4278 *Organometallics* **2007,** *26,* 4278−4286

Trifluoromethyl-Substituted Bis(pyrazolyl)methanes as Ligands for Copper and Silver: Synthesis and Spectroscopic and Structural Characterization

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Received April 3, 2007

New fluorinated bis(pyrazolyl)methanes with the general formula $RCH(Pz^F)_2$ [R = H, Pz^F = 3-(trifluoromethyl)pyrazolyl, 3,5-bis(trifluoromethyl)pyrazolyl; R = Ph, Pz^F = 3,5-bis(trifluoromethyl)pyrazolyl] have been prepared, and their reactivity with copper and silver salts has been studied. Copper derivatives $Cu[RCH(Pz^F)_2](L)(OTf)$ [R = H, Pz^F = 3-(trifluoromethyl)pyrazolyl, 3,5-bis(trifluoromethyl)pyrazolyl; R = Ph, Pz^F = 3,5-bis(trifluoromethyl)pyrazolyl, L = CO, cyclooctene (coe); R = Ph, Pz^F = 3,5-bis(trifluoromethyl)pyrazolyl, L = coe, 4-vinylanisole (van), and triethylvinylsilane (tevs)] have been isolated by reacting $Cu(OTf)(toluene)_{0.5}$ with the bis(pyrazolyl)methane ligand in the presence of olefin or CO. Some of them have been structurally characterized (R = H, Pz^F = 3-(trifluoromethyl)pyrazolyl, 3,5-bis(trifluoromethyl)pyrazolyl, L = CO). These compounds are monomeric and show strong interactions between copper and one oxygen atom of the triflate moiety. [Bis[3,5-bis(trifluoromethyl)pyrazolyl]methyl]silver complexes have been prepared from $AgBF_4$ and the ligand. The coe derivative $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4$ has been obtained in good yields.

Introduction

Within the framework of our research on CO/olefin exchange reactions in transition-metal complexes, we have recently reported on the synthesis of a variety of copper(I) olefin complexes containing trifluoroacetato,[1] hexafluoroacetylacetonato,[2] and poly(pyrazolyl)borato[3] anions and (3,5-dimethylpyrazolyl)methane[4] as ancillary ligands.

Despite the numerous studies on coordination compounds containing fluorinated poly(pyrazolyl)borates,[5] the coordination chemistry of poly(pyrazolyl)methane complexes has been less investigated as clearly stated in recent reviews,[6] and their fluorinated derivatives have never been described. As a matter of fact, fluorinated ligands play an important role in many applications,[7] especially because they often improve the volatility, thermal stability, oxidation resistance, and solubility of their metal adducts. From the synthetic point of view, the use of highly fluorinated tris(pyrazolyl)borates as ligands has allowed the isolation of group 11 carbonyl compounds with the general formula $M[BH(3,5\text{-}(CF_3)_2Pz)_3]CO$ (M = Cu, Ag, Au),[8] which have been reported to be stable with respect to the loss of CO even under reduced pressure. Stable copper(I) and silver(I) ethylene derivatives with the general formula M(L)(ethylene) [M = Cu, L = $BH(3\text{-}CF_3,5\text{-}RPz)_3$; M = Ag; L = $BH(3,5\text{-}(CF_3)_2Pz)_3$] have also been reported.[8b,9]

Aiming to investigate the role played by the ancillary ligand in determining the general properties of olefin and carbonyl derivatives of group 11 metals, we have used neutral bis(CF_3-substituted pyrazolyl)alkane ligands, Scheme 1, to synthesize compounds with the general formula [M{bis(CF_3-substituted pyrazolyl)alkane}(L)]X (X = OTf, BF_4). We have recently shown[3] that attempts to prepare CuL(alkene) [L = $BH(Pz)_3$, $BH(3\text{-}CF_3Pz)_3$, and $BH(3,5\text{-}(CF_3)_2Pz)_3$; alkene = 1,5-cyclooctadiene, diethyl fumarate, methyl cinnamate, and fumaronitrile] failed either because of the absence of any reaction or because of the formation of alkene-free dinuclear derivatives. By taking into consideration that stable compounds

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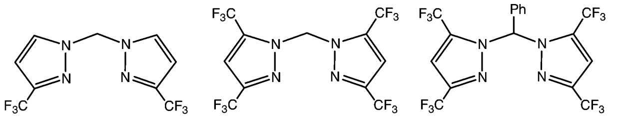
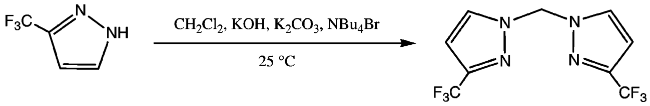
10.1021/om700325t CCC: $37.00

Scheme 1



$CH_2(3\text{-}CF_3Pz)_2$ $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ $PhCH(3,5\text{-}(CF_3)_2Pz)_2$

Scheme 2



were obtained by using the less sterically demanding bis(pyrazolyl)borato anions,[3] we expected the use of bis(pyrazolyl)methanes to be a good choice in the preparation of analogous copper(I) cationic complexes.

In this paper we report on the synthesis and the characterization of the first examples of fluorinated bis(pyrazolyl)alkanes and their copper complexes containing olefins (copper and silver) and carbon monoxide. Some silver complexes containing the ligand [3,5-bis(trifluoromethyl)pyrazolyl]methane are also described here.

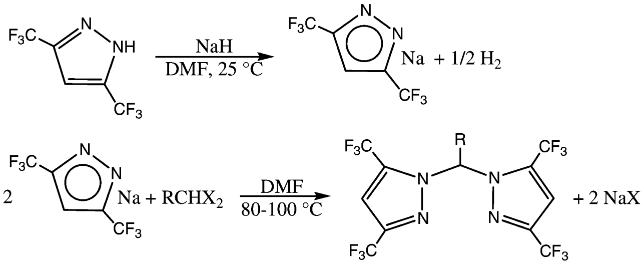
Results and Discussion

Synthesis of Fluorinated Bis(pyrazolyl)alkanes. Bis[3-(trifluoromethyl)pyrazolyl]methane, $CH_2(3\text{-}CF_3Pz)_2$, was prepared following a procedure similar to that reported for the corresponding bismethylated analogue.[10] The in-situ-generated trifluoromethyl-substituted pyrazolato anion reacts with dichloromethane in the presence of a phase-transfer agent (N^nBu_4Br) to yield $CH_2(3\text{-}CF_3Pz)_2$, Scheme 2.

The compound [3,5-bis(trifluoromethyl)pyrazolyl]methane could not be prepared in the same way because the pyrazolate (prepared from 3,5-bis(trifluoromethyl)pyrazole and NaH in THF) did not react with either dichloromethane or diiodomethane. In the latter case, unreacted $Na[3,5\text{-}(CF_3)_2Pz]$ was isolated as a THF adduct and characterized by ^1H NMR spectroscopy [(C_6D_6) δ 6.70 (s, 1H, pyr C*H*), 3.18 (t, 4H, $J =$ 5.8 Hz, OCH_2CH_2), 1.24 (m, 4H, OCH_2CH_2)]. The absence of this reaction can probably be attributed to the lower nucleophilicity of the bis(trifluoromethyl)pyrazolate anion due to the presence of two strong electron-withdrawing substituents. The significant stabilization of carbanions induced by fluoro- or perfluoroaryl substituents is well-known.[11]

On the basis of a reaction reported by Ward and Therrien,[12] bis[3,5-bis(trifluoromethyl)pyrazolyl]methane, $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ (**a**), and α,α-bis[3,5-bis(trifluoromethyl)pyrazolyl]toluene, $PhCH(3,5\text{-}(CF_3)_2Pz)_2$ (**b**), were prepared using reaction conditions typical of nucleophilic substitution, i.e., using DMF as the solvent, as reported in Scheme 3.

Scheme 3



a) R = H, X = I
b) R = Ph, X = Br

The bis(pyrazolyl)methane $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ was isolated (Scheme 3a) after the reaction of $Na[3,5\text{-}(CF_3)_2Pz]$ with CH_2I_2 and the evaporation of the solvent: although the raw material is sufficiently pure to be used in further reactions, it can be purified by recrystallization from hot heptane. In contrast, a purification procedure had to be devised for the synthesis of $PhCH(3,5\text{-}(CF_3)_2Pz)_2$ (Scheme 3b) due to the formation of dibenzylidenehydrazine, $C_6H_5CH{=}NN{=}CHC_6H_5$ (yellow solid identified by GC−MS and comparison of the NMR spectra with those reported in the literature[13]), as the main byproduct in a significant amount. The reaction that led to the formation of dibenzylidenehydrazine was not investigated in detail; however, it seems likely that some decomposition of the pyrazolate occurs within the system, so that hydrazine or intermediates with similar reactivity may react with $PhCHBr_2$ (the starting material) or benzaldehyde (accidentally formed due to traces of water) to give the benzylidene-substituted hydrazine.

