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Versatile Scorpionates—New Developments in the Coordination Chemistry of Pyrazolylborate Ligands

Frank T. Edelmann*

More than 30 years after their discovery poly(pyrazolyl)borate ligands (scorpionates) still belong to the work horses in coordination chemistry.[1] These anions, normally associated with the name Trofimenko, are among the most often used complex ligands.[2, 3] This is true for various main group elements as well as numerous transition metals, lanthanoids, and actinoids. These ligands are so popular due to their reliability and accountability as spectator ligands, which normally do not interfere with the reaction scenarios occurring at the metal centers. Tris(pyrazolyl)borates ($\mathrm{Tp} \equiv \mathrm{HB(pz)_3}$) generally coordinate as tridentate ligands through three nitrogen atoms of the pyrazole rings (κ^3N,N',N''), thereby providing effective steric shielding of the metal center.[3, 4] By introducing suitable substituents (e.g. Me, $\mathrm{CF_3}$, *t*Bu, Ph) particularly in the 3-position of the pyrazolyl rings this effect can be tuned to a large extent. Cone angles much larger than 180° can be achieved with the use of such sterically demanding scorpionate ligands, which, for example, have been utilized to realize unusual bonding (e.g. monomeric zinc hydroxides).[3] Besides the very common κ^3N,N',N'' coordination mode the tridentate $\kappa^3N,N,B\text{-}H$ type[5] and the bidentate κ^2N,N' coordination[6] are also known. Higher hapticities could thus far only be achieved in cases where the substituents in 3-position of the pyrazole rings contained additional donor atoms. For example, the three pyridyl substituents of the ligand $\mathrm{Tp^{py}}$ make it potentially hexadentate.[7] Due to their identical charge, facial coordination, and the fact that both may formally act as six-electron donors, the $\mathrm{Tp^-}$ ions have often been compared to the cyclopentadienyl ligands.[3]

Several recent contributions have demonstrated that the coordination modes of tris(pyrazolyl)borate ligands can be far more versatile than hitherto anticipated. In addition to new findings concerning the electronic properties of the scorpionates, unknown coordination modes as well as novel reaction patterns have been discovered.

1. Electronic Effects

With respect to its steric bulk the hydrotris(3,5-dimethylpyrazolyl)borate anion $(\mathrm{Tp^{Me_2}})^-$ is regarded as a steric equivalent of the pentamethylcyclopentadienyl (Cp*) ligand.[3d] However, conflicting reports can be found in the literature on the electron-donating properties of hydrotris(pyrazolyl)borate (Tp) and $\mathrm{Tp^{Me_2}}$ in comparison to $\mathrm{C_5H_5}$ (Cp) and $\mathrm{C_5Me_5}$ (Cp*).[8] Most researchers claim that the ligands Tp and $\mathrm{Tp^{Me_2}}$ are stronger electron donors than Cp and Cp*. In a recent study on C–H activation reactions by $[(\mathrm{Tp^{Me_2}})\mathrm{Ir}]$ complexes Bergman et al. were able to show the opposite effect, that is that the $\mathrm{Tp^{Me_2}}$ derivatives are *less electron rich* than the corresponding [Cp*Ir] complexes.[9] The starting point for this investigation was the known fact that the iridium(III) complexes $[\mathrm{Cp^*(PMe_3)Ir(Me)}][\mathrm{OTf}]$ (**1**, $\mathrm{OTf} = \mathrm{OSO_2CF_3}$) and $[\mathrm{Cp^*(PMe_3)IrMe(ClCH_2Cl)}][\mathrm{BAr_f}]$ (**2**, $\mathrm{BAr_f} = \mathrm{B[3,5\text{-}(CF_3)_2C_6H_3]_4}$) are capable of cleaving C–H bonds in a wide variety of hydrocarbons under extremely mild conditions.[10] As part of the search for robust ligands for the stabilization of the reactive cationic $\mathrm{Ir^{III}}$ species the triflate **3** was synthesized as the first target molecule (Scheme 1).

