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Monoanionic, Bis(pyrazolyl)methylborate $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]^-$ as a Supporting Ligand for Copper(I)-ethylene, *cis*-2-Butene, and Carbonyl Complexes

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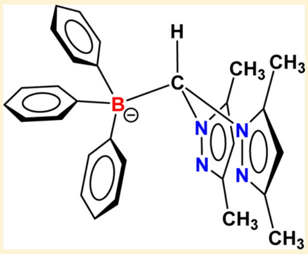
Supporting Information



ABSTRACT: The monoanionic bidentate ligand $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]^-$ has been prepared from lithium bis(pyrazolyl)methanide and triphenylborane. This useful new ligand is closely related to the well-established bis(pyrazolyl)borate and bis(pyrazolyl)methane ligands but has key differences to both analogues as well. The ethylene, *cis*-2-butene, and carbon monoxide adducts $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(L)$ (where L = C_2H_4, *cis*-$CH_3HC{=}CHCH_3$, and CO) have been prepared from $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Li(THF)$, copper(I) triflate, and the corresponding coligand. These complexes have been characterized by NMR spectroscopy and X-ray crystallography. In all cases the bis(pyrazolyl) moiety is bound in κ^2N fashion with the BPh_3 group rotated to sit over the metal center, sometimes coordinating to the metal via phenyl carbons as in $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Li(THF)$ and $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ or simply hovering above the metal site as in $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Cu(C_2H_4)$ and $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$. The ^{13}C and ^1H resonances of the ethylene carbon and protons of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Cu(C_2H_4)$ appear at δ 81.0 and 3.71 ppm in CD_2Cl_2, respectively. The characteristic CO frequency for $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ has been observed at $\bar{\nu}$ 2092 cm^{-1} by infrared spectroscopy and is lower than that of free CO suggesting moderate M → CO π-back-donation. A detailed analysis of these complexes has been presented herein.

INTRODUCTION

Poly(pyrazolyl)borates have been widely explored by inorganic, organometallic, and coordination chemists since their discovery in 1966.[1−6] These monoanionic nitrogen-based ligands are particularly attractive due to the ability to fine-tune their steric and electronic properties and thereby modulate the reactivity of the bound metal center by changing the number and nature of the substituents on the pyrazolyl moieties and on the boron. The bulk of the attention in these ligands has been paid to tris(pyrazolyl)borates (Tp; e.g., $[HB(3,5\text{-}(CH_3)_2Pz)_3]^-$, Figure 1).[1−7] The closely related bis(pyrazolyl)borates (Bp; $[H_2B(3,5\text{-}(CH_3)_2Pz)_2]^-$) are also known and have been found to be useful but have only been moderately explored.[4,8−10] Most of the common tris- and bis(pyrazolyl)borates feature somewhat reactive and reducing B−H functionality, which interferes with certain processes, especially involving easily reducible metal ions.[11,12]

Poly(pyrazolyl)methanes such as tris(pyrazolyl)methanes (e.g., $HC(3,5\text{-}(CH_3)_2Pz)_3$) and bis(pyrazolyl)methanes (e.g., $H_2C(3,5\text{-}(CH_3)_2Pz)_2$; Figure 1) were first reported in the late 1950s and are similar in structure to the tris- and bis(pyrazolyl)borate except that they do not share the borate backbone or carry the formal negative charge (e.g., $H_2C(3,5\text{-}(CH_3)_2Pz)_2$; Figure 1).[4,6,13−18] Poly(pyrazolyl)borates are also widely used in metal coordination chemistry as a supporting ligand. Here we report the design and synthesis of a bidentate ligand analogue of bis(pyrazolyl)borate using the closely related bis(pyrazolyl)methane precursor and triarylboron. These monoanionic, bis(pyrazolyl)methylborate ligands allow the synthesis of neutral metal adducts with M(I) salts including those of copper(I). In particular, we describe the preparation of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]^-$ (Figure 1) and its utility in the synthesis of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]CuL$ complexes containing L = ethylene, carbon monoxide, and cis-2-butene. This bis(pyrazolyl)methylborate ligand does not have the sometimes problematic and reactive B−H moiety found in common bis(pyrazolyl)borates.[11,19] It features a negatively charged third arm that is significantly less prone to coordination in contrast to previously reported monoanionic bis(pyrazolyl)methane versions containing third arms like $-CO_2^-$, $-CS_2^-$, $-CPh_2(C_5H_4)^-$, $-CH_2NDipp^-$ fragments that coordinate readily to metal ions.[8,16] Synthesis of $[(F_3B)C(Pz)_3)]Li$ and its tungsten adducts such as $[(F_3B)C(Pz)_3)]W(CMe)(CO)_2$ has been described by Stone et al.[20] It is the only report on a related poly(pyrazolyl)methylborate to our knowledge. There is no structural data available on these $[(F_3B)C(Pz)_3)]^-$ adducts.

We have focused on the isolation of copper complexes of small, carbon-based molecules because they are of significant fundamental interest and technological importance. For example, copper(I) ethylene adducts serve as models for copper(I)-based ethylene receptor sites in plants,[21,22] and as reaction intermediates in copper-mediated alkene chemistry.[23−25] Copper(I) carbonyl complexes have also attracted

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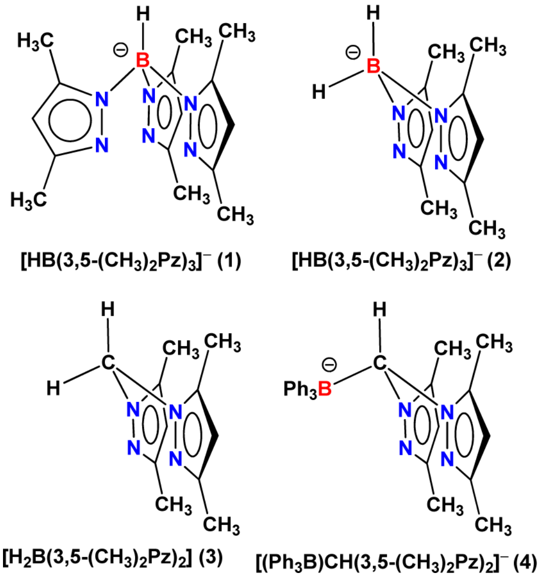

Figure 1. Examples of tris(pyrazolyl)borate (**1**), bis(pyrazolyl)borate (**2**), bis(pyrazolyl)methane (**3**), and bis(pyrazolyl)methyltriphenylborate (**4**) ligands.

