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Dedicated to the 90th birthday of Academician I.I. Moiseev

Hydrogenation of C=C and C=N Bonds of the Amide-Imine Ligand in the Metal Coordination Sphere in the Reaction of Yttrium Bis(alkyl) Complex [2,6-*iso*-$Pr_2C_6H_3NC(=CH_2)C(Me)=NC_6H_3$-*iso*-$Pr_2$-2,6]$Y(CH_2SiMe_3)_2(THF)$ with Molecular Hydrogen

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Abstract—On treatment of the yttrium bis(alkyl) complex [ArNC(=CH_2)C(Me)=NAr]$Y(CH_2SiMe_3)_2$(THF) (**I**, Ar = C_6H_3-*iso*-Pr_2-2.6) containing an amide-imine ligand, with molecular hydrogen, hydrogenation of the C=N and C=C bonds takes place along with hydrogenolysis of Y–C bonds. The reaction is also accompanied by redistribution of nitrogen ligands and results in the formation of the yttrium complexes [ArNCH(Me)CH(Me)NAr]Y[ArN(=CH_2)CH(Me)N(H)Ar](THF) (**II**^{MeMe}) and [ArNCH(Me)C(=CH_2)NAr]Y[ArN(=CH_2)CH(Me)N(H)Ar](THF) (**II**^{MeCH_2}), containing, the monoanionic ene-amide-amine moiety [ArNC(=CH_2)CH(Me)N(H)Ar]$^-$, together with the dianionic diamide ligands [ArNCH(Me)CH(Me)NAr]$^{2-}$ or [ArNCH(Me)C(=CH_2)NAr]$^{2-}$ (CIF file CCDC no. 1873206).

Keywords: rare earth metals, alkyl complexes, hydride complexes, synthesis, structure, reactivity

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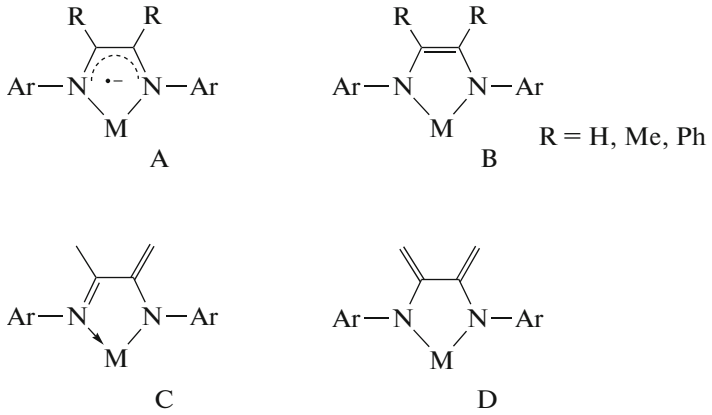
INTRODUCTION

1,4-Disubstituted diazabuta-1,3-dienes and ligand systems based on them have now found wide use in the organic and coordination chemistry of rare earth metals (REMs) [1–9]. The interest in these ligands is caused by their diverse coordination options and redox active nature and also by easy modification of their steric and electronic properties [10]. Owing to the presence of nitrogen lone pairs and C=N bond π-electrons, the diazadiene molecule can act as both n- and p-donor, being coordinated to metal as a neutral ligand [11]. The reduction of diazabutadiene on treatment of one or two molar equivalents of alkali metals gives radical anion [RNC(R')C(R')NR]$^{\cdot -}$ (A, Scheme 1) [12] and ene-diamide [RN–C(R')=C(R')–NR]$^{2-}$ (B, Scheme 1) [13–17] ligands, respectively. Meanwhile, diazabutadienes containing methyl groups at the imine carbon atoms may undergo ligand transformation by an alternative route as a result of activation of one or two CH bonds of these groups to give the monoanionic amide-imine ligand [ArN=C(Me)–C(=CH_2)–NAr]– (C, Scheme 1) [18–20] or diene-diamide ligand [ArN–C(=CH_2)–C(=CH_2)–NAr]$^{2-}$ (D, Scheme 1) [21]. The REM derivatives based on these ligands proved to be efficient catalysis for ring opening polymerization of lactide and b-butyrolactone [22], 2-vinylpyridine polymerization [23], stereoselective polymerization of isoprene [19, 24], and intermolecular hydroamination, hydrophosphination [25], and hydrosilylation [26] of alkenes and alkynes. Recently, first lanthanide (Yb, Dy) complexes with diazabutadiene-based ligands possessing single molecule magnet (SMM) properties were reported [27, 28]. Types of ligand systems based on diazabutadienes (A, B, C, D) are depicted in Scheme 1:



Scheme 1.

