Copper(I) Ethylene Adducts and Aziridination Catalysts Based on Fluorinated Tris(pyrazolyl)borates $[HB(3\text{-}(CF_3),5\text{-}(R)Pz)_3]^-$ (where R = CF_3, C_6H_5, H; Pz = pyrazolyl)

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The ethylene adducts of copper(I) tris(pyrazolyl)borates, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$, $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$, and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$, have been prepared by reacting the corresponding sodium derivative with CF_3SO_3Cu in the presence of ethylene. They were characterized both in the solid state and in solution using ^1H, ^{13}C, and ^{19}F NMR and IR spectroscopy and by X-ray crystallography. Solid samples of these nonionic copper complexes featuring fluorinated tris(pyrazolyl)borate ligands display notably high stability toward air oxidation and ethylene loss. The ^1H NMR chemical shifts of the copper(I)-bonded ethylene protons appear in the 4.8−5.2 ppm region. The ^{13}C signal of copper-coordinated ethylene shows an upfield shift of about 35 ppm, whereas the $^1J_{C-H}$ shows a minor change (an increase of about 2−5 Hz) compared to the values for free ethylene. X-ray structural data show the presence of pseudo-tetrahedral copper ions and η^2-bonded ethylene units and relatively unperturbed ethylene C−C distances. The copper adducts $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ are competent aziridination catalysts, readily converting a variety of olefins into the corresponding *N*-tosyl aziridines with *N*-tosyl phenyliodinane.

Introduction

Metal adducts of the fluorinated ligands often show properties very different from their nonfluorinated counterparts.[1−3] Polyfluorinated ligands commonly improve the volatility, oxidation resistance, thermal stability, and fluorocarbon solubility of metal complexes. They are also known to increase the activity and affect the product distribution of certain metal-mediated reactions. Ligands bearing fluorinated substituents are also desired for applications in fluorous biphase media and in supercritical carbon dioxide.[4,5] Accordingly, there is a considerable amount of interest in the development and applications of ligands bearing fluorinated substituents.

Interestingly, very little is known about the fluorinated versions of one of the most widely used ligands in chemistry, the poly(pyrazolyl)borates.[6] Over the past few years, we and others have reported the synthesis and/or uses of several poly(pyrazolyl)borates containing fluoroalkyl substituents.[2,3,7−19] The ligands we have reported include $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$,[20] $[HB(3\text{-}(CF_3)Pz)_3]^-$,[12] $[HB(3\text{-}(C_2F_5)Pz)_3]^-$,[11] $[HB(3\text{-}(C_3F_7)Pz)_3]^-$,[11] and $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$.[8,12] Their metal adducts show very interesting properties. For example, ν_{CO} of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ is the highest observed for a tris(pyrazolyl)boratocopper(I) complex, and it is about 71 cm^{-1} higher than that of the methylated analogue $[HB(3,5\text{-}(CH_3)_2Pz)_3]CuCO$.[9,21] Furthermore, unlike the air sensitive $[HB(3,5\text{-}(CH_3)_2Pz)_3]CuCO$, the fluorinated analogue $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ is an air stable solid.

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$[HB(3,5-(CF_3)_2Pz)_3]AgCO$ is an example of a nonclassical metal carbonyl complex ($\nu_{CO} = 2178$ cm^{-1}, which is higher than that of free CO, $\nu_{CO} = 2143$ cm^{-1}).[10,13] It is also possible to isolate the $[HB(3,5-(CF_3)_2Pz)_3]AuCO$.[22] Thermally stable silver or gold carbonyls are exceedingly rare, and such complexes are unknown with any other tris(pyrazolyl)borate ligand. Structurally characterized silver adducts containing ethylene,[13] acetylene,[13] organic azides,[16] diazo compounds (e.g., dimethyldiazomalonate),[14] ethylene oxide,[17] and chloro germanium species[15] to date are only known for $[HB(3,5-(CF_3)_2Pz)_3]^-$ systems.

Considering the success we have had with fluorinated tris(pyrazolyl)borates in the stabilization of reactive and/or labile organometallic compounds, we decided to investigate the utility of such ligands in copper ethylene chemistry. Copper ethylene complexes have attracted significant interest due to their importance in biochemistry (e.g., ethylene receptor site of plants, metabolism of ethylene to ethylene oxide),[23−25] in organic synthesis (e.g., copper-catalyzed aziridination, cyclopropanation, and the conjugate addition of Grignards to α,β-unsaturated carbonyls),[26−28] and in industrial applications (e.g., separation and purification of olefins, ethylene oxidation, and oxychlorination).[29,30] However, due to the extremely labile nature of the copper−ethylene interaction, only a limited number of structurally characterized copper(I) ethylene complexes have been reported.[24,25,31−34] The $[HB(3,5-(CH_3)_2Pz)_3]Cu(C_2H_4)$ represents one such example.[24] Recent work from several research groups shows that this compound and the related bis- and tris(pyrazolyl)boratocopper adducts also make very useful aziridination, cyclopropanation, and oxidation catalysts.[6,26,27,35−37] However, oxidative instability of $[HB(3,5-(CH_3)_2Pz)_3]Cu$ systems places limitations on their wider utility. Our work on $[HB(3,5-(CF_3)_2Pz)_3]CuCO$,[9] $[HB(3,5-(CF_3)_2Pz)_3]Ag(C_2H_4)$,[13] and $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$[38] suggests that fluorinated ligands are ideal for improving the oxidative stability and to prevent the facile ethylene dissociation. Here we report full details of the isolation of copper−ethylene adducts of $[HB(3,5-(CF_3)_2Pz)_3]^-$, $[HB(3-(CF_3)Pz)_3]^-$, and $[HB(3-(CF_3),5-(C_6H_5)Pz)_3]^-$. We also show that despite the stability of these copper−ethylene adducts, they function effectively as olefin aziridination catalysts.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using either standard Schlenk techniques or in a Vacuum Atmospheres single station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at room temperature on a JEOL Eclipse 500 (^1H, 500.16 MHz; ^{19}F, 470.62 MHz; ^{13}C, 125.78 MHz) or on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz). Proton and carbon chemical shifts are reported in ppm vs Me_4Si. ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$ standard. Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. $[HB(3,5-(CF_3)_2Pz)_3]Na(THF)$,[12] $[HB(3-(CF_3)Pz)_3]Na$,[12] and *N*-tosyl phenyliodinane[39] were prepared using published procedures. $[HB(3-(CF_3),5-(C_6H_5)Pz)_3]Na(THF)$[40] was prepared from the corresponding pyrazole and $NaBH_4$ following standard methods. Copper(I) trifluoromethanesulfonate salts $[CF_3SO_3Cu]_2\cdot C_6H_6$ and $[CF_3SO_3Cu]_2\cdot C_7H_8$, and ethylene, were purchased from commercial sources and used as received.