similar interest due to their importance in biochemistry, organic synthesis, and several industrial catalytic processes.[23,25−29] Notably, the oxychlorination of ethylene, the synthesis of methanol from syngas, and the selective removal of CO from gas mixtures are a few processes in which copper plays a key role.[30−32] While several copper ethylene and carbonyl complexes are known with tris(pyrazolyl)borates (including their heavier silver and gold counterparts),[23,33−35] and tris(pyrazolyl)methanes,[36−42] only very few examples of copper-alkene or -carbonyl adducts have been successfully stabilized and structurally characterized using the bidentate bis(pyrazolyl)borate and bis(pyrazolyl)methane system.[10,23,43] For example, the fluorinated bis(pyrazolyl)borate ligand supported copper(I) alkene complexes $[H_2B(3,5-(CF_3)_2Pz)_2]$-CuL (L = styrene, cyclooctene, 4-vinylanisole, triethylvinylstyrene) and $\{[H_2B(3,5-(CF_3)_2Pz)_2]Cu\}_2$(1,5-COD), as well as cationic copper(I) olefin complex $\{[CH_2(3,5-(CH_3)_2Pz)_2]$Cu-(cyclooctene)}OTf of bis(pyrazolyl)methane have been reported in the literature.[10,44,45] Copper carbonyl complexes of bis(pyrazolyl)borate and bis(pyrazolyl)methane are also less numerous and include $[CH_2(3,5-(CF_3)_2Pz)_2]Cu(CO)(OTf)$, $[CH_2(3-(CF_3)Pz)_2]Cu(CO)(OTf)$, $[CH_2(3,5-(CH_3)_2Pz)_2]Cu(CO)(OClO_3)$, and $[\{[CH_2(3,5-(CH_3)_2Pz)_2]Cu(CO)\}_2(\mu\text{-pyrazine})](ClO_4)$ as the structurally well authenticated adducts of this type.[44,46]

■ RESULTS AND DISCUSSION

The lithium salt of bis(3,5-dimethylpyrazolyl)methyltriphenylborate, $[(Ph_3B)CH(3,5-(CH_3)_2Pz)_2)]Li$ is obtained in two steps by first treating the bis(3,5-dimethylpyrazolyl)methane with *n*-BuLi in THF at −78 °C for 15 min, followed by the addition of triphenylborane to the resulting methanide. After stirring of the mixture at room temperature overnight, the final product was isolated as a colorless crystalline solid from the concentrated reaction medium layered with hexanes and characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, CHN analysis, and X-ray crystallography. $[(Ph_3B)CH(3,5-(CH_3)_2Pz)_2]Li(THF)$ is a white solid that melts around 142 °C. The complex should be stored under a nitrogen atmosphere to prevent decomposition.

The ^1H NMR spectrum of $[(Ph_3B)CH(3,5-(CH_3)_2Pz)_2]Li(THF)$ in $CDCl_3$ displayed a singlet ^1H resonance at δ 5.68 ppm assigned to the pyrazolyl ring C−H protons. This resonance is shifted upfield from the corresponding peak at δ 5.78 ppm observed for the neutral ligand $H_2C(3,5-(CH_3)_2Pz)_2$ in $CDCl_3$. The methyl groups of the pyrazolyl motifs are observed as two singlets at δ 2.13 and 1.99 ppm, that are shifted only slightly downfield from the parent molecule bis(3,5-dimethylpyrazolyl)methane (δ 2.41 and 2.18 ppm). The pyrazolyl ^{13}C peaks are relatively unchanged; however there are a few features in the ^{13}C spectrum that indicate the formation of $[(Ph_3B)CH(3,5-(CH_3)_2Pz)_2]Li(THF)$. For example, the $CBPh_3$ carbon resonance is observed as a broad peak at δ 71.2 ppm in $CDCl_3$ and is shifted significantly downfield from the original CH_2 backbone resonance observed at δ 60.5 ppm in $CDCl_3$. The single broad ^{11}B resonance observed at δ −8.52 ppm in $CDCl_3$ is indicative of a four coordinate boron center and is shifted dramatically compared to that of the triphenylborane starting material which is observed at δ 60.2 ppm.[47] The CHN analysis is in good agreement with the expected molecule and confirmed by X-ray crystallography.

$[(Ph_3B)CH(3,5-(CH_3)_2Pz)_2]Li(THF)$ crystallizes in the $P2_1/n$ space group and is monomeric (Figure 2). The lithium atom displays distorted tetrahedral geometry and is coordinated to the two nitrogen atoms of the two pyrazolyl groups, the oxygen of THF, and one of the aryl groups attached to boron asymmetrically, essentially in η^1-fashion (with Li−C distances of 2.455(3) and 2.709(3) Å). Although there are no bis(pyrazolyl)methylborate systems for direct comparisons, there are very few lithium adducts like $[(C_5H_4)(Ph)_2CCH(3,5-(CH_3)_2Pz)_2]Li(THF)$ and $[(C_5H_4)(Bu^t)CHCH(3,5-(CH_3)_2Pz)_2]Li(THF)$ that exist with NNOC coordination at

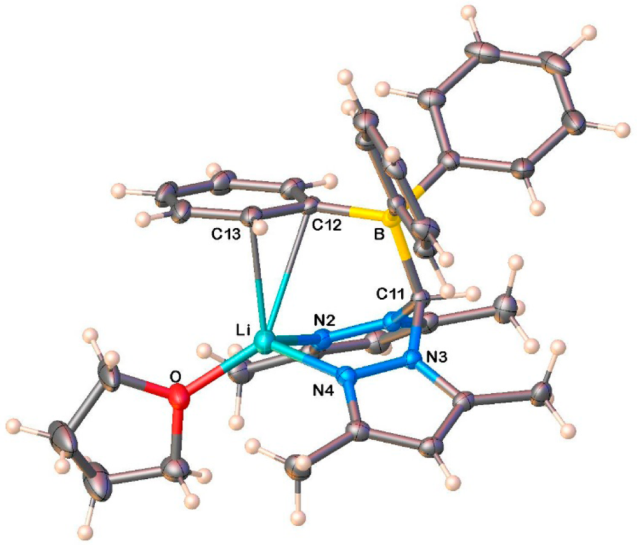

Figure 2. ORTEP diagram of $[(Ph_3B)CH(3,5-(CH_3)_2Pz)_2]Li(THF)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (deg): Li−N2 2.004(3), Li−N4 2.032(3), Li−O 1.927(3), Li−C12 2.709(3), Li−C13 2.455(3), Li−B 3.52, Li−C11 3.042, C11−B 1.7021(18), N2−Li−N4 94.82(10), O−Li−N2 121.55(12), O−Li−N4 114.73(12), N3−C11−N1 107.00(9), N1−C11−B 114.39(9), N3−C11−B 118.35(10), N3−C11−N1 107.00(9).

