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CLUSTER ISSUE

Fluorinated Scorpionates

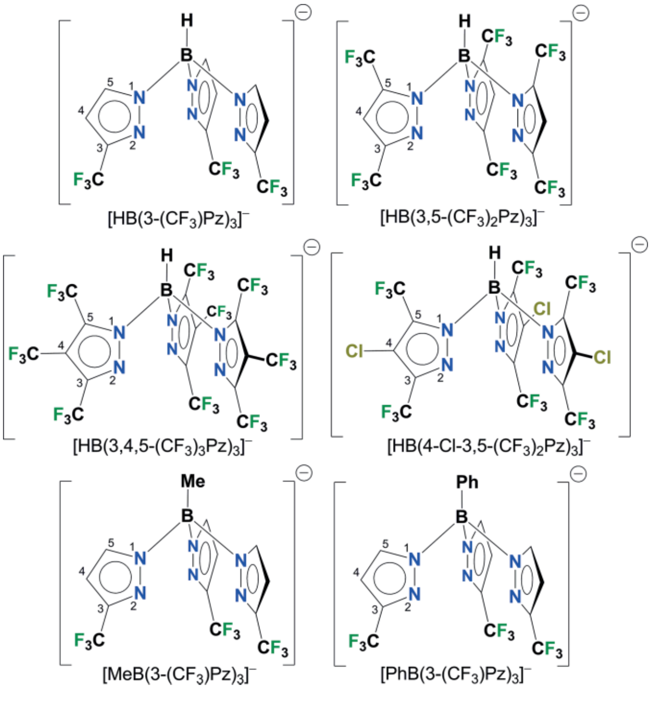
Isolable Ethylene Complexes of Copper(I), Silver(I), and Gold(I) Supported by Fluorinated Scorpionates $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]^-$ and $[HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3]^-$

Shawn G. Ridlen,[a] Jiang Wu,[a] Naveen V. Kulkarni,[a] and H. V. Rasika Dias*[a]

Abstract: The group 11 metal adducts $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]M(C_2H_4)$ (M = Au, Ag, and Cu; Pz = pyrazolyl) have been synthesized via a metathesis process using $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Na$ and CF_3SO_3Cu, CF_3SO_3Ag, AuCl and ethylene. The related $[HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3]Ag(C_2H_4)$ has also been synthesized using $[HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3]Na(THF)$, CF_3SO_3Ag and ethylene. These group 11 metal ethylene complexes are white solids and form colorless crystals. They have been characterized by NMR spectroscopy and X-ray crystallography. The gold-ethylene adduct $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Au(C_2H_4)$ shows large upfield NMR shifts of the ethylene proton and carbon signals relative to the corresponding peaks of the free ethylene, indicating relatively high Au→ethylene backbonding. NMR chemical shift data suggest that the silver complexes of both the tris(pyrazolyl)borate ligands $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]^-$ and $[HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3]^-$ exhibit the weakest interaction with ethylene as compared to the respective copper and gold complexes. X-ray crystal structures reveal that the gold atom in $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Au(C_2H_4)$ binds to scorpionate in κ^2-fashion while the related silver adduct features a κ^3-bonded scorpionate. $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Cu(C_2H_4)$ has a scorpionate that binds to copper with two short Cu–N bonds and one long Cu–N distance.

Introduction

Tris(pyrazolyl)borates, which belong to a class of ligands generally referred to as Scorpionates, are excellent, mono-anionic, nitrogen-based supporting ligands for most metals of the Periodic Table including d-block elements.[1] They are particularly useful because of the ease with which the steric and electronic properties can be modified by varying the substituents on the pyrazolyl moieties and on the boron atom. Our research activities in the field of Scorpionates are mainly focused on the development and applications of fluorinated ligand versions of poly(pyrazolyl)borates[2–5] and other azolyl analogs like tris(triazolyl)borates.[6,7] For example, we have reported the synthesis of $[HB\{3\text{-}(CF_3)Pz\}_3]^-$,[4] $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]^-$,[3,4] $[HB\{3,4,5\text{-}(CF_3)_3Pz\}_3]^-$,[8] $[HB\{3,5\text{-}(CF_3)_2,4\text{-}(Cl)Pz\}_3]^-$,[9] $[HB\{3,5\text{-}(CF_3)_2,4\text{-}(NO_2)Pz\}_3]^-$,[9] as well as the *B*-alkylated and *B*-arylated systems like $[MeB\{3\text{-}(CF_3)Pz\}_3]^-$ and $[PhB\{3\text{-}(CF_3)Pz\}_3]^-$ (Figure 1).[10] Tris(pyrazolyl)borate ligands such as $[HB\{3\text{-}(C_3F_7)Pz\}_3]^-$ and $[PhB\{3\text{-}(C_2F_5)Pz\}_3]^-$ with longer fluoroalkyl substituents are also known.[11]



$[HB(3\text{-}(CF_3)Pz)_3]^-$ $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$
$[HB(3,4,5\text{-}(CF_3)_3Pz)_3]^-$ $[HB(4\text{-}Cl\text{-}3,5\text{-}(CF_3)_2Pz)_3]^-$
$[MeB(3\text{-}(CF_3)Pz)_3]^-$ $[PhB(3\text{-}(CF_3)Pz)_3]^-$

Figure 1. Several examples of fluorinated tris(pyrazolyl)borate ligands.