$[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$. $[HB(3,5-(CF_3)_2Pz)_3]Na(THF)$ (0.270 g, 0.377 mmol) and $[CF_3SO_3Cu]_2\cdot C_6H_6$ (0.086 g, 0.171 mmol) were mixed in toluene (15 mL) at room temperature and stirred for 12 h. The ethylene was bubbled through the solution for a few minutes, and the mixture was stirred for a further 3 h while maintaining an ethylene atmosphere. The resulting mixture was filtered, and the volatiles were removed under vacuum. The residue was extracted into hexane and

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Table 1. Crystal Data and Summary of Data Collection and Refinement for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)\cdot 2(C_6H_6)$, $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$, and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$

	$[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)\cdot 2(C_6H_6)$	$[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$	$[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$
formula	$C_{29}H_{20}BCuF_{18}N_6$	$C_{32}H_{23}BCuF_9N_6$	$C_{14}H_{11}BCuF_9N_6$
fw	868.86	736.91	508.64
space group	*Pnma*	*P*2(1)/*n*	*C*2/*c*
T, K	183(2)	208(2)	188(2)
λ, Å	0.71073	0.71073	0.71073
a, Å	11.2383(14)	9.4219(12)	22.378(3)
b, Å	20.860(8)	23.572(2)	9.756(2)
c, Å	14.733(3)	14.0405(11)	19.748(3)
α, deg	90	90	90
β, deg	90	91.893(11)	118.106(9)
γ, deg	90	90	90
V, $Å^3$	3453.8(15)	3116.6(6)	3802.9(11)
Z	4	4	8
ρ(calc), g/cm^3	1.671	1.571	1.777
μ, mm^{-1}	0.762	0.789	1.249
R1, wR2 $[I>2\sigma(I)]^a$	0.0443, 0.1035	0.0450, 0.1016	0.0463, 0.1062
R1, wR2 (all data)^a	0.0679, 0.1152	0.0674, 0.1127	0.0571, 0.1128

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

filtered, and the filtrate was concentrated to obtain $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ as a colorless solid, 0.209 g, 78% yield. The colorless X-ray quality crystals were grown from hexane/benzene at 5 °C. Mp: 152−156 °C. ^1H NMR (C_6D_6): δ 4.94 (s, 4H, CH_2CH_2), 6.18 (s, 3H, CH). ^1H NMR ($CDCl_3$): δ 4.96 (s, 4H, CH_2CH_2), 6.94 (s, 3H, CH). ^1H NMR (C_6D_{12}): δ 4.98 (s, 4H, CH_2CH_2), 6.82 (s, 3H, CH). ^{13}C NMR (C_6D_{12}): δ 89.5 (t, $^1J(C,H) = 161$ Hz, CH_2CH_2), 107.3 (d, $^1J(C,H) = 186$ Hz, CH), 119.7 (q, $^1J(C,F) = 271$ Hz, CF_3), 120.8 (q, $^1J(C,F) = 270$ Hz, CF_3), 140.8 (br q, CCF_3), 144.5 (q, $^2J(C,F) = 36$ Hz, CCF_3). ^{19}F (C_6D_{12}): δ −61.7 (s), −59.7 (d, $^5J(F,H) = 3$ Hz). IR (KBr): cm^{-1}, 3170, 2919, 2864, *2631* (BH), 1922, 1669, 1557, 1496, 1471, 1432, 1394, 1366, 1278, 1247, 1177, 1147, 1080, 1046, 995, 963, 834, 780, 741, 696, 617, 549, 485, 407. Anal. Calcd for $C_{17}H_8BCuF_{18}N_6$: C, 28.65; H, 1.13; N, 11.79. Found: C, 29.14; H, 1.03; N, 11.82.