Table 1. Spectroscopic Data and Bond Distances for Selected, Three-Coordinate Copper-Ethylene Complexes with κ^2NCu(ethylene) Moiety

compound	$\delta(^{13}C)$ (ppm)	$\delta(^{1}H)$ (ppm)	C=C (Å)	Cu−C (Å)	Cu−N (Å)	ref
$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$	81.0 (CD_2Cl_2)	3.71 (CD_2Cl_2)	1.365(3)	2.0023(18) 2.0025(18)	1.9541(14) 1.9647(13)	this work
$[HC\{C(CH_3)N(2,6\text{-}(CH_3)_2C_6H_3)\}_2]Cu(C_2H_4)$	74.74 (C_6D_6)	2.91 (C_6D_6)	1.365(3)	1.986(2) 1.992(2)	1.917(2) 1.908(1)	55
$[Bu^t_2P(NSiMe_3)_2N]Cu(C_2H_4)$	73.0 (C_6D_6)	3.48 (C_6D_6)	1.362(6)	1.987(3) 1.987(3)	2.0140(16) 2.0140(16)	69
κ^2-$[PhB(3\text{-}(C_2F_5)Pz)_3]Cu(C_2H_4)$	85.5 (C_6D_{12})	3.70 ($CDCl_3$)	1.354(7)	2.033(4) 2.027(4)	2.009(3) 2.008(3)	70
$[N\{(C_3F_7)C((2,6\text{-}(iPr)_2C_6H_3)N\}_2]Cu(C_2H_4)$	86.0 ($CDCl_3$)	3.37 ($CDCl_3$)	1.3518(14)	2.0006(11) 1.9974(11)	1.9406(9) 1.9403(9)	71
$[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$	87.6 ($CDCl_3$)	3.68 ($CDCl_3$)	1.332(12)	2.027(8) 1.997(8)	1.955(5) 1.958(6)	72
$[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$	86.1 ($CDCl_3$)	3.86 ($CDCl_3$)	1.364(4)	2.018(3) 2.010(3)	1.946(2) 1.955(2)	56
$[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Cu(C_2H_4)$	84.20 ($CDCl_3$)	3.53 ($CDCl_3$)	1.364(9)	2.004(6) 2.004(6)	1.958(5) 1.946(5)	73
free ethylene	123.20 (CD_2Cl_2)	5.40 (CD_2Cl_2)	1.313(1) (X-ray) 1.3369(16) (electr. diff.)			50, 57, 74

lithium.[48,49] The geometry of these compounds can be described as distorted tetrahedrons with the lithium coordinated to two pyrazolyl ring nitrogens, cyclopentadienyl ring, and a THF. Cyclopentadienyl groups are bonded to lithium in η^5-fashion somewhat asymmetrically with Li−C bond lengths ranging from 2.25(1)−2.50(6) Å. The Li−C bond lengths of the nearest cyclopentadienyl ring carbon of each complex are 2.25(1) and 2.321(5) Å, and are significantly shorter than that of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$ (2.455(3) Å). This is perhaps due to the better donor ability of anionic cyclopentadienyl groups of the former systems compared to neutral B-phenyl groups of the latter. The Li−N bond distances of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$ are, however, significantly shorter at just 2.004(3) and 2.032(3) Å compared to those of $[(C_5H_4)(Ph)_2CCH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$ (2.13(1) and 2.37(1) Å) and $[(C_5H_4)(Bu^t)CHCH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$ (2.131(5) and 2.131(5) Å).

The copper(I)-L adducts $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]CuL$ (L = C_2H_4 and *cis*-$CH_3HC{=}CHCH_3$) were obtained by treating $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$ with CF_3SO_3Cu in a solution of dichloromethane containing the corresponding coligand, alkene. X-ray quality crystals were obtained from a concentrated dichloromethane solution containing excess alkene, and the products were isolated as white solids. Solid samples of these complexes can be exposed to laboratory atmosphere for several days without obvious signs of decomposition, but should be stored under nitrogen to prevent decomposition during long-term storage. Solid samples of these compounds do not lose the coordinated olefin even under reduced pressure.

The ^{13}C NMR spectrum of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ in CD_2Cl_2 exhibited one singlet resonance at δ 81.0 ppm in CD_2Cl_2, corresponding to the carbons of coordinated ethylene. The proton signals of ethylene were observed at δ 3.71 ppm in CD_2Cl_2. These resonances are shifted significantly upfield from the ^{13}C and ^{1}H signals of free ethylene, which are observed at δ 123.2 and 5.40 ppm in CD_2Cl_2, respectively.[50] The upfield shift of the ethylene carbon resonances is typical for metal-ethylene complexes and has been linked to the metal-to-ligand π-backbonding to the π^* orbital of ethylene.[51−54] The ^{13}C resonances of the structurally authenticated monoethylene adducts, including the cationic species, range from δ 89.5−73.0 ppm.[24] The ^{13}C resonance at δ 81.0 ppm indicates midlevel of metal-to-ligand backbonding between copper and ethylene compared to related complexes. For instance, the ethylene carbon signals of neutral, copper(I) complexes $[HC\{C(CH_3)N(2,6\text{-}(CH_3)_2C_6H_3)\}_2]Cu(C_2H_4)$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ are observed at δ 74.74 (C_6D_6) and 86.1 ($CDCl_3$) ppm, respectively, (Table 1).[55,56] The ^{1}H resonances of the structurally authenticated monoethylene copper(I) adducts, including the cationic species, range from δ 5.22−2.91 ppm.[23,24] The ethylene carbon and proton resonances of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ therefore appear at a normal region expected for copper(I)-ethylene compounds, but analogous bis(pyrazolyl)methane or bis(pyrazolyl)borate adducts are not available for a comparison of more closely related systems.

The solid state structure of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ shows a trigonal planar copper ion coordinated to nitrogens and single ethylene molecule (Figure 3). The $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]^-$, which is bonded to copper in κ^2N fashion via the nitrogen atoms of the pyrazolyl arms, adopts a boat configuration with the BPh_3 moiety rotated toward the metal center. The Cu-ethylene moiety is well behaved and shows that the ethylene molecule coordinated in typical η^2-fashion. The C=C bond length of the coordinate ethylene is 1.365(3) Å, which is slightly longer than that reported for free ethylene (1.3369(16) Å).[57] On the basis of a recent search of the Cambridge Structural Database,[58] the Cu−N and Cu−C bond lengths for three coordinate copper-ethylene complexes range from 1.913 to 2.046, and 1.959 to 2.046 Å, respectively. The Cu−N bond distances of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ are 1.9541(14) and 1.9647(13) Å, and the Cu−C bond lengths of 2.0023(18) and 2.0025(18) Å are in the midrange of the typical Cu−N and Cu−C distances.