The first evidence for a reverse electronic effect of the $\mathrm{Tp^{Me_2}}$ ligand came from the finding that the Ir–O bond (212.8(5) pm) in **3** is shorter than that in the Cp* derivative **1** (221.6(10) pm).[10] In good agreement it was found that the reaction of $[\mathrm{Cp^*(PMe_3)Ir(H)_2}]$ (**4**) with $[(\mathrm{Tp^{Me_2}})(\mathrm{PMe_3})\mathrm{Ir(H)_2H}][\mathrm{OTf}]$ (**5**) results in quantitative formation of $[\mathrm{Cp^*(PMe_3)Ir(H)_3}][\mathrm{OTf}]$ (**6**) and $[(\mathrm{Tp^{Me_2}})(\mathrm{PMe_3})\mathrm{Ir(H)_2}]$ (**7**). Thus the equilibrium lies heavily in favor of the protonated (i.e. more strongly basic) Cp* complex. This result was further confirmed by a comparison of the IR stretching absorbances of $[(\mathrm{Tp^{Me_2}})\mathrm{Ir(CO)_2}]$ (**8**, 2039, 1960 $\mathrm{cm^{-1}}$)[6a] and $[\mathrm{Cp^*Ir(CO)_2}]$ (**9**, 2020, 1953 $\mathrm{cm^{-1}}$) which were reported by Graham et al.[11] Here too it becomes clear that the metal center in the $\mathrm{Tp^{Me_2}}$ compound is *less electron rich*.

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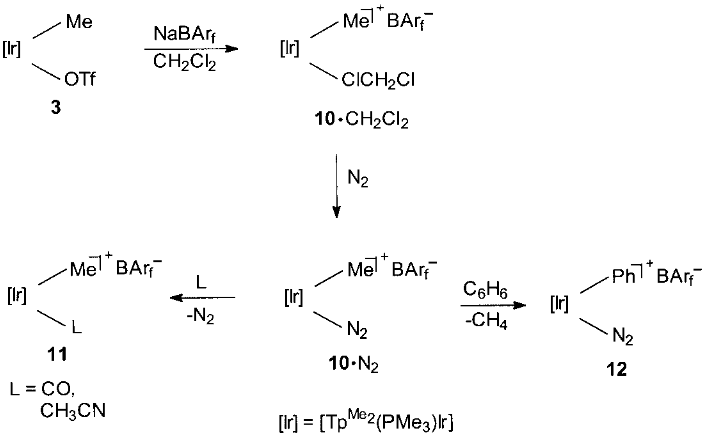
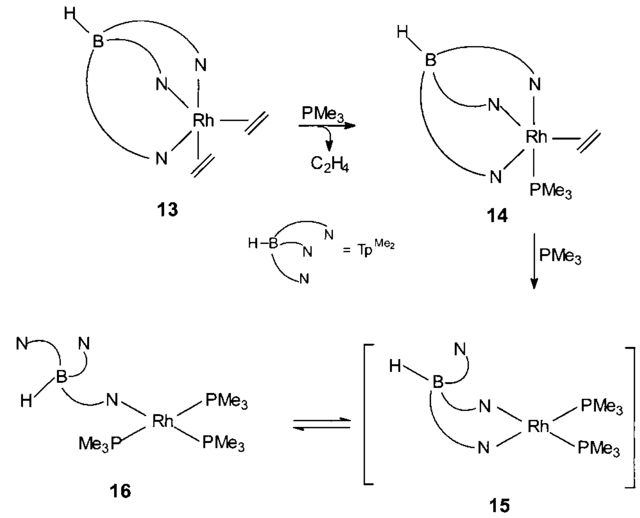
In the case of C–H activation by [Cp*Ir] complexes it was possible to substantially increase the reactivity of [Cp*(PMe$_3$)Ir(Me)][OTf] (**1**) through formation of the cationic complex [Cp*(PMe$_3$)IrMe(ClCH$_2$Cl)][BAr$_f$] (**2**).[10b] Analogous treatment of **3** with NaBAr$_f$ in CH$_2$Cl$_2$ surprisingly afforded the cationic dinitrogen complex **10**·N$_2$ (Scheme 1), which is the first reported structurally characterized complex of this type. The thermally very labile CH$_2$Cl$_2$ complex **10**·CH$_2$Cl$_2$ can be isolated in the absence of N$_2$, while under nitrogen atmosphere **10**·N$_2$ is instantaneously generated again. Both N$_2$ and CH$_2$Cl$_2$ are rapidly displaced by donor ligands such as CO or MeCN under quantitative formation of the cationic complexes **11**. Benzene reacts with **10**·N$_2$ at room temperature to yield the phenyliridium complex **12** and methane.[9]