$[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$. $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Na(THF)$ (0.760 g, 1.09 mmol) was dissolved in THF and added to solid $[CF_3SO_3Cu]_2\cdot C_7H_8$ complex (0.281 g, 0.502 mmol). The resulting mixture stirred for 30 min to ensure complete dissolution of the copper complex. The solution was then saturated with ethylene and allowed to stir overnight. The reaction mixture was filtered over Celite to obtain a yellow solution. Upon removal of volatile materials under reduced pressure, a pale yellow solid was obtained, 0.623 g, 78% yield. X-ray quality crystals of $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ were obtained from a methylene chloride/cyclohexane solution at −6 °C. Mp: dec 141 °C. ^1H NMR (C_6D_6): δ 5.20 (s, 4H, CH_2CH_2), 6.23 (s, 3H, CH), 6.67 (d, $^3J = 8.3$ Hz, Ph), 6.74 (t, $^3J = 7.6$ Hz, Ph), 7.00 (br t, $^3J = 7.3$ Hz, Ph). ^1H NMR ($CDCl_3$): δ 4.91 (s, 4H, CH_2CH_2), 6.56 (s, 3H, CH), 6.87 (d, $^3J = 7.5$ Hz, Ph), 6.93 (t, $^3J = 7.6$ Hz, Ph), 7.25 (m, $^3J = 7.4$ Hz, Ph). ^{19}F NMR ($CDCl_3$): δ −60.9. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 85.7 (s, CH_2CH_2), 105.5 (s, CH), 121.2 (q, $^1J = 269$ Hz, CF_3), 127.9 (s, Ph, C_o), 128.4 (s, Ph, C_m), 129.7 (s, Ph, C_p), 130.5 (s, Ph, C_i), 142.7 (q, $^2J = 38$ Hz, CCF_3), 150.3 (s, C_3). ^{13}C NMR (C_6D_6, ethylene carbons): δ 85.7 (t, $^1J(C,H) = 159$ Hz, CH_2CH_2). IR (KBr), cm^{-1}: 3143, 3068, 3034, 2639 (B−H), 2102, 1955, 1895, 1623, 1545, 1506, 1475, 1446, 1347, 1259, 1168, 1068, 1010, 986, 951, 811, 764, 739, 699, 670, 599, 573, 533, 442. Anal. Calcd for $C_{32}H_{23}BCuF_9N_6$: C, 52.16; H, 3.14; N, 11.41. Found: C, 52.07; H, 3.09; N, 10.98.

$[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$. $[HB(3\text{-}(CF_3)Pz)_3]Na$ (2.50 g, 5.68 mmol) and $[CF_3SO_3Cu]_2\cdot C_6H_6$ complex (1.50 g, 2.98 mmol) were dissolved in toluene (50 mL), and ethylene was bubbled into this solution at room temperature. The resulting mixture was stirred overnight and then filtered through Celite to obtain a pale yellow solution. The toluene was removed under reduced pressure to obtain a white solid. It was recrystallized from hexane at −6 °C to obtain colorless crystals of $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ in 54% yield. Mp: dec 187 °C. ^1H NMR (C_6D_6): δ 4.98 (s, 4 H, CH_2CH_2), 6.02 (d, $^3J = 1.9$ Hz, 3H, CH), 7.06 (br s, 3H, CH). ^1H NMR ($CDCl_3$): δ 4.80 (s, 4 H, CH_2CH_2), 6.50 (d, $^3J = 1.9$ Hz, 3H, CH), 7.69 (s, 3H, CH). ^{19}F NMR (C_6D_6): δ −60.3. ^{13}C NMR (C_6D_6): δ 85.8 (t, $^3J = 158$ Hz, CH_2CH_2), 104.6 (dd, $^1J = 182$ Hz, $^2J = 8$ Hz, CH), 121.4 (q, $^1J = 269$ Hz, CF_3), 135.9 (dd, $^1J = 190$ Hz, $^2J = 6$ Hz, CH), 143.5 (q, $^2J = 38$ Hz, CCF_3). IR (KBr), cm^{-1}: 3157, 3029, 2879, 2641 (B−H), 2500, 2361, 1652, 1375, 1271, 1006, 973, 945, 876, 786, 750, 733, 716. Anal. Calcd for $C_{14}H_{11}BCuF_9N_6$: C, 33.07; H, 2.18; N, 16.54. Found: C, 32.81; H, 1.69; N, 16.94.

General Procedure for the Aziridinations. A solution of styrene (42 mg, 0.40 mmol) and *N*-tosyl phenyliodinane (224 mg, 0.60 mmol) and powdered 4 Å molecular sieves (120 mg) in dry CH_3CN (1 mL) were stirred at room temperature while purging with N_2 for 2 min. $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ (15 mg, 0.02 mmol) was added, and the resulting mixture was stirred at room temperature under N_2 overnight. The reaction mixture was diluted with CH_2Cl_2 (∼20 mL), filtered through Celite, concentrated in vacuo, and subjected to flash chromatography (SiO_2, hexanes/EtOAc, 9:1), giving the product as colorless crystals (108 mg, 99%), mp 87−89 °C (lit. 88−89 °C).[41] ^1H NMR ($CDCl_3$, 500 MHz): δ 7.75 (s, 1H), 7.73 (s, 1H), 7.20−7.08 (m, 7H), 3.65 (dd, $J = 7.2$, 4.5 Hz, 1H), 2.85 (d, $J = 7.2$ Hz, 1H), 2.31 (s, 3H), 2.26 (d, $J = 4.5$ Hz, 1H).

X-ray Structure Determination. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream. Data collections were carried out at low temperature on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit cell parameters of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)\cdot 2(C_6H_6)$, $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$, and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ were determined by least squares refinement of 45, 43, and 30 reflections, respectively. Structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement on F^2 and difference Fourier analysis.