We have synthesized and characterized the *cis*-2-butene adduct $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(cis\text{-}CH_3HC{=}CHCH_3)$ to further explore the natures of these complexes. The olefinic ^{1}H resonance appears as broad peaks at δ 4.90

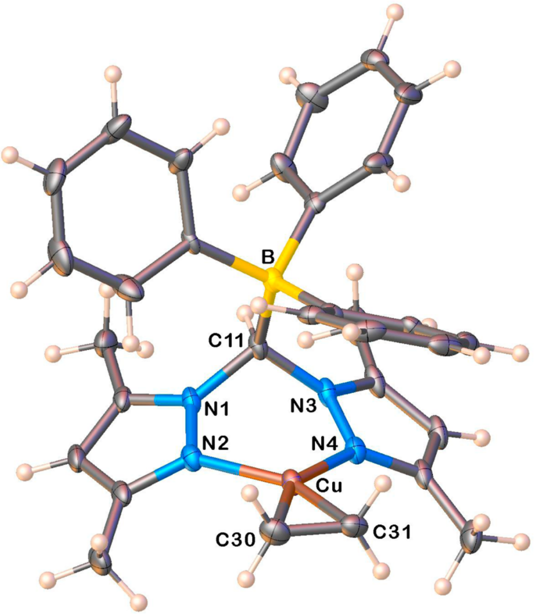

Figure 3. ORTEP diagram of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (deg): Cu−N2 1.9541(14), Cu−N4 1.9647(13), Cu−C30 2.0023(18), Cu−C31 2.0025(18), Cu−C11 3.090, Cu···(C30−C31 centroid) 1.882, C30−C31 1.365(3), Cu−B 3.530, C30−Cu−C31 39.87(8), C11−B 1.703(2), N2−Cu···(C30−C31 centroid) 134.52, N4−Cu···(C30−C31 centroid) 131.24, C11···Cu···(C30−C31 centroid) 155.91, N2−Cu−N4 94.04, N1−C11−B 107.58(12), N3−C11−B 116.11(12), N1−C11−N3 107.49(12).

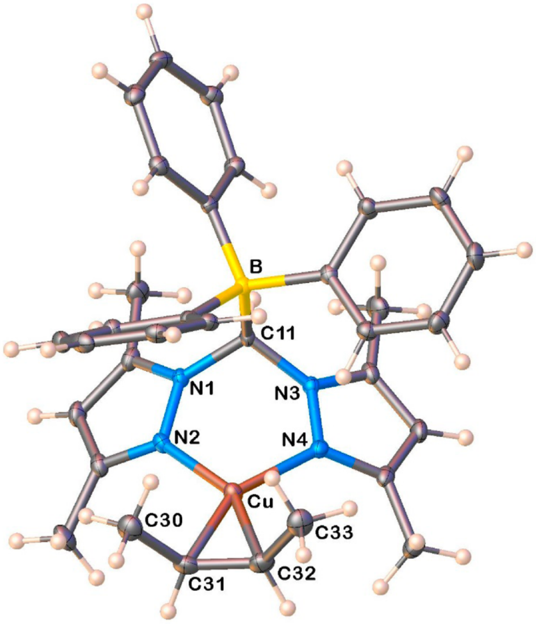

Figure 4. ORTEP diagram of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (deg): Cu−N2 1.9745(13), Cu−N4 1.9569(13), Cu−C31 2.0315(16), Cu−C32 2.0296(17), Cu···(C31−C32 centroid) 1.909, C31−C32 1.382(2), Cu−C11 3.167, Cu−B 3.765, C11−B 1.700(2), C31−Cu−C32 39.78(7), N4−Cu···(C31−C32 centroid) 131.83, N2−Cu···(C31−C32 centroid) 133.68, N2−Cu−N4 94.40(5), N3−C11−N1 107.86(12), N1−C11−B 117.58(12), N3−C11−B 118.15(12), C11−Cu···(C31−C32 centroid) 158.68.

ppm in $CDCl_3$ at room temperature, and at δ 4.64 ppm in CD_2Cl_2 at −40 °C. The corresponding signals for free *cis*-2-butene appear at δ 5.46 ppm in $CDCl_3$. The ^{13}C resonance of the olefinic carbons of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ could not be observed at room temperature, but appears as a broad peak at δ 95.0 ppm in CD_2Cl_2 at −20 °C and as a well-defined singlet at δ 94.2 ppm at −40 °C. This peak shifts upfield, comparably to that observed for the ethylene complex, relative to the free ligand which appears at δ 124.8 ppm in $CDCl_3$. The corresponding peak for example in $[Cu((S,S)\text{-}L)(\textit{cis}\text{-}CH_3HC{=}CHCH_3)]ClO_4$ (L = (1*S*,2*S*)-*N*,*N*′-bis(mesitylmethyl)-1,2-diphenyl-1,2-ethanediamine)[59] and $[K(18\text{-crown-}6)][PtCl_3(\textit{cis}\text{-}CH_3HC{=}CHCH_3)]$[60] has been observed at δ 96.4 and 82.7 ppm, respectively. The ^1H and ^{13}C resonances corresponding to the methyl groups of *cis*-2-butene in $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ are only marginally shifted from those of the free ligand. For example, the methyl protons of the coordinated *cis*-2-butene appear as a doublet centered at δ 1.49 ppm in $CDCl_3$ and the similar peak observed for the free ligand at δ 1.61 ppm in $CDCl_3$. The carbon resonance appears at δ 13.5 ppm in $CDCl_3$ compared to the free ligand at δ 12.5 ppm in $CDCl_3$).

X-ray analysis of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ revealed that it has a similar structure to that of the corresponding ethylene analogue (Figure 4). The ligand $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]^-$ coordinates to copper in κ^2N fashion via the nitrogen atoms of the pyrazolyl arms and adopts a boat configuration with the BPh_3 moiety rotated toward the metal center. Methyl groups of the butene moiety of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ point toward the BPh_3 moiety (see Figure 4) perhaps to avoid the adverse steric interactions with the methyl groups of pyrazolyl moiety at the 3-position. This also significantly reduces the encroachment of the nearby B-phenyl group toward copper. The Cu−C distance to nearest B-phenyl ipso carbon is 3.49 Å, compared to that of 3.01 Å in $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$. The sum of the angles at the metal center in $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ and $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ total 360° indicates that the B-phenyl groups do not interact with copper significantly in these alkene adducts to distort the trigonal planar geometry at copper. The degree of curl-like distortion of the "boat-shaped" bis(pyrazolyl)methyl fragment is reflected in the Cu···B separation, which increases from the ethylene adduct to the *cis*-2-butene adduct (3.53 and 3.77 Å). Selected metrical and spectroscopic data of structurally characterized copper-alkene complexes of bis(pyrazolyl)borate and bis(pyrazolyl)methane ligands are presented in Table 2. $[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(\text{cyclooctene})][OTf]$ is the closest analogue of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ among the reported compounds for a comparison. $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$ has shorter Cu−N distances suggesting that it is somewhat better donating Scorpionate.

