EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Bis(4-methylbenzoxalzol-2-yl)methanide in s-Block Metal Coordination

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201700501

Link to VoR: http://dx.doi.org/10.1002/ejic.201700501

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Bis(4-methylbenzoxazol-2-yl)methanide in s-Block Metal Coordination

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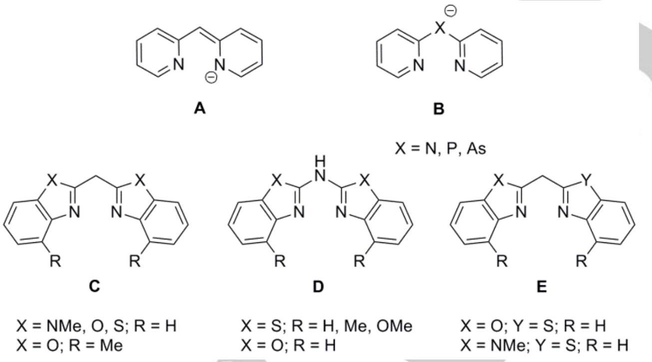
Abstract: On the basis of the bis(4-methylbenzoxazol-2-yl)methanide ligand three new alkali or alkaline earth metal compounds could be synthesized and their solid state structures are discussed in detail. On the way to new alkaline earth metal species a promising potassium precursor complex $[K\{(4\text{-MeNCOC}_6H_3)_2CH\}\ (\eta^5\text{-K}(4\text{-MeNCOC}_6H_3)_2\text{-CH})(THF)]_\infty$ (**2**) and a homoleptic magnesium $[Mg\{(4\text{-MeNCOC}_6H_3)_2\text{-CH}\}_2]$ (**3**) and calcium complex $[Ca\{(4\text{-MeNCOC}_6H_3)_2CH\}_2(THF)_2] \cdot THF$ (**4**) could be obtained.

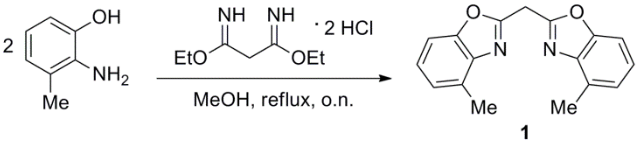
Introduction

Methylene bridged heteroaromatics like the bis(benzothiazol-2-yl)methane[1-2] ligand system and its related bis-benzoxazol and bis-benzimidazol derivatives are well established since many years. The latter were also extensively studied concerning the charge demands of the corresponding heteroaryl substituents in the derived deprotonated forms.[3-5] Despite the fact, that bisheterocyclo methane ligands could act as a suitable platform for transition metal complexes because of their ability to behave as both, neutral and monoanionic ligands[4], they attracted only little attention in the field of main group coordination chemistry in the last three decades.[6]



Scheme 1. β-diketiminate related methylene and amine bridged symmetric and asymmetric heteroaromatic ligand systems.

We embarked to extend the main group chemistry, fired by the ubiquitous β-diketiminate ligand[7-14] and its derivatives, to related bisheterocyclo methane and amine ligand systems. Starting from dipyridyl methane and methanides[15-18] (**A** in Scheme 1) we extended the ligand class to the dipyridyl amides and phosphanides (**B**).[19-24] More recently a variety of Al(III), Ga(III), In(III) and Li(I) complexes containing the bis(benzoxazol-2-yl)- and bis(benzothiazol-2-yl)methanide[25-26] (**C**) or -amide[27] (**D**) ligands could be obtained. Currently this chemistry could also be extended to bis(benzimidazol-2-yl)methanide (**C**) and asymmetric species (**E**) of the abovementioned ligand systems.[28]
In this context especially the bis(4-methylbenzoxazol-2-yl)methane ligand system **1** seems to be most suitable for the generation of low valent main group compounds. **1** is synthesized in a double cyclocondensation reaction starting from 3-methyl-2-aminophenol and ethyl-bisimidate dihydrochloride as the C_3-linker unit according to literature procedures (Scheme 2).[26, 29] Upon metallation its complexes show the least deviation of the metal cation from the chelating ligand plane, indicating the best charge distribution within the aromatic system, advantageous for example for subsequently reduced low oxidation state species. Furthermore the methyl substituents offer a certain amount of shielding to the metal cation while not hampering further substitution reactions.[26] Following up on those investigations we herein present our efforts to exceed this chemistry also to the early main group elements, in particular alkaline earth metals.