Scheme 1. Preparation and reactivity of the cationic [(Tp^{Me_2})Ir^{III}] complexes **10**·CH$_2$Cl$_2$ and **10**·N$_2$.[9]

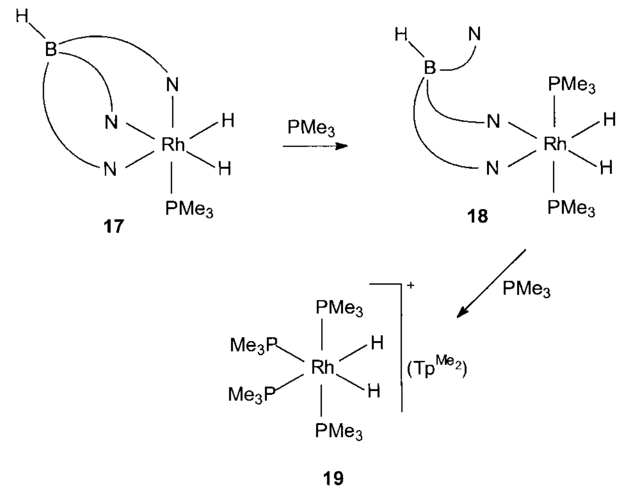
2. Novel Coordination Modes

Recently several authors have reported on new coordination modes of tris(pyrazolyl)borate anions. Both unusually low (κ^1, “κ^0”) and high (κ^5) hapticities have been realized or unambiguously proven for the first time. Here too a comparison with the corresponding cyclopentadienyl complexes is of interest. Variable coordination modes are well documented for cyclopentadienyl complexes.[12] An instructive example is the reaction of [CpRe(NO)(Me)(PMe$_3$)] with PMe$_3$ in which products with η^5-C$_5$H$_5$, η^3-C$_5$H$_5$, and η^1-C$_5$H$_5$ coordination and even ionic “η^0”-C$_5$H$_5^-$ derivatives have been detected.[13] Recently, Paneque, Monge, and Carmona et al. were able to realize similar denticity changes in a rhodium pyrazolylborate system and thereby isolate for the first time an ionic complex containing a “naked” κ^0“-Tp^{Me_2} ligand.[14] In the course of this investigation it was possible to interconvert Tp^{Me_2}-κ^3N, κ^2N, κ^1N, and ”κ^0“ complexes. Treatment of either [(Tp^{Me_2})Rh(C$_2$H$_4$)$_2$] (**13**) or [(Tp^{Me_2})Rh(C$_2$H$_4$)(PMe$_3$)] (**14**) with an excess of PMe$_3$ (ca. 5–6 equivalents, 20 °C) according to Scheme 2 afforded the stable tris(phosphane) complex **16** as the final product. Under modified reaction conditions it was possible to isolate the bis(phosphane) intermediate **15**, albeit not in an analytically pure form.