Fluorinated tris(pyrazolyl)borates like $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]^-$ are significantly weaker donors compared to hydrocarbon counterparts like $[HB\{3,5\text{-}(CH_3)_2Pz\}_3]^-$.[12] Metal adducts of fluorinated tris(pyrazolyl)borates feature more electrophilic metal sites and

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[a] *Department of Chemistry and Biochemistry, The University of Texas at Arlington,
Arlington, Texas 76019, USA
E-mail: dias@uta.edu
https://www.uta.edu/chemistry/faculty/directory/Dias.php*

ORCID(s) from the author(s) for this article is/are available on the WWW under http://dx.doi.org/10.1002/ejic.201501365.

display greater catalytic activity in certain reactions like in the C–H and C–halogen bond functionalization chemistry via carbene insertion, compared to the non-fluorinated, electron rich tris(pyrazolyl)borate analogs.[9,13,14] There are several additional applications involving fluorinated tris(pyrazolyl)borates as well (e.g., model active sites of enzymes and to develop catalysts to mediate other processes like oxidation).[15–17] Fluorinated ligands like $[HB\{3,5-(CF_3)_2Pz\}_3]^-$ have also permitted us to isolate a range of rare group 11 metal adducts (e.g., involving CO,[18–20] *1*-azidoadamantane,[21] ethylene oxide,[22] propylene sulfide,[22] *dimethyl diazomalonate*,[23] Sn^{II} and Ge^{II} species[24]), as well as to prepare compounds with good antimicrobial properties.[25] $[HB\{3,5-(CF_3)_2Pz\}_3]CuCO$ shows relatively high oxidative stability compared to $[HB\{3,5-(CH_3)_2Pz\}_3]CuCO$. The carbonyl stretching frequency of $[HB\{3,5-(CF_3)_2Pz\}_3]CuCO$ appears at 2137 cm^{-1}, which is very close to that of the free CO (2143 cm^{-1}) and about 71 cm^{-1} higher than that of $[HB\{3,5-(CH_3)_2Pz\}_3]CuCO$.[19,26] Related silver(I) adduct $[HB\{3,5-(CF_3)_2Pz\}_3]AgCO$ displays its carbonyl stretching frequency at 2178 cm^{-1}, which is even higher than that of the free CO.[18,27]

Tris(pyrazolyl)borates have played a crucial role in group 11 metal (Cu, Ag, Au) ethylene chemistry. For example, the first structurally authenticated ethylene adducts of copper, $[HB\{3,5-(CH_3)_2Pz\}_3]Cu(C_2H_4)$,[28] silver, $[HB\{3,5-(CF_3)_2Pz\}_3]Ag(C_2H_4)$,[27] and gold, $[HB\{3,5-(CF_3)_2Pz\}_3]Au(C_2H_4)$[29] involve the use of tris(pyrazolyl)borate supporting ligands.[2,30,31] Fluorinated ligand analog of the copper-ethylene adduct $[HB\{3,5-(CF_3)_2Pz\}_3]Cu(C_2H_4)$ is also known.[17] Such isolable complexes are of significant interest as models for likely intermediates in biochemical[28,32,33] and industrial and laboratory processes[34] involving group 11 metals and ethylene or alkenes. For example, ethylene is an important plant hormone and the ethylene receptor site in plants is believed to be a copper center.[33] Partial oxidation of ethylene to ethylene oxide is a major industrial process and silver is the catalyst of choice.[35] Gold is an excellent catalyst for the selective epoxidation of propene and other alkenes.[36] Group 11 metal ethylene adducts supported by scorpionates have also been used in other applications such as in catalysis and sensor development.[14,15,17]

In this paper, we describe the use of $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]^-$ ligand in copper, silver and gold ethylene chemistry as well as the related metal-ethylene adduct of $[HB\{3-(CF_3),5-(Ph)Pz\}_3]^-$ (Figure 2). Group trends of the two isoleptic coinage metal-ethylene adduct series $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]M(C_2H_4)$ and $[HB\{3-(CF_3),5-(Ph)Pz\}_3]M(C_2H_4)$ (M = Cu, Ag, Au) are also described.

Results and Discussion

The copper(I) adduct $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Cu(C_2H_4)$ was obtained by treating $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Na$[37] with CF_3SO_3Cu in THF in the presence of excess ethylene. The analogous Ag^I and Au^I adducts $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Ag(C_2H_4)$ and $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Au(C_2H_4)$ can also be prepared via a metathesis process using CF_3SO_3Ag in dichloromethane and AuCl in hexane, respectively. These group 11 metal ethylene complexes are white solids and form colorless crystals. Solid samples of $[HB\{3-(CF_3),5-(Me)Pz\}_3]Cu(C_2H_4)$, and $[HB\{3-(CF_3),5-(Me)Pz\}_3]Au(C_2H_4)$ can be exposed to air and indoor lighting for several days without obvious signs of decomposition. Similarly, solid samples of $[HB\{3-(CF_3),5-(Me)Pz\}_3]Ag(C_2H_4)$ can be handled in air for short periods, but decompose after several hours of exposure. In all cases, solid samples of these compounds do not lose ethylene under reduced pressure. Silver and gold adducts show greater solution stability in hexanes compared to chlorinated solvents like dichloromethane.

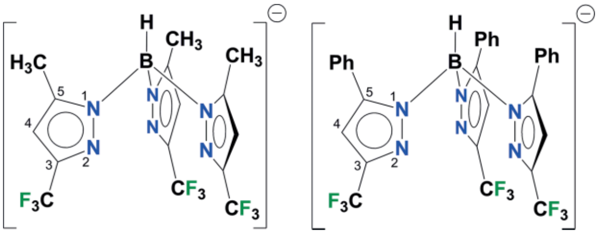

Figure 2. Fluorinated tris(pyrazolyl)borate ligands $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]^-$ and $[HB\{3-(CF_3),5-(Ph)Pz\}_3].^-$.

