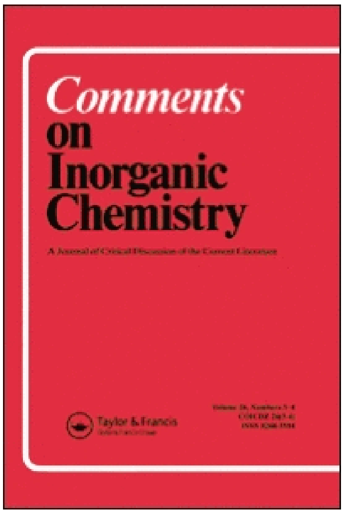

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

FLUORINATED TRIS(PYRAZOLYL)BORATES AND SILVER(I) COMPLEXES OF GROUP 14 LIGANDS

H. V. Rasika Dias[a]; Mauro Fianchini[a]
[a] Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas, USA

To cite this Article Dias, H. V. Rasika and Fianchini, Mauro(2007) 'FLUORINATED TRIS(PYRAZOLYL)BORATES AND SILVER(I) COMPLEXES OF GROUP 14 LIGANDS', Comments on Inorganic Chemistry, 28: 1, 73 — 92

To link to this Article: DOI: 10.1080/02603590701394816

URL: http://dx.doi.org/10.1080/02603590701394816

Comments on Inorganic Chemistry, 28: 73–92, 2007

ISSN: 0260-3594 print
DOI: 10.1080/02603590701394816

FLUORINATED TRIS(PYRAZOLYL)BORATES AND SILVER(I) COMPLEXES OF GROUP 14 LIGANDS

H. V. RASIKA DIAS
MAURO FIANCHINI

Department of Chemistry and Biochemistry,
The University of Texas at Arlington, Arlington,
Texas, USA

This review presents an overview of fluorinated tris(pyrazolyl)borate ligands and their role in the development of silver adducts containing group 14 ligands. Tris(pyrazolyl)borates bearing fluorocarbon substituents are sterically somewhat similar but electronically very different from their hydrocarbon counterparts. They have weakly donating nitrogen sites. Fluorinated hydridotris(pyrazolyl)borates also have less reducing B-H groups. These mono-anionic, nitrogen-based donors are ideal supporting ligands to stabilize silver complexes bearing labile donors. For example, fluorinated tris(pyrazolyl)borates have enabled the isolation of thermally stable Ag(I)-CO, Ag(I)-ethylene, and Ag(I)-acetylene adducts. Compounds with unsupported Ag(I)-Ge(II) and Ag(I)-Sn(II) bonds have also been synthesized. Most of these contain easily removable halide groups and silver atoms in the same molecule, but do not show the silver-halide metathesis. Fluorinated tris(pyrazolyl)borate ligands without the problematic B-H moiety have been reported. They afford silver-tris(pyrazolyl) borates with higher solution stability. The κ^3-coordination mode is the most common for tris(pyrazolyl)borates but κ^2-bonded tris(pyrazolyl)borate silver adducts are also known. Some silver adducts of fluorinated tris(pyrazolyl)borates are excellent tris(pyrazolyl)borato ligand transfer agents, promising homogeneous catalysts and effective antimicrobial agents.

Address correspondence to H. V. Rasika Dias, Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019-0065, USA. E-mail: dias@uta.edu

INTRODUCTION

Tris(pyrazolyl)borates are a very important and hugely popular class of auxiliary ligands in coordination chemistry.[1,2] It is possible to modify the steric and electronic properties of these ligands conveniently, and often predictably, by varying the number and nature of substituents on the pyrazolyl rings and on the boron atom. Among the many varieties, the parent $[HB(Pz)_3]^-$ and the closely related, pyrazolyl ring alkylated systems (e.g., $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$) have attracted the most attention (Figure 1), perhaps because of the ease of synthesis, low cost, and their excellent donor properties.[1,2]

Tris(pyrazolyl)borates readily coordinate, usually as face-capping terdentate ligands (κ^3-*N*,*N*′,*N*″), to a wide variety of metal ions affording thermally stable metal complexes. Although these ligands have been used in chemistry for over forty years, their silver(I) chemistry remains rather poorly developed.[2] The primary reason for this is the inherent instability of such complexes, which contain a strongly oxidizing Ag(I) site and a reducing borohydride functionality.[2] They tend to decompose with the deposition of metallic silver, which is particularly severe in solutions. Light initiated decomposition (i.e., high photosensitivity even in the absence of a B-H moiety) is also a problem for some tris(pyrazolyl)borate silver(I) adducts.

Despite these challenges, Bruce and co-workers reported the first successful isolation of silver(I) tris(pyrazolyl)borates in 1979.[3,4] They described the synthesis of binary adducts containing silver(I) and $[HB(Pz)_3]^-$ or $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$, and a number of tris(pyrazolyl)boratosilver(I)

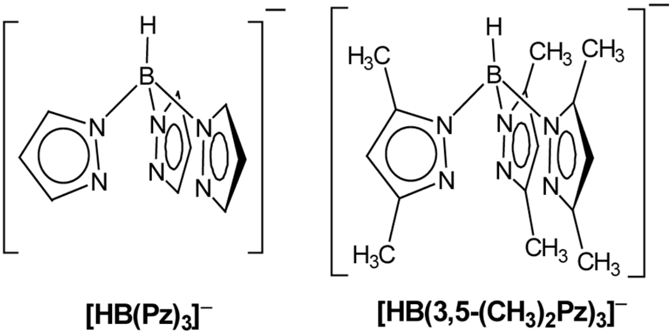

Figure 1. Two widely used tris(pyrazolyl)borate ligands.

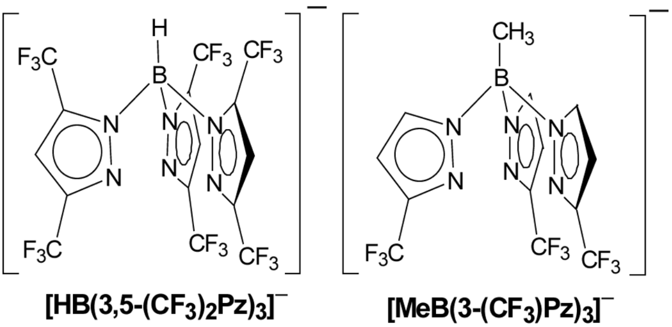

Figure 2. Examples of fluorinated tris(pyrazolyl)borate ligands.

derivatives, which mainly contain phosphine donors. Then, in 1995, Dias et al. demonstrated the utility of a fluorinated tris(pyrazolyl) borate $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (Figure 2) in silver(I) chemistry, including the stabilization of an exceedingly rare silver carbonyl adduct, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$.[5] The interest in the chemistry of silver tris(pyrazolyl)borates has grown steadily since these discoveries. For example, there have been several significant developments in the isolation of novel coordination compounds, homogeneous catalysis, and antimicrobial agents based on silver supported by tris(pyrazolyl)borate ligands (most of which concern fluorinated versions of tris(pyrazolyl)borates).