Copper(I) Derivatives. Copper(I) olefin and carbonyl compounds bearing fluorinated bis(pyrazolyl)methanes were prepared using the same general procedure described in an earlier paper;[4] see eq 1.

$$\mathrm{Cu(OTf)(toluene)_{0.5}} + \mathrm{RCHPz^{F}{}_{2}} + \mathrm{L} \rightarrow \mathrm{Cu(RCHPz^{F}{}_{2})(L)(OTf)} + 0.5\mathrm{toluene} \quad (1)$$

$$\mathrm{RCHPz^{F}{}_{2}} = \mathrm{CH_2(3\text{-}CF_3Pz)_2},\ \mathrm{CH_2(3,5\text{-}(CF_3)_2Pz)_2},\ \mathrm{L} = \mathrm{CO},\ \mathrm{coe};\ \mathrm{RCHPz^{F}{}_{2}} = \mathrm{PhCH(3,5\text{-}(CF_3)_2Pz)_2},\ \mathrm{L} = \mathrm{CO},\ \mathrm{coe},\ \mathrm{tevs},\ \mathrm{van}$$

Moisture and air sensitivities are common features of all of the complexes studied in this investigation, whereas the solubility in aromatic and chlorinated hydrocarbons depends on the bis(pyrazolyl)methane ligands: compounds with the general formula $Cu[CH_2(3\text{-}CF_3Pz)_2](L)(OTf)$ are easily soluble in THF but nearly insoluble in benzene, toluene, dichloromethane, and chloroform, while the corresponding 3,5-trifluoromethyl-substituted compounds show a good degree of solubility in the same media. Some general remarks about IR and NMR spectra are reported in the Spectroscopy section. As far as the carbonyl complexes are concerned, their stability with respect to the loss of carbon monoxide in the solid state allows them to be dried quickly under vacuum; the reversible loss of CO under reduced pressure occurs only in the case of solutions of $Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$ in toluene/heptane. All of the carbonyl derivatives are stable under carbon monoxide, and they are formed quantitatively by reaction of carbon monoxide with the olefin compound; i.e., the equilibrium reported in eq 2

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$$\mathrm{Cu[CHR(Pz^F)_2](olefin)(OTf)} + \mathrm{CO} \rightleftarrows \mathrm{Cu[CHR(Pz^F)_2](CO)(OTf)} + \text{olefin} \quad (2)$$

$\mathrm{R = H, Pz^F = 3\text{-}(CF_3)Pz, 3,5\text{-}(CF_3)_2Pz}$, olefin = cyclooctene; $\mathrm{R = Ph, Pz^F = 3,5\text{-}CF_3}$, olefin = cyclooctene, 4-vinylanisole, triethylvinylsilane

is completely shifted to the right ($\mathrm{CO_{absorbed}}$:Cu molar ratio 1 by gas volumetric methods) even in the presence of excess olefin. During the preparation of $\mathrm{Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)}$, colorless air-sensitive crystals were obtained which did not contain $\mathrm{PhCH(3,5\text{-}(CF_3)_2Pz)_2}$. An X-ray diffraction analysis showed that they actually contained $[\mathrm{Cu}(\mu\text{-OTf})(\mathrm{coe})]_n$ instead, which was obtained independently by the reaction of $\mathrm{Cu(OTf)(toluene)_{0.5}}$ with coe.[14]

The structures of $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ and $\mathrm{Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)}$ have been fully elucidated by X-ray diffraction methods. Views of them are given in Figures 1 and 2, respectively; the most important bond distances and angles are reported and compared in Table 1. The structures of the two compounds are very similar. The copper atom lies in a distorted tetrahedral environment achieved by coordination to two nitrogen atoms of the bis(pyrazolyl)methane ligand, the carbon atom of the carbonyl group, and one oxygen atom of the triflate anion. The structure of $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ has an imposed crystallographic C_s symmetry with the mirror plane passing through the copper atom, the carbonyl, the methylene group of the bis(pyrazolyl)methane, and the O2, S1, C2, and F5 atoms of the triflate. The Cu–N bond distances [2.067(2) Å in $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ and 2.064(4) and 2.075(4) Å in $\mathrm{Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)}$ are very similar but significantly longer than those found in $\mathrm{Cu[CH_2(3,5\text{-}Me_2Pz)_2](CO)(OClO_3)}$ [2.001(3) and 2.007(3) Å][16] and $\mathrm{Cu[CH_2(3,5\text{-}Me_2Pz)_2](coe)(OTf)}$ [2.007(2) and 2.009(2) Å].[4] The Cu–O bond distance in $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ [2.135(3) Å] is longer than in $\mathrm{Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)}$ [2.085(4) Å], but both are significantly shorter than those observed in copper compounds containing the $\mathrm{CH_2(3,5\text{-}Me_2\text{-}Pz)_2}$ ligand, where the triflate anion displays only a weak interaction with the metal center: 2.437(2) Å in $\mathrm{Cu[CH_2(3,5\text{-}Me_2Pz)_2](coe)(OTf)}$ and 2.705(2) Å (mean value) in $[\mathrm{Cu_2\{\mu\text{-}CH_2(3,5\text{-}Me_2Pz)_2\}_2](OTf)_2}$.[4]

The increase of the Cu–N bond distances and the decrease of the Cu–O bond distances on moving from the methyl-substituted to the trifluoromethyl-substituted pyrazolylmethanes suggest that the effect of the fluorinated ligands on the pyrazole rings is to weaken the Lewis basicity of the nitrogen ligand (the Cu–N bond distances increase), thus increasing the Lewis acidity of copper (the Cu–O bond distances decrease, and as suggested by conductivity measurements, vide infra, the interaction $\mathrm{Cu\text{-}OSO_2CF_3}$ persists in diluted solution).

The Cu–C and C–O bond distances within the carbonyl in $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ and $\mathrm{Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)}$ are comparable [1.812(5) and 1.117(6) Å in the former, 1.803(7) and 1.144(7) Å in the latter]. These distances do not differ significantly from those observed in the complex $\mathrm{Cu[CH_2(3,5\text{-}Me_2Pz)_2](CO)(OClO_3)}$ [1.806(5) and 1.124(6) Å],[16] although the CO stretching frequencies indicate a stronger C–O bond in the fluorinated complexes (increase in the $\tilde{\nu}_{\mathrm{CO}}$ value by 12 and 19 cm^{-1} on moving from $\mathrm{Cu[CH_2(3,5\text{-}Me_2Pz)_2](CO)(OClO_3)}$[16] to $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ and $\mathrm{Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)}$.

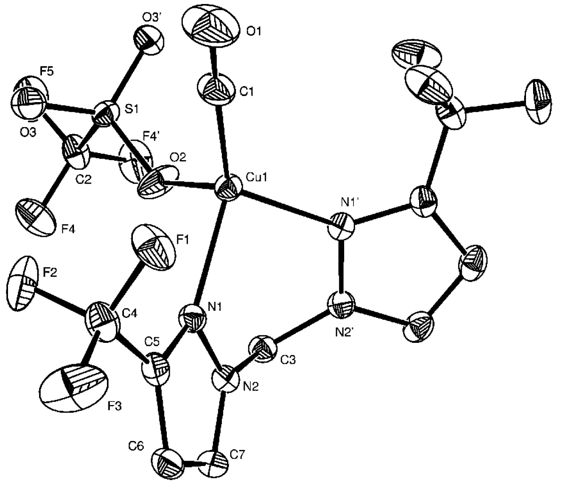

Figure 1. View of the molecular structure of $\mathrm{Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)}$ with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

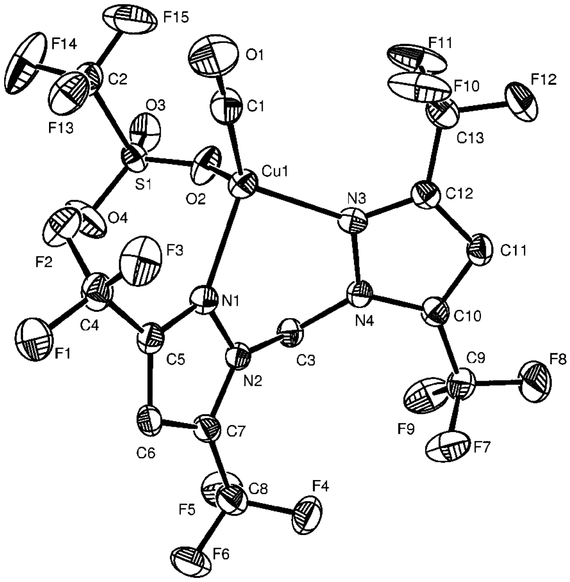

Figure 2. View of the molecular structure of $\mathrm{Cu[CH_2(3,5\text{-}(CF_3)_2\text{-}Pz)_2](CO)(OTf)}$ with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Although all of the reactions reported in eq 1 refer to the syntheses of carbonyl and olefin compounds, some crystals of an unexpected complex not containing either olefin or CO were obtained serendipitously. The crystalline compound which slowly separated out by layering toluene on a diluted dichloromethane solution of $\mathrm{Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](van)(OTf)}$ did not in fact contain vinylanisole, and it was identified as $\mathrm{Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](OTf)}$ on the basis of analytical and spectral (IR and NMR) data. The quality of the crystals did not allow a good structural determination: nevertheless, it was possible to determine the connectivity of the compound and to substantiate the presence of an interaction between the copper and the triflate anion.

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[14] The structure of $[\mathrm{Cu}(\mu\text{-OTf})(\mathrm{coe})]_n$ consists of centrosymmetric dimeric units $[\mathrm{Cu}(\mu\text{-OTf})(\mathrm{coe})]_2$ linked by bridging triflates and is similar to that of the cyclohexene derivative,[15] the main difference being the presence of a tetrameric basic structure in the latter; see the Supporting Information for further details.

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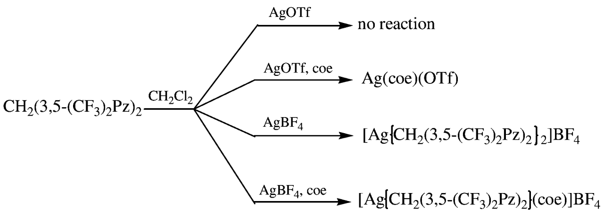
Table 1. Bond Distances (Å) and Angles (deg) for CuL(CO)(OTf) [L = $CH_2(3\text{-}CF_3Pz)_2$, $CH_2(3,5\text{-}(CF_3)_2Pz)_2$][a]

	L = $CH_2(3\text{-}CF_3Pz)_2$	L = $CH_2(3,5\text{-}(CF_3)_2Pz)_2$		L = $CH_2(3\text{-}CF_3Pz)_2$	L = $CH_2(3,5\text{-}(CF_3)_2Pz)_2$
Cu1−C1	1.812(5)	1.803(7)	S1−O2	1.454(3)	1.455(4)
C1−O1	1.117(6)	1.144(7)	S1−O3	1.429(2)	1.425(4)
Cu1−O2	2.135(3)	2.085(4)	S1−O4		1.418(4)
Cu1−N1	2.067(2)	2.064(4)			
Cu1−N3		2.075(4)			
N1−Cu1−N3	92.27(13)	92.01(15)	O2−Cu1−N1	95.15(9)	99.03(17)
C1−Cu1−N1	125.38(10)	122.2(2)	O2−Cu1−N3		92.79(15)
C1−Cu1−N3		124.0(2)	Cu1−C1−O1	177.4(6)	177.9(6)
C1−Cu1−O2	115.88(19)	119.6(2)			

[a] For $Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)$, N3 = N1 and O4 = O3.