X-ray analysis of $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]M(C_2H_4)$ (M = Au, Ag, Cu; Table 1) revealed that all three coinage metal adducts crystallize in the $P\bar{3}$ space group with crystallographically imposed three fold axis of symmetry containing the B–H group (Figures 3, 4, 5). The $M(C_2H_4)$ moiety sits very close to but slightly away from the three fold axis. As a result, $M(C_2H_4)$ unit is disordered over three symmetry related sites with equal occupancy. Although we have modeled this disorder satisfactorily, the metrical parameters at $M(C_2H_4)$ should be treated with due caution and are not suitable for detailed bond length and angle comparisons. Nevertheless, X-ray data show the formation of $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]M(C_2H_4)$ adducts with η^2-bound ethylene molecules. The gold center in $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Au(C_2H_4)$ adopts a trigonal planar geometry with κ^2-bound scorpionate (Au–N distances of 2.214, 2.247, and long 2.727 Å), while $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Ag(C_2H_4)$ has a distorted tetrahedral silver atom and κ^3-bound scorpionate (Ag–N distances of 2.222, 2.383, 2.375 Å). The $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Cu(C_2H_4)$ structure is closer to that of the gold analog (Cu–N distances of 2.024, 2.040, and long 2.279 Å) with an essentially trigonal planar copper site (sum of angles at copper: 352°). In the absence of other interfering factors like steric constrains (e.g., imposed by the substituents on boron), the κ^2 vs. κ^3 bonding of scorpionates in group 11 metal ethylene adducts can be attributable principally to covalent vs. ionic metal-ligand bonding, with the latter type is reflected in symmetrically and κ^3-bound scorpionates and feature close to T-shaped metal-ethylene interaction (rather than metal-ethylene bonding closer to metallacyclopropane regime, with significant σ-bonding and π-backbonding between M and C_2H_4).[30,38] Computational studies and M–ethylene bond strength data of various related and unrelated group 11 metal ethylene systems indicate that Au^I forms the strongest bond with ethylene while Ag^I forms the weakest bond.[38,39] Indeed, the C=C bond lengths of $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]M(C_2H_4)$ adducts in general [despite the uncertainties caused by $M(C_2H_4)$ moiety disorder] show an increase in the order of Ag < Cu < Au, and are in good agreement with bond strength based pre-

Table 1. Crystal Data and Summary of Data Collection and Refinement for [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Cu(C$_2$H$_4$), [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Ag(C$_2$H$_4$), [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Cu(C$_2$H$_4$) and [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Ag(C$_2$H$_4$)·CH$_2$Cl$_2$.

	[HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Cu(C$_2$H$_4$)	[HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Ag(C$_2$H$_4$)	[HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Au(C$_2$H$_4$)	[HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Ag(C$_2$H$_4$)
Empirical formula	$C_{17}H_{17}BCuF_9N_6$	$C_{17}H_{17}AgBF_9N_6$	$C_{17}H_{17}BN_6F_9Au$	$C_{33}H_{25}AgBCl_2F_9N_6$
Formula weight	550.71	595.04	684.14	866.17
Temperature	100(2) K	100(2) K	188(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	trigonal	trigonal	trigonal	orthorhombic
Space group	$P\bar{3}$	$P\bar{3}$	$P\bar{3}$	*Pbcn*
Unit-cell dimension	a = 11.5392(9) b = 11.5392(9) c = 9.5646(7) α = 90° β = 90° γ = 120°	a = 11.3758(10) Å b = 11.3758(10) Å c = 10.0549(9) Å α = 90° β = 90° γ = 120°	a = 11.531(2) Å b = 11.531(2) Å c = 9.981(2) Å α = 90° β = 90° γ = 120°	a = 23.8686(17) Å b = 16.8381(12) Å c = 16.9675(12) Å α = 90° β = 90° γ = 90°
Volume	1102.93(19)	1126.9(2)	1149.3(5)	6819.3(8)
Z	2	2	2	8
Density (cald.)	1.658 Mg/m^3	1.754 Mg/m^3	1.977 Mg/m^3	1.687 Mg/m^3
Absorption coefficient	1.083 mm^{-1}	0.986 mm^{-1}	6.490 mm^{-1}	0.833 mm^{-1}
Final *R* indices [$I \geq 2\sigma(I)$]	R_1 = 0.0341 wR_2 = 0.0975	R_1 = 0.0291 wR_2 = 0.0765	R_1 = 0.0461 wR_2 = 0.1122	R_1 = 0.0360 wR_2 = 0.0835
Final *R* indexes [all data]	R_1 = 0.0394 wR_2 = 0.1011	R_1 = 0.0316 wR_2 = 0.0785	R_1 = 0.0520 wR_2 = 0.1151	R_1 = 0.0384 wR_2 = 0.0853

diction. In addition, the solution NMR chemical shifts of these compounds (especially ^{13}C NMR values for the ethylene moiety; see Table 2) are also consistent with the bonding features reflected in solid state structural data. The Cu–N < Au–N < Ag–N bond length trend in [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]M(C$_2$H$_4$) adducts follow the sizes of covalent radii, as silver is the largest atom and copper is the smallest among group 11 metals[40] [e.g., covalent radii of two-coordinate copper(I), gold(I), and silver(I) are 1.13, 1.25, and 1.33 Å, respectively].[41] The M–C bond lengths also follow the same pattern. It is interesting to note that in addition to κ^2 and κ^3 bonding of scorpionates noted above, closer to κ^1 bonding has also been observed in scorpionate adducts of group 11 like [HB{3,5-(CF$_3$)$_2$Pz}$_3$]Au(CN*t*Bu).[20]

We have synthesized the silver(I) ethylene adduct [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Ag(C$_2$H$_4$) using [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Na-(THF),[26] CF$_3$SO$_3$Ag and ethylene. It is a white solid. X-ray crystal structure of [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Ag(C$_2$H$_4$) shows that it features a κ^3-bonded tris(pyrazolyl)borate and a pseudo-tetrahedral silver site (Figure 6). Unfortunately, the Ag(C$_2$H$_4$) moiety sits on two different sites at 46 % and 54 % occupancy, and is disordered. Although we have modeled this disorder satisfactorily, the metrical parameters of Ag(C$_2$H$_4$) are not ideal for detailed comparisons of bond lengths and angles. [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Ag(C$_2$H$_4$) is the missing member of isoleptic [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]M(C$_2$H$_4$) series as we have reported the copper[17] and gold[29] adducts previously. [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Au(C$_2$H$_4$) has a κ^2-bonded scorpionate just like the [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Au(C$_2$H$_4$) adduct. The copper adduct [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Cu(C$_2$H$_4$) in contrast features a pseudo-tetrahedral copper site, and shows disorder at ethylene moiety.