This article reviews some of the *fluorinated tris(pyrazolyl)borate* ligand synthesis work, and the important role such ligands played in the isolation of *silver(I) complexes with group 14 ligands*. We will also include related silver complexes of non-fluorinated tris(pyrazolyl)borates for comparison. As evident from the following account, they are essentially limited to few isocyanide adducts.[6] More recently, syntheses B-H free tris(pyrazolyl)borates like $[MeB(3\text{-}(CF_3)Pz)_3]^-$ (Figure 2) and $[PhB(3\text{-}(CF_3)Pz)_3]^-$ and their use in silver chemistry have been reported. The silver(I) adducts of these B-H free ligands show relatively higher thermal stability even in solution. Thus, such ligands are particularly suitable for silver(I) chemistry. As we see later, nature of substituent on boron also affects the ligand coordination mode.

FLUORINATED TRIS(PYRAZOLYL)BORATE LIGANDS

Several fluorinated hydridotris(pyrazolyl)borates have been synthesized via the classical route using an alkali metal borohydride (normally

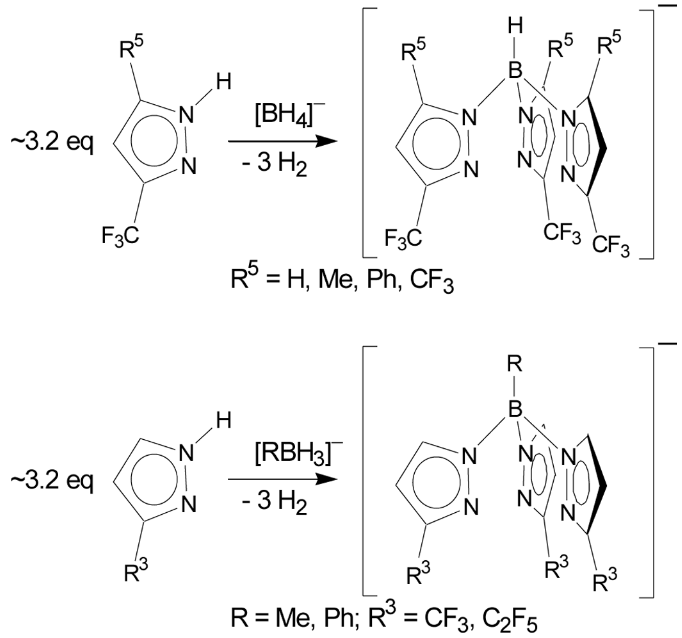

Figure 3. Synthesis of fluorinated tris(pyrazolyl)borate ligands.

$NaBH_4$ or KBH_4) and little more than three equivalents of the corresponding fluorinated pyrazole (Figure 3). They include $[HB(3\text{-}(CF_3)Pz)_3]^-$,[7] $[HB(3\text{-}(C_2F_5)Pz)_3]^-$,[8] $[HB(3\text{-}(C_3F_7)Pz)_3]^-$,[8] $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$,[7,9–11] $[HB(3\text{-}(CF_3),5\text{-}(Me)Pz)_3]^-$,[12,13] $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$,[14,15] and $[HB(3\text{-}(CF_3),5\text{-}(2\text{-thienyl})Pz)_3]^-$.[16] More recently, syntheses B-H free tris (pyrazolyl)borates like $[MeB(3\text{-}(C_2F_5)Pz)_3]^-$,[17] $[MeB(3\text{-}(C_2F_5]^-$ [18] and $[PhB(3\text{-}(CF_3)Pz)_3]^-$[17] have also been reported. They involve the use of $MeBH_3Li$ or $PhBH_3Li$ instead of tetrahydroborate salt precursors (Figure 3).

Compared to the non-fluorinated analogs, the synthesis of fluorinated tris(pyrazolyl)borates requires somewhat lower temperatures since acidic fluorinated pyrazoles react quite readily with the borohydride salts. The moisture can affect the product yield during the ligand assembly step. Some of the fluorinated pyrazoles are also hygroscopic. Thus it is important to use carefully dried pyrazoles in these reactions. In certain cases, the initial stages of the reaction between the metal borohydride (especially when the alkali metal borohydride is fresh and in fine particulate form) and the fluorinated pyrazole is very rapid.

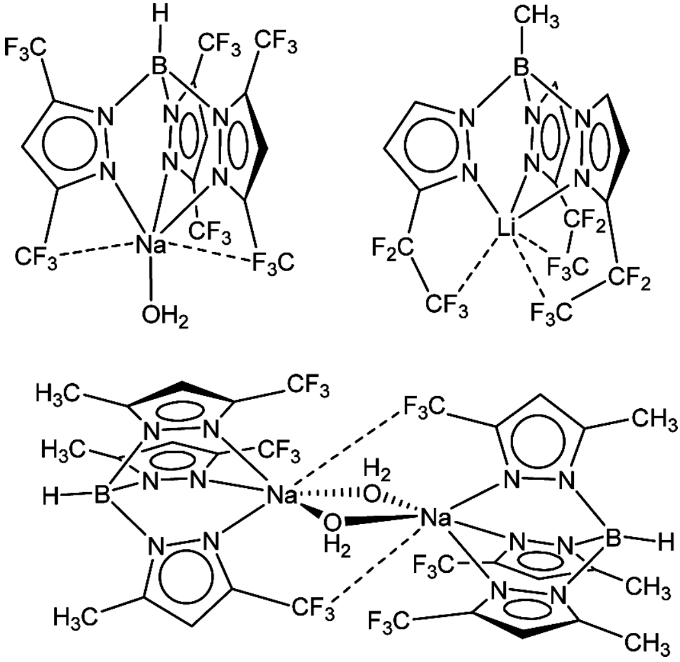

Figure 4. Alkali metal complexes of fluorinated tris(pyrazolyl)borate ligands.

For example, freshly prepared $MeBH_3Li$ and 3-(CF_3)PzH react violently, producing charred material when mixed in the solid state, if they are not pre-cooled and mixed in small portions.