Scheme 4



Silver Derivatives. The results obtained with copper(I) prompted us to investigate the preparation of analogous silver compounds. The use of polyfluorinated pyrazolylmethanes as ancillary ligands was expected to yield carbonyl derivatives of silver, which are known to be stable compounds with highly fluorinated pyrazolylborates.[8a]

Treating a CO-saturated dichloromethane solution of $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ with AgOTf at 1 atm of pressure resulted in a suspension containing nothing more than the unchanged starting materials after the usual workup. The absence of any reaction between $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ and AgOTf was confirmed by the isolation of Ag(coe)(OTf)[17] and unreacted $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ when the $CH_2(3,5\text{-}(CF_3)_2Pz)_2$/AgOTf system was treated with cyclooctene.

When tetrafluoroborate was used instead of triflate as the anion, the silver complex $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}]BF_4$ and its adduct with cyclooctene, $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4$, see Scheme 4, were isolated in high yields. Unfortunately, no CO absorption was observed when a dichloromethane solution of $CH_2(3,5\text{-}(CF_3)_2Pz)_2/AgBF_4$ was exposed to carbon monoxide at 1 atm of pressure, and $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}]BF_4$ was isolated in good yields.

The bisadduct $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}_2]BF_4$ was obtained independent of the $CH_2(3,5\text{-}(CF_3)_2Pz)_2:AgBF_4$ molar ratio (1:1 or 2:1). The crystal structure of the $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}_2]^+$ cation is shown in Figure 3, and the most important bond distances and angles are listed in Table 2.

The silver atom is four-coordinated in a distorted tetrahedral environment, the Ag−N distances ranging from 2.347(7) to 2.467(7) Å and the N−Ag−N angles ranging from 79.5(2)° to 144.1(1)° (the smallest angles are those involved in the chelation of the ligand to the silver atom). These values are comparable to those observed in $[Ag\{CMe_2(Pz)_2\}_2]ClO_4$[19] [2.247(4)−2.432(4) Å and 82.6(1)−145.1(1)°]. As opposed to $[Ag\{CMe_2(Pz)_2\}_2]ClO_4$, where the perchlorate anions are far away from the silver atom, in $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}_2]BF_4$ two of the fluorine atoms of the anion are at distances of 2.743 and 3.083 Å from the metal center, consistent with a higher acidity of the central metal atom due to the introduction of fluorinated groups.

Table 2. Bond Distances (Å) and Angles (deg) for $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}_2]BF_4$

Ag1−N1	2.347(7)	Ag1−N5	2.351(6)
Ag1−N3	2.467(7)	Ag1−N7	2.393(7)
N1−Ag1−N3	80.9(2)	N3−Ag1−N5	105.4(2)
N5−Ag1−N7	79.5(2)	N1−Ag1−N5	132.9(3)
N1−Ag1−N7	122.3(2)	N3−Ag1−N7	144.1(2)

The reaction among $AgBF_4$, $CH_2(3,5\text{-}(CF_3)_2Pz)_2$, and fumaronitrile (fn) in a 1:1:1 molar ratio gives a product which, on the basis of analytical and NMR spectral data, contains a 2:1 $CH_2(3,5\text{-}(CF_3)_2Pz)_2$:fumaronitrile molar ratio. The presence of only one nitrile absorption in the IR spectrum (2264 cm^{-1}) suggests that the coordination of fumaronitrile occurs through both the nitrile groups. Consequently, the structure of this compound might consist of dicationic units in which two $Ag[CH_2(3,5\text{-}(CF_3)_2Pz)_2]^+$ moieties are bridged by one fumaronitrile molecule as observed in the polynuclear compound $[Cu\{BH_2(3,5\text{-}(CF_3)_2Pz)_2\}(fn)]_n$.[3]

Spectroscopy. The IR spectra of the trifluoromethyl-substituted pyrazolylmethanes are characterized by strong absorptions between 1250 and 1100 cm^{-1} due to the CF_3 stretching vibrations. The phenyl-substituted $PhCH(3,5\text{-}(CF_3)_2Pz)_2$ shows an additional cluster of signals between 1500 and 1600 cm^{-1} due to the vibrations of the phenyl ring. The IR spectra of the corresponding copper and silver derivatives do not differ significantly from those of the uncomplexed pyrazolylmethanes, the main differences being the vibrations due to carbon monoxide or to the olefin and to the triflate anion, which shows strong absorptions in the 1270 and 1040 cm^{-1} region.

Strong, sharp absorptions at 2120, 2127, and 2117 cm^{-1} due to the C−O stretching vibration of coordinated carbon monoxide are observed in the IR spectra of $Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)$, $Cu[CH(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$, and $Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$, respectively. Considering that the carbonyl stretching vibration of $Cu[CH_2(3,5\text{-}Me_2Pz)_2](CO)(OClO_3)$ is observed[16] at 2108 cm^{-1}, our new data confirm the expected trend of $\tilde{\nu}_{CO}$ values for Cu[L](CO)(X) [L = $CH_2(3,5\text{-}Me_2Pz)_2$, $CH_2(3\text{-}(CF_3)Pz)_2$), and $CH_2(3,5\text{-}Me_2Pz)_2$] complexes; i.e., the C−O stretching frequencies get higher when the number of electron-withdrawing substituents on the pyrazolyl moieties is increased because of a decrease in the electron density at copper.[20] The fact that the $\tilde{\nu}_{CO}$ value for $Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$ is slightly lower than that of $Cu[CH_2(3\text{-}(CF_3)Pz)_2](CO)(OTf)$ is not a trivial matter, although the steric hindrance due to the phenyl ring on the ligand $PhCH(3,5\text{-}(CF_3)_2Pz)_2$ might have some peculiar effect on the Cu−CO bond.

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[17] The silver olefin complex Ag(coe)(OTf) was reported[18] as obtained by reaction of AgOTf with cyclooctene, but it was not isolated.

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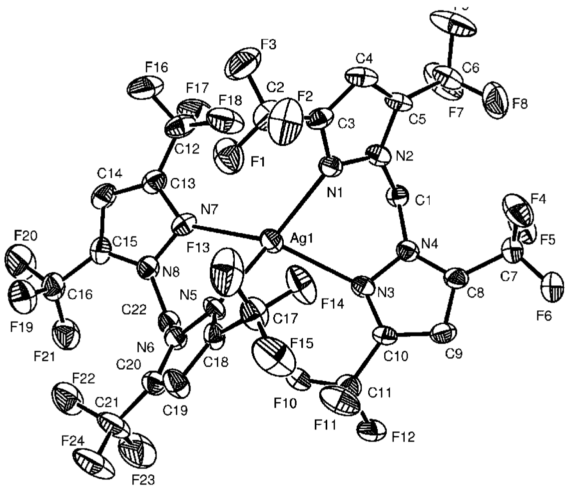

Figure 3. View of the molecular structure of the cation Ag[$CH_2(3,5-(CF_3)_2Pz)_2]_2^+$ in [Ag{$CH_2(3,5-(CF_3)_2Pz)_2$}$_2$]BF_4 with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

The complexes Cu[$BH_2(3,5-(CF_3)_2Pz)_2$](CO)[21] and Cu[$CH_2(3,5-(CF_3)_2Pz)_2$](CO)(OTf) exhibit the same C−O stretching absorption, thus suggesting a similar Cu(I) → CO π-back-donation. Actually, it was expected that the change from a negatively charged bis(pyrazolyl)borate to its neutral analogue would result in an increase in the $\tilde{\nu}_{CO}$ values. As a matter of fact, the C−O stretching vibration increases by about 50 cm^{-1} on going from Cu[$BH(3,5-Me_2Pz)_3$](CO) [$\tilde{\nu}_{CO} = 2066$ cm^{-1}][22] to [Cu[$CH(3,5-Me_2Pz)_3$](CO)]PF_6,] [$\tilde{\nu}_{CO} = 2113$ cm^{-1}].[23] A probable explanation for the almost identical $\tilde{\nu}_{CO}$ values for Cu[$BH_2(3,5-(CF_3)_2Pz)_2$](CO) and Cu[$CH_2(3,5-(CF_3)_2Pz)_2$](CO)(OTf) is that the complexes containing bis(pyrazolyl)methanes we are dealing with are not naked cationic complexes because of the presence of interactions between the triflate and the metal center (vide infra). Hence, the overall electron density on the copper(I) cannot be ascribed only to the (pyrazolyl)methane ligand.

Previous work from our laboratories[1−4] showed that the resonances of the vinyl hydrogen and carbon atoms of the copper-bonded olefinic ligands undergo high-field shifts upon coordination, thus suggesting a shielding of the carbon atoms. Table 3 lists the ^1H and ^{13}C NMR chemical shifts of the vinyl hydrogen and carbon atoms for the alkene in bis[(trifluoromethyl)pyrazolyl]methane complexes of copper(I). The nonfluorinated analogue Cu[$CH_2(3,5-Me_2Pz)_2$](olefin)(OTf) is reported for the sake of comparison.

