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Copper(I) Ethylene Complexes Supported by 1,3,5-Triazapentadienyl Ligands with Electron-Withdrawing Groups

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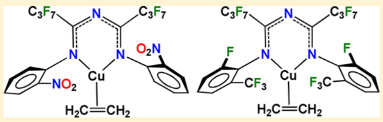
Supporting Information

ABSTRACT: The fluorinated 1,3,5-triazapentadienyl ligands $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]^-$, $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]^-$, $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]^-$, and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ have been used as supporting ligands in copper(I) ethylene chemistry. $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**7**), $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**8**), $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (**9**), and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (**10**) are easily isolable, thermally stable solids and display their ethylene proton and carbon resonances in the δ 3.68–3.48 and 85.2–87.6 ppm regions, respectively. X-ray crystal structures reveal that **7**–**10** feature trigonal-planar copper sites and κ^2-bonded, U-shaped triazapentadienyl ligands. The Cu(I) carbonyl adducts $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (**16**) and $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (**17**) have also been synthesized, and they have pseudotetrahedral copper sites. The CO stretching frequencies of the compounds **16** and **17** and ethylene ^{13}C NMR chemical shift data of **7**–**10** suggest that these molecules have rather acidic copper sites and weakly donating triazapentadienyl ligands.



INTRODUCTION

Copper(I) ethylene complexes are important in many areas, including catalysis, biochemistry, and separation science.[1,2] For example, copper mediates oxychlorination of ethylene, which is an important industrial process.[3,4] Copper(I) ethylene complexes also catalyze very effectively the carbene and nitrene transfer chemistry to a variety of substrates.[5−10] In nature, ethylene is a plant hormone that regulates several aspects of the plant life cycle.[11−13] It is widely believed that the ethylene binding site in plants is a copper center. The alkene coordination ability of copper salts has been explored in chromatography and as an energy-efficient way to separate olefins such as ethylene from paraffins, which is currently achieved via energy-intensive cryogenic distillation.[14,15]

It has been known for many years that copper(I) salts such as cuprous chloride react with ethylene to form adducts, but these compounds have limited stability and decompose unless low temperatures and high ethylene pressures are maintained.[1,16,17] Thompson and co-workers first reported structural data on the copper ethylene complex $[HB(3,5\text{-}(CH_3)_2Pz)_3]Cu(C_2H_4)$ in 1983.[18] However, this adduct also loses ethylene easily under reduced pressure. Overall, there has been significant interest in thermally stable copper(I) ethylene complexes, but the isolation of such adducts is challenging in the absence of proper supporting ligands.

An area of research focus in our laboratory concerns the chemistry of coinage metal (Cu, Ag, Au) adducts involving highly fluorinated ligands and weakly coordinating anions.[1,2,7,19−21] We have discovered that fluorinated tris(pyrazolyl)borate and 1,3,5-triazapentadienyl ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ are good choices to stabilize ethylene adducts **1** and **2** (Figure 1).[6,22] For example, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(C_2H_4)$ (**1**) is an air-stable solid that does not lose the ethylene moiety even under reduced pressure. This feature has been exploited in the development of an ethylene sensor.[23] Copper adducts supported by weakly donating ligands are also excellent carbene and nitrene transfer catalysts.[6−9] In this paper, we report the use of 1,3,5-triazapentadienyl ligands with electron-withdrawing substituents such as fluoroalkyl and nitro groups on the ligand backbone and on an N-aryl group to stabilize copper ethylene adducts as thermally stable solids.

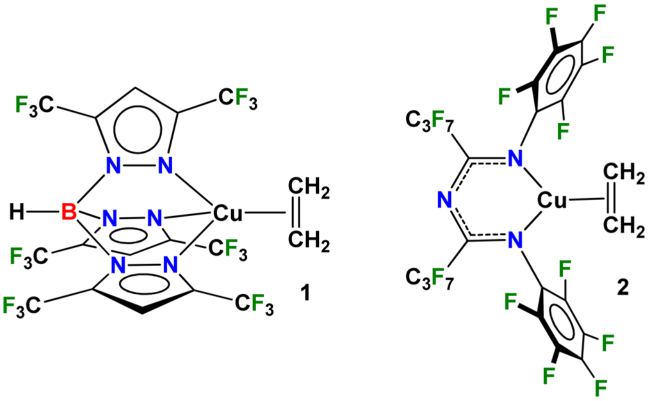


Figure 1. Copper(I) ethylene adducts of the highly fluorinated ligands $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$.