The $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ crystallizes in the *Pnma* space group with a crystallographically imposed plane of symmetry containing Cu, B, and one of the pyrazole rings. It also crystallizes with a molecule of benzene in the asymmetric unit. The ethylene moiety is disordered over two sites. All non-hydrogen atoms except the ethylene carbons were refined anisotropically. The hydrogen atom on the boron was located

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[41] Seden, T. P.; Turner, R. W. *J. Chem. Soc. C* **1968**, 876−878.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$, $[HB(3-(CF_3),5-(C_6H_5)Pz)_3]Cu(C_2H_4)$, and $[HB(3-(CF_3)Pz)_3]Cu(C_2H_4)$

	$Cu(C_2H_4)$	$Cu(C_2H_4)$	$Cu(C_2H_4)$
Cu−C (av)	2.022(6)	2.012(11)	2.009(9)
C(1)−C(2) (av)	1.325(9)	1.30(1)	1.34(1)
Cu−N	2.029(3)	2.076(3)	2.035(3)
	2.152(3)	2.094(3)	2.147(3)
	2.152(3)	2.121(3	2.210(3)
B−N	1.546(6)	1.548(5)	1.547(4)
	1.558(4)	1.557(5)	1.549(5
	1.558(4)	1.546(6)	
Cu···B	3.092	3.072	3.092
N−Cu−N	89.70(9)	87.59(12)	90.82(11)
	89.70(9)	90.55(12)	88.11(10)
	88.70(13)	91.35(12)	91.55(10)
N−B−N	108.9(2)	110.8(3)	109.6(3)
	108.9(2)	109.0(3)	109.7(3)
	109.4(3)	108.5(3)	108.9(3)

from the difference map and included. All the other hydrogen atoms were included at calculated positions.

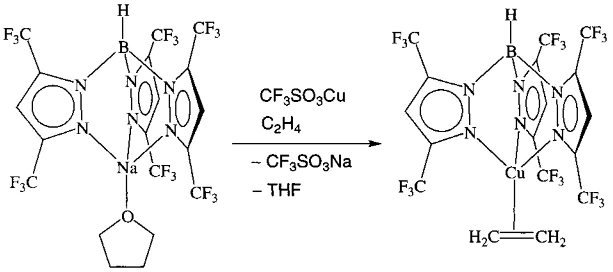
The $[HB(3-(CF_3),5-(C_6H_5)Pz)_3]Cu(C_2H_4)$ crystallizes in the $P2_1/n$ space group. The disordered ethylene unit (over two sites) was modeled successfully, and the occupancies were refined to 48% and 52%. All non-hydrogen atoms except the disordered ethylene carbons were refined anisotropically. The hydrogen atom on the boron was located from the difference map and included. All the other hydrogen atoms were included at calculated positions.

The $[HB(3-(CF_3)Pz)_3]Cu(C_2H_4)$ crystallizes in the $C2/c$ space group. The ethylene unit is disordered over two sites, and the occupancies were refined to 64% and 36%. All non-hydrogen atoms were refined anisotropically. The hydrogen atom on the boron was located from the difference map and included. The remaining hydrogen atoms were included at calculated positions.

Software programs and the sources of scattering factors are contained in the Bruker SHELXTL 5.1 software package provided by Bruker Analytical X-ray Instruments, Inc. Some details of data collection and refinements are given in Table 1. Selected bond distances and angles are given in the Table 2.

Results and Discussion

The treatment of $[HB(3,5-(CF_3)_2Pz)_3]Na(THF)$ with copper(I) trifluoromethanesulfonate under an ethylene atmosphere led to the copper(I) ethylene complex $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$ in very good yield. It is an air stable solid. In contrast, the corresponding methylated analogue $[HB(3,5-(CH_3)_2Pz)_3]Cu(C_2H_4)$[24,36] oxidizes easily upon exposure to air. Furthermore, unlike most copper(I) monoolefin complexes,[31] $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$ does not lose ethylene under reduced pressure. It was characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and by X-ray crystallography.



The ^1H NMR spectrum of $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$ in C_6D_{12} or $CDCl_3$ exhibited a resonance at 4.98 or 4.96 ppm, respectively, which could be assigned to the protons of the ethylene moiety. The ^1H NMR spectrum taken in π-donor solvents such as C_6D_6 also displays a signal at a similar chemical shift value (δ 4.94). More importantly, no free ethylene signal (expected at δ 5.24 in C_6D_6 under similar conditions)[31] was detected in such solutions. A $CDCl_3$ solution of $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$ treated with excess ethylene exhibited two sharp signals at 4.96 and 5.40 ppm for coordinated and free ethylene, signifying only a very slow exchange (if any) on the NMR time scale. These NMR data also indicate that the ^1H NMR resonance due to ethylene protons shift to a lower frequency upon coordination to copper(I). The change, however, is relatively small. The closely related nonfluorinated analogue $[HB(3,5-(CH_3)_2Pz)_3]Cu(C_2H_4)$ exhibits the corresponding peak at a much lower chemical shift value (4.41 ppm).[24] The upfield shift of the ^1H NMR resonance of ethylene protons of copper(I) adducts has been attributed to the increased shielding caused by the copper-to-ethylene π-back-donation.[34] The relative magnitude of the upfield shifts are consistent with the electron-donating ability of the substituents on the tris(pyrazolyl)borate ligand. The carbonyl stretching frequencies of the corresponding copper carbonyl complexes also show a similar trend ($[HB(3,5-(CF_3)_2Pz)_3]CuCO$, $\nu_{CO} = 2137$ cm^{-1}; $[HB(3,5-(CH_3)_2Pz)_3]CuCO$; $\nu_{CO} = 2066$ cm^{-1}).[9,21] An even greater upfield shift of ethylene proton signal has been observed in $[t\text{-}Bu_2P(Me_3SiN)_2]Cu(C_2H_4)$ (3.48 ppm).[31] It features an electron-rich iminophosphanamide ligand. Ethylene complexes of better π-donor metal ions also show a significantly larger upfield shift of ethylene signals (e.g., $[HB(3-(CF_3),5-(CH_3)Pz)_3]Ir(C_2H_4)(CO)$, 2.01, 2.40 ppm;[7] $[HB(3,5-(CH_3)_2Pz)_3]Ir(C_2H_4)(CO)$, 1.76, 2.32 ppm;[42] $[HB(Pz)_3]Rh(C_2H_4)_2$, 2.52 ppm;[43] $[HB(Pz)_3]Rh(C_2H_4)(PPh_3)$, 1.77, 2.39 ppm).[43]