Overall, several fluorinated tris(pyrazolyl)borate ligands are known, and some of their alkali metal complexes have been isolated as water, THF, Et_2O adducts, and as solvent free species, and structurally characterized using X-ray crystallography. They display interesting structures ranging from monomers, dimers to polymers. Some of these adducts feature close alkali metal$\cdots$F-C contacts in the solid state (Figure 4).[7,9,13,14,18]

STERIC AND ELECTRONIC EFFECTS OF FLUORINATED TRIS(PYRAZOLYL)BORATES

The cone angle data provide valuable information about the steric properties of tris(pyrazolyl)borate ligands. Table 1 shows some cone angle values estimated/calculated for select group of ligands using thallium[1] and tri(carbonyl)rhenium tris(pyrazolyl)borate adducts.[19] It is

Table 1. Cone angles (in deg.) of tris(pyrazolyl)borate ligands estimated from their thallium(I) and rhenium(I) adducts[1,19]

L	LTl	LRe(CO)$_3$
[HB(Pz)$_3$]	183	211
[HB(3-(CF$_3$)Pz)$_3$]		241
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]	237	242
[HB(3,5-(Me)$_2$Pz)$_3$]	239	243
[HB(3-(C$_2$F$_5$)Pz)$_3$]		257
[HB(3-(*i*-Pr),5-(Me)Pz)$_3$]		255
[HB(3-(*i*-Pr),4-(Br)Pz)$_3$]	243	262
[HB(3-(*t*-Bu),5-(Me)Pz)$_3$]	243	276
[HB(3-(*t*-Bu)Pz)$_3$]	251	275

important to keep in mind that the cone angle also depends on the metal-N bond length. Nevertheless, these data suggest that although a CF$_3$ group is closer in size to a *i*-Pr group,[20] the *steric effects* of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ is similar to the non-fluorinated analog [HB(3,5-(Me)$_2$Pz)$_3$]$^-$ containing methyl substituents rather than [HB(3,5-(*i*-Pr)$_2$Pz)$_3$]$^-$.

Electronically, however, [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ and [HB(3,5-(Me)$_2$Pz)$_3$]$^-$ are very different. One convenient way to estimate the ligand electronic effects is by examining the position of ν_{CO} band in IR spectra of closely related group of metal carbonyl adducts. Table 2 summarizes

Table 2. Carbonyl stretching frequencies of closely related tris(pyrazolyl)boratocopper(I) carbonyl adducts[14]

CO	2143
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuCO	2137
[HB(3-(C$_2$F$_5$)Pz)$_3$]CuCO	2110
[HB(3-(CF$_3$),5-(Me)Pz)$_3$]CuCO	2109
[HB(3-(CF$_3$),5-(Ph)Pz)$_3$]CuCO	2103
[HB(3-(C$_3$F$_7$)Pz)$_3$]CuCO	2102
[HB(3-(CF$_3$)Pz)$_3$]CuCO	2100
[HB(Pz)$_3$]CuCO	2083
[HB(3,5-(Ph)$_2$Pz)$_3$]CuCO	2080
[HB(3-(Mes)Pz)$_3$]CuCO	2079
[HB(3-(*t*-Bu)Pz)$_3$]CuCO	2069
[HB(3,5-(Me)$_2$Pz)$_3$]CuCO	2066
[HB(3-(*t*-Bu),5-(Me)Pz)$_3$]CuCO	2059
[HB(3-(*t*-Bu),5-(*i*-Pr)Pz)$_3$]CuCO	2057
[HB(3,5-(*i*-Pr)$_2$Pz)$_3$]CuCO	2056

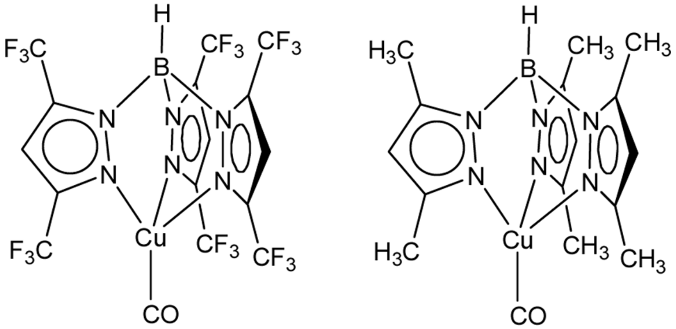

Figure 5. Copper(I) carbonyl adducts supported by $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[HB(3,5\text{-}(Me)_2Pz)_3]^-$.

the CO stretching frequency data from such a series involving well defined copper(I) carbonyl adducts.[14] Tris(pyrazolyl)borate ligand electronic effects have also been studied by using NMR spectroscopy,[21] photoelectron spectroscopy,[22] cyclic voltammetry, and by computational methods.[23]

Overall, data show that fluorinated tris(pyrazolyl)borate ligands are significantly weak donors compared to tris(pyrazolyl)borates with hydrocarbon substituents. For example, the carbonyl stretching frequency of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ is about 71 cm^{-1} higher than that of $[HB(3,5\text{-}(CH_3)_2Pz)_3]CuCO$ (Figure 5). Copper complexes of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand also show relatively high oxidation potentials.[23] The substituents on boron do not appear to play a major role in altering the electronic properties of these ligands. For example, the carbonyl stretching bands of $[HB(3\text{-}(CF_3)Pz)_3]CuCO$ ($\nu_{CO} = 2100\,cm^{-1}$) and $[MeB(3\text{-}(CF_3)Pz)_3]AgCO$ ($\nu_{CO} = 2099\,cm^{-1}$) (or $[HB(3\text{-}(Mes)Pz)_3]CuCO$ ($\nu_{CO} = 2079\,cm^{-1}$) and $[MeB(3\text{-}(Mes)Pz)_3]CuCO$ ($\nu_{CO} = 2075\,cm^{-1}$) appear at a very similar position.[24]

SILVER COMPLEXES OF GROUP 14 LIGANDS

Compared to the common non-fluorinated tris(pyrazolyl)borates such as $[HB(Pz)_3]^-$ or $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$, the fluorinated systems have weakly coordinating donor (nitrogen) sites. Thus, silver complexes supported by fluorinated tris(pyrazolyl)borates are less likely to aggregate (e.g., to form dimers)[25,26] by displacing other secondary ligands as a result of neighboring pyrazolyl nitrogen coordination. This feature is particularly important for the isolation of silver adducts containing fairly labile ligands such as CO and ethylene. Furthermore, fluorinated hydridotris(pyrazolyl)borates also have relatively less reducing borohydride functionality. Thus, the silver adducts of such ligands show lower tendency to decompose via a redox process forming silver metal. Overall, fluorinated systems like $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[MeB(3\text{-}(CF_3)Pz)_3]^-$ are excellent supporting ligands for the stabilization of thermally stable silver(I) tris(pyrazolyl)borates of various types. They essentially act as "Teflon-lined containers" for holding metal ions.