Recently, it was also shown that the dianionic ene-diamide and monoanionic amide-imine ligand systems based on diazabutadienes form an appropriate ligand environment for stabilization of mono- and bis(alkyl) REM derivatives [9, 23, 25]. Moreover, a rare example of metallacyclic yttrium hydride complex was prepared using the dianionic ene-diamide ligand system [25].

This communication reports the reaction of bis(alkyl) yttrium complex stabilized by the amide-imine ligand with molecular hydrogen H_2 and phenylsilane $PhSiH_3$.

EXPERIMENTAL

The complexes were synthesized under conditions ruling out the contact with oxygen and air moisture using standard Schlenk technique. Tetrahydrofuran (THF) and toluene were dried with sodium benzophenone ketyl, while hexane was dried with sodium metal, then thoroughly degassed, and condensed in vacuum into the reaction tube immediately prior to use. The complex $[ArNC(=CH_2)C(Me)=NAr]Y(CH_2SiMe_3)_2(THF)$ (**I**) was prepared by a previously reported procedure [19].

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX 200 MHz and Bruker Avance III 400 MHz instruments. The chemical shifts are given in ppm and referred to the known chemical shifts of the residual protons of deuterated solvents. Elemental analysis was performed on a Perkin-Elmer Series II CHNS/O Analyser 2400 instrument. The REM content was determined by complexometric titration (Trilon B) with xylenol orange as the indicator.

Synthesis of {[2,6-*iso*-$Pr_2C_6H_3$NCH(Me)CH(Me)-NC_6H_3-*iso*-Pr_2-2,6]Y[2,6-*iso*-$Pr_2C_6H_3$-NC(=CH_2)-CH(Me)N(H)C_6H_3-*iso*-Pr_2-2,6]}, {[2,6-*iso*-$Pr_2C_6H_3$NCH(Me)C(=CH_2)NC_6H_3-*iso*-Pr_2-2,6]Y[2,6-*iso*-$Pr_2C_6H_3$NC(=CH_2)CH(Me)N(H)C_6H_3-*iso*-Pr_2-2,6]} ($\mathbf{II}^{MeMe/MeCH_2}$). A solution of complex **I** (0.637 g, 0.86 mmol) in hexane (20 mL) was placed into an evacuated tube equipped with a Teflon valve and a magnetic stirrer and the tube was filled with H_2 up to a pressure of 2 atm. The reaction mixture was stirred for 6 days at room temperature. Recrystallization of the reaction product from a THF–hexane mixture (1 : 1) gave yellow-green crystals. Yield: 0.318 g (38%).

For $C_{60}H_{91}N_4OY$ (M = 972.30)

Anal. calcd., %	C, 74.04	H, 9.42	N, 5.76	Y, 9.13
Found, %	C, 74.39	H, 9.52	N, 5.58	Y, 9.22