Scheme 2. Formation of the tris(phosphane)rhodium(I) complex **16** involving Tp^{Me_2}-κ^1N coordination.[14]

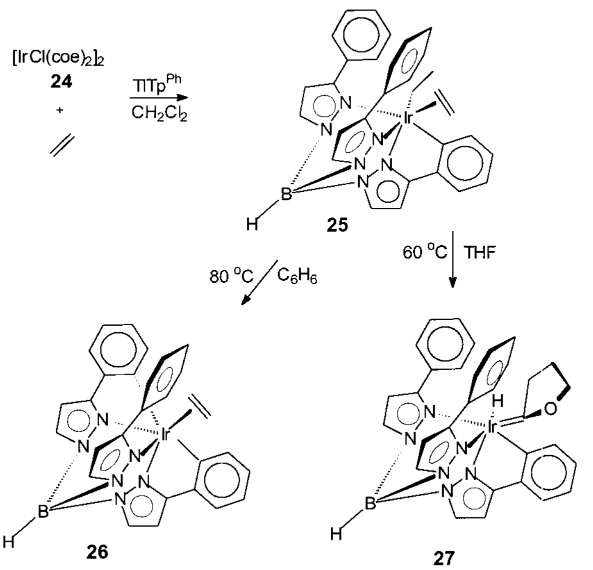
The long Rh···H(B) separation of 259(4) pm in **16** is in agreement with the presence of a Tp^{Me_2} κ^1N coordination.[14] The reaction sequence shown in Scheme 3 produced the most interesting result. Heating of the dihydrido complex [(Tp^{Me_2}-κ^3N)Rh(H)$_2$(PMe$_3$)] (**17**) in the presence of PMe$_3$ initially yielded the isolable bis(phosphane) Tp^{Me_2}-κ^2N complex **18** and subsequently the unusual ionic compound [Rh(H)$_2$(PMe$_3$)$_4$][Tp^{Me_2}] (**19**), which could also be generated by treatment of [Rh(H)$_2$(PMe$_3$)$_4$]Cl (**20**) with KTp^{Me_2}. A crystal structure determination of the analogous complex [Rh(H)$_2$(PMe$_3$)$_4$][Tp] (**21**) confirmed the presence of the first saltlike complex containing “naked” tris(pyrazolyl)borate anions (Tp$^-$-“κ^0”). There is no bonding interaction between the Rh^{III} center and the Tp$^-$ ion. The stepwise change in the denticity of pyrazolylborate ligands from κ^3 to “κ^0” as reported here for the first time may have important implications in catalytic uses of Tp metal complexes. As another novelty among the low-denticity coordination modes of



Scheme 3. Preparation of the saltlike compound **19** containing a “naked” tris(pyrazolyl)borate ion (Tp-“κ^0”).[14]

scorpionate ligands the $\kappa^2N,B\text{-}H$ coordination involving an agostic B – (μ-H) metal interaction should be mentioned here. Two examples have been reported recently, that is the compounds [$(\mathrm{Tp}^{\mathrm{Me_2,4\text{-}Cl}}\text{-}\kappa^2N,B\text{-}H)\mathrm{Rh(CO)(PMePh_2)_2}$] (**22**)[15] and [$\mathrm{Tp}^{\mathrm{Me_2}}\text{-}\kappa^2N,B\text{-}H)\mathrm{Rh\{P(C_7H_7)_3\}}$] (**23**).[16] According to studies by Herberhold et al. **23** is a rhodium(I) complex of the sterically demanding tris(1-cyclohepta-2,4,6-trienyl)phosphane ligand, for which the $\mathrm{Tp}^{\mathrm{Me_2}}\text{-}\kappa^2N,B\text{-}H$ coordination involving a nonlinear B-(μ-H)-Rh bridge could be unambiguously proven by X-ray diffraction.[16]

Denticities beyond κ^4 were unknown for Tp^{R} ligands where R contained no heteroatom. Recently, Slugovc and Carmona et al. reported for the first time on the unusual κ^5 coordination of hydrotris(3-phenylpyrazolyl)borate ligands ($\mathrm{Tp}^{\mathrm{Ph}}$).[17] The reaction of [$\{\mathrm{IrCl(coe)_2}\}_2$] (**24**, coe = cyclooctene) with ethylene and $\mathrm{TlTp}^{\mathrm{Ph}}$ in $\mathrm{CH_2Cl_2}$ initially produced the cyclometalated complex [$(\mathrm{Tp}^{\mathrm{Ph}}\text{-}\kappa^4N,N,N,C^{Ph})\mathrm{Ir(Et)}(\eta^2\text{-}\mathrm{C_2H_4})$] (**25**) (Scheme 4). Prolonged heating (17 h) in refluxing benzene converted **25** into the novel bis-cyclometalated species [$(\mathrm{Tp}^{\mathrm{Ph}}\text{-}\kappa^5N,N,N,C^{Ph},C^{Ph})\mathrm{Ir}(\eta^2\text{-}\mathrm{C_2H_4})$] (**26**) which was formed as the only product. This compound is the first instance of κ^5 coordination of a scorpionate ligand in which the substituents at the pyrazolyl rings contain no donor atoms. If the same thermolysis reaction is carried out in refluxing THF the Fischer-carbene complex **27** is formed as the sole product.