CARBON LIGANDS

The vast majority of the silver adducts of group 14 ligands that have been reported thus far contain $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ as the supporting ligand. This does not mean that other fluorinated tris(pyrazolyl)borates are not suitable for this purpose. However, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ is the most weakly donating tris(pyrazolyl)borate reported to date, and has the least reducing B-H unit. The THF adduct of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ has been obtained from $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ and AgOTf in tetrahydrofuran.[27] The THF in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ can be substituted easily by arenes like toluene (Figure 6) and benzene.[28] $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ can also be synthesized directly from $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(THF)$ and AgOTf in toluene. In general, only silver salts of very weakly coordinating anions form easily isolable adducts with arene ligands. Therefore, neutral hydrocarbon soluble molecules like $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ are not common. The crystal structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ has been reported. It features an η^2-bonded toluene with two different Ag-C distances. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ are excellent precursors to prepare a variety of silver adducts featuring "$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$" unit.[28]

Fluorinated tris(pyrazolyl)borates have enabled the isolation of several thermally stable silver carbonyl adducts. The first among these, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$, was reported in 1995, and has been obtained by bubbling CO into a hexane solution of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ (Figure 7).[5] More recently, the isolation of $[MeB(3\text{-}(C_2F_5)Pz)_3]AgCO$ using a B-methylated ligand was reported.[18] It was synthesized by a direct reaction between $[MeB(3\text{-}(C_2F_5)Pz)_3]Li$ and AgOTf under a carbon monoxide atmosphere. $[MeB(3\text{-}(C_2F_5)Pz)_3]AgCO$ displays a strong absorption

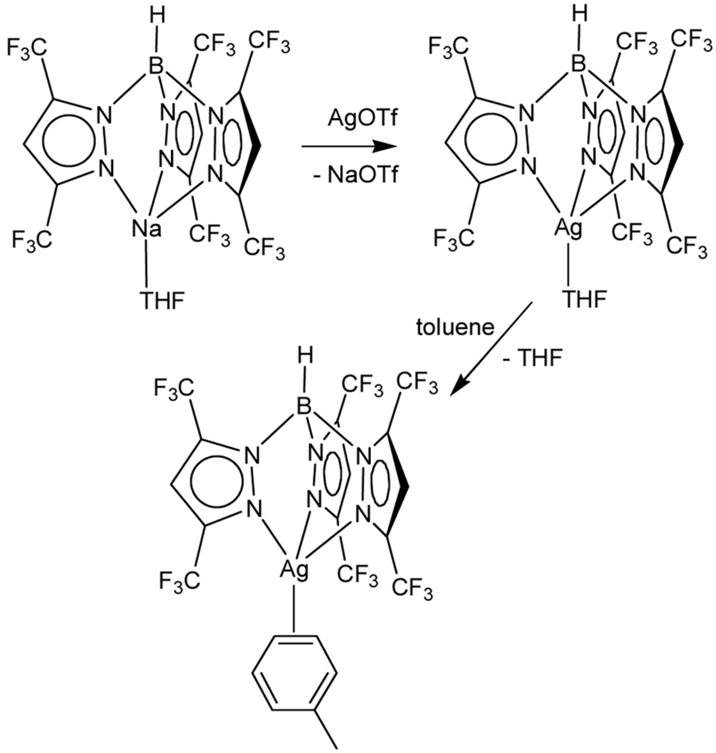

Figure 6. Synthesis of a silver(I)-toluene adduct containing $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand.

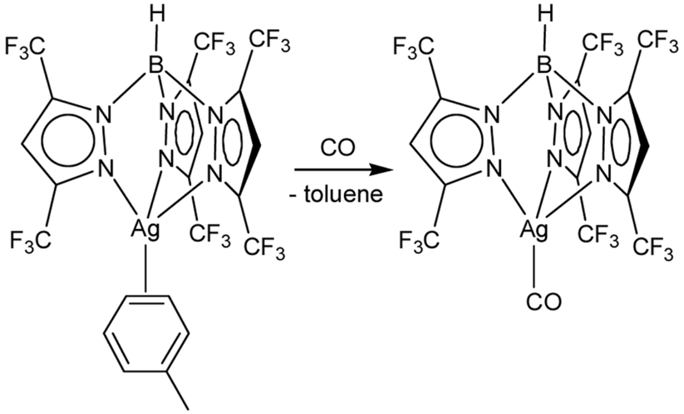

Figure 7. Synthesis of a silver(I)-CO adduct supported by $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$.

band corresponding to the C–O stretch in the IR at 2153 cm^{-1} (KBr), which is significantly lower than the value observed for [HB(3,5-$(CF_3)_2Pz)_3$]AgCO (ν_{CO} = 2178 cm^{-1} Nujol, or 2162 cm^{-1} in hexane).[18] The ^{13}C NMR and IR data suggest that these silver carbonyl adducts belong to a non-classical metal carbonyl family, and show very little, if any, Ag → CO π-backbonding.[29] The formation of [HB(3-(CF_3)),5-(Ph)Pz$)_3$]AgCO in solution (ν_{CO} = 2149 cm^{-1} in hexane) has been noted.[14] However, it has not been isolated as a thermally stable solid. Overall, structurally characterized Ag-CO adducts are rare and examples in the literature include $[Ag(CO)_2][B(OTeF_5)_4]$,[30] $[AgCO][B(OTeF_5)_4]$,[30] and [MeB(3-(Mes)Pz$)_3$]AgCO.[31] [HB(3-(Mes)Pz$)_3$]AgCO is unique among these because it shows a ν_{CO} value (2125 cm^{-1}) lower than that of the free CO (ν_{CO} = 2143 cm^{-1}) as in $Cr(CO)_6$ or $Fe(CO)_5$, and belongs to the classical metal carbonyl family.[29] Structures and properties of [HB(3,5-$(CF_3)_2Pz)_3$]CuCO[32] and [HB(3,5-$(CF_3)_2Pz)_3$]AuCO[33] have also been reported, providing a well authenticated set of coinage metal carbonyls for group trend studies.

Metal isocyanides have often been compared to metal carbonyls due to the isoelectronic relationship between CNH and CO. Although both CO and isocyanide ligands have *sp*-hybridized carbon donor centers, isocyanides display relatively stronger σ-donor character and weaker π-acceptor character. As a result, they form relatively stable complexes with metal ions in high oxidation states where π-back-bonding is of little significance. This is true also for silver(I) as evident from the isolation and the relative stability of several silver isocyanide adducts supported by both fluorinated and non-fluorinated tris(pyrazolyl)borates. Several non-fluorinated tris(pyrazolyl)borate ligand supported silver isocyanides (e.g., [HB(3,5-$(Me)_2Pz)_3$]AgCNBu^t, [HB(3,5-$(Me)_2Pz)_3$]AgCNCy, [HB(3,5-$(Ph)_2Pz)_3$]AgCNBu^t) have been synthesized and structurally

Table 3. Key structural parameters of silver-isocyanides supported by tris(pyrazolyl)borates

Compound	L	Ag-N (av.)	Ag-L	Ref.
[HB(3,5-$(CH_3)_2Pz)_3$]Ag	CN^{t}Bu	2.34 (1)	2.05 (1)	[6]
	CNCy	2.331 (3)	2.063 (5)	[6]
[HB(3,5-$(Ph)_2Pz)_3$]Ag	CN^{t}Bu	2.334 (7)	2.08 (1)	[6]
[HB(3,5-$(CF_3)_2Pz)_3$]Ag	CN^{t}Bu	2.375 (3)	2.059 (4)	[28]