If the electron density at the copper(I) ion had been the only factor that determined the chemical shift change of vinyl hydrogen atoms due to coordination, we would have found that the resonances of the C*H*═C*H* hydrogen atoms of coe followed the order Cu[$CH_2(3,5-Me_2Pz)_2$](coe)(OTf) > Cu[$CH_2(3-CF_3-Pz)_2$](coe)(OTf) > Cu[$CH_2(3,5-(CF_3)_2Pz)_2$](coe)(OTf) ≈ Cu[$PhCH(3,5-(CF_3)_2Pz)_2$](coe)(OTf). Actually, the experimental trend is quite different, and we suggest that it depends on the key role played by the triflate anion and by its interaction with copper in solution.

To substantiate the presence of some interaction between copper and triflate, conductivity measurements were carried out, which provided the data listed in Table 4. As we can observe, solutions of similar concentrations of tetrabutylammonium bromide and Cu[$CH_2(3,5-Me_2Pz)_2$](coe)(OTf) exhibit similar conductivities, thus suggesting that the copper complex is dissociated in these conditions, at least to an extent similar to that of N^nBu_4Br. On the other hand, solutions of the corresponding fluorinated complexes exhibit a significantly smaller conductivity, thus suggesting a smaller extent of dissociation. Therefore, it seems likely that, at least in *sym*-tetrachloroethane solution, the interaction between the triflate anion and the copper atom is stronger in Cu[$CH_2(3,5-(CF_3)_2Pz)_2$](coe)(OTf) and Cu[$PhCH(3,5-(CF_3)_2Pz)_2$](coe)(OTf) complexes than in Cu[$CH_2(3,5-Me_2Pz)_2$](coe)(OTf). Assuming that the same dissociation phenomena are present in $CDCl_3$ solution, the slight chemical shift change (−0.36 ppm) in the vinyl hydrogen atoms of Cu[$CH_2(3,5-Me_2Pz)_2$](coe)(OTf) with respect to uncoordinated coe can be ascribed to the fact that the olefin is ligated to a cationic complex. As a matter of fact, it was found that the cationic complexes [Cu(cod)$_2$]$^+$ and [Cu(cod)(bipy)]$^+$ show slight downfield shifts of the vinyl protons (0.17 and 0.27 ppm, respectively) upon coordination.[24] Strictly related to these observations is the fact that the Cu$\cdots$$OSO_2CF_3$ distances, see Table 5, get smaller on increasing the electron-withdrawing power of the bis(pyrazolyl)methane ligand.

The higher acidity of the silver center in [Ag{$CH_2(3,5-(CF_3)_2Pz)_2$}(coe)]BF_4 with respect to the analogous copper derivative is made clear by the fact that the resonance of the vinylic protons of coordinated coe are high-frequency-shifted upon coordination in the silver complex and low-frequency-shifted in Cu[$CH_2(3,5-(CF_3)_2Pz)_2$](coe)(OTf), Table 3.[25]

Concluding Remarks

Trifluoromethyl-substituted bis(pyrazolyl)methane and bis(pyrazolyl)toluene ligands have been prepared and characterized for the first time. Their reactions with copper(I) and silver(I) precursors in the presence of olefins has allowed the preparation and the characterization of [M{$CHR(Pz^F)_2$}(olefin)]X species [M = Cu, R = H, Pz^F = 3-(trifluoromethyl)pyrazolyl, 3,5-bis(trifluoromethyl)pyrazolyl, olefin = cyclooctene, X = OTf; M = Cu, R = Ph, Pz^F = 3,5-bis(trifluoromethyl)pyrazolyl, olefin = cyclooctene, 4-vinylanisole, triethylvinylsilane, X = OTf; M = Ag, R = H, Pz^F = 3,5-bis(trifluoromethyl)pyrazolyl, olefin = cyclooctene, X = BF_4]. It has been observed that the olefin derivatives of copper(I) reported in this paper are less stable than the corresponding copper(I) compounds containing bis(pyrazolyl)borate[3] or methyl-substituted bis(pyrazolyl)methanes[4] as ancillary ligands as evidenced by the isolation of species such as [Cu(μ-OTf)(coe)]$_n$ not containing the pyrazolylmethane and by the fact that all of the copper(I) olefin derivatives reported above react *quantitatively* with carbon monoxide to afford the corresponding carbonyl derivative. A similar trend, i.e., a decrease of stability of the olefin copper(I) derivatives on increasing the electron-withdrawing power of the ancillary, was

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[21] The carbonyl derivative Cu[$BH_2(3,5-(CF_3)_2Pz)_2$](CO) was formed quantitatively in solution ($\nu_{CO} = 2127$ cm^{-1}, toluene) by carbonylation of Cu[$BH_2(3,5-(CF_3)_2Pz)_2$](olefin) derivatives.[3] It is stable in a CO atmosphere, but it could not be isolated in the solid state due to easy loss of carbon monoxide during the isolation procedures (evaporation of the solvent in vacuo at room temperature or lower).

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Table 3. ^1H and ^{13}C NMR Resonances of the Vinyl Carbon and Hydrogen Atoms in M(L)(olefin) Compounds (ppm, 293 K), $\Delta = \delta_{\text{coordinated olefin}} - \delta_{\text{unoordinated olefin}}$

compound	^1H NMR	$\Delta_{^1H}$	^{13}C NMR	$\Delta_{^{13}C}$
coe[a]	5.64		130.3	
$Cu[CH_2(3,5\text{-}Me_2Pz)_2](coe)(OTf)$[b]	5.28	−0.36	103.5	−26.8
$Cu[CH_2(3\text{-}CF_3Pz)_2](coe)(OTf)$[c]	5.12	−0.52	107.7	−22.6
$Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$[b]	5.23	−0.41		
$Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$[b]	5.27	−0.37	105.3	−25.0
$[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4$	5.79	+0.15	125.1	−5.2
van[a]	6.60, 5.54, 5.04		136.8, 111.4	
$Cu[CH_2(3,5\text{-}Me_2Pz)_2](van)(OTf)$	6.44, 5.08, 4.78[a]	−0.16	*e*, 58.0[c]	*e*, −53.4
tevs[a]	6.03, 5.72, 5.63		136.5, 132.5	
$Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](tevs)(OTf)$[a]	5.2−4.6[d]	≈−1	103.5, 97.8	−33.0, −34.7

[a] C_6D_6. [b] $CDCl_3$. [c] thf-d_8. [d] Multiplet. [e] Overlap with the solvent resonance.

Table 4. Conductivities of Copper(I)-Substituted Pyrazolylmethane Solutions (*sym*-Tetrachloroethane, 293 K)[a]

compound	concn (mM)	conductivity (μS)
$Cu[CH_2(3,5\text{-}Me_2Pz)_2](coe)(OTf)$	3.6	13.6
$Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$	2.6	0.37
$Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$	2.9	1.30

[a] The conductivity of *sym*-tetrachloroethane is 0.03 μS. [b] $NBu^n{}_4Br$ (3.0 mM) has a conductivity of 14.2 μS at 293 K in *sym*-tetrachloroethane.

Table 5. $Cu\cdots OSO_2CF_3$ Distances in Complexes Containing Substituted Bis(pyrazolyl)methanes

compound	$Cu\cdots OSO_2CF_3$ distance (Å)	ref
$Cu[CH_2(3,5\text{-}Me_2Pz)_2](OTf)$	2.706(2)[a]	4
$Cu[CH_2(3,5\text{-}Me_2Pz)_2](coe)(OTf)$	2.437(2)	4
$Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)$	2.135(3)	this work
$Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$	2.085(5)	this work

[a] Average distance.

observed on going from $Cu(CF_3COO)$(olefin) to Cu(hexafluoroacetylacetonate)(olefin) derivatives.[1,2]

Copper(I) carbonyl derivatives of general formula $Cu[CHR(Pz^F)_2](CO)(OTf)$ [R = H, Pz^F = $3\text{-}(CF_3)Pz$, $3,5\text{-}(CF_3)_2Pz$; R = Ph, Pz^F = $3,5\text{-}CF_3$] are stable compounds which can be isolated and fully characterized. It is noteworthy that such carbonyl derivatives become more stable than the corresponding bis(pyrazolyl)borato derivative $Cu[BH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)$, which has been reported[3,21] but not isolated in the solid state.

The electronic properties of the ancillary ligand play a fundamental role in the stabilization of the silver(I) complexes. As a matter of fact, AgOTf does not react with $CH_2(3,5\text{-}(CF_3)_2Pz)_2$, while it does, in fact, react with the more basic L = $CH_2(3,5\text{-}Me_2Pz)_2$ to form $Ag_2(\mu\text{-}L)_2(OH_2)_2(OTf)_2$ and $[AgL_2](OTf)$.[26]

As far as copper(I) olefin derivatives are concerned, the combination of solution (NMR and conductivity measurements) and solid-state (X-ray crystallography) studies has shown that the trifluoromethyl subsituents on pyrazolylmethanes weaken their Lewis basicity (the Cu−N bond distances increase) and increase, consequently, the Lewis acidity of copper (the $Cu-O_{\text{triflate}}$ bond distances decrease together with the conductivity of their solutions). The triflate anion−copper interaction in solution plays a key role as evidenced by the fact that the observed chemical shift change of vinyl hydrogen atoms due to coordination is not the one expected on the basis of the simple electron density at copper(I); see Table 4. Moreover, the fact that the resonance of the vinylic protons is shifted to high or to low frequencies in $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4$ and in $Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$, respectively, Table 4, with respect to that of free coe, indicates the higher acidity of the silver center in $[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4$ with respect to the analogous copper derivative.