There are a fair number of well characterized copper carbonyl adducts presently known in the literature including a few involving tris(pyrazoyl)borate supporting ligands.[23,26] In contrast, copper carbonyl complexes of bis(pyrazolyl)borate and bis(pyrazolyl)methane ligands are much less common. The $[CH_2(3,5\text{-}(CF_3)_2Pz)_2]Cu(CO)(OTf)$, $[CH_2(3\text{-}(CF_3)Pz)_2]Cu(CO)(OTf)$, $[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)(OClO_3)$, and $[\{[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)\}_2(\mu\text{-pyrazine})](ClO_4)$ rep-

Table 2. Spectroscopic Data and Bond Distances for Selected Copper-Olefin Complexes

compound	$\delta(^{13}C)$ (ppm)	$\delta(^{1}H)$ (ppm)	C=C (Å)	Cu−C (Å)	Cu−N (Å)	ref
$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$	94.2 (CD_2Cl_2)	4.64 (CD_2Cl_2)	1.382(2)	2.0315(16), 2.0296(17)	1.9745(13), 1.9569(13)	this work
$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(cyclooctene)$	102.6 (C_6D_6)	4.90 (C_6D_6)	1.338(5)	2.035(3), 2.046(3)	1.998(3), 1.995(3)	45
$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(PhCH{=}CH_2)$	76.0, 105.0 ($CDCl_3$)	4.61, 4.98 ($CDCl_3$)	1.368(5)	2.055(3), 2.020(3)	1.993(3), 2.000(3)	10
$\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu\}_2(1,5\text{-}COD)$		5.01 (C_6D_6)	1.370(4) 1.374(4)	2.030(3), 2.021(3) 2.023(3), 2.025(3)	1.989(3), 1.994(3) 1.989(3), 1.985(2)	10
$[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(cyclooctene)][OTf]$	103.5 ($CDCl_3$)	5.28 ($CDCl_3$)	1.362(3)	2.072(2), 2.050(2)	2.009(2), 2.007(2)	75

Table 3. Infrared Spectroscopy Data and Selected Bond Distances for Copper CO Complexes

Cu(CO) complex	$\bar{\upsilon}$ (CO) (IR, cm^{-1})	Cu−C (Å)	C−O (Å)	Cu−N (Å)	reference
$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$	2092 (neat)	1.8055(18)	1.123(2)	1.9939(14) 1.9827(13)	this work
$[CH_2(3,5\text{-}(CF_3)_2Pz)_2]Cu(CO)$ (OTf)	2127 (neat)	1.803(7)	1.144(7)	2.064(4) 2.075(4)	44
$[CH_2(3\text{-}(CF_3)Pz)_2]Cu(CO)$ (OTf)	2120 (neat)	1.812(5)	1.117(6)	2.067(2)	44
$[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ ($OClO_3$)	2108 (neat)	1.806(5)	1.124(6)	2.001(3) 2.007(3)	46
$\{[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)\ (OClO_3)\}_2(\mu\text{-pyrazine})$	2119 (Nujol)	1.835(8)	1.121(8)	2.043(6) 2.046(6) 2.056(5)	46
$[CH(3,5\text{-}(CH_3)_2Pz)_3]Cu(CO)$ (PF_6)	2113 (Nujol)				36
$[CH(3\text{-}(\textit{t}\text{-}Bu)Pz)_3]Cu(CO)$ (PF_6)	2100 (Nujol)	1.778(10)	1.133(9)	2.076(6) 2.075(5) 2.088(5)	36
free CO	2143		1.12822(7)		76

resent well authenticated copper−carbonyl adducts of this type (Table 3).[44,46] In these systems, the CO stretching frequency of metal carbonyl adducts serves as a good measure of relative electron density at a metal site (or the electron acceptor/back-donation ability of a metal ion). It also provides information about the donor properties of the auxiliary ligands coordinated to a metal ion. Considering these reasons, we also explored the copper(I) carbonyl chemistry of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]^-$.

The carbonyl adduct was obtained by treating $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$ with CF_3SO_3Cu in a solution of dichloromethane saturated with carbon monoxide. X-ray quality crystals were obtained from a concentrated dichloromethane solution containing the CO, and the product was isolated as colorless crystals. $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ can be handled in air for several days without obvious signs of decomposition, and solid samples do not lose CO under reduced pressure. However, samples should be stored under nitrogen for long-term storage. The ^{13}C and ^{1}H NMR spectra of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ is similar to that of the analogous ethylene and *cis*-2-butene analogues. The ^{13}C resonance of copper bound CO was not observed, which is not uncommon in copper adducts.[33,39]

X-ray analysis of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ revealed that this Cu-CO adduct has the deepest $Cu(N{-}N)_2C$ boat with a Cu···B distance of 3.33 Å and the nearest $Cu{-}C_{Phenyl}$ distance at just 2.61 Å (Figure 5). The trigonal-planar geometry of the Cu-CO adduct is distorted, and the sum of the angles around the copper center is 354°. The geometry around copper can better be described as trigonally distorted tetrahedron, with the approaching B-phenyl group as the fourth electron domain. This is further evident from the (N2/N4 centroid)-Cu-CO angle of 160°. For comparison, (N2/N4 centroid)-Cu-(C30/C31 centroid) angle of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ is essentially linear at 176°. The Cu−C bond distance of the reported three coordinate copper(I)−carbonyl complexes chelated by nitrogen range from 1.749 to

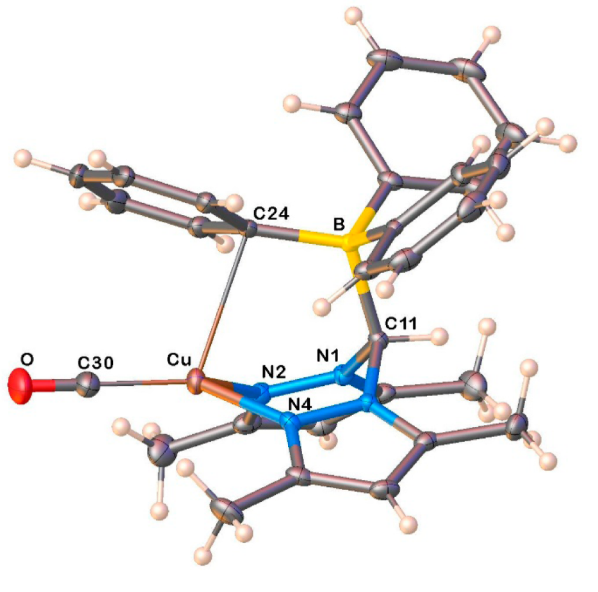

Figure 5. ORTEP diagram of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ (thermal ellipsoids set at 50% probability). Selected bond distances (Å) and angles (deg): Cu−N2 1.9939(14), Cu−N4 1.9827(13), Cu−C30 1.8055(18), O−C30 1.123(2), Cu−C24 2.609, Cu−B 3.334, Cu−C11 3.309, C11−B 1.692(2), N4−Cu−N2 91.68(6), C30−Cu−N2 134.53(7), C30−Cu−N4 127.55(7), O−C30−Cu 177.77(19), C11−Cu−C30 167.57, N1−C11−B 118.24(12), N3−C11−B 114.67(12), N3−C11−N1 106.99(12).