1

Scheme 2. Synthesis of bis(4-methylbenzoxazol-2-yl)methane **1**.

Results and Discussion

When **1** is added to a suspension of KH in THF (Scheme 3) the corresponding four-fold coordinated potassium precursor complex **2** can be obtained in good yields of 73%. Subsequent transmetallation (Scheme 4) gives the related alkaline earth metal complexes. **2** crystalizes in the orthorhombic space group P*bca* containing two molecules in the asymmetric unit. They form infinite zig-zag strands (see ESI). The central potassium cation shows a distorted tetrahedral coordination by two ring nitrogen atoms of a monoanionic methanide ligand, a THF molecule and an additional η^5-coordination to the central C_3N_2 plane of a second ligand (Figure 1).

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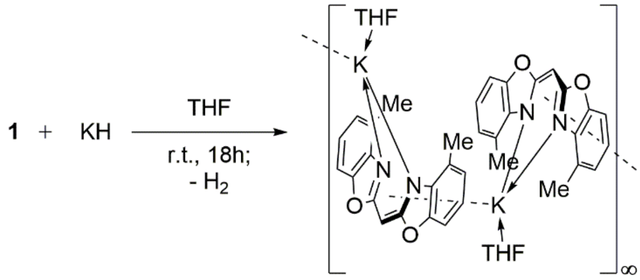


2

73%

Scheme 3. Synthesis of compound **2**.

In comparison to the free uncharged ligand **1**[26] (1.487 Å) the averaged C1-C$_{ipso}$ distance in **2** (1.393 Å) decreases due to the formation of a conjugated π-system and the change in hybridization of the bridging carbon atom from sp^3 to sp^2 upon deprotonation. The opposite is true for the averaged N-C$_{ipso}$ distance (1.332 Å) which gets longer in comparison to **1** (1.291 Å). Furthermore, to facilitate the additional η^5-coordination to a second ligand molecule the potassium atom shows a strong dislocation (1.33(3) Å) from the chelating C_3N_2 plane that fits quite well to a related homoleptic β-diketiminate barium complex [Ba(NacNac)$_2$][30] **IV**, exhibiting almost the same dislocation of 1.222(1) Å. Further structural features like an averaged M-N distance (2.795 Å (M = K) to 2.712 Å (M = Ba)) and an averaged N-M-N bite angle (67.6° to 68.89°) are also in good agreement. These observations are not surprising according to the similar effective ionic radii of both cations (K^+ = 137 pm to Ba^{2+} = 135 pm[31]). The η^6-coordination of the potassium atom in [(PMDETA)(THF)KPyCPh$_2$], (Py = pyridyl, PMDETA = ($Me_2NCH_2CH_2)_2NMe$) gives a slightly longer K-N distance of 2.809(5) Å.[32]