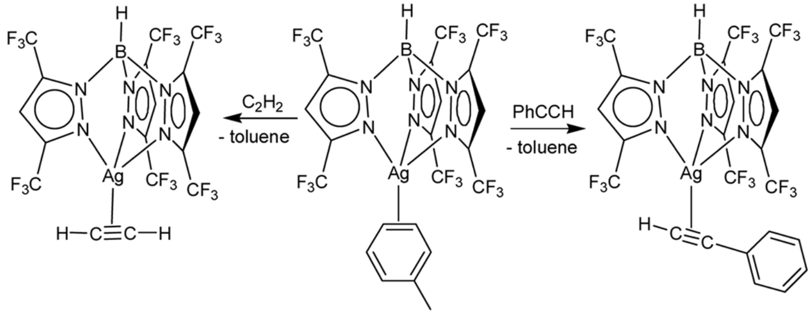

Figure 8. Silver(I)-alkyne complexes of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand.

characterized (Table 3).[6] $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCNBu^t$ is the only one that features a fluorinated tris(pyrazolyl)borate ligands, and it is stable both in solution and as a pure solid, and in contrast to $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$, donors such as benzene or toluene do not displace the secondary ligand $CNBu^t$ from the silver ion.[5] The ν_{CN} of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCNBu^t$,[5] $[HB(3,5\text{-}(Me)_2Pz)_3]AgCNBu^t$,[6] and free $CNBu^t$ [5] are 2214, 2178, 2138 cm^{-1}, respectively.

Thermally stable silver(I) acetylene and phenyl acetylene adducts have been isolated using $[HB(3,5\text{-}(CF_3)_2Pz)_3)]^-$ supporting ligand (Figure 8).[28] They have been prepared by displacing toluene from $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$. The ^{13}C signal due to coordinated acetylene in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ was observed at δ66.3 (compared with free acetylene at δ71.9). The C–H coupling constant suggests the presence of essentially *sp*-hybridized carbon atoms in the silver bound acetylene. The $\nu_{C\equiv C}$ stretching band of the silver-phenyl acetylene adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$ has been observed at 2041 cm^{-1}, which is only about 69 cm^{-1} lower than the $\nu_{C\equiv C}$ band for the free $HC{\equiv}CPh$ ligand (2110 cm^{-1}). This is a sign of a weak silver-alkyne interaction.[28] X-ray crystal structures of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$ have also been reported. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ has a symmetrically and η^2-bonded alkyne whereas in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CPh)$ the $HC{\equiv}CPh$ coordinates to the silver atom in an asymmetric manner with one short and one long Ag-C distance. Structural and spectroscopic data suggest very little Ag → alkyne π-backbonding in these silver-alkyne complexes.

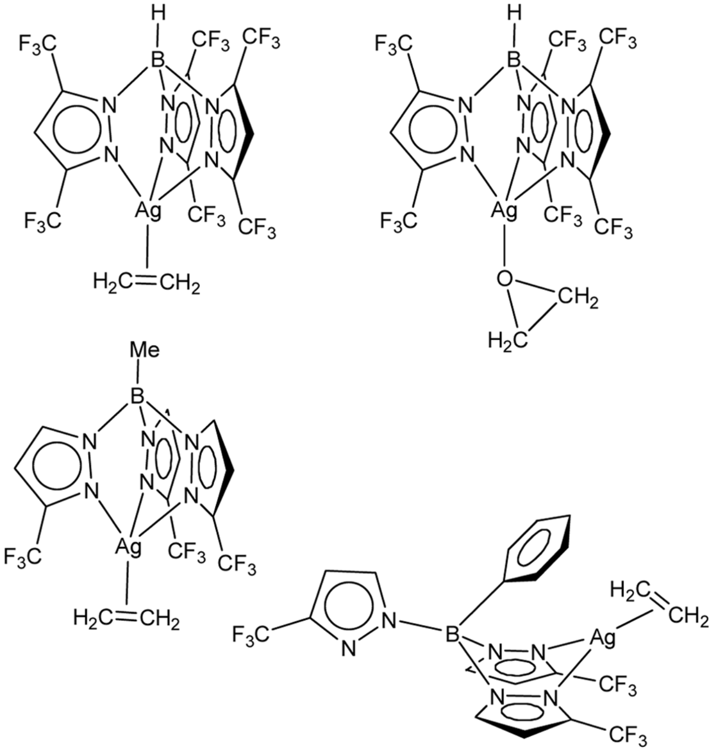

Figure 9. Silver(I)-ethylene and silver(I)-ethylene oxide adducts supported by fluorinated tris(pyrazolyl)borates.

In general, structurally characterized silver alkynes adducts like $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(HC{\equiv}CH)$ are rare as a result of weak Ag-alkyne interaction. Further difficulty is the secondary reactions of acetylene and terminal alkynes with silver ions leading to the formation of insoluble, sometimes explosive, silver acetylides. Relatively stable silver(I)-alkyne adducts found in the literature usually contain polyalkyne ligands and/or or ionic silver salts.[28]

Silver(I)-ethylene complexes represent yet another very important class of compounds stabilized by fluorinated tris(pyrazolyl)borate ligands. Silver plays an important role in the ethylene epoxidation and olefin separation.[18] In addition, there are numerous spectroscopic investigations and computational studies of $Ag(I)\text{-}(C_2H_4)$ adducts.[18] Yet, there were no structurally characterized silver(I) ethylene adducts in the literature prior to the report by Dias et al. on the isolation of [HB(3,5-$(CF_3)_2Pz)_3$]Ag($CH_2{=}CH_2$) (Figure 9).[28] It is not easy to obtain such isolable silver-ethylene adducts because silver(I) in general forms very labile ethylene adducts. Light sensitivity of silver adducts, oxidizing nature of silver, and the easy displacement of the coordinated C_2H_4 by other weakly donating species (including common solvents) present further synthetic challenges. More recently, the synthesis and isolation of [MeB(3-$(C_2F_5)Pz)_3$]Ag(CH_2=CH_2),[18] [PhB(3-(CF_3)Pz)]Ag(CH_2=CH_2)[17] and [MeB(3-(CF_3)$Pz)_3$]Ag(CH_2=CH_2)[17] were reported. Unlike [HB(3,5-$(CF_3)_2Pz)_3$]Ag(CH_2=CH_2) and [MeB(3-(C_2F_5)$Pz)_3$]Ag(CH_2=CH_2), solid samples of [PhB(3-(CF_3)$Pz)_3$]Ag(CH_2=CH_2) and [MeB(3-(CF_3)$Pz)_3$]Ag(CH_2=CH_2) lose ethylene under reduced pressure. All these adducts have typical η^2-bonded ethylene ligands. The tris(pyrazolyl)borate ligand in the B-phenylated complex [PhB(3-(CF_3)$Pz)_3$]Ag(CH_2=CH_2) shows κ^2-coordination to silver which is unusual, whereas other silver ethylene adducts described above feature tris(pyrazolyl)borates with more common tripodal κ^3-bonding mode (Figure 9).[17] In all these adducts, the C=C bond length does not show a significant change upon coordination to silver(I). The ^{1}H NMR signal of the ethylene protons in [HB(3,5-$(CF_3)_2Pz)_3$]Ag(CH_2=CH_2) appears at 5.56 ppm, which is at a downfield position relative to that of the free ethyleneb (5.40 ppm).[5,28] The related copper adduct [HB(3,5-$(CF_3)_2Pz)_3$]Cu(CH_2=CH_2) shows a small upfield shift (e.g., ethylene protons observed at 4.96 ppm in $CDCl_3$ compared to the free ethylene.[15] There are few other structurally characterized silver-ethylene adducts now known, and they include [HC{(CF_3)C(3,5-$(CF_3)_2C_6H_3$)N}$_2$]Ag(CH_2=CH_2),[34] [Ag(CH_2=CH_2)$_3$][Al{OC(CF_3)$_3$}$_4$],[35] and [MeB(3-(Mes)$Pz)_3$]Ag(CH_2=CH_2).[31]