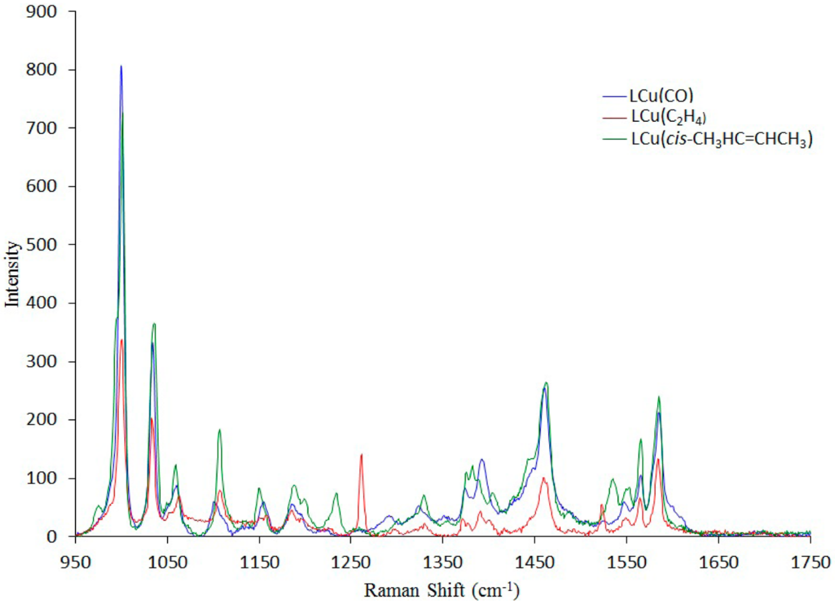

Figure 6. Raman spectra for $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$, $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$, and $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$.

1.813 Å, while the Cu−C bond distance of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ is 1.8055(18) Å. The cationic copper−carbonyl complex based on bis(pyrazolyl)methane ligand $[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)(OClO_3)$[46] is perhaps the most closely related to $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$. It also features a pseudotetrahedral copper site as a result of the Cu−O interaction with weakly coordinating $OClO_3^-$ counterion. The Cu−N and Cu−C bond distances of these two adducts are similar (e.g., the Cu−C and Cu−N distances of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ are 1.80555(18) (Cu−C), 1.9939(14) (Cu−N), and 1.9827(13) Å (Cu−N), and the Cu−C and Cu−N distances of $[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)(OClO_3)$ are 1.806(5) (Cu−C), 2.001(3) (Cu−N), and 2.007(3) Å (Cu−N)).

The CO stretching frequency of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ was observed at 2092 cm^{-1} by infrared spectroscopy, which is lower than that of the free CO ($\overline{\upsilon}$ 2143 cm^{-1}). For comparison, the CO absorptions for the pseudo-four-coordinate and closely related complexes $[CH_2(3,5\text{-}(CF_3)_2Pz)_2]Cu(CO)(OTf)$[44] and $[CH_2(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)(OClO_3)$[46] appear at 2127 and 2108 cm^{-1}, respectively. These data indicate that $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ has a somewhat electron-rich and better back-donating copper site. The CO band of $(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ was observed at 2091 cm^{-1} by Raman spectroscopy and is in good agreement with the infrared data.

A comparison of Raman spectra of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]CuL$ (L = CO, ethylene and *cis*-$CH_3HC{=}CHCH_3$) show that two copper-alkene adducts have an extra peak in the 1500−1650 cm^{-1} region (Figure 6). These bands, observed at 1523 and 1535 cm^{-1} respectively, for $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ and $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$, may correspond to the alkene C=C stretching frequency. For comparison, free ethylene ($\overline{\upsilon}$ 1623 cm^{-1}) and free *cis*-2-butene ($\overline{\upsilon}$ 1660 cm^{-1}) have higher C=C stretching frequencies.[61] The lowering of the C=C stretching frequency upon coordination to copper(I) is expected because of the ethylene → Cu and Cu → ethylene σ-donor/π-acceptor interactions. The $\overline{\upsilon}$ (C=C) value observed for $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ is slightly lower than the values observed for $[Cu(Ph_2bpm)(C_2H_4)]^+$ ($\overline{\upsilon}$ 1529−1531 cm^{-1}, for various counterions; Ph_2bpm = 6,6-diphenyl-4,4-bipyrimidine) and in the same range as typical, trigonal planar, mono(ethylene) complexes of copper(I) ($\overline{\upsilon}$ 1515−1537 cm^{-1}).[62] The lower C=C stretching frequency in $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ relative to $[Cu(Ph_2bpm)(C_2H_4)]^+$ is understandable as latter adducts feature more Lewis acidic, cationic copper(I) sites that would show relatively less Cu → ethylene backbonding. It has been noted that the C=C stretch and the metal-ethylene bonding relationship is not straightforward, as the ethylene CH_2 scissoring action couples with the C=C stretch.[24,63,64] It is advisable to consider these vibrational data in combination with other supporting evidence such as those from ^{13}C NMR spectroscopy and X-ray crystallography for the analysis of metal-ethylene bonding.

In summary we have described the preparation and characterization of the ligand $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]^-$, as well as its value in the stabilization of the copper(I) ethylene, *cis*-2-butene, and carbon monoxide adducts $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(L)$ (where L = C_2H_4, *cis*-$CH_3HC{=}CHCH_3$, and CO). In the case of the copper-olefin adducts, the Scorpionate ligand is bound in κ^2 fashion with the BPh_3 moiety rotated to sit over the metal center. Isolable ethylene adducts like $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Cu(C_2H_4)$ have not been reported using closely related bis(pyrazolyl)borate and bis(pyrazolyl)methane ligands. The ^{13}C resonance of ethylene carbons of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$ and CO frequency for $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$ indicate moderately strong M → L π-back-donation for these copper adducts. We are continuing to explore the various other metal complexes of bis(pyrazolyl)methyltriphenylborate ligands as well as the effects of ligand steric-electronic properties on coordinated metal site and chemistry.

■ EXPERIMENTAL SECTION

General Methods. 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 and purified by conventional methods prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on JEOL Eclipse 500 (^{1}H, 500.16 MHz; ^{13}C, 125.77 MHz) or JEOL Eclipse 300 (^{11}B, 96.42 MHz) spectrometers, unless otherwise noted. Proton and carbon chemical shifts are referenced using the residual proton or carbon signals of the deuterated solvent and ^{11}B NMR values were referenced to an external $BF_3{\cdot}Et_2O$ standard. Melting points were obtained on a Mel-Temp II apparatus. Elemental analyses were performed at Intertek Pharmaceutical Services. IR spectra were collected at room temperature on a Shimadzu IRPrestige-21 FTIR containing an ATR attachment. Raman spectra were collected on HORIBA Jobin Yvon LabRam ARAMIS spectrometer using 633 nm laser. Copper(I) trifluoromethanesulfonate benzene complex ($(CF_3SO_3Cu)_2{\cdot}C_6H_6$)[65] and bis(3,5-dimethylpyrazolyl)methane[66] were prepared via literature procedure. Carbon monoxide gas was purchased from Airgas, ethylene gas was purchased from Matheson, and *cis*-2-butene was purchased from Sigma-Aldrich.