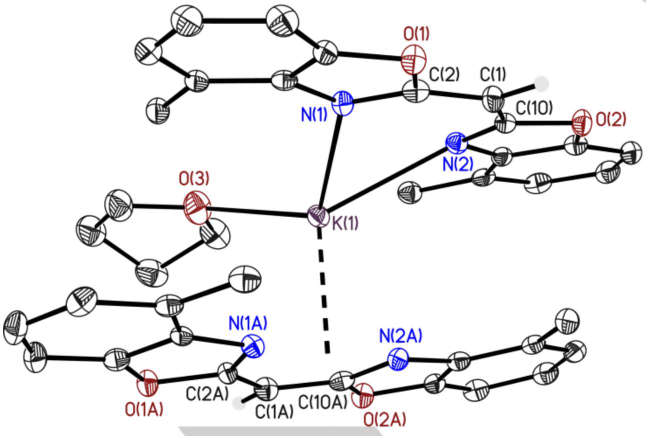
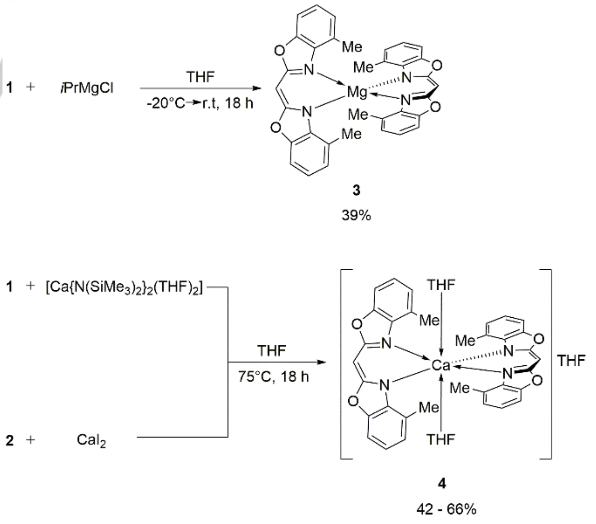


Figure 1. Excerpt of the polymeric structure of [K{(4-MeNCOC$_6$H$_3$)$_2$CH}(η^5-K(4-MeNCOC$_6$H$_3$)$_2$CH)(THF)]$_\infty$ (**2**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity except for those at the bridging methanide position. Structural data are given in Tables 1 and 2, respectively. Additional selected averaged bond lengths [Å]: C1-C$_{ipso}$ 1.394(3), N-C$_{ipso}$ 1.332(2), O-C$_{ipso}$ 1.395(2), K-O$_{THF}$ 2.672(2).

Table 1. Selected averaged bond lengths [Å] and angles [°] for **1**-**4** and related NacNac species **II**-**IV**.

	N–M	C$_{ipso}$–C1–C$_{ipso}$	N-M-N	M–plane distance
1	--	110.79(12)	--	--
2	2.795	125.0	67.6	1.33
3	2.057	123.3	94.0	0.07
4	2.472	124.9	78.6	1.34
II	2.111	--	92.97	0.907
III	2.379	--	83.09	1.291
IV	2.712	--	68.89	1.222

Contrary to expectations, adding ligand **1** to a solution of a slight excess of *i*PrMgCl in THF at -20 °C does not give the heteroleptic chloride complex of the parent ligand system as the product but the disubstituted homoleptic species **3** (Scheme 4). **3** crystalizes in the monoclinic space group P*2₁/n* with one molecule in the asymmetric unit (Figure 2). The central magnesium(II) cation adopts a slightly distorted tetrahedral coordination sphere resulting in the two planar ligand molecules arranged almost perfectly perpendicular (85.42(4) °). Additionally, in contrast to **2**, **4** and the reference NacNac structures **II**-**IV** the cation in **3** shares both C_3N_2 planes with only a marginal av. deviation of 0.07 Å. This is also reflected by the shortest averaged Mg-N distance of 2.057 Å.



Scheme 4. Synthesis of compounds **3** and **4**.

Comparing **3** to the related homoleptic structure [Mg(NacNac)$_2$][30] **II**, again similar structural features (Mg-N distance: 2.0565 Å to 2.379 Å and N-Mg-N bite angle of 94.06 ° and 92.97 °) can be found. Interestingly, in the hexa coordinated [Mg{(pz*)$_3$C}$_2$] (pz*

