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Highly basic alkyl-substituted bis(benzhydryl) Ca^{II} and Yb^{II} complexes with β-CH–M agostic interactions

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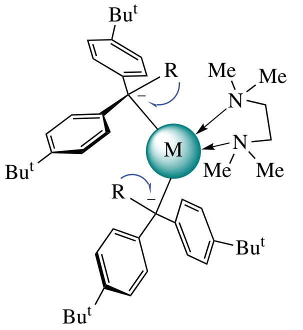
The reaction between potassium derivative $\{[(4\text{-Bu}^tC_6H_4)_2CH]^-K^+\}_n$ and alkyl iodides gives new 1,1-bis(4-*tert*-butylphenyl)alkanes which can be deprotonated with Bu^nNa to produce species $[(4\text{-Bu}^tC_6H_4)_2CR]^-Na^+$ (R = Me, Bu^i). The salt metathesis of the latter with base-free CaI_2 or YbI_2 affords novel bis(hydrocarbyl) complexes $[(4\text{-Bu}^tC_6H_4)_2CR]_2M(TMEDA)$ (M = Ca, R = Me; M = Yb, R = Bu^i). The hyperconjugation of the central carbanion with alkyl groups pronouncedly enhances the basic properties of the compounds which would perform CH bond activation in toluene and thiophene, in distinction to the related 'non-alkylated' analogues with $(4\text{-Bu}^tC_6H_4)_2CH^-$ ligand.

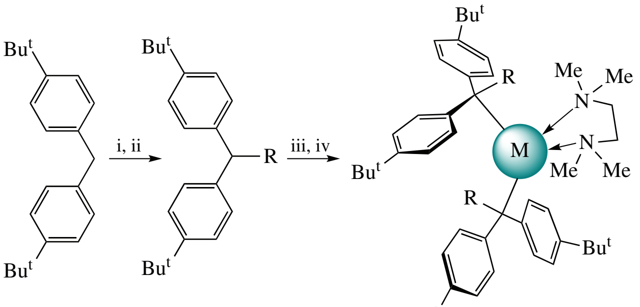


Highly-basic bis(hydrocarbyl) complexes
M = Yb^{II}, Ca^{II}
R = Me, Bu^i

Keywords: rare-earth metals, alkaline earth metals, calcium complexes, ytterbium complexes, alkyl ligands, agostic interactions, CH bond activation.

Highly reactive hydrocarbyl derivatives of large and electropositive M^{II} rare- and heavy alkaline-earth metals despite their powerful potential in numerous catalytic applications[1] still remain poorly explored.[2] The presence of highly reactive M–C bonds which readily undergo insertions into multiple C=C and C=E bonds,[3] σ-bond metathesis[4] and enable activation of normally inert CH-bonds[5] provides unique reactivity of these complexes and makes them exciting objects of research. However, the development of this field is slowed down by the extremely high air-sensitivity of the complexes as well as by the synthetic problems associated with the difficulties in stabilization of the coordination sphere of large metal ions[6] prone to ligand redistribution and β-hydrogen elimination or β-hydrogen abstraction of hydrocarbyl ligands.[7] Rational selection of the sterically demanding silyl-[8] and aryl-substituted methanide ligands[9] lacking β-hydrogen atoms allowed one to expand significantly the family of M^{II} alkyl complexes.[2] Recently the synthesis of extremely reactive methyl ytterbium(II)[10] and calcium(II)[11] complexes was reported. Scarce Ca^{II} species with hydrocarbyl fragments containing hydrogen atoms[1(*e*),12] in β-position to metallocentre were obtained by addition of calcium hydrides at C=C bonds.[12] However, no Yb^{II} analogues are known so far. Successful application of sterically demanding benzhydryl anion $[(4\text{-Bu}^tC_6H_4)_2CH]^-$ in Ln^{II}, Ln^{III} and Ca^{II} chemistry made it possible to obtain isolable thermally stable hydrocarbyl complexes.[13] Cationic benzhydryl Ln^{III} complexes proved to be highly efficient, regio- and chemoselective catalysts for hydroarylation and hydrobenzylation of C=C bonds of a variety of substrates with substituted pyridines.[14] Herein, we report on the synthesis, structures and reactivity of Yb^{II} and Ca^{II} complexes with highly basic carbanions of type $[(4\text{-Bu}^tC_6H_4)_2C^-R]_2M^{2+}(TMEDA)$ (M = Ca, Yb).