Scheme 4. Preparation of the cyclometalated complexes [$(\mathrm{Tp}^{\mathrm{Ph}}\text{-}\kappa^4N,N,N,C^{Ph})\mathrm{Ir(Et)}(\eta^2\text{-}\mathrm{C_2H_4})$] (**25**) and [$(\mathrm{Tp}^{\mathrm{Ph}}\text{-}\kappa^5N,N,N,C^{Ph},C^{Ph})\mathrm{Ir}(\eta^2\text{-}\mathrm{C_2H_4})$] (**26**).[17]

Yet another entirely new aspect of scorpionate coordination chemistry is the η^5 coordination of a pyrazole ring. Despite the formal similarities with the cyclopentadienyl ligands (vide supra),[3] a π interaction between a pyrazolylborate ligand and a metal center has never been encountered. A first successful approach was recently reported by Gorun et al.[18] The reaction of CuCl with $\mathrm{KTp}^{\mathrm{CF_3,Me}}$ ($\mathrm{Tp}^{\mathrm{CF_3,Me}}$ = hydrotris(3-trifluoromethyl-5-methylpyrazolyl)borate) unexpectedly afforded a blue complex of the composition [$\{(\mathrm{KTp}^{\mathrm{CF_3,Me}})_2(\mathrm{CuCO_3})\}_2$] (**28**) in 11% yield. Atmospheric $\mathrm{CO_2}$ must be responsible for the formation of the carbonato ligand, since the preparation of **28** was carried out in air. A [$(\mu^4\text{-}\mathrm{CO_3})_2\mathrm{Cu_2K_4}$] unit forms the central part of the complex molecule. Of special interest is the coordination environment around the potassium center (Figure 1). One of the coordination hemispheres of K1 is occupied by two carbonate oxygen atoms, one N atom of the $\mathrm{Tp}^{\mathrm{CF_3,Me}}$ ligand, and three fluorine atoms. On the opposite side the potassium ion is located directly above the center of a pyrazole ring, thus allowing a comparison with the η^5-cyclopentadienyl coordination in polymeric KCp.[19] With an average value of 337 pm the corresponding K–C (pyrazolyl) distances are somewhat longer than those in KCp (av 305.6 pm). Nevertheless these values clearly indicate for the first time the presence of η^5 coordination involving a scorpionate pyrazole ring, which results in a formal coordination number of 9 around the K1 center.

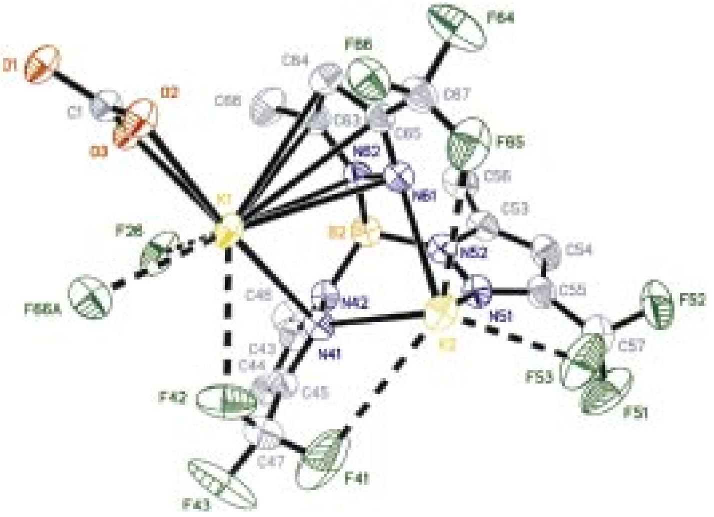
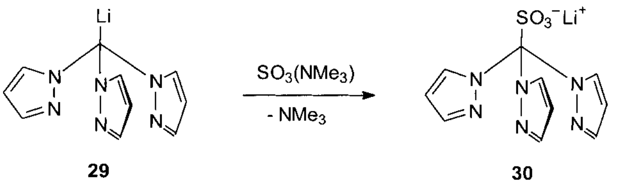