^1H NMR for $\mathbf{II}^{MeMe}$ (400 MHz; pyridine-d_5; 293 K; δ, ppm (*J,* Hz)): 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3-*iso*-Pr), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3-*iso*-Pr), 1.16 (m, 15H, CH_3-*iso*-Pr and CHCH_3), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH_3-*iso*-Pr), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH_3-*iso*-Pr), 1.28 (m, 6H, CHCH_3), 1.56 (m, 4H, β-CH_2THF), 2.82 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*-*iso*-Pr), 2.90 (sept., $^3J_{HH}$ = 6.8 Hz, 2H, C*H*-*iso*-Pr), 3.60 (m, 10H, NC*H*CH_3, C*H*-*iso*-Pr and α-CH_2THF), 3.87 (m, 2H, N(H)C*H*CH_3 and C=CH_2), 4.37 (m, 1H, C=CH_2), 5.08 (d, $^3J_{HH}$ = 8.8 Hz, N*H*), 7.20 (m, 12H, C*H*C_6H_3). $^{13}C\{^1H\}$ NMR for $\mathbf{II}^{MeMe}$ (400 MHz; pyridine-d_5; 293 K; δ, ppm): 15.6 (s, NHCH*C*H_3), 18.8 (s, NCH*C*H_3), 22.6 (s, *C*H_3-*iso*-Pr), 22.7 (s, *C*H_3-*iso*-Pr), 23.2 (s, *C*H_3-*iso*-Pr), 23.3 (s, *C*H_3-*iso*-Pr), 23.8 (s, *C*H_3-*iso*-Pr), 23.9 (s, β-*C*H_2THF), 24.1 (s, *C*H_3-*iso*-Pr), 27.7 (s, *C*H-*iso*-Pr), 27.9 (s, *C*H-*iso*-Pr), 28.1 (s, *C*H*i*Pr), 59.7 (s, NH*C*(H)Me), 60.6 (s, N*C*(H)Me), 67.6 (s, α-*C*H_2THF), 112.3 (s, NC=*C*H_2 Ar), 116.6 (s, *C*HAr), 122.7 (s, *C*HAr), 123.7 (s, *C*HAr), 123.8 (s, *C*HAr), 128.4 (s, *C*HAr), 129.2 (s, *C*HAr), 136.3 (s, *C*Ar), 141.6 (s, *C*Ar), 142.4 (s, *C*Ar), 143.2 (s, *C*Ar), 145.9 (s, *C*Ar), 158.3 (s, *C*Ar), 173.3 (s, N*C*=CH_2). The content of $\mathbf{II}^{MeCH_2}$ in the crystalline powder was less than 5% according to NMR data, which precludes correct description of its ^1H NMR and $^{13}C\{^1H\}$ NMR spectra.

Table 1. Crystallographic data and X-ray diffraction experiment and structure refinement details for complex **II**

Parameter	Value
Formula	$1/2(C_{60}H_{89}N_4OY)$, $1/2(C_{60}H_{91}N_4OY)$
M	972.26
Space group	$P\bar{1}$
a, Å	12.9100(3)
b, Å	14.7126(3)
c, Å	14.8157(3)
α, deg	77.906(2)
β, deg	87.430(2)
γ, deg	85.626(2)
V, Å^3	2742.41(10)
Z	2
ρ(calcd.), mg/m^3	1.177
μ, mm^{-1}	1.105
Scan mode of θ, deg	2.88–26.02
Number of measured reflections	41266
Number of reflections with $I > 2\sigma(I)$	10 778
R_{int}	0.1176
Number of refined parameters	633
$S(F^2)$	1.002
R_1 ($I > 2\sigma(I)$)	0.0712
wR_2 (for all data)	0.1413
Residual electron density (min/max), e/Å^3	−0.756/0.968

The X-ray diffraction study of II was carried out on at Agilent XcaliburE diffractometer (ω-scan mode, MoK_α-radiation, λ = 0.71073 Å, T = 100 K). The measurement of experimental reflection intensities, applying absorption corrections, and structure refinement were carried out using CrysAlisPro [29] and SHELX [30] packages. The structures were solved by the direct methods and refined by the full-matrix least-squares method on F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed into geometrically calculated positions and refined isotropically with fixed thermal parameters $U(H)_{iso}$ = $1.2U(C)_{equiv}$ ($U(H)_{iso}$ = $1.5U(C)_{equiv}$ for methyl groups). The atom coordinates in the disordered diamide moiety were found from electron density maps. Some bond lengths and anisotropic thermal parameters of disordered C atoms were restrained by the DFIX, RIGU, ISOR, and EADP instructions. The crystallographic data and X-ay diffraction experiments and structure refinement details are summarized in Table 1; selected bond lengths and bond angles are in Table 2.

Atom coordinates and other structural parameters of **II** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1873206; ccdc.cam.ac.uk/getstructures).