Experimental Section

General Considerations. Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. *cis*-Cyclooctene (coe; Aldrich), 4-vinylanisole (van; Aldrich), triethylvinylsilane (tevs; Aldrich), α,α′-dibromotoluene (Aldrich), and diiodomethane (C. Erba, Milan) were distilled under reduced pressure and stored at ca. −30 °C. The compounds 3-(trifluoromethyl)pyrazole (Aldrich), Cu_2O (Aldrich), AgOTf (Aldrich), and $AgBF_4$ (Aldrich) were used as received. The derivatives $Cu(OTf)(toluene)_{0.5}$[27] and 3,5-bis(trifluoromethyl)pyrazole[10] were prepared according to the literature. IR spectra were recorded on an FTIR spectrometer equipped with a Perkin-Elmer UATR sampling accessory. NMR spectra (^1H, 200 MHz; ^{13}C, 50.31 MHz, with TMS as the reference; ^{19}F, 188 MHz, with C_6F_6 as the reference) were recorded with a Varian Gemini 200BB spectrometer. The gas volumetric measurements were performed with the apparatus described by Calderazzo and Cotton.[28]

Synthesis of Bis[3-(trifluoromethyl)-1-pyrazolyl]methane, $CH_2(3\text{-}CF_3Pz)_2$. Dichloromethane (30 mL) was added to a mixture of 3-(trifluoromethyl)pyrazole (2.31 g, 16.9 mmol), tetrabutylammonium bromide (0.771 g, 2.50 mmol), powdered KOH (2.70 g, 48.2 mmol), and K_2CO_3 (6.62 g, 48.1 mmol). The reaction mixture was stirred and heated under reflux for 36 h. After filtration, the solid was washed with hot CH_2Cl_2 (50 mL), and the organic portions were combined. The solvent was removed by evaporation under reduced pressure. The resulting solid (which also contained traces of tetrabutylammonium bromide) was recrystallized from hot heptane to give $CH_2(3\text{-}CF_3\text{-}Pz)_2$ as a colorless crystalline compound (2.10 g, 87%). Anal. Calcd for $C_9H_6F_6N_4$: C, 38.0; H, 2.1; N, 19.7. Found: C, 38.1; H, 1.9; N, 19.5. IR ($\tilde{\nu}$/cm^{-1}, neat): 3160w, 3119w, 3034w, 1532w, 1486m, 1432m,w, 1422m,w, 1372m, 1306m,w, 1238vs, 1205m, 1172s, 1118vs, 1062s, 1057s, 1006s, 961s, 793m, 769vs, 752m, 722m. ^1H NMR ($CDCl_3$): δ 7.76 (d, 2H, ^3J = 2.4 Hz, pyr 5-C*H*), 6.56 (d, ^3J = 2.4 Hz, pyr 4-C*H*), 6.34 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 144.2 (q, $^2J_{C-F}$ = 39 Hz, *C*CF_3), 131.6 (s, pyr 5-*C*H), 120.8 (q, $^2J_{C-F}$ = 270 Hz, C*C*F_3), 106.1 (s, pyr 4-*C*H), 65.8 (s, *C*H_2). EI-MS: 284 *m/z* [M^+, 37], 265 *m/z* [M^+ − F, 12], 215 *m/z* [M^+ − CF_3, 1], 149 *m/z* [M^+ − 3-CF_3Pz, 2].

Synthesis of Bis[3,5-bis(trifluoromethyl)-1-pyrazolyl]methane, $CH_2(3,5\text{-}(CF_3)_2Pz)_2$. A solution of 3,5-bis(trifluoromethyl)pyrazole

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(6.89 g, 33.7 mmol) in DMF (20 mL) was added dropwise to a well-stirred suspension of NaH (0.815 g, 33.9 mmol) in DMF (10 mL). Diiodomethane (2 mL, 25.1 mmol) was added to the resulting pale yellow solution, and the reaction mixture was allowed to stir at 80 °C for 4 days. Diethyl ether (100 mL) was added. The organic phase was washed with a water solution of K_2CO_3 (5 × 50 mL). The solvent was removed under reduced pressure to give a pale yellow solid. $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ was obtained as a colorless crystalline compound (3.70 g, 52%) by recrystallization from hot heptane. Anal. Calcd for $C_{11}H_4F_{12}N_4$: C, 31.4; H, 1.0; N, 13.3. Found: C, 31.0; H, 0.9; N, 13.5. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3169w, 3043w, 1676w, 1574m, 1480w, 1468m,w, 1397m,w, 1383m, 1280m,s, 1271m,s, 1227s, 1219s, 1186s, 1122vs, 1107vs, 1086s, 1042vs, 973s, 843vs, 804m,w, 784m, 737m,w, 719m,s, 696m. ^{1}H NMR ($CDCl_3$): δ 6.79 (s, 2H, pyr C*H*), 6.57 (s, 2H, C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 143.9 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 134.7 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 119.9 (q, $^1J_{C-F} = 269$ Hz, *C*F$_3$), 118.8 (q, $^1J_{C-F} = 270$ Hz, *C*F$_3$), 107.8 (s, pyr *C*H), 63.7 (s, *C*H$_2$). EI-MS: 217 *m/z* [M$^+$ − 3,5-(CF$_3$)$_2$Pz, 100], 147 *m/z* [M$^+$ − 3,5-(CF$_3$)$_2$Pz − HCF$_3$, 9], 69 *m/z* [14].

Synthesis of α,α′-Bis[3,5-bis(trifluoromethyl)-1-pyrazolyl]toluene, $PhCH(3,5\text{-}(CF_3)_2Pz)_2$. A solution of 3,5-bis(trifluoromethyl)pyrazole (8.82 g, 43.2 mmol) in DMF (10 mL) was added dropwise to a well-stirred suspension of NaH (1.03 g, 42.9 mmol) in DMF (15 mL). α,α′-Dibromotoluene (5.44 g, 21.7 mmol) was added to the resulting pale yellow solution, and the reaction mixture was allowed to stir at 80 °C for 3 days and at 100 °C for the following 36 h. Diethyl ether (100 mL) was added. The organic phase was washed with a water solution of K_2CO_3 (5 × 50 mL). The solvent was removed under reduced pressure to give a brown-yellow solid. $PhCH(3,5\text{-}(CF_3)_2Pz)_2$ was obtained as a pale yellow crystalline compound (4.29 g, 40%) by sublimation of the crude product (70 °C, 10^{-2} Torr). Anal. Calcd for $C_{17}H_8F_{12}N_4$: C, 41.1; H, 1.6; N, 11.3. Found: C, 41.0; H, 1.5; N, 10.9. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3153w, 1742w, 1624w, 1573m,w, 1494m, 1456w, 1390w, 1275m,s, 1245m, 1216s, 1096s, 1041vs, 975s, 862m, 838m,s, 754m,s, 730s, 690s. ^{1}H NMR ($CDCl_3$): δ 7.85 (s, 1H, PhC*H*), 7.52−7.22 (m, 5H, Ph), 7.04 (s, 2H, pyr C*H*). ^{13}C NMR ($CDCl_3$): δ 143.0 (q, $^2J_{C-F} = 42$ Hz, *C*CF$_3$), 133.7 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 131.7 (s, 1-*C*$_{Ph}$), 130.5 (s, *C*H$_{Ph}$), 128.8 (s, *C*H$_{Ph}$), 128.1 (s, *C*H$_{Ph}$), 119.9 (q, $^1J_{C-F} = 269$ Hz, *C*F$_3$), 118.8 (q, $^1J_{C-F} = 270$ Hz, *C*F$_3$), 107.0 (s, pyr *C*H), 75.7 (s, Ph*C*H). EI-MS: 496 *m/z* [M$^+$, 2], 427 *m/z* [M$^+$ − CF$_3$, 8], 293 *m/z* [M$^+$ − 3,5-(CF$_3$)$_2$Pz, 100], 223 *m/z* [M$^+$ − 3,5-(CF$_3$)$_2$Pz − CF$_3$, 2].

Synthesis of $Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)$. Cu(OTf)(toluene)$_{0.5}$ (0.280 g, 1.08 mmol) was dissolved in toluene (20 mL); the solution was saturated with CO, and a colorless solid formed. After addition of $CH_2(3\text{-}CF_3Pz)_2$ (0.291 g, 1.02 mmol), the suspension was stirred for 24 h at room temperature. The solid was recovered by filtration, dried in vacuo for a short time, and identified as $Cu[CH_2(3\text{-}CF_3Pz)_2](CO)(OTf)$ (0.392 g, 74%). Crystals suitable for X-ray diffraction were grown from THF/toluene. Anal. Calcd for $C_{11}H_6CuF_9N_4O_4S$: C, 25.2; H, 1.2; N, 10.7. Found: C, 25.0; H, 1.5; N, 10.9. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3157w, 3135w, 3048w, 2120s, 1496m,w, 1426w, 1383m, 1339w, 1321m, 1290m,s, 1235vs, 1221s, 1207s, 1188s, 1139vs, 1075m,s, 1066s, 1021vs, 973s, 891w, 788s, 756m,s, 743m, 723m,w. ^{1}H NMR (thf-*d*$_8$): δ 8.45 (s, 2H, pyr 5*H*), 6.92 (d, 2H, $^3J = 1.8$ Hz), 6.79 (s, 2H, NC*H*$_2$N). ^{13}C NMR (thf-*d*$_8$): δ 144.8 (q, $^2J_{C-F} = 38$ Hz, *C*CF$_3$), 136.2 (s, pyr 5*C*H), 121.1 (q, $^1J_{C-F} = 269$ Hz, *C*F$_3$), 106.8 (s, pyr 4*C*H), 64.3 (s, N*C*H$_2$N).

