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Polyfluorinated ligand-supported organometallic complexes of copper, silver, and gold*

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Abstract: The tris(pyrazolyl)borate $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ prepared using highly fluorinated 3,5-bis(trifluoromethyl)pyrazole and BH_4^- is an excellent supporting ligand for the stabilization of a number of rare organometallic complexes of coinage metals. For example, it has enabled the isolation of Cu(I), Ag(I), and Au(I) complexes of CO and ethylene as crystalline solids. Syntheses, spectroscopic and structural features, and properties of $[HB(3,5\text{-}(CF_3)_2Pz)_3]ML$ (M = Cu, Ag, Au; L = CO, C_2H_4) are the main focus of this discussion. Several metal adducts based on the tris(triazolyl)borate $[HB(3,5\text{-}(CF_3)_2Tz)_3]^-$ supporting ligand as well as the cationic, coinage metal multi-alkene complexes containing the $[SbF_6]^-$ counterion are also discussed.

Keywords: alkenes; carbon monoxide; copper; fluorinated ligands; gold; silver.

Coinage metals (Cu, Ag, and Au) mediate many important chemical processes involving unsaturated, C-based compounds like CO and olefins [1,2]. For example, Cu plays an important role in the synthesis of methanol from CO and hydrogen and in the selective removal of CO from gas mixtures [3,4]. Cu(I), Ag(I), and Au(I) salts are also capable of catalyzing carbonylation reactions of olefins and alcohols [5–8]. Silver-mediated highly selective oxidation of ethylene to ethylene oxide and olefin-paraffin separation are processes of significant industrial importance [9–13]. Gold-based materials serve as excellent catalysts for the low-temperature oxidation of CO and selective epoxidation of propene [14–19]. Ethylene (which is a plant hormone) receptor site in plants is believed to be a Cu center [20–22]. In these reactions and many other reported processes in the literature which involve coinage metals and CO or alkenes, Cu, Ag, or Au complexes with bonds to CO or alkene are believed to be one of the key intermediates or the main focus. Structures and properties of such species, therefore, are of significant interest.

Isolation of thermally stable species with bonds between coinage metal ions and CO or alkenes like ethylene is challenging due to their high reactivity and/or lability. An area of research focus in our laboratory concerns the development and use of highly fluorinated ligands and weakly coordinating anions for the stabilization of such species in crystalline and “bottle-able” form (i.e., preferably, molecules that are stable at room temperature and in air) and to characterize them using routinely used analytical tools such as NMR spectroscopy and X-ray crystallography [1,2,23]. Easily isolable Cu, Ag, and Au adducts of CO and ethylene would serve as excellent models for the proposed intermediates in processes involving coinage metal ions and C-based unsaturated molecules, provide valuable structural and spectroscopic information, and permit convenient reactivity studies.

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Polyfluorinated tris(pyrazolyl)borate (e.g., $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, **1**) [1,23], tris(triazolyl)borate (e.g., $[HB(3,5\text{-}(CF_3)_2Tz)_3]^-$, **2**) [24,25], and 1,3,5-triazapentadienyl ligands (e.g., $[N\{(C_3F_7)C(Dipp)N\}_2]^-$, **3**) [26–29] and weakly coordinating anions [30–32] like $[SbF_6]^-$ (**4**) have been the most useful in our hands thus far for the stabilization of Cu, Ag, and Au adducts of unsaturated carbon-based molecules (Fig. 1). Here we mainly focus on one of these ligands, fluorinated tris(pyrazolyl)borate $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, and its utility in the successful isolation of Cu(I), Ag(I), and Au(I) complexes of CO and ethylene.