^{1}H NMR signal corresponding to the coordinated ethylene of [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]Cu(C$_2$H$_4$) in CDCl$_3$ appears at δ = 4.71 ppm (Table 2), while the related silver and gold analogs display this peak at δ = 5.45 and 3.47 *ppm*, respectively. For comparison, [HB{3,5-(CH$_3$)$_2$Pz}$_3$]Cu(C$_2$H$_4$) and [HB{3,5-(CF$_3$)$_2$Pz}$_3$]-Cu(C$_2$H$_4$) ethylene proton signals have been observed at δ = 4.41 and 4.96 ppm, respectively. It appears that the upfield shift of ethylene proton signal follows the relative donor-properties of the scorpionate ligand on copper(I).[12,26] The copper supported by electron rich [HB{3,5-(CH$_3$)$_2$Pz}$_3$]$^-$ shields the ethylene protons most while the Lewis acidic [HB{3,5-(CF$_3$)$_2$Pz}$_3$]Cu moiety provides the least amount of shielding. In the isoleptic [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]M(C$_2$H$_4$) series (M = Cu, Ag, Au), the gold adduct shows the largest upfield shift of the ethylene proton signal from that of free ethylene protons (δ = 5.40 ppm in CDCl$_3$) followed by the copper adduct, while silver adduct shows a small downfield shift. The ^{13}C NMR resonance of the metal bound ethylene carbon of [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]-M(C$_2$H$_4$) appear at δ = 84.8, 103.5, and 58.3 ppm, respectively for M = Cu, Ag, and Au. The upfield shift of the carbon resonance in the gold adduct relative to that of free ethylene (δ = 123.5 ppm) is particularly large. For example, $\Delta\delta$(C) [where $\Delta\delta(C) = \delta(C)_{complex} - \delta(C)_{ethylene}$] for these Au, Ag, and Cu adducts are –39, –20, –65 ppm, respectively. The upfield shift of the ^{13}C and ^{1}H NMR resonance of ethylene signal has been attributed to the increased metal-to-ethylene π-back-donation contribution.[38,42] Overall, these NMR spectroscopic data point to a significantly higher π-back-donation component in the gold(I)–ethylene bond than in the lighter members, and are in good agreement with the latest computational work and structural features observed above.

^{1}H and ^{13}C NMR spectra of [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]Ag(C$_2$H$_4$) in CD$_2$Cl$_2$ exhibited the resonance attributable to ethylene protons and carbons at δ = 5.56 and 104.0 ppm, respectively. As evident from the data presented in Table 2, [HB{3-(CF$_3$),5-(Ph)Pz}$_3$]M(C$_2$H$_4$) adducts also follow trends similar to that of the [HB{3-(CF$_3$),5-(CH$_3$)Pz}$_3$]M(C$_2$H$_4$) series.

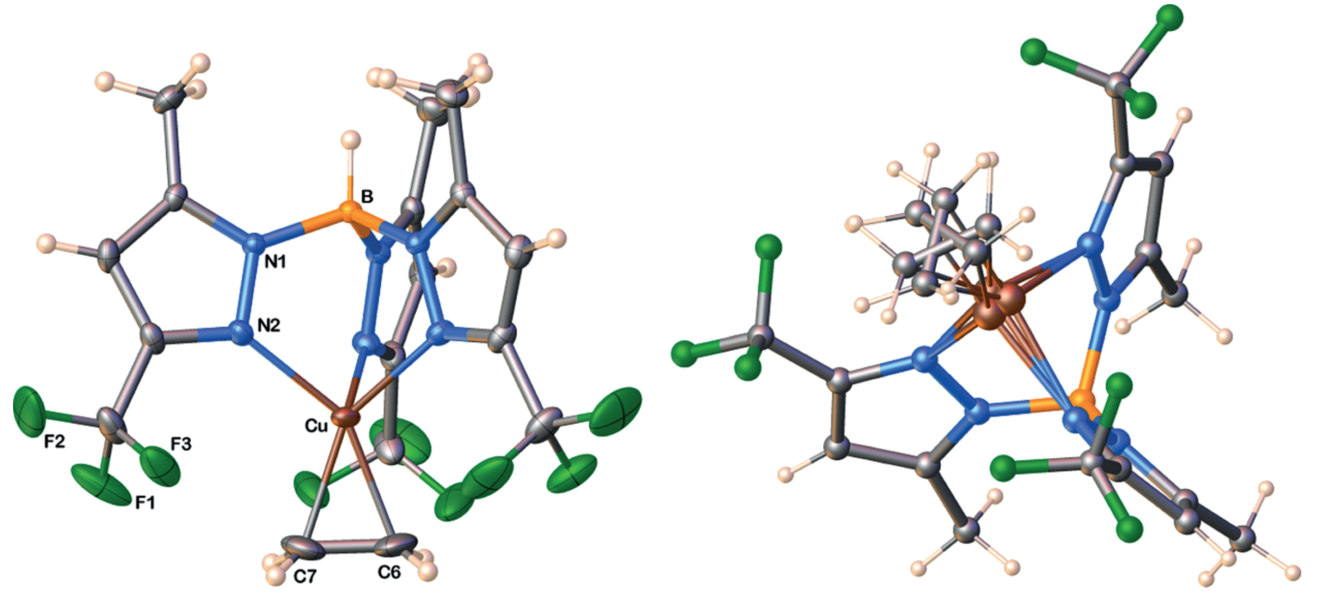

Figure 3. ORTEP diagram of [HB{3-(CF_3),5-(CH_3)Pz}$_3$]Cu(C_2H_4) (thermal ellipsoids set at 50 % probability) and a view showing the disordered copper-ethylene moiety.