The proton-coupled ^{13}C NMR spectrum of $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$ displayed a triplet centered at 89.5 ppm. This can be assigned to the carbon atoms of the ethylene moiety. The corresponding peak in free ethylene appears at a much higher frequency (123.5 ppm).[44] The $^1J_{C-H}$ coupling constant of ethylene increases very slightly upon coordination (Table 3). The $^1J_{C-H}$ values provide useful information about the hybridization state at the carbon.[45] These data suggest that in $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$ the hybridization at the ethylene carbons remains essentially sp^2. For comparison, metal adducts such as $(PPh_3)_2Pt(C_2H_4)$ and $[HB(3,5-(CH_3)_2Pz)_3]Ir(C_2H_4)(PMe_2Ph)$ show a $^1J_{C-H}$ of about 145 Hz, which is *lower* than that for free ethylene.[42,45] In some cases, an increase of $^1J_{C-H}$ as a result of π-coordination has also been observed (e.g., in $(C_6H_6)_2Cr$, $(C_6H_6)Cr(CO)_3$), and a simple explanation for such behavior is not available.[45]

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(43) Oldham, W. J., Jr.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467−474.

(44) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: New York, 1993.

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Table 3. Selected ^{1}H and ^{13}C NMR Spectroscopic (chemical shifts in ppm; coupling constants in Hz) and Solid State Structural Data (bond distances in Å)

compound[f]	$C_2\mathit{H}_4$	C_2H_4	$^{1}J_{C-H}$	Pz(4-H)	C=C (Å)	Cu−C (Å)	ref
$[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$	4.98[a]	89.5[a]	161	6.82	1.325(9)	2.022(6)	this work
	4.94[b]			6.18			
	4.96[c]	89.1[c]		6.94			
$[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$	5.20[b]	85.7[b]	159	6.23	1.30(1)	2.012(11)	this work
	4.91[c]	85.7[c]		6.56			
$[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$	4.98[b]	85.8[b]	158	6.02	1.34(1)	2.009(9)	this work
	4.80[c]	85.7[c]		6.50			
$[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$	4.41[d]			5.68	1.329(9)	2.017(6)	24
$[HB(Pz)_3]Cu(C_2H_4)\cdot CuCl$	4.43[d]			6.26	1.347(5)	1.999(3)	24
$[t\text{-}Bu_2P(Me_3SiN)_2]Cu(C_2H_4)$	3.48[b]	73.0[b]	158		1.362(6)	1.987(3)	31
$[(tmen)Cu(C_2H_4)]ClO_4$	4.16[e]				1.36(1)	1.96(1)	34
$[\{NH(py)_2\}Cu(C_2H_4)]ClO_4$	4.70[e]				1.359(7)	2.019(3)	48
$[(bpy)Cu(C_2H_4)]ClO_4$	4.92[e]				1.353(15)	1.992(12)	32, 47
$[(phen)Cu(C_2H_4)]ClO_4$	5.00[e]				1.361(22)	2.010(13)	32, 47
$[(Hhq)Cu(C_2H_4)]ClO_4$	5.22[e]				1.32(1)	2.046(6)	33
C_2H_4	5.24[b]	123.5	156		1.3369(16)		44, 46
	5.40[c]						this work
	5.43[e]						34
$[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$	5.56[c]	104.9[c]	164	6.79	1.30(1)		13
$[HB(3,5\text{-}(CH_3)_2Pz)_3]Ir(C_2H_4)(PMe_2Ph)$	1.73[b]	−7.2[b]	145		1.44(2)		42
	2.78						

[a] C_6D_{12} solvent. [b] C_6D_6 solvent. [c] $CDCl_3$ solvent. [d] CD_2Cl_2 solvent. [e] $(CD_3)_2CO$ solvent. [f] Abbreviations: Pz(4-H) = protons at the pyrazolyl ring 4-position, tmen = tetramethylethylenediamine, $NH(py)_2$ = di-2-pyridylamine, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Hhq = 2-hydroxyquinoxaline

It is noteworthy that due to the highly labile nature of copper−olefin bonding interaction, very little is known about the ^{13}C NMR chemical shifts or the C−H coupling constant values of copper-coordinated ethylene (see Table 3). The only report in the literature containing $^{1}J_{C-H}$ values of a stable copper−ethylene unit concerns $[t\text{-}Bu_2P(Me_3SiN)_2]Cu(C_2H_4)$.[31]

The ^{19}F NMR spectrum of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ shows two signals as expected for the CF_3 groups on the 3- and 5-positions of the pyrazole ring. One of the peaks, which corresponds to the trifluoromethyl groups on the pyrazole ring 5-position, appears as a doublet. Similar splitting was observed for most of the metal complexes derived from the $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ ligand.[2,12] This is believed to be due to long-range coupling to the hydrogen atom on boron.