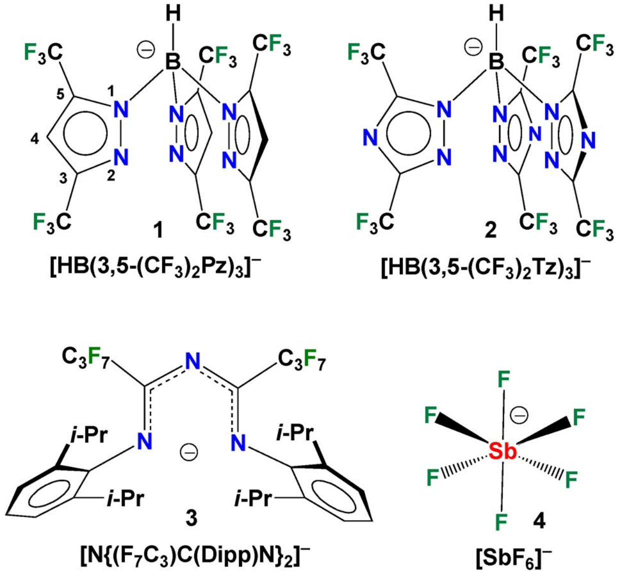
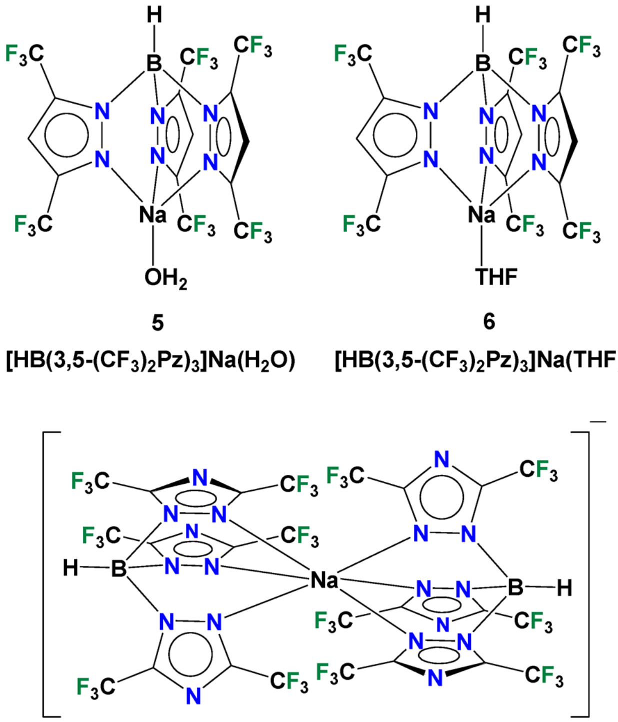


Fig. 1 A few examples of polyfluorinated ligands and weakly coordinating anions utilized successfully in Dias Laboratory for the isolation of CO and olefin adducts of Cu(I), Ag(I), and Au(I).

Tris(azolyl)borates are widely used as auxiliary ligands in coordination chemistry [33,34]. They are particularly attractive because steric and electronic properties of the ligand can be modified conveniently by changing the nitrogen-based heterocycle or by varying the substituents on the azolyl ring and/or on the B atom. The Na salt of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ can be synthesized in high yield using the parent pyrazole $3,5\text{-}(CF_3)_2PzH$ and $NaBH_4$ [23,35]. It is important to use dry, freshly sublimed (or distilled) $3,5\text{-}(CF_3)_2PzH$ since the pyrazole is hygroscopic and extra moisture can drastically reduce the yield of the $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na$. Once formed, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na$ is fairly tolerant of moisture since it could even be crystallized as its water adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na(OH_2)$ (**5**, Fig. 2). The diethyl ether and tetrahydrofuran (THF) coordinated $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na$ can also be isolated (e.g., **6**) [36]. The potassium salt of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (e.g., $[HB(3,5\text{-}(CF_3)_2Pz)_3]K(DMAC)$, DMAC = dimethyl acetamide) is also known [37]. The related tris(triazolyl)borate $[HB(3,5\text{-}(CF_3)_2Tz)_3]Na$ has been synthesized using $3,5\text{-}(CF_3)_2TzH$ and $NaBH_4$ [25]. Crystallization of $[HB(3,5\text{-}(CF_3)_2Tz)_3]Na$ from THF led to a very interesting ionic compound that has a tris(triazolyl)borate sandwiched Na anion $\{[HB(3,5\text{-}(CF_3)_2Tz)_3]_2Na\}^-$ (**7**, Fig. 2) and a $[Na(THF)_6]^+$ cation [25].



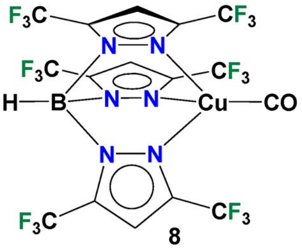
5 $[HB(3,5-(CF_3)_2Pz)_3]Na(H_2O)$

6 $[HB(3,5-(CF_3)_2Pz)_3]Na(THF)$

7 $\{[HB(3,5-(CF_3)_2Tz)_3]_2Na\}^-$

Fig. 2 Several Na complexes of polyfluorinated tris(azolyl)borates.