Figure 1. Section of the molecular structure of [$\{(\mathrm{KTp}^{\mathrm{CF_3,Me}})_2(\mathrm{CuCO_3})\}_2$] (**28**) clearly showing the π coordination of a pyrazolyl ring.[18]

3. New Ligands

Very recent work on scorpionate coordination chemistry has also made important contributions to increase the number of potentially useful ligands, either through deliberate syntheses or by unexpected transformations of coordinated ligands. The most interesting achievements in this area will be discussed here. A hitherto unsolved problem in the chemistry of hydrotris(pyrazolyl)borates and related anions was the preparation of water-soluble ligands by introduction of suitable substituents. Such derivatives are expected to be highly useful in the synthesis of enzyme model complexes, which are soluble and stable under physiological conditions. Two recent papers by Kläui et al.[19] as well as Mews et al.[20] provide decisive new impulses. Both synthetic routes are remarkably simple.

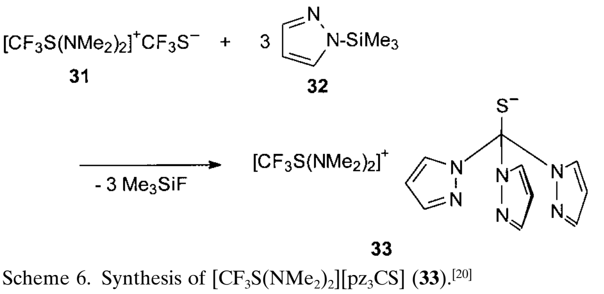
Kläui's approach involves treatment of lithiated tris(pyrazolyl)methane (**29**) with sulfur trioxide – triethylamine complex to afford the lithium salt of tris(pyrazolyl)methane sulfonic acid (**30**) in one step (Scheme 5, 48% yield).[19]



Scheme 5. Preparation of tris(pyrazolyl)methanesulfonate (**30**).[19]

Compound **30** is highly water-soluble and the solutions are stable over a wide pH range. At pH 0 traces of free pyrazole can be detected only after several weeks, while at pH 13 no decomposition is observed at all. The analogous potassium salt can be prepared from **30** through a metathetical reaction with K_2CO_3. With respect to potentially useful ligands for enzyme models[3c, 21] the lithium salt of the sterically demanding tris(3-*tert*-butylpyrazolyl)methane sulfonate anion $(\text{Tpms}^{t\text{Bu}})^-$ was also prepared according to Scheme 5. Treatment of this compound with $TlNO_3$ in methanol/water afforded the thallium salt $\text{TlTpms}^{t\text{Bu}}$, which was shown to adopt a dimeric structure in the solid state. Initial experiments already revealed that the new anions may act as tripodal nitrogen donor ligands in transition metal complexes.

A completely different, though no less straightforward synthetic route was reported by Mews et al.[20] The basic idea of this work is the nucleophilic substitution of the fluorine atoms in the CF_3S^- ion (present as the $[CF_3S(NMe_2)_2]^+$ salt **31**) by five-membered nitrogen heterocycles, which are employed as their N-silylated derivatives (**32**). For example, treatment with three equivalents of *N*-trimethylsilylpyrazole yields the hitherto unknown tris(pyrazolyl)methane thiolate (pz_3CS) ion (present as the $[CF_3S(NMe_2)_2]^+$ salt **33**; Scheme 6). This synthesis is highly variable since different cations as well as other *N*-trimethylsilyl azoles can be successfully employed. These new anions too can be expected to exhibit a rich coordination chemistry with main group and transition metals.