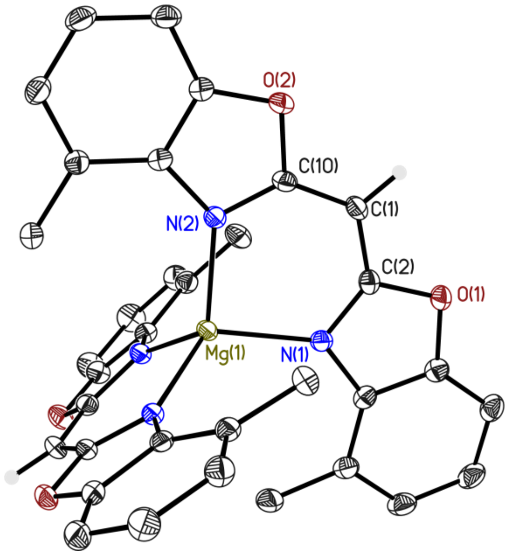


Figure 2. Molecular structure of [Mg{(4-MeNCOC$_6$H$_3$)$_2$CH}$_2$] (**3**). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity except for those at the bridging methanide position. Structural data are given in Tables 1 and 2, respectively. Additional selected averaged bond lengths [Å]: C1-C$_{ipso}$ 1.392(2), N-C$_{ipso}$ 1.341(2), O-C$_{ipso}$ 1.376(2).

= 3,5-dimethylpyrazolyl), the Mg-N bond path of 2.1973 Å is only slightly longer.[33]

The reactions of **1** with calcium hexamethyldisilazane, as well as of the potassium precursor complex **2** with CaI$_2$ beads, both give the homoleptic calcium compound **4** (Scheme 4). **4** contains one molecule per asymmetric unit and is depicted in Figure 3. The central calcium cation shows a distorted octahedral coordination made up from two ligands and two THF molecules. Steric crowding causes the average dislocation of 1.34 Å from the C$_3$N$_2$ plane. The two ligands show an almost perfect parallel arrangement with a twisting angle of only 7.25(9) °. The values for the Ca-N distance of 2.472 Å and the N-Ca-N bite angle of 78.6 ° are half way between those of compound **2** and **3**, because the effective ionic radius of Ca^{2+} of 100 pm is located between those of Mg^{2+} (72 pm) and K^{+} (137 pm). They are in good agreement with those found for a related homoleptic β-diketiminate compound [Ca(NacNac)$_2$] **III**. Some general trends for **2**-**4** can be deduced, predominantly caused by the increasing size of the cation: On the one hand the N-M distances and C$_{ipso}$–C1–C$_{ipso}$ angles are increasing while on the other hand the N-M-N bite angle is decreasing. In contrast, due to different coordination modes no such trend can be determined for the deviation of the metal ions from the C$_3$N$_2$ plane.

Compounds **2**-**4** were additionally characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, LIFDI-MS and elemental analysis. In the ^{1}H NMR spectra, for the aromatic protons all compounds display resonances within a range of 7.07 and 6.55 ppm. Counter-intuitively, in comparison to the chemical shift of 4.70 ppm[25] found for the methylene-bridging moiety in **1**, upon deprotonation this resonance experiences a slight up-field shift (4.65 ppm) in **2**. This observation is most likely due to the additionally present η^5-coordination of the potassium cation decreasing the net electronic deshielding per methylene bridge proton. As expected, upon deprotonation this signal experiences a significant down-field shift in **3** and **4** showing resonances of 5.05 and 5.07 ppm, respectively. Furthermore, at 3.62 and 1.77 ppm resonances of the attached THF molecules in **2** and **4** can be found. Interestingly, the chemical shift of the methyl groups of 2.41 ppm in **2** is in-between those of 2.62 and 1.91 ppm found in **3** and **4**. The ^{13}C NMR spectra of **2**-**4** revealed resonances of 57.0, 60.4 and 59.0 ppm, respectively for the bridging carbon atom.