The product resulting from the loss of ethylene from [PhB(3-(CF_3)$Pz)_3$]Ag(CH_2=CH_2) have been isolated and characterized. It is a polymer with a very interesting helical structure.[17] Each [PhB (3-(CF_3)$Pz)_3$]$^-$ acts as a bridge between two silver ions. It is possible to convert the polymeric {[PhB(3-(CF_3)$Pz)_3$]Ag}$_n$ back to [PhB(3-(CF_3)$Pz)_3$]Ag(CH_2=CH_2) by exposing to ethylene.[17]

As indicated earlier, silver plays an important role in the industrial ethylene epoxidation process.[18,35] Silver adducts like [HB(3,5-$(CF_3)_2Pz)_3$]Ag(CH_2=CH_2) are useful models for possible intermediates in this process. The [HB(3,5-$(CF_3)_2Pz)_3$]$^-$ has also enabled the isolation of a rare ethylene oxide adduct of silver, [HB(3,5-$(CF_3)_2Pz)_3$]Ag(OC_2H_4) (Figure 9).[36]

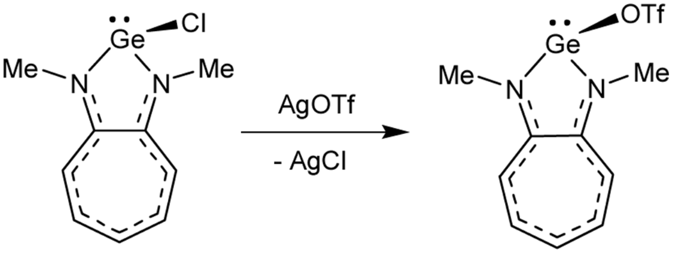

Figure 10. Successful chloride ion abstraction from $[(Me)_2ATI]GeCl$ by AgOTf.

SILVER COMPLEXES OF GERMANIUM AND TIN LIGANDS

Halide derivatives of germanium(II) and tin(II) aminotroponiminate (ATI) complexes like $[(n\text{-}Pr)_2ATI]GeCl$, $[(Me)_2ATI]GeCl$, and $[(n\text{-}Pr)_2ATI]SnCl$ undergo rapid metathesis with CF_3SO_3Ag,[37,38] leading to the corresponding trifluoromethanesulfonate salts $\{[(n\text{-}Pr)_2ATI]Ge\}[SO_3CF_3]$, $\{[(Me)_2ATI]Ge\}[SO_3CF_3]$ and $\{[(n\text{-}Pr)_2ATI]Sn\}[SO_3CF_3]$, and silver chloride (Figure 10). However, when the silver source $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ is used, rather than undergoing metathesis, very stable 1:1 adducts $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Ge(Cl)[(n\text{-}Pr)_2ATI]$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Ge(Cl)[(Me)_2ATI]$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Sn(Cl)[(n\text{-}Pr)_2ATI]$ are formed (Figure 11). The iodide derivative $[(n\text{-}Pr)_2ATI]SnI$ also forms a simple adduct with $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ rather than generating silver halide (in this case, AgI) precipitate.[37,38]

The reaction between $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Ge(Cl)[(Me)_2ATI]$ and AgOTf has been investigated.[37] It affords the chloride-free product $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Ge(OSO_2CF_3)[(Me)_2ATI]$ and AgCl. The X-ray structures have also been reported and they feature rare unsupported Ag-Ge and Ag-Sn bonds. The M-X and M-N_{ring} (M = Ge or Sn, X = Cl or I) bonds of these aminotroponiminate adducts shorten upon coordination to silver. Some of these molecules are believed to be good models for intermediates in silver-halide metathesis process involving Ge(II) and Sn(II) halides and silver salts like AgOTf.

The chemistry between $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ and $[(n\text{-}Pr)_2ATI]GeN_3$ or $[(n\text{-}Pr)_2ATI]SnN_3$ has also been described.[39] Interestingly, rather than undergoing metathesis (leading to AgN_3) or nitrogen elimination or silver ion coordination to the nitrogen atoms of the azide moiety (as in $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow N(Ad)NN$),[40] they form

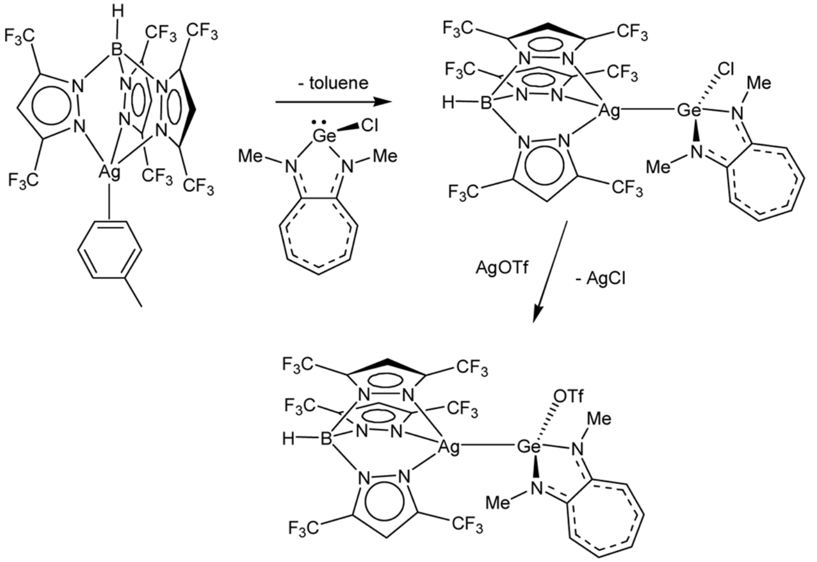

Figure 11. Retarded and successful silver halide metathesis involving $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ and AgOTf.

adducts $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow M(N_3)[(n\text{-}Pr)_2ATI]$ (M = Ge and Sn) featuring unsupported silver–germanium and silver–tin bonds. Crystal structures of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Ge(N_3)[(n\text{-}Pr)_2ATI]$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag \leftarrow Sn(N_3)[(n\text{-}Pr)_2ATI]$ have been reported.[39]

Related Ag–Si or Ag–Pb bonded adducts supported by tris(pyrazolyl)borates have not been reported yet. Luminescence properties of silver adducts containing heavier group 14 members are also of potential interest, considering that they feature bonds between atoms of d^{10} and pseudo-d^{10} configurations.

