

Syntheses and Structural Diversity of Group 2 and Group 12 Tris(pyrazolyl)methane and Zwitterionic Tris(pyrazolyl)methanide Compounds

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Reaction of $\text{HC}(\text{Me}_2\text{pz})_3$ with $\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2$ gave the zwitterionic amide complex $\text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiMe}_3)_2\}$ (**13**), containing a “free” pyramidal carbanion and a cationic $\{\text{Mg}-\text{N}(\text{SiMe}_3)_2\}^+$ moiety. Reaction of the less bulky amide $\text{Mg}\{\text{N}(\text{SiHMe}_2)_2\}_2$ with $\text{RC}(\text{Me}_2\text{pz})_3$ ($\text{R} = \text{H}$ or D) gave the four-coordinate adducts $\text{Mg}\{\kappa^2\text{N}-\text{RC}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiHMe}_2)_2\}_2$ ($\text{R} = \text{H}$ (**15**) or D (**15-d**)). A similar complex, $\text{Mg}\{\kappa^2\text{N}-\text{HC}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**14**), was observed by NMR spectroscopy at low temperatures. On warming, **15**, **15-d**, and **14** eliminated $\text{RN}(\text{SiR}'\text{Me}_2)_2$ ($\text{R}' = \text{H}$ or Me) to form $\text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiR}'\text{Me}_2)_2\}$ (**13** or **17**). The reactions of **15** and **15-d** followed first-order kinetics with a primary kinetic isotope effect ($k(\text{H})/k(\text{D})$) of 1.91(2). Reaction of **13** or **17** with a further equivalent of $\text{HC}(\text{Me}_2\text{pz})_3$ gave the homoleptic sandwich complex $\text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}_2$ (previously reported), containing two free carbanions and a dicationic metal center. The reaction of **17** with an excess of $\text{RC}(\text{Me}_2\text{pz})_3$ ($\text{R} = \text{H}$ or D) followed pseudo-first-order kinetics with a primary kinetic isotope effect of 1.51(4). The corresponding reactions of $\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$ with 1 or 2 equiv of $\text{HC}(\text{Me}_2\text{pz})_3$ gave $\text{Ca}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})$ (**18**) or $\text{Ca}\{\text{C}(\text{Me}_2\text{pz})_3\}_2$ (**19**). In contrast, $\text{Zn}\{\text{N}(\text{SiMe}_3)_2\}_2$ was effectively unreactive toward $\text{HC}(\text{Me}_2\text{pz})_3$. However, reaction of ZnCl_2 with 1 or 2 equiv of $\text{Li}\{\text{C}(\text{Me}_2\text{pz})_3\}(\text{THF})$ afforded $\text{Zn}\{\text{C}(\text{Me}_2\text{pz})_3\}\text{Cl}$ (**20**) or $\text{Zn}\{\text{C}(\text{Me}_2\text{pz})_3\}_2$ (**23**), respectively. Subsequent reaction of **20** with $\text{NaN}(\text{SiMe}_3)_2$ or $\text{LiN}(\text{SiHMe}_2)_2$ formed $\text{Zn}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiR}'\text{Me}_2)_2\}$ ($\text{R} = \text{Me}$ (**21**) or H). $\text{Cd}\{\text{N}(\text{SiMe}_3)_2\}_2$ reacted with 1 or 2 equiv of $\text{HC}(\text{Me}_2\text{pz})_3$ to form $\text{Cd}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}(\text{SiMe}_3)_2\}$ (**24**) or $\text{Cd}\{\text{C}(\text{Me}_2\text{pz})_3\}_2$ (**25**). Reaction of **13** or **18** with $\text{HC}(\text{pz})_3$ gave the heteroleptic zwitterions $\text{M}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{C}(\text{pz})_3\}$ ($\text{M} = \text{Mg}$ (**26**) or Ca (**27**)), containing $\kappa^3\text{N}$ -coordinated $\text{C}(\text{Me}_2\text{pz})_3$ and $\text{C}(\text{pz})_3$ ligands. In contrast, reaction of **24** with $\text{HC}(\text{pz})_3$ formed $\text{Cd}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\kappa^1\text{C}, \kappa^2\text{N}-\text{C}(\text{pz})_3\}$ (**28**), containing two different coordination modes for the tris(pyrazolyl)methanide ligands and a $\text{Cd}-\text{C}(\text{pz})_3$ bond. The solid-state structures of **13**, **15**, **18**, **19**, **20**, **21**, **23**, **24**, **26**, and **28** have been determined.

Introduction

The anionic poly(pyrazolyl)borates and their neutral poly(pyrazolyl)methane counterparts are among the most widely used ligands in coordination and organometallic chemistry. Figure 1 depicts in general terms the tris(pyrazolyl)hydroborate (**I**) and tris(pyrazolyl)methane (**II**) homologues. The development of these and other scorpionate-type ligands,

and the synthesis and reactions of their complexes, have been recorded through many reviews.^{1–8}

Removal of the C-bound apical proton from **II** generates the anionic tris(pyrazolyl)methanide **III** (Figure 1). **III** is isoelectronic with the hydroborate system **I**, but features ambidentate characteristics and two possible binding sites, namely, the anionic carbon or the pyrazolyl ring nitrogens.⁹ Stone was the first to report a structurally authenticated derivative of tris(pyrazolyl)methanide, namely, the trimetallic species **1** (Figure 2), which has an anionic $\text{C}(\text{pz})_3$ moiety bound through both the apical carbon and all three 2-position pyrazolyl nitrogens.^{10,11} Compound **1** was prepared from $\text{Pt}(\text{norbornene})(\text{PMe}_2\text{Ph})_2$ and $\text{Ar}^{\text{F}}\text{Au}\{\kappa^1\text{C}, \kappa^3\text{N}-\text{C}(\text{pz})_3\}$

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