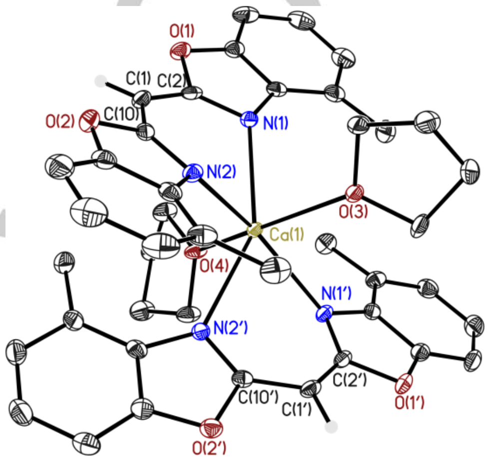


Figure 3. Molecular structure of [Ca{(4-MeNCOC$_6$H$_3$)$_2$CH}$_2$(THF)$_2$] · THF (**4**). Anisotropic displacement parameters are depicted at the 50% probability level. A co-crystallized THF molecule and hydrogen atoms are omitted for clarity except for those at the bridging methanide position. Structural data are given in Tables 1 and 2, respectively. Additional selected averaged bond lengths [Å]: C1-C$_{ipso}$ 1.388(3), N-C$_{ipso}$ 1.333(3), O-C$_{ipso}$ 1.390(2), Ca-O$_{THF}$ 2.386(2).

Conclusions

In this work the successful syntheses and solid-state structure determination of three metallated bis(4-methylbenzoxazol-2-yl)-methanides **2**–**4** could be presented. With the potassium complex **2** a promising precursor complex for subsequent transmetallation reactions could be introduced. Moreover, two new homoleptic alkaline earth metal complexes **3** and **4** could be obtained. Currently, ongoing efforts are made to synthesize more bulky bis(benzoxazol-2-yl)methane ligand systems bearing sterically demanding substituents at the four position to facilitate the formation of heteroleptic alkaline earth metal halide complexes for subsequent reduction to give the corresponding low oxidation state species, not yet realized in the current endeavor.

Experimental Section

Procedures: All manipulations were carried out under an inert argon atmosphere by using Schlenk techniques[34] or were handled in an argon dry box. All solvents used within metallation reactions were distilled from Na or K before use. The starting materials were purchased commercially and used as received if not stated otherwise. [Ca{N(SiMe$_3$)$_2$}$_2$] x 2 THF was synthesized according to literature procedures.[35] ^{1}H and ^{13}C spectroscopic data were recorded on a Bruker Avance 300 MHz spectrometer and referenced to the residual proton signal of the deuterated solvent (THF-d_8).[36] Deuterated solvents were dried over activated molecular sieve (3Å) and were additionally stored in an argon dry box. Elemental analyses (C, H and N) were carried out on a Vario EL3 at the Mikroanalytisches Labor, Institut für Anorganische Chemie, University of Göttingen. All LIFDI-MS spectra (70 eV) were recorded on a Jeol AccuTOF spectrometer.

[K{(4-MeNCOC$_6$H$_3$)$_2$CH}(η^5-K(4-MeNCOC$_6$H$_3$)$_2$CH) (THF)]$_\infty$ (**2**). KH (48.0 mg, 1.19 mmol, 1.10 eq.) was suspended in THF (10 mL) and **1** (300 mg, 1.08 mmol, 1.00 eq.) dissolved in THF (10 mL) was slowly drop wise added. A red suspension forms upon gas evolution. The mixture was left stirring at r.t. overnight. The resulting orange-brownish suspension was filtered via cannula and the solvent was removed under reduced pressure. The residue was washed with pentane (3 x 10 mL) and dried. For analysis the residue was recrystallized by slow evaporation of pentane into a sat. THF solution at r.t.. Colorless needle shaped crystals were obtained in a yield of 306 mg (788 µmol, 73%).