1,1-Bis(4-*tert*-butylphenyl)ethane **1a** and 1,1-bis(4-*tert*-butylphenyl)-4-methylbutane **1b** were synthesized by nucleophilic substitution reaction of $\{[(4\text{-Bu}^tC_6H_4)_2CH]^-K\}_n$ with the appropriate alkyl iodides (Scheme 1). After flash chromatography on silica gel, hydrocarbons **1a**,**b** were isolated in 82–90% yields. Deprotonation of these diarylmethanes **1a**,**b** with Bu^nNa[15] (24 h for **1a** and 100 h for **1b**) and subsequent salt metathesis of the resulting $[(4\text{-Bu}^tC_6H_4)_2CR]^-Na^+$ with base-free MI_2 (2 : 1 molar ratio, TMEDA–PhH) allowed for the preparation of $[(4\text{-Bu}^tC_6H_4)_2CMe]_2Ca(TMEDA)$ **2a** and $[(4\text{-Bu}^tC_6H_4)_2CBu^i]_2Yb(TMEDA)$ **2b** as orange and bloody-red



1a,**b**
a R = Me, 82%
b R = Bu^i, 90%

2a,**b**
a M = Ca, R = Me, 53%
b M = Yb, R = Bu^i, 85%

Scheme 1 *Reagents and conditions*: i, Bu^nLi, Bu^tOK, hexane, 0 → 20 °C; ii, RI, THF, 0 °C; iii, Bu^nNa, TMEDA, hexane, room temperature, 24–100 h; iv, 1/2 MI_2, TMEDA, PhH, room temperature.

crystals, respectively (see Scheme 1). The moderate yield of **2a** (53%) can be explained by its high solubility in benzene from which its crystallization was performed. Complexes **2a**,**b** are non-pyrophoric, highly air- and moisture-sensitive compounds. Their solutions in benzene and aliphatic hydrocarbons are stable at room temperature.

In the $^{13}C\{^1H\}$ NMR spectrum of **2a**, the signal at 60.9 ppm corresponds to the carbon atom bonded to Ca^{II}. It is significantly shifted upfield in comparison to those in the related Ca^{II} complexes [dipp-NacNac]Ca(CPh$_2$Me)(THF) (88.5 ppm)[12(*a*)] and [(Tp$^{Ad,Pr^i}$)Ca{CPh$_2$Me}] (72.01 ppm).[12(*c*)] The chemical shift of the central carbon in the $^{13}C\{^1H\}$ NMR spectrum of **2b** (71.2 ppm), surprisingly, completely coincides with that for the bis(benzhydryl) complex [(4-Bu^{t}C$_6$H$_4$)$_2$CH]$_2$Yb(TMEDA).[13(*a*)] The 2D ^{171}Yb–^{1}H NMR long-range correlation of **2b** revealed that the ^{171}Yb chemical shift extracted from the 2D spectrum (329 ppm) proved to be noticeably shifted to upfield region, compared to the values previously published for Yb^{II} alkyl complexes.[8(*a*),(*b*),(*g*),13] It is noteworthy that intensive cross-peaks are observed for the CH$_2$ protons and the coordinated TMEDA ligand. Due to the parameters of the experiment used, this should mean that s-orbitals are significantly involved into the coordination bond formation, or the mechanism of spin–spin interaction is other than Fermi-contact in this case. These interactions can be regarded as β-agostic,[16,17] however no cross-peaks of ytterbium with protons for the CHMe$_2$ groups corresponding to γ- and δ-CH–Yb agostic interactions were detected.

The molecular structures of complexes **2a**,**b** (Figures 1, 2) were determined by X-ray diffraction analysis.[†] X-ray data revealed that the coordination environment of the Yb^{II} ion in **2b** consists of two isobutyl-substituted benzhydryl ligands and a TMEDA molecule (Figure 1).

