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Concept for Enhancement of the Stability of Calcium-Bound Pyrazolyl-Substituted Methanides

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Supporting Information

ABSTRACT: Metalation of bis(3-thiophen-2-ylpyrazol-1-yl)phenylmethane [**2**, which is accessible from the reaction of bis(3-thien-2-ylpyrazol-1-yl)methanone (**1**) with triphosgene] with [(thf)$_2$Ca{N(SiMe$_3$)$_2$}$_2$] in tetrahydrofuran and subsequent crystallization from a mixture of toluene and 1,2-dimethoxyethane yield [(dme)Ca{C(Pz$^{\text{th}}$)$_2$Ph}{N(SiMe$_3$)$_2$}] (**3**). The α,α-bis(3-thiophen-2-ylpyrazol-1-yl)benzyl ligand exhibits a $\kappa^2N,\kappa C$-coordination mode with a Ca−C σ-bond length of 262.8(2) pm. The crystalline compound is stable if air and moisture is strictly excluded; however, in solution; this calcium complex slowly degrades.

Scorpionate ligands have been introduced to coordination chemistry by the pioneering work of the Trofimenko group[1] and employed thereafter by many others.[2] These tridentate tris(pyrazolyl)borate ligands commonly bind facially to metal ions via the pyrazolyl bases. In this context, the isoelectronic tridentate tris(pyrazolyl)methanes and -methanides have attracted interest from numerous coordination chemists.[3] Recent developments focus on the behavior of such tridentate bases, where one pyrazolyl unit is substituted by another Lewis base, so-called heteroscorpionates.[4] The removal of one pyrazolyl moiety leads to bis(pyrazolyl)borates as well as to isoelectronic bis(pyrazolyl)methanes and -methanides.[5]

Tris(pyrazolyl)methanides commonly show a coordination chemistry similar to that of borate-based scorpionates. However, the heteroleptic cadmium derivative [Cd($\kappa^2N,\kappa C$-CPz$_3$)(κ^3N-CPz$^{\text{Me2}}_3$)] contained two scorpionate ligands with different binding modes.[6] In addition, Au$^{\text{I}}$ binds to the C atom of tris(3,5-dimethylpyrazolyl)methanide, whereas the homologous Cu and Ag atoms coordinate to the pyrazolyl bases.[7] In addition, the coordination mode of tris(pyrazolyl)methanides depends on the substitution pattern of the pyrazolyl rings. Alkyl substituents stabilize a κ^3N binding mode at alkaline-earth metals,[8] whereas aromatic groups in the 3 position such as phenyl[9] and thienyl[10] change the coordination to a $\kappa^2N,\kappa C$ mode with one noncoordinating pyrazolyl moiety. In heteroleptic calcium complexes, the alkyl-substituted tris(pyrazolyl)methanides also bind via all pyrazolyl bases.[3] The formation of a Ca−C bond initiates degradation of the tris(pyrazolyl)methanide anion, yielding calcium bis(pyrazolates) and tetrakis(pyrazolyl)ethene. This degradation reaction of the anion seems to be an intramolecular process with intermediately formed bis(pyrazolyl)carbene species bound to the alkaline-earth metal ion. Dimerization of this carbene yields tetrakis(pyrazolyl)ethene, which is a very poor ligand for s-block metal ions and, hence, is liberated.[10]

Several factors enable enhancement of the stability of calcium-bound tris(pyrazolyl)methanides (Scheme 1). Heteroleptic calcium complexes of the type (Pz$_3$C)CaX with only one pryrazolyl-substituted methanide should exhibit enhanced stability because the intramolecular release of tetrakis(pyrazolyl)ethene is impossible. Steric shielding by a bulky pseudohalide X and demanding substituents R in the 3 position of the pyrazolyl moieties prevent ligand scrambling known as Schlenk-type equilibrium and, hence, additionally stabilize this complex. In addition, coordination sites can be blocked by demanding coligands L such as bidentate 1,2-dimethoxyethane (DME) in order to complete a preferred (distorted) octahedral environment of calcium. Because of the fact that one pyrazolyl-substituted side arm is turned to the outside of the molecule without coordination to the cation, it can be replaced by another group, enabling charge delocalization and reduction of the nucleophilicity of the carbanion. For this purpose, phenyl groups seem to be ideal, and the resulting anion represents a bis(pyrazolyl)benzyl derivative. Benzylcalcium complexes as well as their substituted derivatives are well-known and have been studied by several research groups.[11−14] In these compounds, charge delocalization reduces the reactivity, and ether cleavage has not been observed; nevertheless, these organometallics are still reactive and represent, e.g., valuable styrene polymerization initiators.[12−14]