The Cu(I) carbonyl complex $[HB(3,5-(CF_3)_2Pz)_3]CuCO$ (**8**) could be obtained from a reaction between $[HB(3,5-(CF_3)_2Pz)_3]K(DMAC)$ and CuOTf under a CO atmosphere [38]. It is a rare, air and thermally stable Cu-CO complex and shows one of the highest carbonyl stretching frequencies ($\nu_{CO} = 2137\ cm^{-1}$) for a Cu carbonyl species [1]. This value is about 71 cm^{-1} higher than that of the nonfluorinated analog $[HB(3,5-(CH_3)_2Pz)_3]CuCO$ [39].



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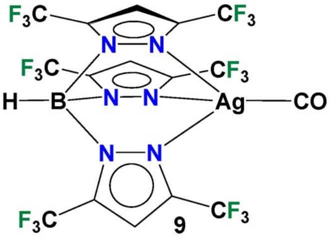
$[HB(3,5-(CF_3)_2Pz)_3]CuCO$

$\nu_{CO} = 2137\ cm^{-1}$



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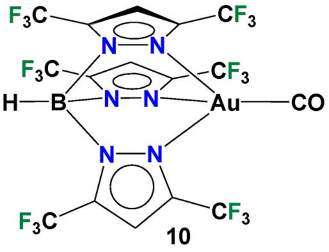
$[HB(3,5-(CF_3)_2Pz)_3]AgCO$

$\nu_{CO} = 2178\ cm^{-1}$



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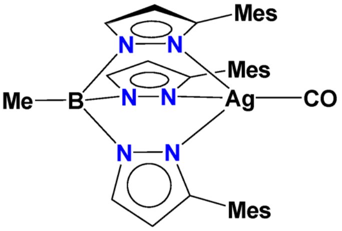
$[HB(3,5-(CF_3)_2Pz)_3]AuCO$

$\nu_{CO} = 2144\ cm^{-1}$

The Ag and Au carbonyl adducts of $[HB(3,5-(CF_3)_2Pz)_3]^-$ can also be prepared. $[HB(3,5-(CF_3)_2Pz)_3]AgCO$ (**9**) was synthesized by treating the corresponding Ag-toluene adduct $[HB(3,5-(CF_3)_2Pz)_3]Ag(toluene)$ with CO while the reaction between $[HB(3,5-(CF_3)_2Pz)_3]AgCO$ and

AuCl affords the $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$ (**10**) [40,41]. Unlike the Cu carbonyl adduct, these Ag and Au carbonyl complexes are rather reactive molecules and decompose easily. The CO stretching band of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ appears at 2178 cm^{-1}, suggesting very little (if any) back-bonding between the Ag(I) and CO. It is an example of a "non-classical" metal carbonyl complex [42]. In fact, almost all structurally authenticated or spectroscopically detected Ag(I)-CO adducts reported thus far belong to this category. $[MeB(3\text{-}(Mes)Pz)_3]AgCO$ (**11**, Mes = Mesityl; 2,4,6-$Me_3C_6H_2$) is a rare exception [43] The ν_{CO} band of this adduct has been observed at 2125 cm^{-1}, which is lower than that of the free CO (ν_{CO} = 2143 cm^{-1}). It is a Ag-carbonyl that belongs to the "classical" metal carbonyl family.

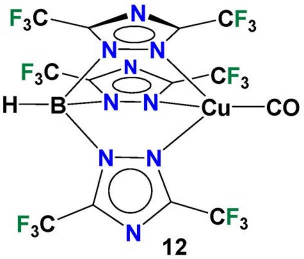


11

$[MeB(3\text{-}(Mes)Pz)_3]AgCO$
ν_{CO} = 2125 cm^{-1}

The Au adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$ features a pseudo-tetrahedral metal site (similar to the analogous Cu and Ag adducts) and displays ν_{CO} band at 2144 cm^{-1}. Compounds $[HB(3,5\text{-}(CF_3)_2Pz)_3]MCO$ (M = Cu, Ag, Au) represent the first complete series of well-authenticated, isoleptic coinage metal carbonyl adducts. The Ag adduct has the longest coinage metal–CO bond while the Cu analog displays the shortest M–C distance.