The benzhydryl ligands in **2b** are bound to the metal atom *via* central carbon atom; however, their coordination modes are somewhat different. In contrast to the previously published complex [(4-Bu^{t}C$_6$H$_4$)$_2$CH]$_2$Yb(TMEDA)[13(*a*)] featuring η^3-interaction of both benzhydryl ligands with the metal ion, in compound **2b** the increased steric demand of the ligands results in realization of η^3-mode only for one ligand [Yb–C(Bu^i): 2.638(3) Å; Yb–C$_{ipso}$: 2.845(3) Å; Yb–C$_{ortho}$: 2.817(3) Å]. The second one is η^2-coordinated and demonstrates a short contact only with one *ipso* aryl carbon atom [Yb–C(Bu^i): 2.593(3) Å; Yb–C$_{ipso}$: 2.884(3) Å]. The Yb–C bond distances in **2b** and [(4-Bu^{t}C$_6$H$_4$)$_2$CH]$_2$Yb(TMEDA) have similar values. The C–H bond length in the methylene group involved into the interaction with Yb^{II} is 0.88(4) Å and the Yb···H distance is 2.63(3) Å. Both ligands in **2b** are strongly distorted: the dihedral angles between the benzene planes are 41.4(2) and 46.9(2)°. The Yb–N bonds [2.570(2), 2.596(3) Å] are comparable with those in four-coordinate Yb^{II} complexes [(4-Bu^{t}C$_6$H$_4$)$_2$CH]$_2$Yb(TMEDA)[13(*a*)] and (Bu$^t_4$Carb)Yb[(4-Bu^{t}C$_6$H$_4$)$_2$CH](TMEDA)[13(*b*)] [2.519(2)–2.617(3) Å].

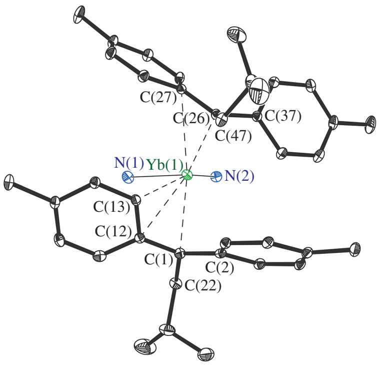


Figure 1 Molecular structure of complex **2b**. Thermal ellipsoids are given at 30% probability level. Methyl and methylene groups of *tert*-butyl substituents and TMEDA, and all hydrogen atoms are omitted for clarity.

The single crystal X-ray diffraction data obtained for **2a** provide confidence in the molecular and crystal structure of this compound (Figure 2), but do not allow one to discuss in details its geometric parameters.

Complexes **2a**,**b** demonstrate high thermal stability: no decomposition was observed after heating at 70 °C for 48 h (C$_6$D$_6$, ^{1}H NMR-control). However, raising the temperature to 100 °C leads to decomposition with a half-life of 14 and 12 h,

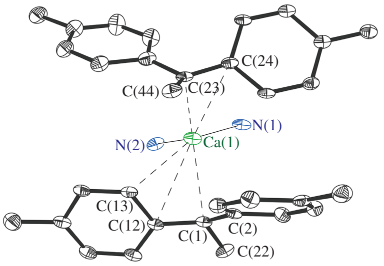


Figure 2 Molecular structure of complex **2a**. Thermal ellipsoids are given at 30% probability level. Methyl and methylene groups of *tert*-butyl substituents and TMEDA, and all hydrogen atoms are omitted for clarity.

[†] *Crystal data for* **2a**. C$_{50}$H$_{74}$CaN$_2$ · 1/4 C$_6$H$_6$, $M = 762.71$, space group $P\bar{1}$, $T = 120$ K, $a = 17.737(6)$, $b = 18.065(5)$ and $c = 31.270(10)$ Å, $\alpha = 99.577(9)°$, $\beta = 101.372(7)°$, $\gamma = 91.142(8)°$, $V = 9671(5)$ Å^3, $Z = 8$, $d_{calc} = 1.048$ g cm^{-3}, $F_{000} = 3348$. Colourless needle-shaped single crystal with dimensions 0.15 × 0.01 × 0.01 mm was selected and intensities of 110551 reflections were measured using Bruker APEXII DUO CCD diffractometer (ω-scans technique, MoK$_\alpha$-radiation, $\lambda = 0.71073$ Å, $\mu = 0.163$ mm^{-1}, $2\theta_{max} = 50.06°$). After merging of equivalents and absorption correction, 33746 independent reflections ($R_{int} = 0.8047$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.1741$ [6442 reflections with $I > 2\sigma(I)$], $wR_2 = 0.2677$ (all reflections), $S = 0.905$, largest diff. peak and hole are 0.52 and –0.44 e Å^{-3}, respectively. High R-factors result from the best available crystals being twinned, small and, hence, of an extremely low reflective power; however, the quality of the obtained dataset was still enough to unambiguously establish the crystal and molecular structure of **2a**.