The solid state structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ shows a pseudo-tetrahedral copper ion coordinated to three pyrazole nitrogens and to the ethylene molecule. The $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu$ moiety shows the common C_{3v} symmetry. Unfortunately, the ethylene moiety is disorderd over two sites. Therefore, it is unwise to interpret the structural parameters of the ethylene unit in great detail. Nevertheless, the structure shows that the ethylene molecule coordinates to copper(I) in typical η^2-fashion. The C=C bond distance of the coordinated ethylene (average 1.325(9) Å) is essentially the same as that for the free molecule (1.3369(16) Å).[46] These data are consistent with the C−H coupling constant value. The related copper analogue $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$[24] featuring the nonfluorinated ligand and the silver analogue $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$[13] of the same fluorinated ligand have been characterized by X-ray crystallography, and they both show no notable changes in the C=C bond distance upon coordination (Table 3).

Considering the relatively high stability of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$, we have decided to explore the chemistry of copper ethylene complexes of various other fluorinated tris(pyrazolyl)borates. Accordingly, we prepared $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ using the corresponding sodium salts, copper trifluoromethanesulfonate, and ethylene. These copper ethylene adducts have been obtained as colorless solids in good yield. Like $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$, $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ are soluble in most organic solvents such as toluene, THF, and chloroform. Solutions of $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ are, however, less stable toward oxidation compared to that of the highly fluorinated analogue $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$. For example, benzene solutions of $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ show green color within an hour, whereas the solution containing $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ remains colorless even after several days. This is not surprising considering the high air sensitivity of the nonfluorinated analogue $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$ and the relative donor properties of the tris(pyrazolyl)borate ligands.[2,24] Nevertheless, solid samples of $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ can be handled in air for a short periods (several hours) and can be stored under nitrogen indefinitely, without any apparent sign of decomposition.

No free ethylene was detected by ^{1}H NMR in $CDCl_3$ or C_6D_6 solutions of $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ or $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$. We have also treated C_6D_6 solutions of $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$ with excess ethylene. ^{1}H NMR spectra of these solutions at room temperature show two separate signals, one at the coordinated ethylene chemical shift value of the copper adduct (δ 5.20 or 4.98) and the second peak at δ 5.24 corresponding to the free ethylene. The proton chemical shifts of coordinated ethylene protons are much closer to those observed for ionic copper salts of ethylene than that observed for neutral molecular compounds such as $[t\text{-}Bu_2P(Me_3SiN)_2]$-

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(46) Bartell, L. S.; Roth, E. A.; Hollowell, C. D.; Kuchitsu, K.; Young, J. E., Jr. *J. Chem. Phys.* **1965**, *42*, 2683−2686.

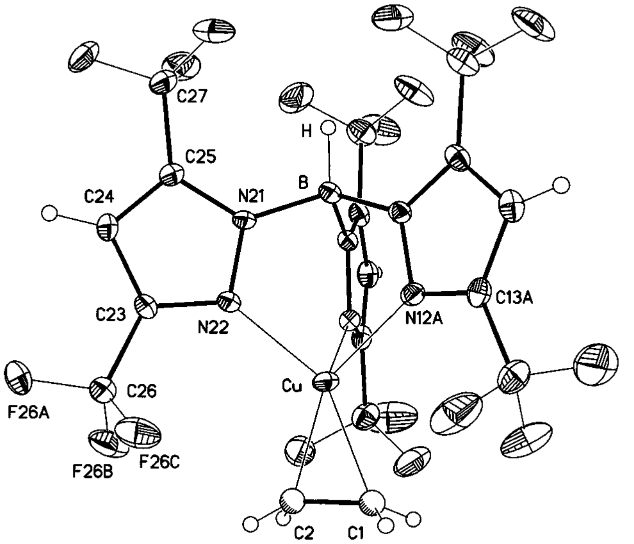

Figure 1. Molecular structure of [HB(3,5-$(CF_3)_2$Pz)$_3$]Cu(C_2H_4) (thermal ellipsoids at 30% level).

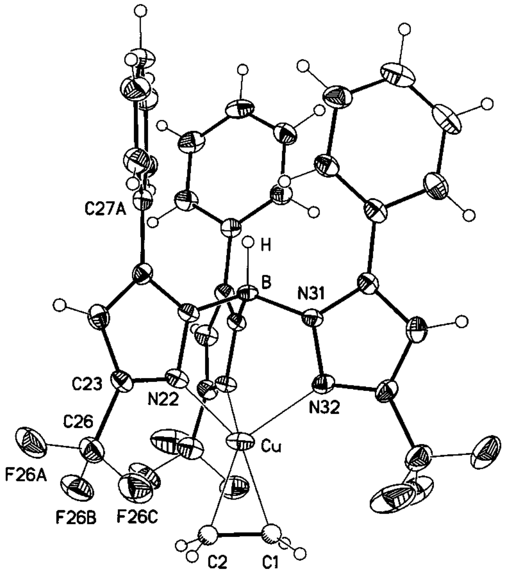

Figure 2. Molecular structure of [HB(3-(CF_3),5-(C_6H_5)Pz)$_3$]Cu(C_2H_4) (thermal ellipsoids at 30% level).

Cu(C_2H_4) (see Table 3).[25,33,34,47,48] The ^{13}C chemical shift and C−H coupling constant data of the ethylene unit are similar to the corresponding parameters for [HB(3,5-$(CF_3)_2$Pz)$_3$]Cu(C_2H_4).