APPLICATIONS

Most of the applications based on silver supported by fluorinated tris(pyrazolyl)borates concern the THF adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$. However, it is not difficult to replace THF by most other ligands. For example, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ has been obtained during the crystallization of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ from toluene. Thus, compounds like $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgL'$ where $L' = $ THF, toluene, ethylene, CO, C_2H_2 are good precursors for

"$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$" moiety, and most likely behave in a similar manner in following reactions.[28]

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ has been used as a good ligand transfer agent in the preparation of a large variety of metal complexes. It reacts with ClAuCO in carbon monoxide saturated dichloromethane to give the first tris(pyrazolyl)boratogold carbonyl adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$.[33] Silver salt metathesis between $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ and metal halides like $BrMn(CO)_5$,[23] InCl, GaI have also been investigated.[27,41] These reactions lead to $[HB(3,5\text{-}(CF_3)_2Pz)_3]Mn(CO)_3$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$, and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$. Alkyl group metathesis involving $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ is also known. Reactions between $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ and $AlMe_3$ or $Zn(CH_2CH_3)_2$ afford $[HB(3,5\text{-}(CF_3)_2Pz)_3]AlMe_2$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Zn(CH_2CH_3)$.[42]

$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ activates fairly inert C–H and C–X (X = Cl, Br) bonds via a carbene transfer process under remarkably mild conditions.[43,44] Ethyl diazoacetate serves as the carbene source in these reactions. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ also catalyzes carbene transfer to primary allylic and propargylic halides resulting in a net addition-rearrangement sequence[45] and to arenes leading to Büchner reaction.[46] $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(OSMe_2)$ have been used as anti-bacterial agents. They show excellent antibacterial activity against certain classes of pathogens (e.g., *Staphylococcus aureus*), which is comparable and even superior to common agents like silver sulfadiazine and silver nitrate.[47]

SUMMARY AND CONCLUSION

As we saw from the preceding account, fluorinated tris(pyrazolyl)borates have led to major advances in silver coordination chemistry. They have afforded a number of rare (often for the first time), thermally stable and structurally characterized silver adducts featuring important group 14 donors like CO, ethylene, and acetylene. Key structural parameters of some of the molecules highlighted in this review are presented in Table 4.

These adducts feature pseudo-tetrahedral silver sites (except $[PhB(3\text{-}(CF_3)Pz)_3]Ag(CH_2{=}CH_2)$). The Ag-N distances vary only within a small range. Although we have not discussed it here in detail, fluorinated tris (pyrazolyl)borates are excellent supporting ligands for the isolation

Table 4. Key structural parameters of silver tris(pyrazolyl)borates containing group 14 ligands

L	Compound	Ag-N bond distance (Å, average)	Ag-L bond distance (Å)	Ref.
C-Ligand	$[HB(3,5-(CF_3)_2Pz)_3]AgCO$	2.328 (4)	2.037 (5)	[28]
	$[MeB(3-(C_2F_5)Pz)_3]AgCO$	2.314 (3)	2.030 (4)	[18]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2-C_2H_4)$	2.358 (4)	2.294 (7), 2.307 (7)	[28]
	$[MeB(3-(CF_3)Pz)_3]Ag(\eta^2-C_2H_4)$	2.3453 (13)	2.2853 (18), 2.2791 (19)	[17]
	κ^2-$[PhB(3-(CF_3)Pz)_3]Ag(\eta^2-C_2H_4)$	2.261 (3)	2.262 (4), 2.267 (4)	[17]
	$[MeB(3-(C_2F_5)Pz)_3]Ag(\eta^2-C_2H_4)$	2.3544 (14)	2.301 (2), 2.300 (2)	[18]
	$[HB(3,5-(CF_3)_2Pz)_3]AgCN^tBu$	2.375 (3)	2.059 (4)	[28]
	$[HB(3-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) *two molecules in the asymmetric unit*	2.390 (2)	2.414 (4), 2.506 (4); 2.392 (4), 2.480 (4)	[28]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2-C_2H_2)$	2.353 (3)	2.293 (4), 2.293 (4)	[28]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2-CHCPh)$	2.371 (3)	2.263 (5), 2.407 (5)	[28]
Ge-Ligand	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow GeCl[(Me)_2ATI]$	2.402 (4)	2.4215 (9)	[37]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow Ge(OSO_2CF_3)[(Me)_2ATI]$	2.379 (6)	2.4116 (10)	[37]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow GeCl[(n-Pr)_2ATI]$	2.383 (3)	2.4142 (6)	[38]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow Ge(N_3)[(n-Pr)_2ATI]$	2.411 (4)	2.4146 (7)	[39]
Sn-Ligand	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow SnCl[(n-Pr)_2ATI]$	2.383 (4)	2.5863 (6)	[38]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow SnI[(n-Pr)_2ATI]$	2.367 (7)	2.5880 (10)	[38]
	$[HB(3,5-(CF_3)_2Pz)_3]Ag \leftarrow Sn(N_3)[(n-Pr)_2ATI]$	2.385 (3)	2.5943 (6)	[39]

of silver adducts featuring ligands from other groups (e.g., dimethyl diazomalonate,[48] adamantyl azide,[40] ethylene oxide,[36] propylene sulfide.[36]) $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ is the ligand that has been used most widely in these reports. Some of these molecules show long–range coupling involving fluorine atoms in the NMR spectra. Very little has been done using other fluorinated ligands including B-protected versions. Silver chemistry based on such ligands as well as detailed computational work on these interesting silver complexes, and new processes catalyzed by some of fluorinated tris(pyrazolyl)borates, are likely avenues for future research.

ACKNOWLEDGEMENT

This work has been supported by the Robert A. Welch Foundation (grant Y-1289). We are also grateful to the very talented postdoctoral fellows, graduate students and undergraduate students whose names appear in the references.