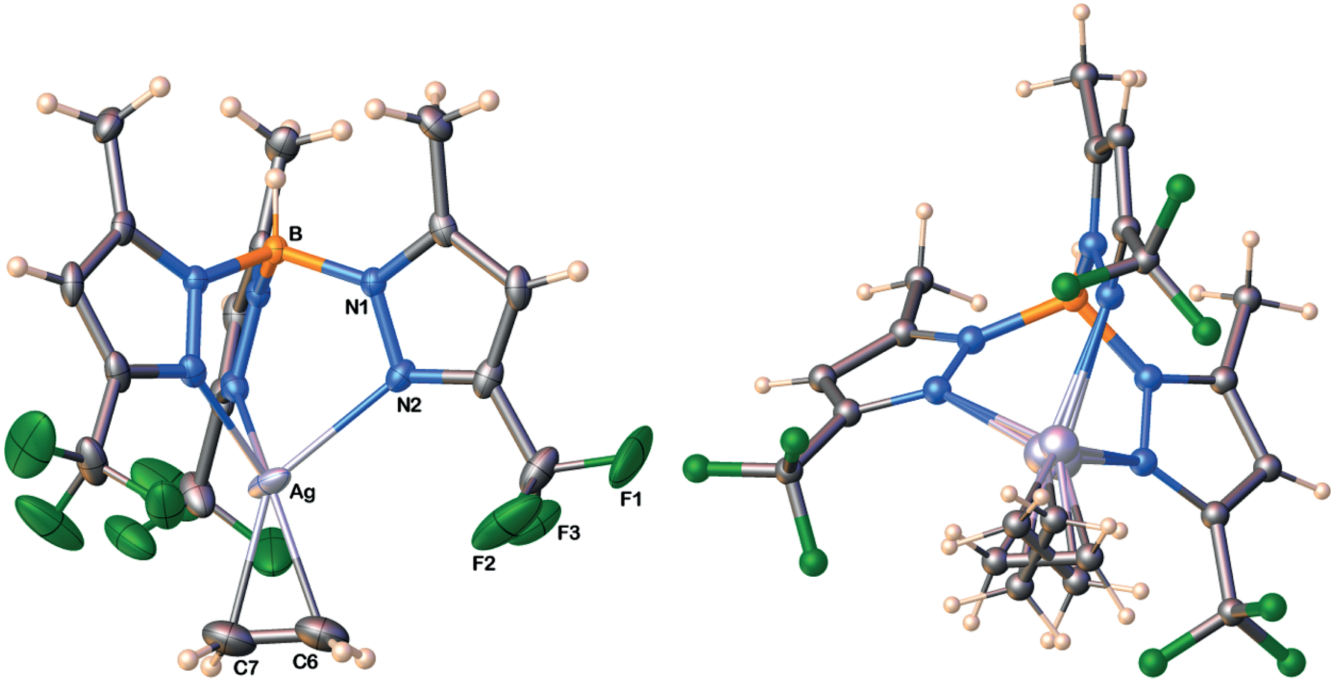

Figure 4. ORTEP diagram of [HB{3-(CF_3),5-(CH_3)Pz}$_3$]Ag(C_2H_4) (thermal ellipsoids set at 50 % probability) and a view showing the disordered silver-ethylene moiety.

Conclusions

In summary, we have reported the isolation and characterization of a series of thermally stable, isoleptic group 11 metal–ethylene adducts, [HB{3-(CF_3),5-(CH_3)Pz}$_3$]M(C_2H_4) (M = Au, Ag, and Cu). The related [HB{3-(CF_3),5-(Ph)Pz}$_3$]Ag(C_2H_4) has also been isolated completing a second set of isoleptic group 11 metal ethylene adducts. The gold atoms bind to scorpionates in κ^2-fashion while silver feature essentially κ^3-bonded scorpionates. [HB{3-(CF_3),5-(CH_3)Pz}$_3$]Cu(C_2H_4) shows scorpionate coordination approaching the κ^2-mode. Unfortunately, M(C_2H_4) fragments in [HB{3-(CF_3),5-(CH_3)Pz}$_3$]M(C_2H_4) (M = Au, Ag, and Cu) and [HB{3-(CF_3),5-(Ph)Pz}$_3$]Ag(C_2H_4) are disordered. Nevertheless, M–C and M–N distances of the [HB{3-(CF_3),5-(CH_3)Pz}$_3$]M(C_2H_4) and [HB{3-(CF_3),5-(Ph)Pz}$_3$]M(C_2H_4) complexes show that they follow the same trend as the covalent radii of M^I. The gold-ethylene adducts [HB{3-(CF_3),5-(CH_3)Pz}$_3$]Au(C_2H_4) and [HB{3-(CF_3),5-(Ph)Pz}$_3$]Au(C_2H_4) show large upfield NMR shifts of the ethylene proton and carbon signals, indicating rela-