Synthesis of $Cu[CH_2(3\text{-}CF_3Pz)_2](coe)(OTf)$. Cu(OTf)(toluene)$_{0.5}$ (0.830 g, 3.20 mmol) was added to a mixture of $CH_2(3\text{-}CF_3Pz)_2$ (0.911 g, 3.20 mmol) and coe (0.39 g, 3.50 mmol) in toluene (15 mL). A colorless solid separated out. After 24 h of stirring at room temperature, heptane was added (30 mL), and the colorless suspension was filtered. The solid was recovered, dried in vacuo, and identified as $Cu[CH_2(3\text{-}CF_3Pz)_2](coe)(OTf)$ (1.52 g, 77%). Mp: 118−125 °C. Anal. Calcd for $C_{18}H_{20}CuF_9N_4O_3S$: C, 35.6; H, 3.3; N, 9.2. Found: C, 35.0; H, 3.5; N, 9.1. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3130w, 3034w, 2963w, 1492m,w, 1446w, 1423w, 1385m, 1341w, 1319m,w, 1269m,s, 1236vs, 1206s, 1139vs, 1065m,s, 1028s, 1013s, 970m,s, 864m,w, 794s, 784vs, 757m,s, 742m, 722m,w. ^{1}H NMR (C_6D_6): δ 8.17 (s, 2H, pyr 5-*H*), 7.01 (s, 2H, pyr 4-*H*), 5.86 (s, 2H, C*H*$_2$), 5.1−4.8 (m, 2H, C*H*═C*H*), 2.4−2.0 (m, 4H, C*H*$_2$CH═), 1.19 (s, 8H). ^{1}H NMR (thf-*d*$_8$): δ 8.48 (s, 2H, pyr 5-*H*), 6.85 (s, 4H, pyr 4-*H* and C*H*$_2$), 5.2−5.0 (m, 2H, C*H*═C*H*), 2.23 (s, 4H, C*H*$_2$CH═), 1.50 (s, 8H). ^{13}C NMR (thf-*d*$_8$): δ 147.5 (q, $^2J_{C-F} = 39$ Hz, *C*CF$_3$), 138.6 (s, pyr 5-*C*H), 124.3 (q, $^1J_{C-F} = 270$ Hz, *C*F$_3$), 109.6 (s, pyr 4-*C*H), 107.7 (s, *C*H═*C*H), 68.0 (s, *C*H$_2$CH═), 33.5 (s, *C*H$_2$), 30.0 (s, *C*H$_2$), 29.8 (s, CH$_2$).

Synthesis of $Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$. $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ (0.357 g, 0.850 mmol) was dissolved in CH_2Cl_2 (10 mL). The solution was saturated with CO at atmospheric pressure, and Cu(OTf)(toluene)$_{0.5}$ (0.220 g, 0.851 mmol) was added. A colorless solid separated out. After 24 h of stirring at room temperature, pentane (20 mL) was added, and the colorless precipitate was recovered by filtration, dried quickly under vacuum, and identified as $Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$ (0.323 g, 58%). Anal. Calcd for $C_{13}H_4CuF_{15}N_4O_4S$: C, 23.6; H, 0.6; N, 8.5. Found: C, 23.8; H, 0.5; N, 8.1. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3106w, 2127s, 1654w, 1572w, 1488w, 1446w, 1412, 1312m, 1272s, 1213vs, 1194s, 1148vs, 1109m,s, 1056s, 1025vs, 1000m, 986m,w, 975w, 868m,w, 835w, 797w, 749m,w, 736w, 725w, 697w. ^{1}H NMR (C_6D_6): δ 6.60 (s, 2H, pyr C*H*), 5.34 (s, 2H, NC*H*$_2$N). ^{1}H NMR (thf-*d*$_8$): δ 7.33 (s, 2H, pyr C*H*), 6.79 (s, 2H, NC*H*$_2$N). ^{13}C NMR (thf-*d*$_8$): δ 143.7 (q, $^2J_{C-F} = 39$ Hz, *C*CF$_3$), 134.9 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 120.8 (q, $^1J_{C-F} = 269$ Hz, *C*F$_3$), 119.6 (q, $^1J_{C-F} = 270$ Hz, *C*F$_3$), 108.3 (s, pyr *C*H), 64.6 (s, N*C*H$_2$N).

Synthesis of $Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$. Cu(OTf)(toluene)$_{0.5}$ (0.804 g, 3.12 mmol) was added to a mixture of $CH_2(3,5\text{-}(CF_3)_2Pz)_2$ (1.31 g, 3.12 mmol) and coe (0.462 g, 4.20 mmol) in toluene (25 mL). After 24 h of stirring at room temperature, heptane was added (30 mL), and the resulting colorless suspension was filtered. The solid was recovered, dried in vacuo, and identified as $Cu[CH_2(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)$ (1.10 g, 48%). Anal. Calcd for $C_{20}H_{18}CuF_{15}N_4O_3S$: C, 32.3; H, 2.4; N, 7.5. Found: C, 32.0; H, 2.5; N, 7.9. Mp: 126−131 °C. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3100w, 2938m,w, 2856w, 1573w, 1483w, 1464w, 1411w, 1399w, 1317m, 1267m,s, 1243m, 1219m,s, 1178vs, 1158vs, 1143vs, 1100m,s, 1050m,s, 1031m,s, 1012s, 991m,s, 898w, 874m,w, 841m, 796m, 749m, 734w, 723w, 693w, 629s, 582m, 566m. ^{1}H NMR ($CDCl_3$): δ 7.03 (s, 2H, pyr C*H*), 6.69 (s, 2H, NC*H*$_2$N), 5.23 (m, 2H, C*H*═C*H*), 2.4−2.0 (m, 4H, C*H*$_2$CH═), 1.47 (s, 8H). ^{13}C NMR (thf-*d*$_8$): δ 143.8 (q, $^2J_{C-F} = 39$ Hz, *C*CF$_3$), 134.8 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 119.7 (q, $^1J_{C-F} = 269$ Hz, *C*F$_3$), 117.9 (q, $^1J_{C-F} = 270$ Hz, *C*F$_3$), 108.3 (s, pyr *C*H), 106.3 (s, *C*H═*C*H), 64.6 (s, N*C*H$_2$N), 29.7 (s, *C*H$_2$CH═), 26.0 (s, *C*H$_2$), 25.9 (s, *C*H$_2$).

Synthesis of $Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$. $PhCH(3,5\text{-}(CF_3)_2Pz)_2$ (0.262 g, 0.521 mmol) was dissolved in toluene (10 mL). The solution was saturated with CO at atmospheric pressure, and Cu(OTf)(toluene)$_{0.5}$ (0.132 g, 0.53 mmol) was added. After 24 h of stirring at room temperature, heptane (20 mL) was added, and a colorless precipitate formed. After filtration, the solid was dried quickly under vacuum and identified as $Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](CO)(OTf)$ (0.172 g, 45%). Anal. Calcd for $C_{19}H_8CuF_{15}N_4O_4S$: C, 31.0; H, 1.1; N, 7.6. Found: C, 30.8; H, 1.5; N, 7.9. IR ($\tilde{\nu}/\mathrm{cm}^{-1}$, neat): 3066w, 2117s, 2108s, 1644w, 1610m, 1575m,w, 1496w, 1449m,w, 1286s, 1259s, 1214vs, 1167vs, 1079m,w, 1016vs, 980m, 926m,w, 896w, 875m,w, 752s, 734m, 692s. ^{1}H NMR ($CDCl_3$): δ 8.04 (s, 1H, PhC*H*), 7.7−7.1 (m, 5H, Ph), 6.34 (s, 1H, pyr C*H*), 6.31 (s, 1H, pyr C*H*). ^{13}C NMR ($CDCl_3$): δ 168.3 (s, *C*O), 166.3 (s, *C*O), 146.1 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 137.8 (q, $^2J_{C-F} = 41$ Hz, *C*CF$_3$), 133.8 (s, 1-*C*$_{Ph}$) 131.5(s, *C*H$_{Ph}$), 130.1 (s, *C*H$_{Ph}$), 124.8 (s,

$C\mathrm{H_{Ph}}$),118.6 (q, $^{1}J_{\mathrm{C-F}} = 271$ Hz, $C\mathrm{F_3}$), 118.0 (q, $^{1}J_{\mathrm{C-F}} = 271$ Hz, $C\mathrm{F_3}$), 108.6 (s, pyr *C*H), 73.6 (s, Ph*C*H).

Synthesis of $\mathbf{Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](coe)(OTf)}$. Cu(OTf)(toluene)$_{0.5}$ (0.720 g, 2.80 mmol) was added to a mixture of PhCH(3,5-$\mathrm{(CF_3)_2Pz)_2}$ (1.37 g, 2.81 mmol) and coe (0.380 g, 3.40 mmol) in toluene (20 mL). After 24 h of stirring at room temperature, the volume of the pale rose solution was reduced to 10 mL by evaporation of the solvent, and heptane (50 mL) was added. Cu[PhCH(3,5-$\mathrm{(CF_3)_2Pz)_2}$](coe)(OTf) separated out as a colorless solid, which was recovered by filtration and dried in vacuo (1.22 g, 54%). Mp: 138−142 °C. Anal. Calcd for $\mathrm{C_{26}H_{22}CuF_{15}N_4O_3S}$: C, 38.1; H, 2.7; N, 6.8. Found: C, 38.0; H, 2.9; N, 6.9. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 3105w, 2929m,w, 2855w, 1611w, 1574w, 1496w, 1469m,w, 1453m,w, 1313m,s, 1275s, 1211vs, 1149vs, 1109m,s, 1051s, 1029vs, 994m,s, 976m, 959m,w, 858m,w, 843m,w, 826m,w, 757m,s, 737m, 693m. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.00 (s, 1H, PhC*H*), 7.7−7.1 (m, 5H, Ph), 6.80 (s, 1H, pyr C*H*), 6.76 (s, 1H, pyr C*H*), 5.27 (m, 2H, C*H*═C*H*), 1.74 (s, 4H, $\mathrm{C}H_2\mathrm{CH}$═), 1.6−1.2 (m, 8H). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 143.3 (q, $^{2}J_{\mathrm{C-F}} = 42$ Hz, $C\mathrm{CF_3}$), 134.4 (q, $^{2}J_{\mathrm{C-F}} = 41$ Hz, $C\mathrm{CF_3}$), 131.9 (s, 1-C_{Ph}), 130.7 (s, $C\mathrm{H_{Ph}}$), 129.1 (s, $C\mathrm{H_{Ph}}$), 127.7 (s, $C\mathrm{H_{Ph}}$),120.2 (q, $^{1}J_{\mathrm{C-F}} = 270$ Hz, $C\mathrm{F_3}$), 118.7 (q, $^{1}J_{\mathrm{C-F}} = 269$ Hz, $C\mathrm{F_3}$), 110.9 108.2 (s, pyr *C*H), 105.3 (s, *C*H═*C*H), 75.4 (s, Ph*C*H), 66.2 29.6 (s, $C\mathrm{H_2}$), 26.0 (s, $C\mathrm{H_2}$), 15.1 (s, $C\mathrm{H_2}$).