Compounds [HB(3-(CF_3),5-(C_6H_5)Pz)$_3$]Cu(C_2H_4) and [HB(3-(CF_3)Pz)$_3$]Cu(C_2H_4) afford good X-ray quality crystals. Their solid state structures are depicted in Figures 2 and 3, respectively. Although we were hoping for a more ordered ethylene moiety, both these adducts unfortunately show disorder of the ethylene unit similar to that observed in [HB(3,5-$(CF_3)_2$Pz)$_3$]Cu(C_2H_4) (see Figure 4). The ethylene group in these adducts appears to sit in a pocket with a significant amount of vibrational/rotational freedom. Interestingly, unusually large thermal parameters have been observed for ethylene carbons of [HB(3,5-$(CH_3)_2$Pz)$_3$]Cu(C_2H_4).[24] The Cu−C, C=C, or Cu−N bond distances are essentially identical in all these tris(pyrazolyl)boratocopper ethylene adducts. In particular, fluoro substituents on the tris(pyrazolyl)borate ligand backbone do not cause a noticeable effect on these parameters.

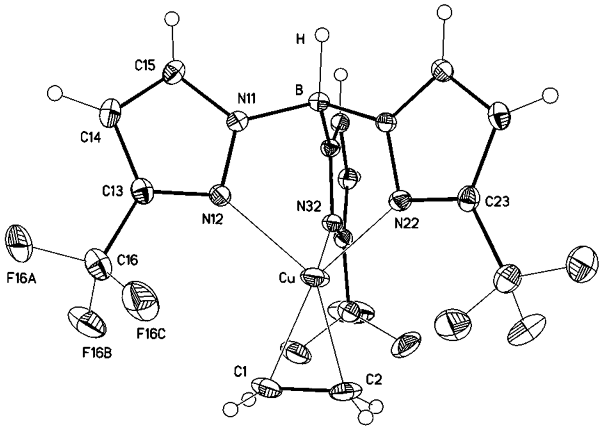

Figure 3. Molecular structure of [HB(3-(CF_3)Pz)$_3$]Cu(C_2H_4) (thermal ellipsoids at 30% level).

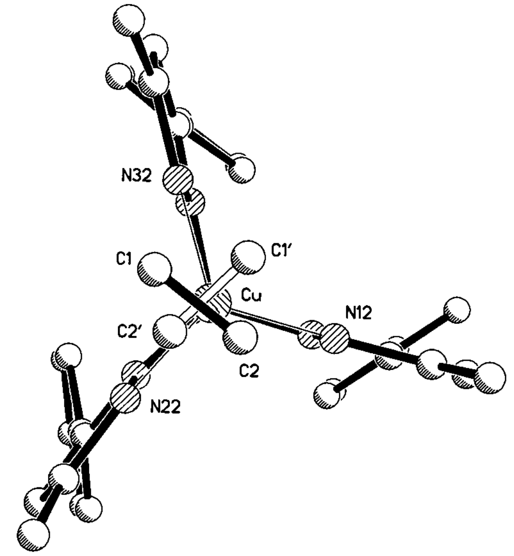

Figure 4. View of [HB(3-(CF_3),5-(C_6H_5)Pz)$_3$]Cu(C_2H_4) down the Cu−B axis showing disorder of the ethylene unit (hydrogen and fluorine atoms have been omitted for clarity).

It is possible to compare ^{1}H and ^{13} NMR spectroscopic data of [HB(3,5-$(CF_3)_2$Pz)$_3$]Cu(C_2H_4) with the closely related Ag(I) adduct [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(C_2H_4). The ethylene protons of [HB(3,5-$(CF_3)_2$Pz)$_3$]Ag(C_2H_4) resonate at 5.56 ppm (see Table 3). This opposite shift of vinyl protons in Ag and Cu systems (compared to that in free ethylene) is believed to be due to the difference in Ag(I)−olefin and Cu(I)−olefin bonding.[13,16,49] The σ-bonding predominates in silver systems, whereas in copper(I) adducts, back-bonding is also somewhat important.[50] The difference in silver− and copper−ligand bonding is also evident from ν_{CO} data of carbonyl adducts. For example, [HB(3,5-$(CF_3)_2$Pz)$_3$]AgCO shows ν_{CO} at 2178 cm^{-1}, which is *higher* than that of free CO (ν_{CO} = 2143 cm^{-1}).[10] The copper analogues exhibit the ν_{CO} at relatively lower values, e.g., [HB(3,5-$(CH_3)_2$Pz)$_3$]-

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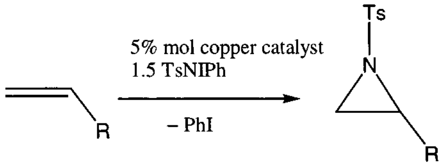
Table 4. Aziridination Results from Copper Complexes $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$[a]

		catalyst			
		$[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$		$[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$	
entry	substrate	time/h	yield/%	time/h	yield/%
1	styrene	16	99	16	99
2	styrene	144	63[b]		
3	*trans*-stilbene	16	24	16	28
4	*trans*-stilbene	16	39[c]		
5	*cis*-stilbene	16	55 (3.6:1)[d]	16	45 (7.5:1)[d]
6	cyclohexene	72	26	72	17
7	cyclohexene	12[e]	93		
8	cyclohexene	2[f]	17		
9	1,2-dihydronaphthalene	72	28	72	34
10	1-octene	96	28	96	34