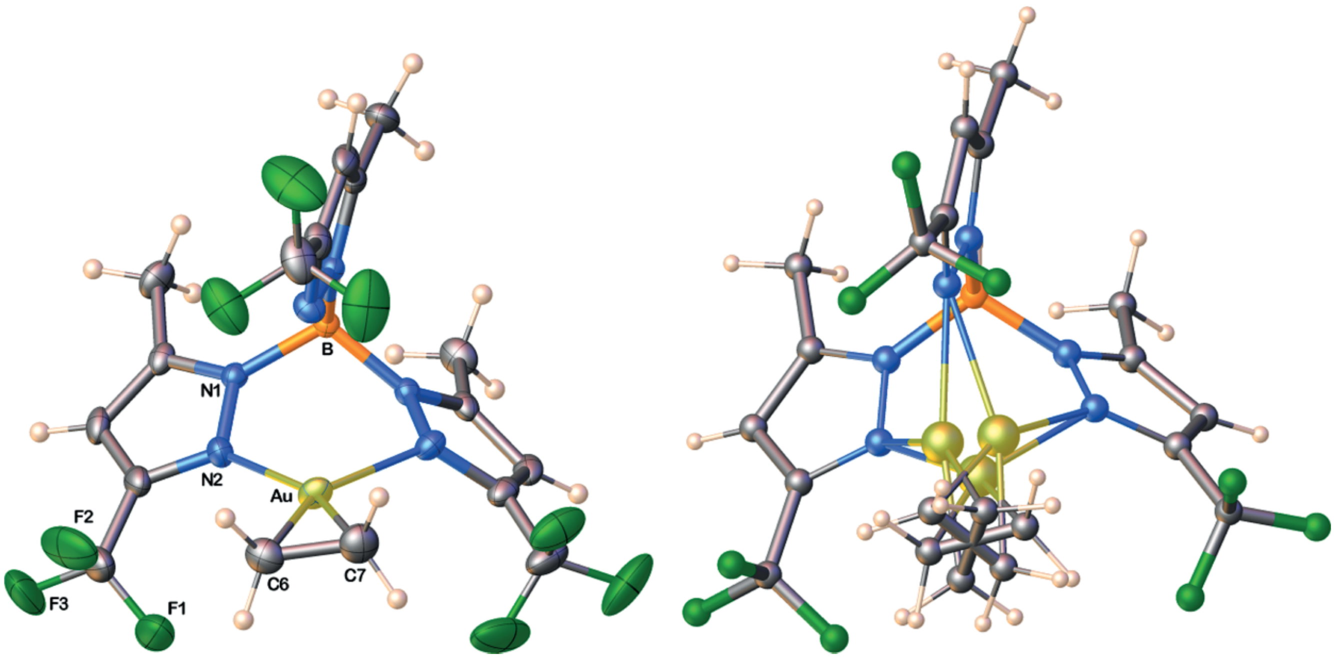

Figure 5. ORTEP diagram of [HB{3-(CF_3),5-(CH_3)Pz}$_3$]Au(C_2H_4) (thermal ellipsoids set at 30 % probability) and a view showing the disordered gold-ethylene moiety.

Table 2. Selected ^{1}H and ^{13}C NMR Spectroscopic data of the ethylene group of the copper, silver and gold ethylene adducts supported by fluorinated scorpionates LM(C_2H_4) (M = Cu, Ag, Au; L = fluorinated scorpionate). Chemical shifts are given in ppm.

LM(C_2H_4)	^{1}H NMR spectroscopic data of C_2H_4 moiety			^{13}C NMR spectroscopic data of C_2H_4 moiety			Reference
Supporting ligand L	Cu	Ag	Au	Cu	Ag	Au	
[HB{3-(CF_3),5-(CH_3)Pz}$_3$]	4.71 ($CDCl_3$)	5.45 (CD_2Cl_2)	3.47 ($CDCl_3$)	84.8 ($CDCl_3$)	103.5 (CD_2Cl_2)	58.3 ($CDCl_3$)	this work
[HB{3-(CF_3),5-(Ph)Pz}$_3$]	4.91 ($CDCl_3$)	5.56 (CD_2Cl_2)	3.69 ($CDCl_3$)	85.7 (C_6D_6)	104.0 (CD_2Cl_2)	59.3 ($CDCl_3$)	this work,[2,17,29]
[HB{3,5-(CF_3)$_2$Pz}$_3$]	4.96 ($CDCl_3$)	5.56 (C_6D_{12})	3.81 ($CDCl_3$)	89.5 (C_6D_{12})	104.9 (C_6D_{12})	63.7 ($CDCl_3$)	[2,17,29]
[HB{3,4,5-(CF_3)$_3$Pz}$_3$]	5.06 ($CDCl_3$)	5.65 (CD_2Cl_2)		94.9 ($CDCl_3$)	111.1 (CD_2Cl_2)		[8]
[HB{3,5-(CF_3)$_2$Tz}$_3$]	5.12 ($CDCl_3$)	5.70 ($CDCl_3$)		92.6 (CD_2Cl_2)	109.7 ($CDCl_3$)		[7]
Free C_2H_4	5.40 ($CDCl_3$), 5.25 (C_6D_6)			123.13 ($CDCl_3$), 122.96 (C_6D_6)			[47]

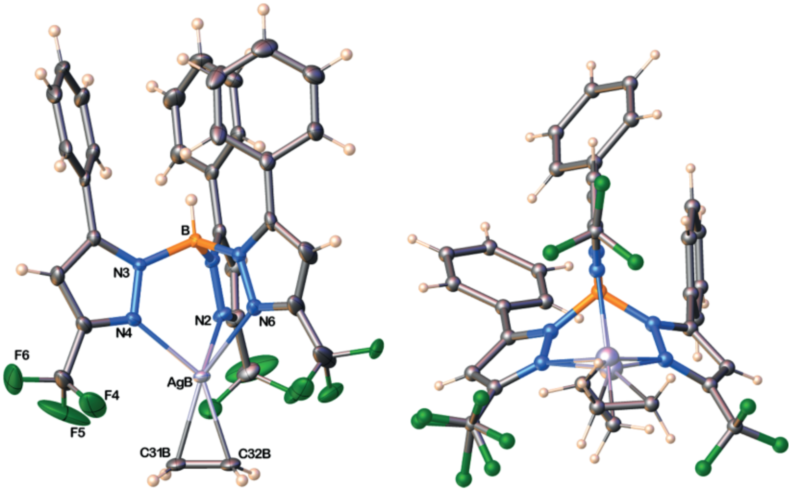

Figure 6. ORTEP diagram of [HB{3-(CF_3),5-(Ph)Pz}$_3$]Ag(C_2H_4) (thermal ellipsoids set at 50 % probability) and a view showing the disordered silver-ethylene moiety.

tively high Au→ethylene backbonding. NMR spectroscopic data suggest that silver complexes of both the tris(pyrazolyl)borate ligands [HB{3-(CF_3),5-(CH_3)Pz}$_3$]$^-$ and [HB{3-(CF_3),5-(Ph)Pz}$_3$]$^-$ exhibit the weakest interaction with ethylene as compared to the respective copper and gold complexes.