^{1}H NMR (300 MHz, [D$_8$]THF, r.t.): δ=6.85 (m, 2H, H7), 6.71 (m, 2H, H5), 6.60 (m, 2H, H6), 4.65 (s, 1H, H10), 3.62 (m, 4H, THF) 2.41 (s, 6H, Me), 1.77 (m, 4H, THF); ^{13}C NMR (75 MHz, [D$_8$]THF, r.t.): δ=170.3 (C2), 149.9 (C8), 146.5 (C3), 123.9 (C5), 122.5 (C4), 118.5 (C6), 105.6 (C7), 57.0 (C10), 17.5 (Me); LIFDI-MS: *m/z* (%): 316.1 (100) [*M–2THF*], 632.1 (40) 2[*M–2THF*], 671.1 (12) {2[*M–2THF*] + K$^+$}; elemental analysis calcd (%) for $C_{21}H_{21}KN_2O_3$: C 64.92, H 5.45, N 7.21; found: C 64.71, H 5.31, N 7.38.

[Mg{(4-MeNCOC$_6$H$_3$)$_2$CH}$_2$] (**3**). *i*PrMgCl (2 M in THF, 1.00 mL, 1.98 mmol, 1.11 eq.) was diluted in THF (10 mL) and cooled to -20 °C. **1** (500 mg, 1.80 mmol, 1.00 eq.) dissolved in THF (10 mL) was then slowly drop wise added. After completed addition the cooling bath was removed and the mixture was left stirring at r.t. overnight. The solvent was removed under reduced pressure and the residue was extracted with toluene (3 x 10 mL) and filtered via cannula. The volume of the toluene extract was reduced to a minimum and a formed precipitate was again dissolved by gentle heating. From this solution colorless prism shaped crystals were obtained at r.t. in a yield of 405 mg (702 µmol, 39%).

^{1}H NMR (300 MHz, [D$_8$]THF, r.t.): δ=7.07 (m, 4H, H7), 6.92 (m, 8H, H5 + H6), 5.05 (s, 2H, H10), 2.69 (s, 12H, Me); ^{13}C NMR (75 MHz, [D$_8$]THF, r.t.): δ=169.9 (C2), 149.1 (C8), 140.8 (C3), 125.6 (C5), 124.6 (C4), 121.6 (C6), 108.6 (C7), 60.4 (C10), 19.2 (Me); LIFDI-MS: *m/z* (%): 278.1 (20) [*(4-MeNCOC$_6$H$_3$)$_2$CH*], 578.1 (100) [*M*]; elemental analysis calcd (%) for $C_{34}H_{26}MgN_4O_4$: C 70.54, H 4.53, N 9.68; found: C 69.95, H 4.31, N 9.29.

[Ca{(4-MeNCOC$_6$H$_3$)$_2$CH}$_2$(THF)$_2$] x THF (**4**).

Method A: 2 (290 mg, 747 µmol, 1.00 eq.) and anhydrous CaI$_2$ beads (241 mg, 821 µmol, 1.10 eq.) were suspended in THF (15 mL). The suspension was heated under reflux at 75 °C overnight. The solvent was removed under reduced pressure. The residue was washed with pentane (2 x 10 mL) and extracted with toluene (3 x 10 mL). The solvent from the toluene extract was removed and the crude product was recrystallized by slow evaporation of pentane into a sat. THF solution at -30 °C. From this solution colorless prism shaped crystals were obtained in a yield of 255 mg (314 µmol, 42%).

Method B: Ca{N(SiMe$_3$)$_2$}$_2$ x 2 THF (200 mg, 396 µmol, 1.00 eq.) was suspended in THF (10 mL). Then **1** (110 mg, 396 µmol, 1.00 eq.) dissolved in THF (5 mL) was drop wise added. The mixture was left stirring at r.t. for 2 h and was then heated under reflux at 75 °C overnight. The formed suspension was filtered via cannula and the solvent removed under reduced pressure. Recrystallization following the above mentioned method yielded **4** in an amount of 212 mg (261 µmol, 66%).