Colorless crystals formed in the mother liquor after 10 days at room temperature. The crystals were collected by filtration and shortly dried in vacuo at room temperature, giving 0.150 g of Cu(coe)(OTf) in the form of a colorless air-sensitive compound. Anal. Calcd for $\mathrm{C_9H_{14}CuF_3O_3S}$: C, 33.7; H, 3.8. Found: C, 34.0; H, 4.0. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 2932m,w, 2854w, 1634w, 1466w, 1448w, 1289s, 1228s, 1208vs, 1182vs, 1028s, 974w, 765w. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.22 (m, 2H, C*H*═C*H*), 2.19 (d, 4H, $^{3}J = 5.4$ Hz, $\mathrm{C}H_2\mathrm{CH}$═), 1.3−1.7 (m, 8H). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 128.3 (s, *C*H═*C*H), 29.4 (s, $C\mathrm{H_2CH}$═), 26.0 (s, $C\mathrm{H_2}$).

Synthesis of $\mathbf{Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](van)(OTf)}$. This compound was prepared as described for the analogous coe derivative, using 4-vinylanisole instead of cyclooctene. The pale rose microcrystalline solid Cu[PhCH(3,5-$\mathrm{(CF_3)_2Pz)_2}$](van)(OTf) was obtained in 83% yield. Anal. Calcd for $\mathrm{C_{27}H_{18}CuF_{15}N_4O_4S}$: C, 38.5; H, 2.2; N, 6.7. Found: C, 38.0; H, 2.3; N, 6.9. Mp: ca. 60 °C dec. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 2925w, 2835w, 1659w, 1610m,w, 1574m,w, 1510m,s, 1457m,w, 1417w, 1407w, 1330m,w, 1271s, 1224vs, 1168vs, 1146vs, 1097m,s, 1027vs, 994m,s, 976m,s, 853m, 828m,s, 755m,s, 732m,s, 688m. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.01 (s, 1H, PhC*H*), 7.6−6.9 (m, 9H, Ph), 6.80 (d, 2H, *o*-C*H*), 6.60 (m, 1H, C*H*═$\mathrm{CH_2}$), 6.35 (s, 2H, pyr C*H*), 4.95 (s, br, 2H, CH═$\mathrm{C}H_2$), 3.72 (s, 3H, $\mathrm{OC}H_3$).

Synthesis of $\mathbf{Cu[PhCH(3,5\text{-}(CF_3)_2Pz)_2](tevs)(OTf)}$. This compound was prepared as described for the analogous coe derivative, using triethylvinylsilane instead of cyclooctene. The pale yellow solid was obtained in 60% yield. Anal. Calcd for $\mathrm{C_{26}H_{26}CuF_{15}N_4O_3SSi}$: C, 36.7; H, 3.1; N, 6.6. Found: C, 37.0; H, 3.0; N, 6.9. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 3091w, 2962w, 1663w, 1619m,w, 1571m,w, 1456m,w, 1401w, 1274s, 1220vs, 1142vs, 1049s, 1028vs, 989m,s, 976m,s, 868m, 838m, 803m, 753s, 730s, 688m,s. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.85 (s, 1H, PhC*H*), 7.5−7.3 (m, 3H, Ph), 7.3−7.1 (m, 2H, Ph), 7.04 (s, 2H, pyr C*H*), 5.2−4.6 (m, 3H, C*H*═$\mathrm{C}H_2$), 0.97 (t, 9H, $\mathrm{CH_2C}H_3$), 0.65 (q, 6H, $\mathrm{C}H_2\mathrm{CH_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 143.1 (q, $^{2}J_{\mathrm{C-F}} = 41$ Hz, $C\mathrm{CF_3}$), 133.9 (q, $^{2}J_{\mathrm{C-F}} = 41$ Hz, $C\mathrm{CF_3}$), 131.6 (s, 1-C_{Ph}), 130.7 (s, $C\mathrm{H_{Ph}}$), 129.0 (s, $C\mathrm{H_{Ph}}$), 127.8 (s, $C\mathrm{H_{Ph}}$), 119.8 (q, $^{1}J_{\mathrm{C-F}} = 271$ Hz, $C\mathrm{F_3}$), 118.7 (q, $^{1}J_{\mathrm{C-F}} = 270$ Hz, $C\mathrm{F_3}$), 108.0 (s, pyr *C*H), 103.5 (s, *C*H═$\mathrm{CH_2}$), 97.8 (s, CH═$C\mathrm{H_2}$), 75.5 (s, Ph*C*H), 7.3 (s, $C\mathrm{H_2}$), 3.3 (s, $C\mathrm{H_3}$).

Carbonylation Reactions of $\mathbf{Cu[CHR(Pz^F)_2](L)(OTf)}$ (R = H, $\mathbf{Pz^F}$ = 3-$\mathbf{CF_3}$, 3,5-$\mathbf{CF_3}$, L = coe; R = Ph, $\mathbf{Pz^F}$ = 3,5-$\mathbf{CF_3}$, L = coe, tevs, van). Toluene ($\mathrm{Pz^F}$ = 3-$\mathrm{CF_3}$, 50 mL) or THF ($\mathrm{Pz^F}$ = 3,5-$\mathrm{CF_3}$, 50 mL) and a thin-walled sealed glass container containing the copper(I) derivative were introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric buret and saturated with CO at atmospheric pressure at the temperature of the experiment. The glass container was then broken by mechanical stirring, and the absorption of gas was measured. The presence of the carbonyl derivative was established by IR at the end of the reaction.

Reaction of $\mathbf{CH_2(3,5\text{-}(CF_3)_2Pz)_2}$ with AgOTf in the Presence of coe. Isolation of Ag(coe)(OTf). AgOTf (0.282 g, 1.11 mmol) was added to a mixture of $\mathrm{CH_2(3,5\text{-}(CF_3)_2Pz)_2}$ (0.461 g, 1.11 mmol) and coe (1.21 mmol) in THF (20 mL). After 20 h of stirring at room temperature, the solution was partially evaporated in vacuo, and heptane was added. A small amount of colorless solid formed which was recovered by filtration, dried in vacuo, and identified (see below) as Ag(coe)(OTf) (ca. 0.032 g).

Synthesis of Ag(coe)(OTf). coe was added (0.2 mL, 1.5 mmol) to a stirred suspension of AgOTf (0.34 g, 1.3 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL). The colorless solid dissolved in a few minutes. After 4 h of stirring at room temperature, the solvent was evaporated in vacuo, and the resulting colorless solid was dried in vacuo and identified as Ag(coe)(OTf) (0.433 g, 89%). Anal. Found: C, 29.5; H, 3.6. Calcd for $\mathrm{C_9H_{14}AgF_3O_3S}$: C, 29.5; H, 3.8. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 2928m, 2856m,w, 1580w, 1469m,w, 1448w, 1301s, 1221s, 1182vs, 1121m, 1012vs, 899m, 876w, 820m, 794m,s, 763m. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 6.07 (m, 2H, C*H*═C*H*), 2.34 (d, 4H, $^{3}J = 4.4$ Hz, $\mathrm{C}H_2\mathrm{CH}$═), 1.3−1.7 (m, 8H). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 124.0 (s, *C*H═*C*H), 29.5 (s, $C\mathrm{H_2CH}$═), 26.2 (s, $C\mathrm{H_2}$), 25.8 (s, $C\mathrm{H_2}$).

Synthesis of $\mathbf{[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}]BF_4}$. $\mathrm{AgBF_4}$ (0.120 g, 0.621 mmol) was added to a THF solution (15 mL) of $\mathrm{CH_2(3,5\text{-}(CF_3)_2Pz)_2}$ (0.263 g, 0.625 mmol). After 18 h of stirring at room temperature, the solvent was evaporated in vacuo, and the resulting colorless solid was dried in vacuo and identified as $\mathrm{[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}]BF_4}$ (0.321 g, 85%). Mp: 146−152 °C with darkening. Anal. Calcd for $\mathrm{C_{11}H_4AgBF_{16}N_4}$: C, 21.5; H, 0.7; N, 9.1. Found: C, 22.0; H, 1.0; N, 8.9. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 3154w, 2993w, 1574m,w, 1483w, 1451w, 1408w, 1294m,w, 1270s, 1209s, 1136vs, 1096s, 1046vs, 988s, 982s, 865m,s, 843m,w, 791m, 747m, 723m, 694m,w. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.09 (s, 2H, pyr C*H*), 5.35 (s, 2H, $\mathrm{NC}H_2\mathrm{N}$). ^{13}C NMR (thf-d_8): δ 143.7 (q, $^{2}J_{\mathrm{C-F}} = 39$ Hz, $C\mathrm{CF_3}$), 134.1 (q, $^{2}J_{\mathrm{C-F}} = 41$ Hz, $C\mathrm{CF_3}$), 120.5 (q, $^{1}J_{\mathrm{C-F}} = 269$ Hz, $C\mathrm{F_3}$), 118.9 (q, $^{1}J_{\mathrm{C-F}} = 270$ Hz, $C\mathrm{F_3}$), 107.7 (s, pyr *C*H), 62.9 (s, $\mathrm{N}C\mathrm{H_2N}$). ^{19}F NMR (thf-d_8): δ −59.4 (s, 6F, $\mathrm{C}F_3$), −63.2 (s, 6F, $\mathrm{C}F_3$), −149.5 (s, 4F, $\mathrm{B}F_4$).