The ligand with the desired requirements is easily available via a two-step synthesis. Thienylpyrazole was reacted with triphosgene in tetrahydrofuran (THF) in the presence of triethylamine. Bis(3-thienylpyrazolyl)methanone (Pz$^{\text{th}}_2$C=O, **1**) was dissolved in THF and precipitated during the addition of pentane. The reaction of compound **1** with benzaldehyde after the addition of catalytic amounts of cobalt(II) chloride hexahydrate yielded bis(3-thiophen-2-ylpyrazol-1-yl)phenylmethane [HC(Ph)(Pz$^{\text{th}}$)$_2$, **2**]. This compound was metalated with stoichiometric amounts of [(thf)$_2$Ca{N(SiMe$_3$)$_2$}$_2$][15−17] and the resulting complex recrystallized from a mixture of toluene and DME, yielding yellow crystals of heteroleptic [(dme)Ca{C(Pz$^{\text{th}}$)$_2$Ph}{N(SiMe$_3$)$_2$}] (**3**) according to Scheme 2. Complex **3** is stable as a crystalline solid. However, in solution very slow degradation over several weeks is observed, yielding 1,2-diphenyl-1,2-bis(thienylpyrazolyl)ethene and thienylpyrazolates of calcium, whereas homoleptic complexes degrade within very few days.

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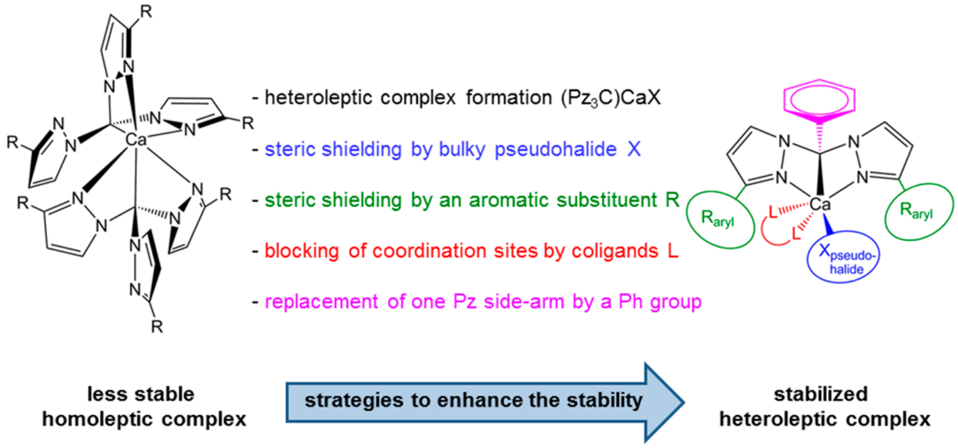
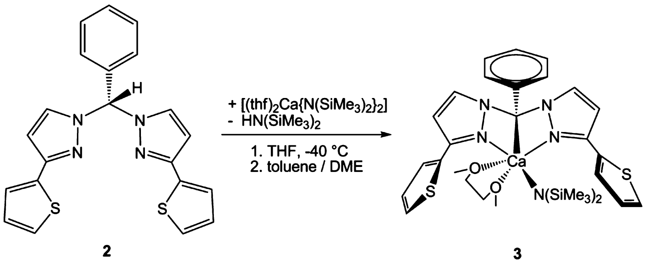
Scheme 1. Strategies (Middle) To Enhance the Stability of Calcium Complexes with $\kappa^2N,\kappa C$-Bound Bis(pyrazolyl)methanide Anions (See the Text), Leading to a Stabilized Heteroleptic Complex (Right)



Scheme 2. Synthesis of Heteroleptic 3



In the NMR spectra of **3** (see the Supporting Information, SI), two resonances at δ 0.01 and 0.05 (^{1}H NMR) and at δ 2.5 and 5.9 (^{13}C{^{1}H} NMR) are observed for the bis(trimethylsilyl)amide anion. This finding verifies the crowded environment of the Ca ion with a hindered rotation around the Ca–N bond. In addition, fast exchange processes via dissociation can be excluded as well.