^{1}H NMR (300 MHz, [D$_8$]THF, r.t.): δ=6.97 (m, 4H, H7), 6.73 (t, ^3J(H,H)=7.8 Hz, 4H, H6), 6.55 (m, 4H, H5), 5.07 (s, 2H, H10), 3.62 (m, 8H, THF), 1.91 (s, 12H, Me), 1.77 (m, 8H, THF); ^{13}C NMR (75 MHz, [D$_8$]THF, r.t.): δ=170.2 (C2), 149.6 (C8), 142.8 (C3), 125.4 (C5), 124.8 (C4), 121.3 (C6), 106.3 (C7), 59.0 (C10), 17.1 (Me); LIFDI-MS: *m/z* (%): 594.1 (100) [*M*]; elemental analysis calcd (%) for $C_{42}H_{42}CaN_4O_6$: C 68.27, H 5.73, N 7.58; found: C 67.73, H 5.51, N 7.69.

Crystallographic details

Shock cooled crystals were selected from a Schlenk flask under argon atmosphere using the X-TEMP2 device.[37-39] The data were collected on an IµS microfocus diffractometer.[40] All data were integrated with SAINT.[41] A multi-scan absorption correction (SADABS)[42] and a 3λ correction were applied.[43] The structures were solved by direct methods (SHELXT)[44] and refined on F^2 using the full-matrix least-squares methods of SHELXL[45] within the SHELXLE GUI.[46] More details about the crystallographic data and the refinement can be found in the supporting information. These data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data-request/cif.

Table 2. Crystal structure data for **2**-**4**.

	2	**3**	**4** · THF
Formula	$C_{21}H_{21}KN_2O_3$	$C_{34}H_{26}MgN_4O_4$	$C_{46}H_{50}CaN_4O_7$
MW, gmol^{-1}	388.50	578.90	810.98
CCDC no.	1536931	1536929	15369230
Space group	Pbca	P2$_1$/n	Pbca
a, Å	7.103(2)	11.336(2)	18.297(2)
b, Å	28.522(2)	15.002(2)	15.994(2)
c, Å	38.061(3)	16.777(2)	27.504(3)
β,°	90	93.10(2)	90
V, Å^3	7711.(2)	2849.0(7)	8048.8(16)
Z	16	4	8
Abs. coeff., mm^{-1}	0.299	0.110	0.214
Theta max, °	25.352	30.042	26.369
Refl. meas.	61122	58293	50606
Refl. uniq.	7074	8328	8215
R_{int}	0.0659	0.0466	0.0634
Data/restr./para.	7074/0/492	8328/0/392	8215/11/535
R_1 [I>2σ(I)][a]	0.0366	0.0398	0.0441
wR_2 (all)[b]	0.0891	0.1034	0.1230
$\Delta\rho_{fin}$, e Å^{-3}	0.234/-0.263	0.416/-0.301	0.599/-0.280

[a] $R1 = \frac{\sum \lVert F_o \rvert - \lvert F_c \rVert}{\sum \lvert F_o \rvert}$ [b] $wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$

Acknowledgements

Thanks to the Danish National Research Foundation (DNRF93) funded *Centre for Materials Crystallography* (CMC) for partial support and the federal state of Lower Saxony, Germany for providing a fellowship in the CaSuS PhD program.

Keywords: Organometallic synthesis, s-Block chemistry, heteroaromatic substituted methanides, X-ray

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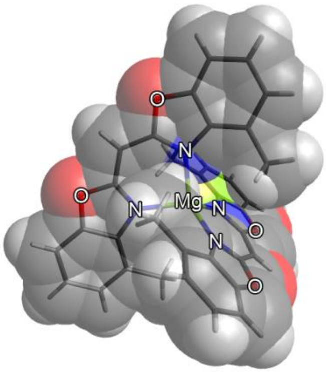
FULL PAPER

New s-Block Complexes derived from heteroaromatic substituted methanides! They are based on the versatile bis-(4-methylbenzoxazol-2-yl)methane ligand. Metallation of the bridging methylene moiety with Group 1 and 2 organometallics gives the *N*,*N*-chelating anions comprising further O-donor centres in the periphery of the complex. Structural features are compared to the omnipresent monoanionic NacNac ligand.



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Bis(4-methylbenzoxazol-2-yl)methanide in s-Block Metal Coordination