Synthesis of $\mathbf{[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}_2]BF_4}$. $\mathrm{AgBF_4}$ (0.061 g, 0.311 mmol) was added to a THF solution (10 mL) of $\mathrm{CH_2(3,5\text{-}(CF_3)_2Pz)_2}$ (0.260 g, 0.620 mmol). After 18 h of stirring at room temperature, the solvent was evaporated in vacuo, and the resulting colorless solid was dried in vacuo and identified as $\mathrm{[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}_2]BF_4}$ (0.262 g, 82%). Mp: 166−171 °C with darkening. Anal. Calcd for $\mathrm{C_{22}H_8AgBF_{28}N_8}$: C, 25.5; H, 0.8; N, 10.8. Found: C, 25.3; H, 1.0; N, 10.5. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 3150w, 2998w, 1570m,w, 1487w, 1453w, 1287m,w, 1270s, 1208s, 1131vs, 1096s, 1046vs, 985s, 981s, 868m,s, 791m, 742m, 721m. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.21 (s, 2H, pyr C*H*), 5.25 (s, 2H, $\mathrm{NC}H_2\mathrm{N}$).

Synthesis of $\mathbf{[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4}$. $\mathrm{AgBF_4}$ (0.150 g, 0.770 mmol) was added to a mixture of $\mathrm{CH_2(3,5\text{-}(CF_3)_2Pz)_2}$ (0.331 g, 0.780 mmol) and coe (1.55 mmol) in THF (15 mL). After 20 h of stirring at room temperature, the solution was partially evaporated in vacuo, and heptane was added. A colorless solid formed. The mixture was kept at −30 °C for some hours, and the colorless precipitate was then recovered by filtration, dried in vacuo, and identified as $\mathrm{[Ag\{CH_2(3,5\text{-}(CF_3)_2Pz)_2\}(coe)]BF_4}$ (0.451 g, 80%). Mp: 126−131 °C with darkening. Anal. Calcd for $\mathrm{C_{19}H_{18}AgBF_{16}N_4}$: C, 31.5; H, 2.5; N, 7.7. Found: C, 31.6; H, 2.7; N, 7.5. IR ($\tilde{\nu}/\mathrm{cm^{-1}}$, neat): 3145w, 3114w, 2994w, 2938w, 2860w, 1569m,w, 1486w, 1467w, 1454w, 1409w, 1273m,s, 1223s, 1211s, 1175m,s, 1138vs, 1129vs, 1050vs, 1021s, 982s, 898m,w, 871m,

Table 6. Crystallographic Data for Cu[CH$_2$(3-CF$_3$Pz)$_2$](CO)(OTf), Cu[CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$](CO)(OTf), and [Ag{CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$]BF$_4$

	Cu[CH$_2$(3-CF$_3$Pz)$_2$](C O)(OTf)	Cu[CH$_2$(3,5-CF$_3$Pz)$_2$](C O)(OTf)	[Ag{CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$]BF$_4$
empirical formula	$C_{11}H_6CuF_9O_4N_4S$	$C_{13}H_4CuF_{15}N_4O_4S$	$C_{22}H_8AgBF_{28}N_8$
fw	524.80	660.80	1035.04
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pnma*	$P2_1/n$	$P2_1/c$
a, Å	14.748(5)	10.818(3)	10.027(3)
b, Å	13.785(5)	14.758(5)	19.543(5)
c, Å	8.820(3)	13.283(3)	17.572(4)
α, deg	90	90	90
β, deg	90	95.41(5)	92.71(5)
γ, deg	90	90	90
V, Å^3	1793(1)	2111(1)	3439(2)
Z, D_{calcd}, g cm^{-3}	4, 1.944	4, 2.079	4, 1.999
$F(000)$	1032	1288	2000
μ, cm^{-1}	39.76	39.77	64.61
no. of reflns collected	1767	4138	5297
no. of unique reflns	1759 [$R_{int} = 0.05$]	3968 [$R_{int} = 0.04$]	5108 [$R_{int} = 0.05$]
no. of obsd reflns [$I > 2\sigma(I)$]	1550	2395	2458
no. of params	175	370	541
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0429, wR2 = 0.1210	R1 = 0.0488, wR2 = 0.1126	R1 = 0.0451, wR2 = 0.0860
final R indices[a] (all data)	R1 = 0.0473, wR2 = 0.1247	R1 = 0.0960, wR2 = 0.1446	R1 = 0.1357, wR2 = 0.1196

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

794m, 748m, 724m, 696m,w. ^{1}H NMR (thf-d_8): δ 7.42 (s, 2H, pyr C*H*), 6.83 (s, 2H, NC*H*$_2$N), 5.79 (m, 2H, C*H*═C*H*), 2.23 (s, 4H, C*H*$_2$CH═), 1.52 (s, 8H). ^{13}C NMR (thf-d_8): δ 143.9 (q, $^2J_{C-F}$ = 40 Hz, *C*CF$_3$), 135.1 (q, $^2J_{C-F}$ = 41 Hz, *C*CF$_3$), 125.1 (s, *C*H═*C*H), 121.1 (q, $^1J_{C-F}$ = 269 Hz, *C*F$_3$), 119.9 (q, $^1J_{C-F}$ = 270 Hz, *C*F$_3$), 108.6 (s, pyr *C*H), 64.9 (s, N*C*H$_2$N), 30.3 (s, *C*H$_2$CH═), 26.7 (*C*H$_2$). ^{19}F NMR (thf-d_8): δ −56.8 (s, 6F, C*F*$_3$), −60.7 (s, 6F, C*F*$_3$), −152.5 (2, 4F, B*F*$_4$).

Synthesis of [Ag$_2${CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$(fn)](BF$_4$)$_2$. AgBF$_4$ (0.120 g, 0.621 mmol) was added to a mixture of CH$_2$(3,5-(CF$_3$)$_2$-Pz)$_2$ (0.260 g, 0.620 mmol) and fumaronitrile (0.081 g, 1.0 mmol) in THF (15 mL). After 20 h of stirring at room temperature, the solvent was evaporated in vacuo, and the resulting colorless solid was dried in vacuo and identified as [Ag$_2${CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$-(fn)](BF$_4$)$_2$ (0.36 g, 87%). Anal. Found: C, 25.6; H, 1.1; N, 12.5. Calcd for $C_{15}H_6AgBF_{16}N_6$: C, 26.0; H, 0.9; N, 12.1. IR ($\tilde{\nu}$/cm^{-1}, neat): 3166w, 3067w, 2964w, 2264w, 1574m,w, 1484w, 1398w, 1384w, 1267m,s, 1224m,s, 1135s, 1044vs, 983m,s, 974m,s, 953m, 835m,s, 800m,s, 721 m, 695m,w. ^{1}H NMR (thf-d_8): δ 7.39 (s, 2H, pyr C*H*), 6.82 (s, 2H, NC*H*$_2$N), 6.76 (s, 1H, C*H*═C*H*). ^{13}C NMR (thf-d_8): δ 143.9 (q, $^2J_{C-F}$ = 40 Hz, *C*CF$_3$), 135.1 (q, $^2J_{C-F}$ = 41 Hz, *C*CF$_3$), 121.0 (q, $^1J_{C-F}$ = 269 Hz, *C*F$_3$), 118.9 (q, $^1J_{C-F}$ = 270 Hz, *C*F$_3$), 120.4 (s, *C*HCN), 119.8 (q, $^1J_{C-F}$ = 270 Hz, *C*F$_3$), 108.6 (s, pyr *C*H), 64.8 (s, N*C*H$_2$N). ^{19}F NMR (thf-d_8): δ −56.8 (s, 6F, C*F*$_3$), −60.7 (s, 6F, C*F*$_3$), −151.8 (2, 4F, B*F*$_4$).

X-ray Structure Determination of Cu[CH$_2$(3-CF$_3$Pz)$_2$](CO)(OTf), Cu[CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$](CO)(OTf), [Cu(μ-OTf)(coe)]$_n$, and [Ag{CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$]BF$_4$. Mixtures of THF/toluene, CH$_2$Cl$_2$/heptane, and toluene/heptane were used to grow single crystals of Cu[CH$_2$(3-CF$_3$Pz)$_2$](CO)(OTf), Cu[CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$]-(CO)(OTf), and [Cu(μ-OTf)(coe)]$_n$, respectively. Single crystals of the silver compound [Ag[CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$]BF$_4$ was obtained from benzene at room temperature.

Data were collected at 203 K on an Enraf Nonius CAD 4 single-crystal diffractometer (Cu Kα radiation, λ = 1.54183 Å). Details for the X-ray data collections are collected in Table 6. The structures were solved by Patterson and direct methods with SHELXS-97 and refined against F^2 with SHELXL-97,[25] with anisotropic thermal parameters for all non-hydrogen atoms. The fluorine atoms of one of the trifluoromethyl groups in Cu[CH$_2$(3-CF$_3$Pz)$_2$](CO)(OTf) and in Cu[CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$](CO)(OTf) were disordered and distributed in two positions.

Acknowledgment. We thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Roma), Programmi di Ricerca Scientifica di Notevole Interesse Nazionale, Cofinanziamento 2004-2005, and Consiglio Nazionale delle Ricerche (CNR), Progetto CNR-MIUR "Sviluppo di microcelle a combustibile", for financial support.

Supporting Information Available: Discussion of the crystal structure of [Cu(μ-OTf)(coe)]$_n$ and X-ray crystallographic data for Cu[CH$_2$(3-CF$_3$Pz)$_2$](CO)(OTf), Cu[CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$](CO)(OTf), [Cu(μ-OTf)(coe)]$_n$, and [Ag{CH$_2$(3,5-(CF$_3$)$_2$Pz)$_2$}$_2$]BF$_4$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700325T