Crystal data for **2b**. C$_{56}$H$_{86}$N$_2$Yb, $M = 960.30$, space group $Fdd2$, $T = 100$ K, $a = 34.9243(15)$, $b = 50.360(2)$ and $c = 12.0265(5)$ Å, $V = 21152.1(15)$ Å^3, $Z = 16$, $d_{calc} = 1.206$ g cm^{-3}, $F_{000} = 8096$. Brown prism-shaped single crystal with dimensions 0.65 × 0.42 × 0.28 mm was selected and intensities of 82179 reflections were measured using Bruker D8 Quest diffractometer (ω-scans technique, MoK$_\alpha$-radiation, $\lambda = 0.71073$ Å, $\mu = 1.803$ mm^{-1}, $2\theta_{max} = 61.01°$). After merging of equivalents and absorption correction, 16071 independent reflections ($R_{int} = 0.0316$) were used for the structure solution and refinement. Final R factors: $R_1 = 0.0220$ [15093 reflections with $I > 2\sigma(I)$], $wR_2 = 0.0518$ (all reflections), $S = 1.047$, Flack parameter = 0.012(2), largest diff. peak and hole are 1.53 and –0.80 e Å^{-3}, respectively.

The intensity data for **2a**,**b** were integrated by APEX3[18] software package. SADABS[19] was used to absorption corrections. The structures were solved *via* intrinsic phasing algorithm and refined by full-matrix least squares on F^2 using SHELX[20] and Olex2.[21] All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. The H atoms were placed in the calculated positions and refined in the 'riding' model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms [$U(H)_{iso} = 1.5U_{eq}$ for methyl groups] except for H(3A), H(7A), H(13A), H(17A), H(28A), H(32A), H(38A) and H(42A) atoms in **2a** located from the difference Fourier synthesis of the electron density. All hydrogen atoms were refined isotropically.

CCDC 2055806 (**2a**) and 2055470 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

respectively. In the contrary to the prevailing opinion about the tendency of alkyl derivatives of lanthanides to undergo intramolecular β-elimination reactions,[7] no products with multiple bonds were detected in the reaction mixture. Instead, the parent hydrocarbons **1a**,**b** formed in quantitative yields. Highly likely, due to the high basicity of anions Ar_2CR^- (R = Me, Bu^i) the abstraction of a proton from the solvent or TMEDA takes place. To support this hypothesis, the reactions of complex **2b** with a 5-fold molar excess of toluene and thiophene (pK_a 43 and 42) which are prone to CH bond activation in benzylic and α-hetaryl positions were performed. The reactions lead to the rapid release of alkane, however all our trials to isolate and characterize the metal-containing products failed due to their low solubility.

In summary, new hydrocarbyl Yb^{II} and Ca^{II} complexes $[(4\text{-}Bu^tC_6H_4)_2CR]_2M(TMEDA)$ (M = Ca, R = Me; M = Yb, R = Bu^i) have been synthesized and characterized. Complex **2b** is the first example of a hydrocarbyl derivative featuring β-agostic interactions of Yb^{II} with the protons of the methylene group $Yb–C–CH_2$. Despite the presence of hydrogen atoms in the β-positions, the complexes are thermally stable up to 70 °C, while further raising the temperature leads to decomposition and the formation of the parent hydrocarbons. Complex **2b** when treated with toluene and thiophene readily undergoes Yb–C bond protolysis accompanied by the elimination of $(4\text{-}Bu^tC_6H_4)_2CHBu^i$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.017.

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