/deg	3.8—55.8	4.34—49.426
h, k, l Ranges	$-13 \leqslant h \leqslant 10$, $-21 \leqslant k \leqslant 21$, $-15 \leqslant l \leqslant 15$	$-12 \leqslant h \leqslant 8$, $-37 \leqslant k \leqslant 37$, $-14 \leqslant l \leqslant 14$
Number of reflections		
measured	18968	27621
unique	8244	6479
(R_{int})	(0.042)	(0.0801)
$R_σ$	0.0545	0.0751
Number of constraints	54	5
Number of refined parameters	442	425
GOOF on F^2	1.033	1.013
R factor ($I > 2σ(I)$)		
R_1	0.0422	0.0505
wR_2	0.1019	0.1011
R factor (all reflections)		
R_1	0.0504	0.0800
wR_2	0.1088	0.1136
Residual electron density ($ρ_{max}/ρ_{min}$)/e Å^{-3}	0.23/–0.37	0.28/–0.25
Flack parameter	0.006(11)	—

added to a solution of complex **5** (0.2 g, 0.37 mmol) in toluene (20 mL) cooled to –30 °C. The reaction mixture was stirred with cooling for 20 min and then heated to room temperature and stirred for 2 h. The resulting dark-brown solution was concentrated *in vacuo* to dryness. The dry residue was extracted with two portions of hexane (5 mL and 2 mL). The resulting solution was kept for 7 days at –30 °C. The crystals of compound **6** that precipitated were separated from the mother liquor by decantation and dried *in vacuo*. The yield was 0.086 g (38%). Found (%): C, 73.6; H, 10.4; N, 4.8. $C_{35}H_{56}BN_2VO$. Calculated (%): C, 74.2; H, 10.0; N, 4.9. IR, ν/cm^{-1}: 3057 m, 2962 s, 2868 s, 2816 w, 2733 w, 1935 w, 1864 w, 1814 w, 1748 w, 1623 w, 1533 s, 1463 s, 1437 s, 1384 v.s, 1318 s, 1258 s, 1173 m, 1102 v.s, 1055 v.s, 1022 v.s, 934 m, 904 w, 856 m, 797 v.s, 760 s, 705 w.

(Diethyldihydroborato-μ-H,μ-H′)[*N*-(2,6-diisopropylphenyl)-*N*-{4-[(2,6-diisopropylphenyl)imino]pent-2-en-2-yl}amido-κ^2-*N*,*N*′](tetrahydrofuran)vanadium(II), [(^{Me}nacnac^{Dipp})V(μ-H)$_2$BEt$_2$(THF)] (7). A solution of Na[HBEt$_3$], which was prepared by mixing the commercial 1 *M* Na[HBEt$_3$] solution in THF (0.9 mL, 0.9 mmol) and toluene (3 mL), was added dropwise for 10 min to a solution of complex **3** (0.2 g, 0.37 mmol) in toluene (10 mL) cooled to –40 °C. The reaction mixture was stirred with cooling for 30 min and then heated to room temperature and stirred for 1 h. The resulting brown solution was filtered off and concentrated *in vacuo* to dryness. The residue was dissolved in THF (~2 mL), and the solution was kept at –30 °C. Black crystals of complex **7** that precipitated were separated from the mother liquor by decantation and dried *in vacuo*. The yield was 0.05 g (22%). Found (%): C, 72.1; H, 9.8; N, 4.3. $C_{37}H_{61}BVN_2O$. Calculated (%): C, 72.7; H, 10.1; N, 4.6. IR, ν/cm^{-1}: 3057 m, 2962 s, 2868 s, 2689 w, 1921 s, 1867 s, 1622 m, 1531 s, 1509 s, 1462 v.s, 1436 v.s, 1402 v.s, 1314 s, 1259 v.s, 1172 s, 1021 v.s, 933 m, 866 m, 799 v.s, 760 s.

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