The molecular structure of **3** is shown in Figure 1. The tridentate bis(thienylpyrazolyl)phenylmethanide anion binds in a facial manner to the hexacoordinate Ca atom. The bulky bis(trimethylsilyl)amido ligand and the bidentate dme molecule complete the distorted octahedral coordination sphere. The Ca1–C1 bond length of 262.8(2) pm resembles a characteristic value observed in other calcium-based organometallics[12−14,18−21] (see Table S1 in the SI).

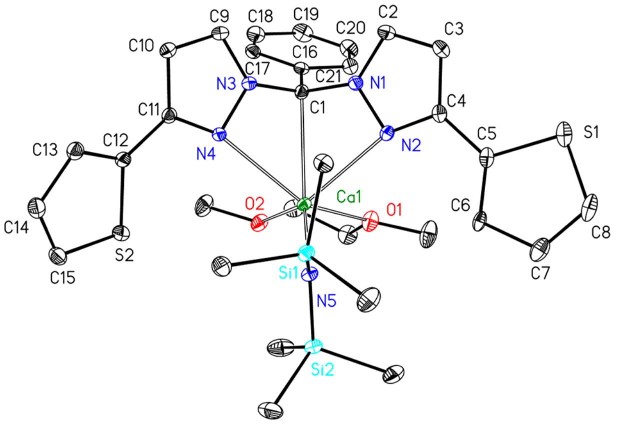


Figure 1. Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 30%; H atoms are omitted for clarity reasons.

Because of electrostatic attraction, the Ca1–N5 bond to the bis(trimethylsilyl)amido anion [231.7(1) pm] is significantly shorter than the bonds to the electroneutral pyrazolyl bases [251.4(1) and 254.6(1) pm]. As observed also for other highly ionic s-block metal bis(trimethylsilyl)amides, short N–Si bond lengths result from electrostatic attraction and hyperconjugation from the N-centered p_z(N) lone pair into σ^*(Si–C) bonds of the trimethylsilyl groups.[22] Steric requirements lead to significantly different proximal and distal Ca1–N5–Si2 and Ca1–N5–Si1 bond angles of 113.09(7)° and 122.02(7)°, respectively.

The α,α-bis(thienylpyrazolyl)phenylmethanide anion shows a slight charge delocalization and, hence, a shortened C1–C16 bond length of 145.1(2) pm (7 pm shorter than that in **2**). This rather small bond length between the α-C and *ipso*-C atoms represents a characteristic feature of Ca-bound benzyl anions regardless of the substitution pattern (Table S1 in the SI). Even bridging benzyl ligands display similar bond lengths despite the distorted tetrahedral environment of the α-C atom.[13] The yellow color of the crystals is typical for benzyl anions and is directly related to the extent of charge delocalization.[23]

Metalation of **2** with [(thf)$_2$Ca{N(SiMe$_3$)$_2$}$_2$] in THF yields the desired heteroleptic α,α-bis(3-thiophen-2-yl-pyrazol-1-yl)-benzylcalcium bis(trimethylsilyl)amide. Recrystallization from a solvent mixture of toluene and DME leads to crystalline yellow **3**. The solid material is stable under strict exclusion of air and moisture; however, this complex degrades once dissolved in common organic solvents, leading to the formation of 1,2-diphenyl-1,2-bis(3-thienylpyrazol-2-yl)ethene and calcium bis(3-thienylpyrazolate).

The $\kappa^2N,\kappa C$-coordination behavior of tris(pyrazolyl)-methanide ligands[9,10] and the bis(pyrazolyl)methanide ions of **3** toward Ca ions is very similar if aromatic groups are bound to the pyrazolyl rings. A phenyl substituent at the central C atom stabilizes this complex, leading to an α,α-bis(pyrazolyl)-substituted benzylcalcium derivative with Ca–C σ bonds, which exhibit characteristic bond lengths, as is also observed for "simpler" benzylcalcium derivatives. The anionic charge is partly delocalized into the aromatic rings, leading to a shortening of the C_α–C_{ipso} bond for all of these congeners.

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■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and NMR spectra of **1**−**3** and CIF files of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the following supplementary publications: CCDC 1038733 for **2** and CCDC 1038734 for **3**; copies of this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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Notes

The authors declare no competing financial interest.

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