Experimental Section

General: All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmosphere single-station glovebox equipped with a –25 °C refrigerator. Solvents were purchased from commercial sources, purified prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on a JEOL Eclipse 500 and JEOL Eclipse 300 spectrometer (^1H, 500.16 MHz and 300.53 MHz; ^{13}C, 125.78 MHz, and 75.59 MHz; ^{19}F, 470.62 MHz, and 282.78 MHz). Proton and carbon chemical shifts are reported in ppm, and referenced using the residual proton or carbon signals of the deuterated solvent. ^{19}F NMR values were referenced to external $CFCl_3$. Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at Intertek Pharmaceutical Services. Melting points were obtained on a Mel-Temp II apparatus. IR spectra were collected on a Shimadzu IRPrestige-21 FTIR spectrometer containing an ATR attachment. Silver(I) triflate, and AuCl were purchased from Aldrich and ethylene gas was purchased from Matheson. $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Na$,[37] $[HB\{3-(CF_3),5-(Ph)Pz\}_3]Na(THF)$,[26] and $[CF_3SO_3Cu]_2{\cdot}C_6H_6$[43,44] were prepared via reported procedures.

$[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Cu(C_2H_4)$: $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Na$ (0.100 g, 0.207 mmol) was dissolved in THF (10 mL) and the solution was saturated with ethylene. This solution was slowly added to solid $[CF_3SO_3Cu]_2{\cdot}C_6H_6$ (0.054 g, 0.107) via syringe under a flow of ethylene. The resulting mixture was allowed to stir overnight under an ethylene atmosphere at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. $Na(CF_3SO_3)$ was removed by filtration through a bed of Celite and the pale green filtrate was concentrated by bubbling ethylene and stored at –20 °C under an ethylene atmosphere for crystallization, yield 0.195 g, 86 %; m.p. 147 °C (decomposition). ^1H NMR ($CDCl_3$, 500.16 MHz, 298 K): δ = 6.27 (s, 3 H, C*H*), 4.71 (s, 4 H, $CH_2{=}CH_2$), 2.45 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 125.77 MHz, 298 K): δ = 145.0 (s, CCH_3), 142.4 (q, ^2J = 38 Hz, CCF_3) 121.3 (q, ^1J = 277 Hz, CF_3), 104.9 (s, CH), 84.8 (s, $CH_2{=}CH_2$), 13.0 (s, CH_3) ppm. ^{19}F NMR ($CDCl_3$, 470.62 MHz, 298 K): δ = –60.5 (s) ppm. ATR-FTIR (selected peak): $\tilde{\nu}$ = 2562 (B–H) cm^{-1}. $C_{17}H_{17}BCuF_9N_6$ (550.70): calcd. C 37.08, H 3.11, N 15.26; found C 37.01, H 3.01, N 15.11.

$[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Ag(C_2H_4)$: CF_3SO_3Ag (0.108 g, 0.420 mmol), and $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Na$ (0.200 g, 0.415 mmol) were dissolved in dichloromethane (10 mL) under a flow of ethylene. The resulting mixture was wrapped in aluminum foil to protect it from light and stirred overnight under an ethylene atmosphere at room temperature. Over the course of the reaction a black precipitate formed and was removed by filtration. The resulting clear colorless filtrate was concentrated by bubbling ethylene and stored at –20 °C under an ethylene atmosphere for crystallization, yield 0.098 g, 80 %; m.p. 105 °C (decomposition). ^1H NMR (CD_2Cl_2, 500.16 MHz, 298 K): δ = 6.29 (s, 3 H, C*H*), 5.45 (s, 4 H, $CH_2{=}CH_2$), 2.47 (s, 9 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 125.77 MHz, 298 K): δ = 146.8 (s, CCH_3), 142.7 (q, ^2J = 38 Hz, CCF_3), 122.2 (q, ^1J = 250 Hz, CF_3), 104.4 (s, CH), 103.5 (s, $CH_2{=}CH_2$), 13.4 (s, CH_3) ppm. ^{19}F NMR (CD_2Cl_2, 470.62 MHz, 298 K): δ = –61.5 (s) ppm. ATR-FTIR (selected peak): $\tilde{\nu}$ = 2540 (B–H) cm^{-1}. $C_{17}H_{17}AgBF_9N_6$ (595.02): calcd. C 34.32, H 2.88, N 14.12; found C 34.38, H 2.77, N 13.74.

$[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Au(C_2H_4)$: AuCl (0.062 g, 0.270 mmol) and freshly sublimed $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Na$ (0.13 g, 0.270 mmol) were dissolved in ethylene saturated hexane at room temperature. The mixture was protected from light using aluminum foil, and stirred at room temperature for 4 h while periodically passing ethylene through the solution. Over the course of the reaction the yellow solution became gray with an off white precipitate. The mixture was filtered through a bed of Celite, and the clear colorless filtrate was dried under reduced pressure to obtain $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Au(C_2H_4)$ as a white solid. X-ray quality crystals were obtained from a hexane solution saturated with ethylene at –20 °C, yield 0.110 g, 80 %; m.p. 130 °C (decomposition). ^1H NMR (CD_2Cl_2, 500.16 MHz, 298 K): δ = 6.38 (s, 3 H, C*H*), 3.49 (s, 4 H, $CH_2{=}CH_2$), 2.45 (s, 9 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 125.77 MHz, 298 K): δ = 146.9 (s, CCH_3), 142.7 (q, ^2J = 38 Hz, CCF_3), 121.8 (q, ^1J = 269 Hz, CF_3), 105.4 (s, CH), 58.6 (s, $CH_2{=}CH_2$), 13.4 (s, CH_3) ppm. ^{19}F NMR (CD_2Cl_2, 470.62 MHz, 298 K): δ = –61.3 (s) ppm. ^1H NMR ($CDCl_3$, 500.16 MHz, 298 K): δ = 6.31 (s, 3 H, C*H*), 3.47 (s, 4 H, $CH_2{=}CH_2$), 2.42 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 125.77 MHz, 298 K, selected peak): δ = 58.3 (br., $CH_2{=}CH_2$) ppm. ^{19}F NMR ($CDCl_3$, 470.62 MHz, 298 K): δ = –61.3 (s) ppm. $C_{17}H_{17}AuBF_9N_6$ (684.12): calcd. C 29.85, H 2.50, N 12.28; found C 29.66, H 3.01, N 12.11.