We also reported the isolation of $[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$ (**12**) and $[HB(3,5\text{-}(CF_3)_2Tz)_3]AgCO$ (**13**) using the closely related tris(triazolyl)borate-supporting ligand [24,25]. Surprisingly, these adducts and the corresponding tris(pyrazolyl)borate counterparts show essentially identical CO stretching frequency values (although the tris(triazolyl)borate ligand is a relatively weaker donor). NMR data of the corresponding ethylene complexes showed a clear difference consistent with the weakly donating nature of tris(triazolyl)borate ligand support. Thus, this work shows that in certain situations, one has to be careful when using CO stretching frequency data as a convenient indicator of the metal site electron density [24,25].



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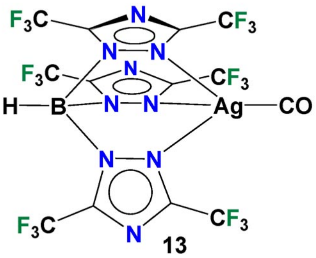
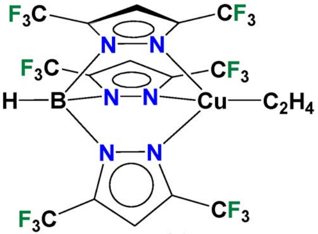
$[HB(3,5\text{-}(CF_3)_2Tz)_3]CuCO$



13

$[HB(3,5\text{-}(CF_3)_2Tz)_3]AgCO$

The Cu(I) ethylene adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ (**14**) can be obtained by reacting the corresponding Na derivative with CuOTf in the presence of ethylene [44]. Closely related Ag complex $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ (**15**) was synthesized by treating $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ (which was obtained from a reaction between [HB(3,5-$(CF_3)_2Pz)_3$]Na(THF) and AgOTf) with ethylene [45]. The reaction of [HB(3,5-$(CF_3)_2Pz)_3$]Na with AuCl under an ethylene atmosphere led to the Au analog [HB(3,5-$(CF_3)_2Pz)_3$]Au(C_2H_4) (**16**) [46]. These three coinage metal ethylene complexes show remarkable stability. Solid samples of [HB(3,5-$(CF_3)_2Pz)_3$]M(C_2H_4) (M = Cu, Ag, Au) are thermally stable at room temperature, can be handled in open air and under light for short periods without noticeable decomposition, and do not lose ethylene under reduced pressure. Notably, [HB(3,5-$(CF_3)_2Pz)_3$]Ag(C_2H_4) and [HB(3,5-$(CF_3)_2Pz)_3$]Au(C_2H_4) are the first structurally characterized Ag- and Au-ethylene complexes.



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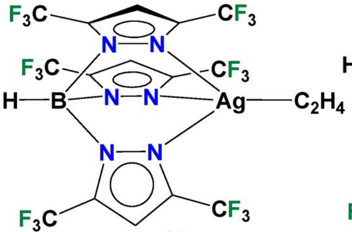
[HB(3,5-$(CF_3)_2Pz)_3$]Cu(C_2H_4)



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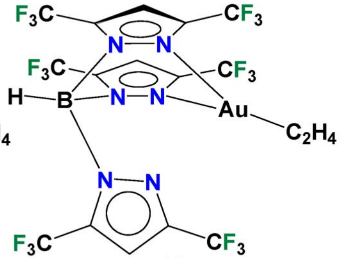
[HB(3,5-$(CF_3)_2Pz)_3$]Ag(C_2H_4)



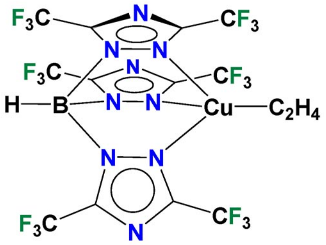
16

[HB(3,5-$(CF_3)_2Pz)_3$]Au(C_2H_4)

Compared to free ethylene, CD_2Cl_2 solutions of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(C_2H_4) shows *downfield*-shifted ^1H and upfield-shifted ^{13}C NMR signals for the Ag coordinated ethylene. In contrast, metal-coordinated ethylene of [HB(3,5-$(CF_3)_2Pz)_3$]Cu(C_2H_4) and [HB(3,5-$(CF_3)_2Pz)_3$]Au(C_2H_4) display upfield-shifted signals in both ^1H and ^{13}C NMR spectra. ^{13}C NMR data of ethylene carbons are useful for probing M-ethylene backbonding interactions [2]. Among these coinage metal complexes, ethylene ^{13}C NMR signal of [HB(3,5-$(CF_3)_2Pz)_3$]Au(C_2H_4) (63.7 ppm) shows an upfield shift of about 60 ppm from the free ethylene (123.3 ppm). This points to significant Au(I) → ethylene backbonding (despite having a highly fluorinated supporting ligand on Au) [2]. The related [HB(3,5-$(CF_3)_2Pz)_3$]Cu(C_2H_4) and HB(3,5-$(CF_3)_2Pz)_3$]Ag(C_2H_4) show much smaller upfield shifts from the free ethylene (34 and 18 ppm, respectively) [1].