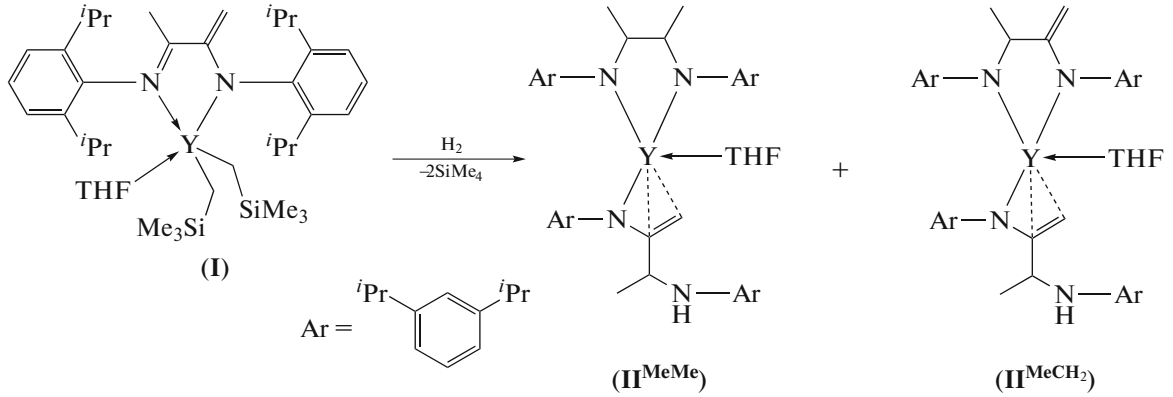
RESULTS AND DISCUSSION

The REM hydride complexes containing reactive Ln–H bonds are of interest for both fundamental research and application in the reactions of unsaturated substrates [31–37]. The sandwich and half-sandwich metallocene complexes were the first REM hydride derivatives [38–40]. The subsequent studies concerning REM hydride derivatives were focused on the synthesis of hydrides in a non-cyclopentadienyl ligand environment [40–43]. It was clearly demonstrated in some studies that the stability of REM hydride derivatives is largely determined by the nature of the ancillary ligand environment, whose variation can serve for modulating the reactivity of Ln–H bonds.

The most popular synthetic method for the preparation of REM hydride complexes is the σ-bond metathesis between the appropriate alkyl complex and

molecular hydrogen or phenylsilane. In order to prepare yttrium dihydride derivative stabilized by the amide-imine ligand based on diazabutadiene, we studied the reactions of bis(alkyl) complex **I** with molecular hydrogen and $PhSiH_3$.

Complex **I** was found to readily react with molecular hydrogen in hexane at room temperature ($P(H_2)$ = 2 atm, 6 days) (Scheme 2) to give a finely crystalline yellow powder. Recrystallization of the solid products from a THF–hexane mixture (1 : 1) by slow diffusion of hexane into a THF solution of the complex furnished greenish-yellow crystals in a 38% yield based on the starting amount of **I** (Scheme 2). The obtained crystals were readily soluble in THF and pyridine, sparingly soluble in toluene, insoluble in hexane, and sensitive to oxygen and air moisture.



Scheme 2.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **II**

Bond	$\mathbf{II}^{MeMe}$	$\mathbf{II}^{MeCH_2}$
	d, Å	
Y(1)–N(1)	2.191(3)	
Y(1)–N(2)	2.209(3)	
N(1)–C(1)	1.467(5)	
N(2)–C(2)	1.43(2)	1.49(2)
C(1)–C(2)	1.501(8)	1.519(8)
C(1)–C(3)	1.367(8)	1.533(8)
C(2)–C(4)	1.525(9)	1.528(9)
Y(1)–N(3)	2.301(3)	
Y(1)–C(29)	2.828(4)	
Y(1)–C(31)	2.749(5)	
Y(1)–O(1)	2.363(3)	
Angle	ω, deg	
N(1)Y(1)N(2)	77.8(2)	
N(1)Y(1)O(1)	103.7(2)	
N(2)Y(1)O(1)	103.9(2)	
O(1)Y(1)N(3)	117.4(2)	
N(1)C(1)C(2)	114.0(5)	114.1(5)
N(1)C(1)C(3)	119.5(8)	114.0(8)
C(2)C(1)C(3)	126.4(9)	102.5(8)
N(2)C(2)C(1)	116.1(7)	111.4(7)
N(2)C(2)C(4)	117(2)	111(2)
C(4)C(2)C(1)	116(2)	109(2)