[a] The aziridination reactions were conducted with 5 mol % of catalyst (except where noted) and employing 1.0 equiv of alkene and 1.5 equiv of *N*-tosyliodinane in acetonitrile at 25 °C. [b] This run was performed with 1 mol % of catalyst. [c] This reaction was performed at 50 °C. [d] *Cis/trans* ratio of the aziridine product. This ratio seems to depend on the batch of iodinane used. [e] 5 equiv of the cyclohexene was used, cf. Handy et al.[36] [f] 10 equiv of cyclohexene and much shorter reaction time (2 h) were used, cf. Perez et al.[26]

CuCO; $\nu_{CO} = 2066\ cm^{-1}$; $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]CuCO$, $\nu_{CO} = 2102\ cm^{-1}$; $[HB(3\text{-}(CF_3)Pz)_3]CuCO$, $\nu_{CO} = 2100\ cm^{-1}$; $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$, $\nu_{CO} = 2137\ cm^{-1}$.[2,9,21,40]

Copper complexes of tris(pyrazolyl)borates are important catalysts in various processes.[6,26,27,35,36,51,52] For example, copper adducts of the nonfluorinated poly(pyrazolyl)borate derivatives (e.g., $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$) are useful catalysts for the conversion of alkenes into aziridines, cyclopropanes, and epoxides. However, most of the complexes used in these studies are very air sensitive and either difficult to prepare or must be prepared in situ.[36] In contrast, the copper(I) derivatives of the fluorinated tris(pyrazolyl)borate ligands described here are much more stable and easier to handle. Thus, it is useful to find out whether these adducts show catalytic activity. Accordingly, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ and $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$ were evaluated as aziridination catalysts utilizing a variety of olefins and *N*-tosyliodinane as the nitrene source.



Our initial experiments were performed utilizing 5 mol % of the catalysts, 1.5 equiv of the nitrene source, and 1.0 equiv of the alkene in acetonitrile and in the presence of molecular sieves. We were delighted to find that under these conditions styrene gave essentially a quantitative yield of the aziridine with both catalysts after stirring overnight at room temperature (Table 4). On lowering the catalyst loading to 1 mol %, it was found that $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ still catalyzed the aziridination of styrene, although the yield was reduced and the reaction time was significantly extended.

We investigated the generality and stereospecificity of this reaction and found that both complexes were able to convert a number of alkenes into the corresponding aziridines. Both *cis* and *trans* stilbene undergo aziridination, with the *cis* isomer providing better yields of the products. Interestingly, it was found that the stereospecificity of the reaction depended on the stereochemistry of the stilbene employed.[53] The *trans* isomer gave exclusively the *trans* aziridine with both catalysts; none of the *cis* isomer was observed in a ^1H NMR spectrum of the crude reaction mixture. On the other hand, the *cis* stilbene provided a mixture of both the *cis* and *trans* isomer. The $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ complex provided a 1.2:1 (*cis/trans*) mixture of aziridines (crude product), which upon purification provided the aziridine in 55% yield (3.6:1 *cis/trans*). With the other complex, $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$, the *cis/trans* ratios were variable from run to run but were generally in the range 1−1.4:0.7−1 (*cis/trans*). The isolation of the aziridine from a run producing an excess of the *cis* isomer gave 45% of the product (7.5:1 *cis/trans*).

In addition to styrene derivatives, the aziridination reactions of simple cyclic and acyclic alkenes were investigated. Both complexes catalyze nitrene transfer, providing the expected aziridines in moderate to low yields. Although these examples appear to be relatively low yielding, it should be pointed out that the ratio of alkene to the nitrene source is significantly lower than in many other reports (e.g., 5−10:1).[26,36] When the aziridination of cyclohexene was repeated according to the conditions of Handy,[36] the yield of the aziridine increased to an excellent 93%. No enhancement in yields was found with this substrate when the conditions reported by Perez were employed.[26]

Summary and Conclusion

We have described the synthesis, properties, and X-ray crystal structures of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$, $[HB(3\text{-}(CF_3),5\text{-}(C_6H_5)Pz)_3]Cu(C_2H_4)$, and $[HB(3\text{-}(CF_3)Pz)_3]Cu(C_2H_4)$. Despite the importance of copper ethylene adducts, very few examples of well-authenticated

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copper(I)−ethylene adducts are available. Most are either very reactive toward air and/or easily lose ethylene. Compounds described in this paper are neutral molecular compounds containing strong copper−ethylene interactions. These adducts are also significantly more air stable compared to the nonfluorinated analogue $[HB(3,5-(CH_3)_2Pz)_3]Cu(C_2H_4)$. Their stability may be attributed mainly to the unique electronic properties of the fluorinated tris(pyrazolyl)borate ligands. In addition to the preparation and characterization of the complexes, we have investigated their ability to catalyze olefin aziridination. These electron-poor copper complexes are competent aziridination catalysts, readily converting a variety of olefins into the corresponding *N*-tosyl aziridines with *N*-tosyl phenyliodinane. In general these complexes appear to have activity comparable to nonfluorinated tris(pyrazolyl)borato derivatives previously reported. This reactivity is very interesting in view of their stability and the electron-deficient nature of the copper center. We are currently exploring the catalytic activity of these copper adducts in other chemical processes. Preliminary experiments indicate that these complexes will catalyze carbene transfer employing ethyl diazoacetate.[54]

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Supporting Information Available: Full details of the X-ray structures of complexes $[HB(3,5-(CF_3)_2Pz)_3]Cu(C_2H_4)$, $[HB(3-(CF_3),5-(C_6H_5)Pz)_3]Cu(C_2H_4)$, and $[HB(3-(CF_3)Pz)_3]Cu(C_2H_4)$ including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010886V

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