[HB(3,5-$(CF_3)_2Pz)_3$]M(C_2H_4) also represents the first complete series of structurally characterized isoleptic coinage metal ethylene complexes. The Cu and Ag adducts show pseudo-tetrahedral metal sites while the Au complex features an uncommon three-coordinate, trigonal planar, Au site. The tris(pyrazolyl)borate ligand in [HB(3,5-$(CF_3)_2Pz)_3$]M(C_2H_4) shows κ^2-bonding [47]. [HB(3,5-$(CF_3)_2Pz)_3$]Cu(C_2H_4) and [HB(3,5-$(CF_3)_2Pz)_3$]Ag(C_2H_4) also serve as excellent catalysts for several transformations. For example, [HB(3,5-$(CF_3)_2Pz)_3$]Ag(C_2H_4) catalyzes the insertion of carbene moiety of ethyl diazoacetate to unactivated C–H bonds of hydrocarbons at room temperature in very high yields [1,48].

[HB(3,5-$(CF_3)_2Tz)_3$]Cu(C_2H_4) (**17**) and [HB(3,5-$(CF_3)_2Tz)_3$]Ag(C_2H_4) (**18**) have a fluorinated tris(triazolyl)borate ligand [24]. Compared to the corresponding tris(pyrazolyl)borate analogs [HB(3,5-$(CF_3)_2Pz)_3$]M(C_2H_4), ethylene proton and carbon signals of these adducts in ^1H and ^{13}C NMR spectra appear at relatively upfield positions. [HB(3,5-$(CF_3)_2Tz)_3$]Ag(C_2H_4) displays one of the highest ethylene ^{13}C NMR chemical shift values for a coordinated ethylene moiety (109.7 ppm) of a metal complex [47].



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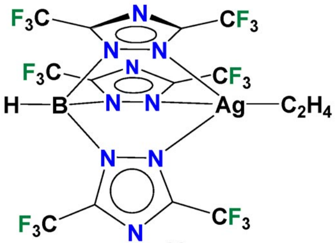
[HB(3,5-$(CF_3)_2$Tz$)_3$]Cu(C_2H_4)



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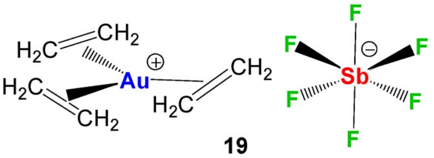
[HB(3,5-$(CF_3)_2$Tz$)_3$]Ag(C_2H_4)

More recently, we have described the isolation of several cationic coinage metal complexes containing three alkene donors using commercially available $[SbF_6]^-$ counter ion [30–32]. $[Au(C_2H_4)_3][SbF_6]$ (**19**) is one such example [30]. The cationic $[Au(C_2H_4)_3]^+$ moiety of this compound is planar, and the six ethylene carbon atoms and the Au form a spoke wheel structure. It is also possible to isolate tris(alkene) complexes of coinage metal ions using larger alkenes like norbornene [31]. X-ray data show that the basic structural features of [M(norbornene$)_3$][SbF_6] (**20**, M = Cu, Ag, Au) are remarkably similar between the three coinage metal family members. They also feature spoke wheel structures. In this group of compounds, the Ag adduct has the longest M-C(alkene) bonds while the Cu system has the shortest M-C(alkene) contacts.



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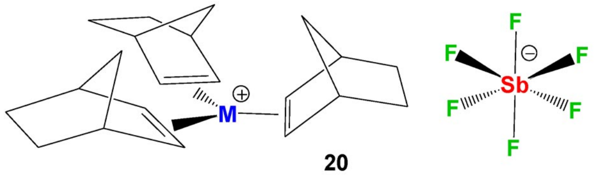
$[Au(C_2H_4)_3][SbF_6]$



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[M(norbornene$)_3$][SbF_6], M = Cu, Ag, Au

Overall, we have been able to synthesize a variety of coinage metal complexes featuring coordinated CO or alkenes, isolate them as crystalline solids, and investigate the structures and properties. Fluorinated ligands and anions have played a major role in this work.

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