According to X-ray diffraction data, the independent part of the unit cell of a single crystalline sample of product **II** contains two molecules of two different Y complexes disordered in 50 : 50% ratio and superimposed onto each other: {[ArNCH(Me)CH(Me)NAr]Y[ArNC(=CH_2)CH(Me)N(H)Ar](THF)} ($\mathbf{II}^{MeMe}$; Ar = C_6H_3-*iso*-Pr_2-2,6; Fig. 1a) and {[ArNCH(Me)C(=CH_2)NAr]Y[ArNC(=CH_2)CH(Me)N(H)Ar](THF)} ($\mathbf{II}^{MeCH_2}$; Ar = C_6H_3-*iso*-Pr_2-2,6; Fig. 1b). Compounds $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ differ by substituents at the carbon atoms in the diamide ligand: [ArN–CH(Me)–CH(Me)–NAr] or [ArN–CH(Me)–C(=CH_2)–NAr], respectively. Compounds $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ are formed upon hydrogenolysis of Y–C bonds resulting in intermediate hydride complexes as well as hydrogenation of C=C and C=N bond lengths of the amide-imine ligand and redistribution of N-containing ligands. Unfortunately, other yttrium-containing products could not be isolated from the reaction mixture.

Despite the presence of two different compounds (in approximately equal amounts) in the single crystalline sample of the reaction product, the ^{1}H NMR spectrum of the finely crystalline powder **II** (C_5D_5N, 293 K) shows signals for complex $\mathbf{II}^{MeMe}$, while the content of complex $\mathbf{II}^{MeCH_2}$ is low (<5%). Apparently, $\mathbf{II}^{MeMe}$ containing a diamide ligand with fully hydrogenated C=N and C=C bonds is the major reaction product, whereas $\mathbf{II}^{MeCH_2}$ is a minor product.