Scheme 6. Synthesis of $[CF_3S(NMe_2)_2][pz_3CS]$ (**33**).[20]

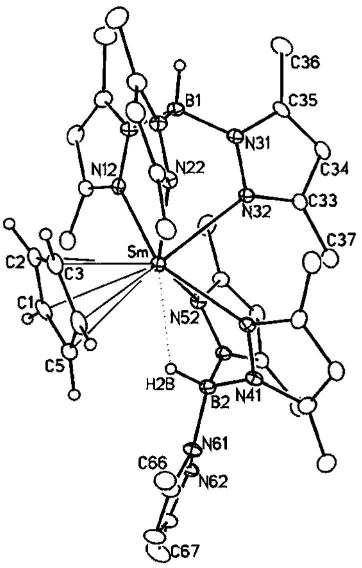


Figure 2. Molecular structure of $[(\text{Tp}^{\text{Me}_2})_2\text{Sm(Cp)}]$ (**35**).[22]

The synthesis of the unprecedented cyclopentadienylbis(pyrazolyl)borate ligand in the coordination sphere of samarium, which was reported by Marques and Takats et al,[22] was certainly not anticipated. Despite its insolubility in the usual organic solvents the samarium(II) complex $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ (**34**) is highly reactive.[23] Treatment with [TlCp] in THF solution leads to precipitation of metallic thallium and formation of the first mixed Tp/Cp lanthanoid complex, $[(\text{Tp}^{\text{Me}_2})_2\text{Sm(Cp)}]$ (**35**), which could be structurally characterized by X-ray diffraction (Figure 2). The cyclopentadienyl ligand in **35** is η^5-coordinated to samarium. As a response one of the Tp^{Me_2} ligands partially peals off by adopting a κ^3*N,N,B-H* coordination mode. Prolonged heating of **35** under vacuum at 165 °C transformed it into an intensely yellow colored solid, from which the novel complex $[(\text{Tp}^{\text{Me}_2})\text{Sm}\{\text{HB}(3,5\text{-Me}_2\text{pz})_2(C_5H_4)\}]$ (**36**; 3,5-Me_2pz = 3,5-dimethylpyrazolyl) could be isolated by fractional crystallization from a toluene/hexane mixture. A single-crystal X-ray structure analysis (Figure 3) revealed the presence of one intact Tp^{Me_2} unit and one uniquely modified ligand in which a pyrazolyl moiety has been replaced by a C_5H_4 ring. The synthesis of the new dianionic $[\text{HB}(3,5\text{-Me}_2\text{pz})_2(C_5H_4)]^{2-}$ ligand by thermally induced intramolecular C–H activation in **35** opens the way to a new class of "heteroscorpionates" which can be expected to offer versatile applications in coordination chemistry.

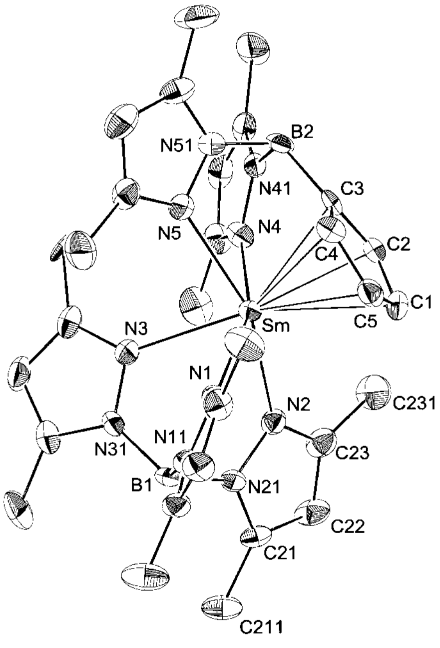


Figure 3. Molecular structure of $[(\text{Tp}^{\text{Me}_2})\text{Sm}\{\text{HB}(3,5\text{-Me}_2\text{pz})_2(C_5H_4)\}]$ (**36**).[22]

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