REFERENCES

1. Trofimenko, S. 1999. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London.
2. Pettinari, C. and C. Santini, 2004. *Comprehensive Coordination Chemistry II*, **1**, 159–210.
3. Abu Salah, O. M., G. S. Ashby, M. I. Bruce, E. A. Pederzolli, and J. D. Walsh, 1979. *Australian Journal of Chemistry*, **32**, 1613–1619.
4. Bruce, M. I. and J. D. Walsh, 1979. *Australian Journal of Chemistry*, **32**, 2753–2756.
5. Dias, H. V. R. and W. Jin, 1995. *Journal of the American Chemical Society*, **117**, 11381–11382.
6. Gioia Lobbia, G., C. Pettinari, C. Santini, B. W. Skelton, and A. H. White, 2000. *Inorganica Chimica Acta*, **298**, 146–153.
7. Dias, H. V. R., W. Jin, H.-J. Kim, and H.-L. Lu, 1996. *Inorganic Chemistry*, **35**, 2317–2328.
8. Dias, H. V. R. and H.-J. Kim, 1996. *Organometallics*, **15**, 5374–5379.
9. Dias, H. V. R., H.-L. Lu, R. E. Ratcliff, and S. G. Bott, 1995, *Inorganic Chemistry*, **34**, 1975–1976.
10. Renn, O., L. M. Vananci, A. Marteletti, and V. Gramlich, 1995. *Helvetica Chimica Acta*, **78**, 993–1000.
11. Fekl, U., R. van Eldik, S. Lovell, and K. I. Goldberg, 2000. *Organometallics*, **19**, 3535–3542.

12. Ghosh, C. K., J. K. Hoyano, R. Krentz, and W. A. G. Graham, 1989. *Journal of the American Chemical Society*, **111**, 5480–5481.
13. Hu, Z. and S. M. Gorun, 2001. *Inorganic Chemistry*, **40**, 667–671.
14. Dias, H. V. R. and T. K. H. H. Goh, 2004. *Polyhedron*, **23**, 273–282, and the references therein.
15. Dias, H. V. R., H.-L. Lu, H.-J. Kim, S. A. Polach, T. K. H. H. Goh, R. G. Browning, and C. J. Lovely, 2002. *Organometallics*, **21**, 1466–1473.
16. Han, R., P. Ghosh, P. J. Desrosiers, S. Trofimenko, and G. Parkin, 1997. *Journal of the Chemical Society, Dalton Transactions*, 3713–3717.
17. Dias, H. V. R., J. Wu, X. Wang, and K. Rangan, 2007. *Inorganic Chemistry*, **46**, 1960–1962.
18. Dias, H. V. R. and X. Wang, 2005. *Dalton Transactions*, 2985–2987, and the references therein.
19. Bergman, R. G., T. R. Cundari, A. M. Gillespie, T. B. Gunnoe, W. D. Harman, T. R. Klinckman, M. D. Temple, and D. P. White, 2003. *Organometallics*, **22**, 2331–2337.
20. Smart, B. E. 2001. *Journal of Fluorine Chemistry*, **109**, 3–11.
21. Imai, S., K. Fujisawa, T. Kobayashi, N. Shirasawa, H. Fujii, T. Yoshimura, N. Kitajima, and Y. Moro-oka, 1998. *Inorganic Chemistry*, **37**, 3066–3070.
22. Joshi, H. K., M. E. Arvin, J. C. Durivage, N. E. Gruhn, M. D. Carducci, B. L. Westcott, D. L. Lichtenberger, and J. H. Enemark, 2004. *Polyhedron*, **23**, 429–438.
23. Dias, H. V. R., H.-J. Kim, H.-L. Lu, K. Rajeshwar, N. R. de Tacconi, A. Derecskei-Kovacs, and D. S. Marynick, 1996. *Organometallics*, **15**, 2994–3003.
24. Dias, H. V. and R. X. Wang, 2004. *Polyhedron*, **23**, 2533–2539.
25. Humphrey, E. R., Z. Reeves, J. C. Jeffery, J. A. McCleverty, and M. D. Ward, 1999. *Polyhedron*, **18**, 1335–1338.
26. Effendy Lobbia, G. G., C. Pettinari, C. Santini, B. W. Skelton, and A. H. White, 2000. *Inorganica Chimica Acta*, **308**, 65–72.
27. Dias, H. V. R. and W. Jin, 1996. *Inorganic Chemistry*, **35**, 267–268.
28. Dias, H. V. R., Z. Wang, and W. Jin, 1997. *Inorganic Chemistry*, **36**, 6205–6215.
29. Lupinetti, A. J., S. H. Strauss, and G. Frenking, 2001. *Progress in Inorganic Chemistry*, **49**, 1–112.
30. Hurlburt, P. K., J. J. Rack, J. S. Luck, S. F. Dec, J. D. Webb, O. P. Anderson, and S. H. Strauss, 1994. *Journal of the American Chemical Society*, **116**, 10003–14.
31. Dias, H. V. R. and M. Fianchini, 2007. *Angewandte Chemie, International Edition*, **46**, 2188–2191.
32. Dias, H. V. R. and H.-L. Lu, 1995. *Inorganic Chemistry*, **34**, 5380–5382.
33. Dias, H. V. R. and W. Jin, 1996. *Inorganic Chemistry*, **35**, 3687–3694.

34. Chiong, H. A. and O. Daugulis, 2006. *Organometallics*, **25**, 4054–4057.
35. Krossing, I. and A. Reisinger, 2003. *Angewandte Chemie, International Edition*, **42**, 5725–5728.
36. Dias, H. V. R. and Z. Wang, 2000. *Inorganic Chemistry*, **39**, 3724–3727.
37. Dias, H. V. R. and Z. Wang, 2000. *Inorganic Chemistry*, **39**, 3890–3893.
38. Ayers, A. E. and H. V. R. Dias, 2002. *Inorganic Chemistry*, **41**, 3259–3268.
39. Dias, H. V. R. and A. E. Ayers, 2002. *Polyhedron*, **21**, 611–618.
40. Dias, H. V. R., S. A. Polach, S.-K. Goh, E. F. Archibong, and D. S. Marynick, 2000. *Inorganic Chemistry*, **39**, 3894–3901.
41. Dias, H. V. R. and W. Jin, 2000. *Inorganic Chemistry*, **39**, 815–819.
42. Dias, H. V. R. and W. Jin, 2003. *Inorganic Chemistry*, **42**, 5034–5036.
43. Dias, H. V. R., R. G. Browning, S. A. Polach, H. V. K. Diyabalanage, and C. J. Lovely, 2003. *Journal of the American Chemical Society*, **125**, 9270–9271.
44. Dias, H. V. R., R. G. Browning, S. A. Richey, and C. J. Lovely, 2004. *Organometallics*, **23**, 1200–1202.
45. Krishnamoorthy, P., R. G. Browning, S. Singh, R. Sivappa, C. J. Lovely, and H. V. R. Dias, 2007. *Chemical Communications*, 731–733.
46. Lovely, C. J., R. G. Browning, V. Badarinarayana, and H. V. R. Dias, 2005. *Tetrahedron Letters*, **46**, 2453–2455.
47. Dias, H. V. R., K. H. Batdorf, M. Fianchini, H. V. K. Diyabalanage, S. Carnahan, R. Mulcahy, A. Rabiee, K. Nelson, and L. G. van Waasbergen, 2006. *Journal of Inorganic Biochemistry*, **100**, 158–160.
48. Dias, H. V. R. and S. A. Polach, 2000. *Inorganic Chemistry*, **39**, 4676–4677.