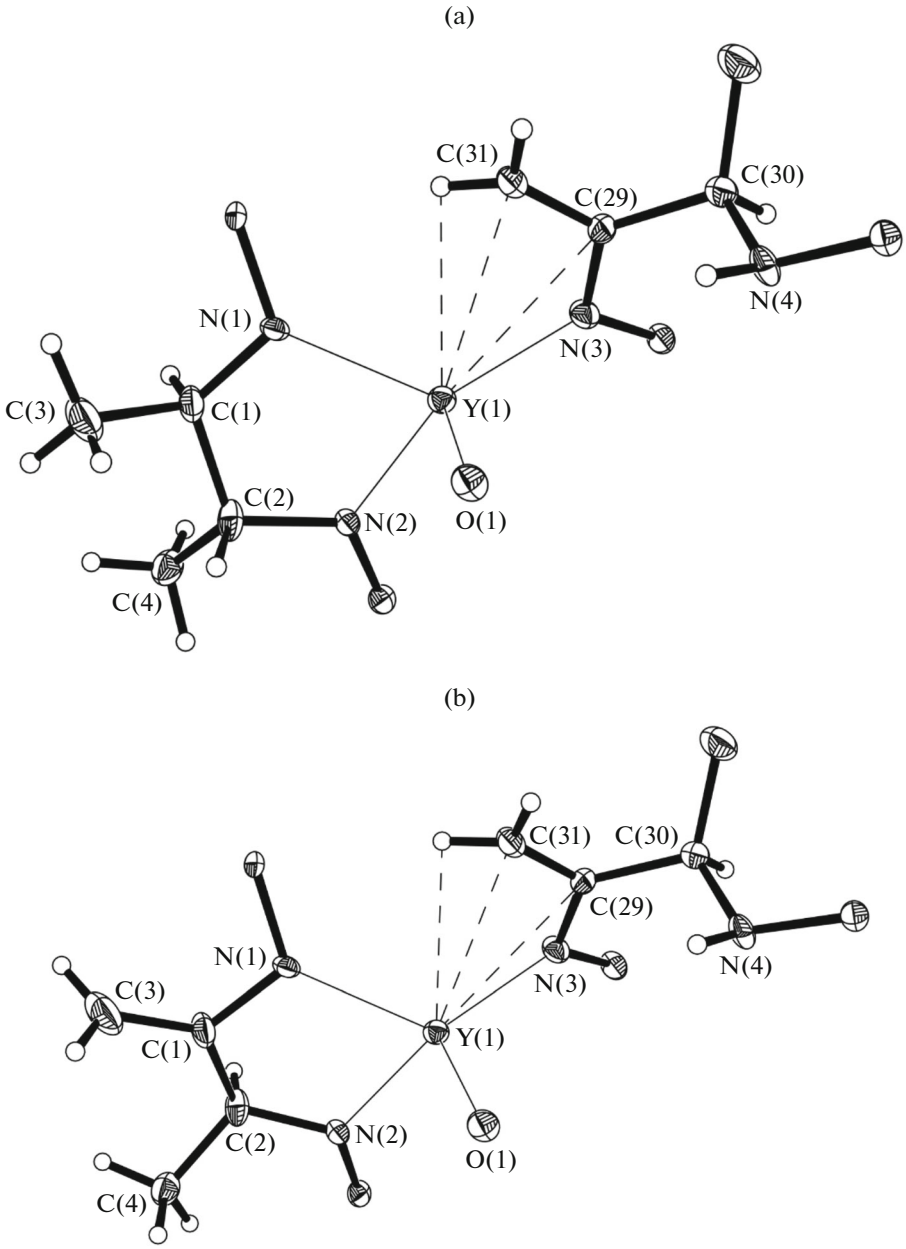


Fig. 1. Molecular structure of complex (a) $\mathbf{II}^{\mathbf{MeMe}}$ and (b) $\mathbf{II}^{\mathbf{MeCH_2}}$. The thermal ellipsoids are given at 30% probability level. 2,6-Diisopropylphenyl substituents and THF carbon atoms are omitted.

The molecular structures of compounds $\mathbf{II}^{\mathbf{MeMe}}$ and $\mathbf{II}^{\mathbf{MeCH_2}}$ are presented in Fig. 1. According to X-ray diffraction data, $\mathbf{II}^{\mathbf{MeMe}}$ and $\mathbf{II}^{\mathbf{MeCH_2}}$ crystallize in space group $P\bar{1}$ (Table 1). Both compounds are monomeric and contain monoanionic ene-amide-amine ligand $[ArN{-}C(=CH_2){-}CH(Me){-}N(H)Ar]^-$ coordinated to yttrium via one anilide nitrogen atom and the $C{=}CH_2$ double bond, giving rise to η^3-aza-allyl coordination mode. The ene-amide-amine ligand $[ArN{-}C(=CH_2){-}CH(Me){-}N(H)Ar]^-$ is apparently formed upon hydrogenation of the C=N bond in the initial complex **I**. Meanwhile, the Y–N bond cleavage induced by H_2 gives the amino group, which is not involved in the metal–ligand interaction. Furthermore, yttrium ion in both compounds is linked to the dianionic diamide ligand, which also results from hydrogenation of the skeleton of the initial amide-imine ligand $[ArN{-}C(=CH_2){-}C(Me){=}NAr]$. However, in $\mathbf{II}^{\mathbf{MeMe}}$, the C=N and C=C bonds of the initial moiety are hydrogenated to $[N(Ar){-}C(H)Me{-}C(H)Me{-}N(Ar)]^{2-}$, whereas in $\mathbf{II}^{\mathbf{MeCH_2}}$,

the C=C bond of the $[ArN{-}C(=CH_2){-}C(H)Me{-}NAr]^{2-}$ moiety remains intact. Also, the yttrium ion in both compounds is coordinated to one THF molecule.

The aza-allyl coordination mode is untypical of REM complexes; however, there are reported examples of formation of aza-allyl complexes via the addition of either ketimines or nitriles to the Ln–C σ-bonds [44, 45]. Comparison of the Y–N and Y–C distances in the $YN{-}C{=}CH_2$ moiety with the previously known values unambiguously attests to the aza-allyl coordination mode. The Y–N bond length between the yttrium and nitrogen atoms of the η^3-coordinated ene-amide-amine ligand in complexes $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ is 2.299(2) Å, which is longer than the usual Y–N covalent bond lengths in metallacyclic ene-diamide (2.167(3)–2.256(2) Å) [8, 9, 16, 22, 23, 25] and diamide (2.149(3)–2.219(4) Å) derivatives [46, 47], but is comparable with the values detected in aza-allyl yttrium derivatives (2.295(6)–2.414(3) Å) [44, 45]. The short distances between the yttrium and carbon atoms of the $N{-}C{-}CH_2$ moiety of the ene-amide-imine ligand in $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ (Y(1)–C(31), 2.749(5); Y(1)–C(29), 2.828(4) Å) are also in line with the values found in the aza-allyl derivatives (2.613(6)–2.927(8) Å) [44, 45]. Negative charge delocalization over the aza-allyl $N{-}C{-}CH_2$ moiety results in C–N bond shortening (C(29)–N(3), 1.371(5) Å) and $C{=}CH_2$ bond elongation (C(29)–C(31), 1.355(4) Å) in comparison with the standard single C–N (1.469 Å) and double C=C (1.322 Å) bond lengths [48].