$[HB\{3-(CF_3),5-(Ph)Pz\}_3]Ag(C_2H_4)$: CF_3SO_3Ag (0.036 g, 0.140 mmol), and $[HB\{3-(CF_3),5-(Ph)Pz\}_3]Na(THF)$ (0.100 g, 0.135 mmol) were dissolved in hexanes (10 mL) under a flow of ethylene. The resulting mixture was covered with aluminium foil to protect it from light and stirred overnight under an ethylene atmosphere at room temperature. Over the course of the reaction a white precipitate formed and was removed by filtration. The resulting clear colorless filtrate was concentrated by bubbling ethylene and stored at –20 °C under an ethylene atmosphere for crystallization, yield 0.078 g, 72 %; m.p. 124 °C (decomposition). ^1H NMR (500.16 MHz, C_6D_{12}): δ = 7.10 (br., 3 H, Ph-*H*), 6.84 (br., 12 H, Ph-*H*), 6.40 (s, 3 H, C*H*), 5.55 (s, 4 H, $CH_2{=}CH_2$) ppm. ^{13}C NMR (C_6D_{12}, 125.77 MHz, 298 K): δ = 151.7 (s, CCH_3), 143.7 (q, ^2J = 38 Hz, CCF_3), 132.3 (s, Ph), 130.4 (s, Ph), 128.3 (s, Ph), 122.4 (q, ^1J = 264 Hz, CF_3), 105.0 (s, CH), 102.4 (s, $CH_2{=}CH_2$) ppm. ^{19}F NMR (CD_2Cl_2, 470.62 MHz, 298 K): δ = –62.1 (s) ppm. ^1H NMR (500.16 MHz, CD_2Cl_2): δ = 7.23 (t, $^3J_{HH}$ = 5.0 Hz, 3 H, Ph-*H*), 6.94 (t, $^3J_{HH}$ = 10.0 Hz, 6 H, Ph-*H*), 6.89 (d, $^3J_{HH}$ = 10.0 Hz, 6 H, Ph-*H*), 6.57 (s, 3 H, C*H*), 5.56 (s, 4 H, $CH_2{=}CH_2$) ppm. ^{13}C NMR (CD_2Cl_2, 125.76 MHz, 298 K, selected peak): δ = 104.0 (s, $CH_2{=}CH_2$) ppm. ^{19}F NMR (CD_2Cl_2, 470.62 MHz, 298 K): δ = –61.4 (s) ppm. ATR-FTIR (selected peak): $\tilde{\nu}$ = 2626 (B–H) cm^{-1}. $C_{32}H_{23}AgBF_9N_6{\cdot}0.5CH_2Cl_2$ (823.7): calcd. C 47.39, H 2.94, N 10.20; found C 47.26, H 2.84, N 9.92.

X-ray Crystallographic Data: A suitable crystal covered with a layer of hydrocarbon/paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data for $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Cu(C_2H_4)$, $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Ag(C_2H_4)$ and $[HB\{3-(CF_3),5-(Ph)Pz\}_3]Ag(C_2H_4)$ were measured at 100(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo-K_α fine-focus sealed tube (λ = 0.71073 Å). X-ray intensity data for $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]Au(C_2H_4)$ were measured at 188(2) K (because crystals crack at 100 K) on a SMART APEX II CCD area detector system equipped with an Oxford Cryosystems 700 series cooler, a graphite monochromator, and a Mo-K_α fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker ApexII program suite. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using SHELXL.[45] Absorption corrections were applied by using SADABS. All the non-hydrogen atoms were refined anisotropically. X-ray structural figures were generated using Olex2.[46] Further details are given in Table 1. All three coinage metal compounds $[HB\{3-(CF_3),5-(CH_3)Pz\}_3]M(C_2H_4)$ (M = Cu, Ag, Au) crystallize in the $P\bar{3}$ space group with crystallographically imposed three fold axis of symmetry containing B–H moiety (for a *Z* value of 2). Unfortunately, M-ethylene fragment lies slightly off threefold axis in these adducts, and therefore is disordered equally over three symmetry related positions. The disordered M-ethylene units in these adducts were modeled successfully. The $[HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3]Ag(C_2H_4)$ crystallizes in *Pbcn* space group with a CH_2Cl_2 molecule of crystallization. The Ag–ethylene moiety is also disordered but over two sites, and was modeled satisfactorily and the occupancies were refined to 46 % and 54 %. The fluorine atoms of one CF_3 group and CH_2Cl_2 also show positional disorder over two sites, and were modeled well. Hydrogen atoms on boron and pyrazolyl ring of $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Cu(C_2H_4)$ as well as the hydrogen atom on boron of $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Au(C_2H_4)$ were located from difference maps and included. All the other hydrogen atoms of the crystal structures reported here including those of the ethylene moieties were placed at calculated positions and refined using a riding model. CCDC 1437975 {for $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Cu(C_2H_4)$}, 1437976 {for $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Ag(C_2H_4)$}, 1437977 {for $[HB\{3\text{-}(CF_3),5\text{-}(CH_3)Pz\}_3]Au(C_2H_4)$}, and 1437978 {for $[HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3]Ag(C_2H_4)$} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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