[(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$]Li(THF). Bis(3,5-dimethylpyrazolyl)-methane (0.204 g, 1.0 mmol) was added to a Schlenk flask and dissolved in THF (10 mL, dry). The solution was cooled to −78 °C using a dry ice-acetone bath and 1.6 M ethereal solution of *n*-BuLi (1.1 equiv) was added dropwise via syringe. The contents were vigorously stirred while maintaining the reaction temperature below −70 °C for 15 min and triphenylborane (0.242 g, 1.0 mmol) of was added at once using a solid addition funnel. The mixture was slowly allowed to attain room temperature and stirred overnight. The solution was concentrated under a vacuum, layered with hexanes and kept in −20 °C freezer to obtain the colorless crystals. Yield: 0.419 g, 80%; mp 142 °C (melts at this temperature and begins to decompose at 170 °C). ^{1}H NMR ($CDCl_3$, 500.16 MHz) δ (ppm): 7.10 (m, 13H, aromatic (BPh_3), 7.09 (m, 2H, aromatic (BPh_3)), 6.43 (s, 1H, C*H*-BPh_3), 5.68 (s, 2H, Pz-*H*), 3.56 (m, 4H, THF), 2.13 (s, 6H, CH_3), 1.99 (s, 6H, CH_3), 1.81 (m, 4H, THF). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.76 MHz) δ (ppm): 145.7 (CCH_3), 139.6 (CCH_3), 136.7 (BPh_3), 126.0 (BPh_3), 123.8 (BPh_3), 104.3 (CH-Pz), 71.2 (CH-BPh_3) 68.4 (THF), 25.4 (THF), 13.2 (CH_3), 11.8 (CH_3). ^{11}B NMR ($CDCl_3$, 96.42 MHz) δ (ppm): −8.52. ^{1}H NMR (C_6D_6, 500.16 MHz) δ (ppm): 7.58 (d, 6H, Ph, $^{3}J_{HH}$ = 7.15 Hz), 7.25 (t, 6H, Ph, $^{3}J_{HH}$ = 7.45 Hz), 6.65 (s, 1H, C*H*-BPh_3), 5.57 (s, 2H, Pz-*H*), 3.18 (m, 4H, THF), 1.94 (s, C*H*$_3$), 1.80 (s, CH_3), 1.20 (m, 4H, THF). ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz) δ (ppm): 145.7 (s, CCH_3), 140.0 (s, CCH_3), 137.4 (s, BPh_3), 126.6 (s, BPh_3), 124.3 (s, BPh_3), 104.6 (s, CH-Pz), 72.0 (CH-BPh_3), 68.1 (THF), 25.4 (THF) 13.3 (CH_3), 11.7 (CH_3). Anal. Calcd for $C_{33}H_{38}BLiN_4O$: C, 75.58; H, 7.30; N, 10.68. Found: C, 75.13; H, 7.01; N, 10.52.

[(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$]Cu(C$_2$H$_4$). [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$]-Li(THF) (0.262 g, 0.5 mmol) and $(CF_3SO_3Cu)_2{\cdot}C_6H_6$ (0.125, 0.5 mmol) were added to Schlenk flask and dissolved in DCM (10 mL, dry) saturated with the C_2H_4. The mixture was stirred under positive pressure of C_2H_4 for 2 h. The resulting white precipitate (LiOTf) was removed by filtration through a bed of Celite, and the colorless filtrate was concentrated by bubbling C_2H_4. The concentrated solution was stored under C_2H_4 atmosphere in a −20 °C freezer to obtain X-ray quality crystals. Yield: 0.188 g, 70%, mp 125 °C (slowly starts to turn brown at this temperature and completely decomposes at 138 °C). ^{1}H NMR (CD_2Cl_2, 500.16 MHz) δ (ppm): 7.02 (m, 10H, (BPh_3), 6.87 (m, 5H, BPh_3), 6.66 (s, 1H, C*H*-BPh_3), 5.81 (s, 2H, Pz-*H*), 3.71 (s, 4H, C_2H_4), 2.15 (s, 6H, CH_3), 2.06 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.76 MHz) δ (ppm): 148.3 (CCH_3), 141.4 (CCH_3), 137.3 (BPh_3), 126.4 (BPh_3), 124.3 (BPh_3), 106.1 (CH-Pz), 81.0 (C_2H_4), 68.5 (CH-BPh_3), 14.4 (CH_3), 12.3 (CH_3). ^{11}B NMR (CD_2Cl_2, 96.42 MHz) δ (ppm): −8.19. ^{1}H NMR ($CDCl_3$, 500.16 MHz) δ (ppm): 6.98 (m, 15H, BPh_3), 6.68 (s, 1H, C*H*-BPh_3), 5.78 (s, 2H, Pz-*H*), 3.69 (s, 4H, C_2H_4), 2.16 (s, 6H, C*H*$_3$), 2.05 (s, 6H, C*H*$_3$). Raman (Selected peak, cm^{-1}): $\overline{\upsilon}$ = 1523 (C=C). Anal. Calcd for $C_{31}H_{32}BCuN_4$: C, 69.60; H, 6.03; N, 10.47%. Found: C, 69.32; H, 5.63; N, 10.17%.

[(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$]Cu(cis-CH$_3$HC=CHCH$_3$). [(Ph$_3$B)CH-(3,5-(CH$_3$)$_2$Pz)$_2$]Li(THF) (0.100 g, 0.191 mmol) and $(CF_3SO_3Cu)_2{\cdot}C_6H_6$ (0.048 g, 0.095 mmol) were added to Schlenk flask under a nitrogen atmosphere and *cis*-2-butene was gently bubbled through dichloromethane (10 mL, dry) in a separate flask for ∼2 min and the resulting solution was slowly added via syringe. After the addition, 2-butene was gently bubbled for ∼2 min and the mixture was stirred for 2 h. The resulting white precipitate (LiOTf) was removed by filtration through a bed of Celite and the filtrate was concentrated under reduced pressure. The concentrated solution was stored at −20 °C freezer after bubbling 2-butene for ∼1 min to obtain X-ray quality crystals. Yield: 0.085 g, 79%, mp 134 °C (slowly starts to melt at this temperature and completely decomposes at 146 °C). ^{1}H NMR ($CDCl_3$, 500.16 MHz) δ (ppm): 7.02 (m, 10H, BPh_3), 6.90 (m, 5H, BPh_3), 6.76 (s, 1H, C*H*-BPh_3), 5.72 (s, 2H, Pz-*H*), 4.90 (br, 2H, $(CH_3)_2C_2H_2$), 2.23 (s, 6H, CH_3), 2.01 (s, 6H, CH_3) 1.49 (d, 6H, $(CH_3)_2C_2H_2$, $^{3}J_{HH}$ = 4.60). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.77 MHz) δ (ppm): 146.9 (CCH_3), 140.8 (CCH_3), 136.6 (BPh_3), 126.1 (BPh_3), 123.8 (BPh_3), 105.7 (CH-Pz), 14.0 (CH_3), 13.5 (CH_3), 12.3 (CH_3). ^{11}B NMR ($CDCl_3$, 96.42 MHz): δ −7.96. ^{1}H NMR (CD_2Cl_2, 500.16 MHz, 233 K) δ (ppm): 6.98 (m, 10H, BPh_3), 6.79 (m, 5H, BPh_3), 6.74 (s, 1H, C*H*-BPh_3), 5.73 (s, 2H, Pz-*H*), 4.64 (br, 2H, $(CH_3)_2C_2H_2$), 2.22 (s, 6H, C*H*$_3$), 2.02 (s, 6H, C*H*$_3$) 1.34 (s, 6H, $(CH_3)_2C_2H_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.77 MHz, 233 K): δ 147.3 (CCH_3), 140.4 (CCH_3), 136.3 (BPh_3), 125.9 (BPh_3), 123.7 (BPh_3), 105.4 (CH-Pz), 94.2 (s, $(CH_3)_2C_2H_2$), 74.0 (br, CH-BPh_3), 13.7 (CH_3), 12.2 (CH_3), 12.2 (CH_3). Raman (selected peak, cm^{-1}): $\overline{\upsilon}$ = 1535 (C=C). Anal. Calcd for $C_{33}H_{38}BCuN_4{\cdot}0.1CH_2Cl_2$: C, 69.32; H, 6.71; N, 9.77%. Found: C, 69.96; H, 6.53; N, 8.56%.