The second ligand coordinated to yttrium ions in $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ according to the κ^2-N,N mode is a dianionic diamide species. The Y–N distances in $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ are 2.191(3) and 2.209(3) Å, which corresponds to Y–N covalent bond length [8, 9, 16, 22, 23, 25, 46, 47]. The dianionic diamide ligands in complexes $\mathbf{II}^{MeMe}$ and $\mathbf{II}^{MeCH_2}$ are different. The molecule of $\mathbf{II}^{MeMe}$ contains the $[ArN{-}CH(Me){-}CH(Me){-}NAr]^{2-}$ ligand in which the multiple C=N and $C{=}CH_2$ bonds have been hydrogenated to single bonds (CH–N, 1.467(5) and 1.492(12); $CH{-}CH_3$, 1.525(9) and 1.533(8) Å). The methyl groups at the central carbon atoms point to different directions relative to the NCCN moiety. Molecule $\mathbf{II}^{MeCH_2}$ contains the $[ArN{-}C(=CH_2){-}CH(Me){-}NAr]^{2-}$ ligand in which only C=N bond has been hydrogenated (C(1)–N(1), 1.467(5) Å), whereas the double $C{=}CH_2$ bond remains intact (C(1)–C(3), 1.367(8) Å).

The ^{1}H NMR spectrum of the finely crystalline reaction product recorded in pyridine-d_5 exhibits signals for $\mathbf{II}^{MeMe}$. The methyl protons of the isopropyl groups and the protons of methyl substituents of the NCCN moiety of $\mathbf{II}^{MeMe}$ are manifested in the ^{1}H NMR spectrum as overlapping doublets in the range of 1.05 to 1.30 ppm. The methine protons of the isopropyl groups give rise to four septets. Two of them have chemical shifts of 2.82 and 2.90 ppm ($^3J_{HH}$ = 6.8 Hz), while the other two overlap with the signal corresponding to the THF α-CH_2 protons (3.60 ppm). The methine protons of the ligand NCCN moiety give rise to a complex multiplet between 3.51 and 3.68 ppm, which also overlaps with the α-CH_2 proton signals of the coordinated THF molecule. The signals with chemical shifts of 3.87 and 4.37 ppm correspond to diastereotopic methylene protons of the aza-allylic moiety. The aromatic protons occur as a set of signals at 6.89–7.35 ppm.

The reactions of REM alkyl derivatives with $PhSiH_3$ are also widely used as a synthetic approach to hydrides [40, 41]. The reaction of **I** with 2 molar equiv. of $PhSiH_3$ in hexane at 0°C affords viscous oily products. Unfortunately, all our attempts to isolate pure compounds from the reaction mixture failed. Conducting the reaction between complex **I** and 2 molar equiv. of $PhSiH_3$ in benzene-d^6 with NMR monitoring proved that the reaction had occurred. Within 1 h after the sample preparation, the ^{1}H NMR spectrum of the reaction mixture exhibited no signals corresponding to yttrium-bonded alkyl groups, but showed the appearance of the expected amount of the Y–C σ-bond metathesis product, $PhSiH_2CH_2SiMe_3$. However, no signals for hydride ligands attached to yttrium appeared.

Thus, it was found that the reaction of yttrium bis(alkyl) complex **I** containing an amide-imine ligand based on diazabutadiene with molecular hydrogen is accompanied by hydrogenolysis of Y–C bonds and hydrogenation of the C=C and C=N bonds of the amide-imine ligand. The reaction give yttrium complexes containing a new ene-amide-amine ligand ($[ArNC(=CH_2)CH(Me)N(H)Ar]^-$) and dianionic diamide ($[ArNCH(Me)CH(Me)NAr]^{2-}$ or $[ArNCH(Me)C(=CH_2)NAr]^{2-}$) ligands.

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