[(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$]Cu(CO). [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$]Li-(THF) (0.250 g, 0.477 mmol) and $(CF_3SO_3Cu)_2{\cdot}C_6H_6$ (0.075, 0.238 mmol) were added to Schlenk flask and dissolved in DCM (10 mL, dry) saturated with carbon monoxide (CO). The mixture was stirred under positive pressure of CO for 2 h. The resulting white precipitate (LiOTf) was removed by filtration through a bed of Celite, and the filtrate was concentrated by bubbling CO. The concentrated solution was stored under a CO atmosphere in a −20 °C freezer to obtain X-ray quality crystals. Yield: 0.190 g, 74%, mp 105−118 °C (slowly melts over this wide range and decomposes at 172 °C). ^{1}H NMR ($CDCl_3$, 500.16 MHz) δ (ppm): 7.12−7.01 (m, 15H, BPh_3), 6.31 (s, 1H, C*H*-BPh_3), 5.80 (s, 2H, Pz-*H*), 2.15 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.76 MHz) δ (ppm): 146.4 (s, CCH_3), 140.3 (s, CCH_3), 136.9 (BPh_3), 126.4 (BPh_3), 124.2 (BPh_3), 105.0 (CH-Pz), 13.8 (CH_3), 11.7 (CH_3). ^{11}B NMR ($CDCl_3$, 96.42 MHz) δ (ppm): −8.46. ATR-FTIR (Selected peak, cm^{-1}): $\overline{\upsilon}$ = 2092 (CO). Anal. Calcd for $C_{30}H_{30}BCuN_4O{\cdot}0.3CH_2Cl_2$: C, 64.71; H, 5.48; N, 9.96%. Found: C, 65.07; H, 5.00; N, 8.72%.

X-ray Crystallography. 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 [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Li(THF), [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(C$_2$H$_4$), [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(*cis*-CH$_3$HC=CHCH$_3$), and [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(CO) were collected 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 Kα 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.[67] Absorption corrections were applied by using SADABS. All the non-hydrogen atoms were refined anisotropically. X-ray structural figures were generated using Olex2.[68]

The hydrogen atom of ethylene moiety in [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(C$_2$H$_4$) were located in a Fourier difference synthesis and refined satisfactorily. All the remaining hydrogen atoms of [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(C$_2$H$_4$) and hydrogen atoms of [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Li(THF), [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(*cis*-CH$_3$HC=CHCH$_3$), and [(Ph$_3$B)CH(3,5-(CH$_3$)$_2$Pz)$_2$)]Cu(CO) were placed at calculated positions and refined using a riding model. Carbon atoms of THF in [(Ph$_3$B)CH(3,5-

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Table 4. Crystal Data and Summary of Data Collection and Refinement for $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$, $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$, $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$, and $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO)$

compound	$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Li(THF)$	$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(C_2H_4)$	$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(\textit{cis}\text{-}CH_3HC{=}CHCH_3)$	$[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2]Cu(CO){\cdot}CH_2Cl_2$
empirical formula	$C_{33}H_{38}BLiN_4O$	$C_{28}H_{34}BN_4Cu$	$C_{33}H_{38}BCuN_4$	$C_{31}H_{32}BCl_2CuN_4O$
formula weight	524.42	500.94	565.02	621.85
temperature (K)	100	99.96	101.73	101.53
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
unit-cell dimensions	$a = 12.0600(5)$ Å	$a = 8.3862(12)$ Å	$a = 8.6761(5)$ Å	$a = 10.1293(5)$ Å
	$b = 14.1103(6)$ Å	$b = 10.5732(15)$ Å	$b = 10.7866(7)$ Å	$b = 19.1290(9)$ Å
	$c = 17.3524(8)$ Å	$c = 16.695(2)$ Å	$c = 16.3429(10)$ Å	$c = 16.0586(7)$ Å
	$\alpha = 90°$	$\alpha = 77.206(2)°$	$\alpha = 92.498(2)°$	$\alpha = 90°$
	$\beta = 98.9860(11)°$	$\beta = 84.276(2)°$	$\beta = 104.506(2)°$	$\beta = 104.024(2)°$
	$\gamma = 90°$	$\gamma = 68.071(2)°$	$\gamma = 104.528(2)°$	$\gamma = 90°$
volume, $Å^3$	2916.6(2)	1338.9(3)	1424.09(15)	3018.8(2)
Z	4	2	2	4
density (calculated) (Mg/m^3)	1.194	1.243	1.318	1.368
absorption coefficient (mm^{-1})	0.072	0.838	0.796	0.931
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0424$	$R_1 = 0.0283$	$R_1 = 0.0304$	$R_1 = 0.0352$
	$wR_2 = 0.1090$	$wR_2 = 0.0702$	$wR_2 = 0.0732$	$wR_2 = 0.0965$
R indices (all data)	$R_1 = 0.0485$	$R_1 = 0.0338$	$R_1 = 0.0339$	$R_1 = 0.0371$
	$wR_2 = 0.1137$	$wR_2 = 0.0725$	$wR_2 = 0.0750$	$wR_2 = 0.0981$

$(CH_3)_2Pz)_2)]Li(THF)$ and one of the phenyl groups of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Cu(C_2H_4)$ were disordered over two sites. These positional disorders were modeled quite well. There is a residual electron density (0.83 $eÅ^{-3}$) near C32 (i.e., 0.92 Å away) of disordered THF of $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Li(THF)$ generating a type-B alert which is not unusual. $[(Ph_3B)CH(3,5\text{-}(CH_3)_2Pz)_2)]Cu(CO)$ crystallizes with a molecule of CH_2Cl_2 in the asymmetric unit. The CH_2Cl_2 shows positional disorder over two sites, which was treated satisfactorily. Additional data collection, structure solution, and refinement data are presented in Table 4. Figures showing disordered atoms are given in Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00878.

Additional figures (PDF)

Accession Codes

CCDC 1548861−1548864 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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