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■ RESULTS AND DISCUSSION

The synthesis of $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$ has been reported.[24] The related $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]H$, $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]H$, and $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$ were synthesized via a similar route using perfluoro-5-aza-4-nonene, the corresponding aniline $2\text{-}(CF_3)\text{-}C_6H_4NH_2$, $2\text{-}(NO_2)C_6H_4NH_2$, or $4\text{-}(NO_2)C_6H_4NH_2$, and triethylamine. The synthesis of $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)\text{-}N\}_2]H$ has been mentioned as a footnote in a publication, but no other details are available.[25] $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)\text{-}N\}_2]H$ (**3**) and $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$ (**4**) are yellow solids, while $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]H$ (**5**) and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$ (**6**) are white solids. The room-temperature ^{19}F NMR spectra of these compounds are somewhat complex, as noted earlier for other fluorinated 1,3,5-triazapentadienes, due to the possible existence of different conformers and tautomers in solution.[25−32]

These fluorinated triazapentadienes are weak monoprotic acids.[25] Their copper ethylene adducts can be prepared using copper(I) oxide as the copper source.[22] For example, reaction of **3** with Cu_2O and acetonitrile followed by the treatment of the resulting copper adduct (presumably, the copper(I) acetonitrile complex $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu\text{-}(NCCH_3)$, as established for other triazapentadienyl ligands)[31] with ethylene led to $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu\text{-}(C_2H_4)$ (**7**) in 58% yield (Figure 2). The analogous $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**8**) was synthesized via a similar route using the triazapentadiene **4**. Compounds **7** and **8** are thermally stable solids, do not lose ethylene during sample drying for chemical analysis, and can be handled in air briefly without decomposition. The ^{13}C and ^1H NMR signals of copper(I)-coordinated ethylene in $CDCl_3$ solution for **7** were observed at δ 85.4 and 3.51 ppm, respectively. The corresponding resonances of **8** appear at δ 87.6 and 3.68 ppm, respectively.

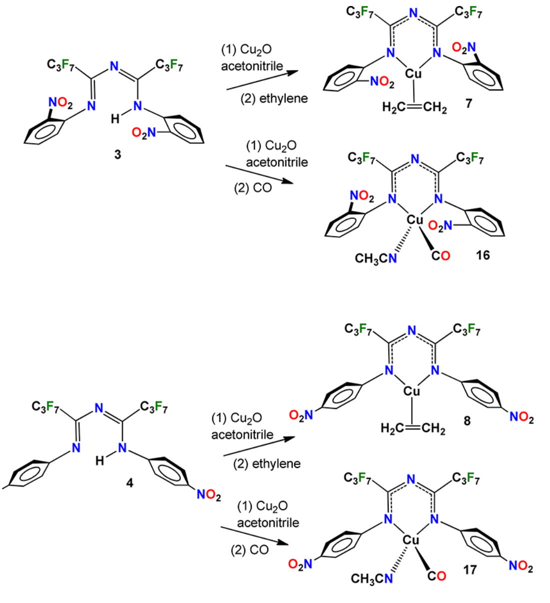

Figure 2. Synthesis of copper(I) ethylene complexes **7** and **8** and copper(I) carbonyl complexes **16** and **17**.

We have also investigated the copper ethylene adducts of $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]H$ (**5**) and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$ (**6**). $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]\text{-}Cu(C_2H_4)$ (**9**) and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu\text{-}(C_2H_4)$ (**10**) can be prepared via an route analogous to that described for **7** and **8**, using copper(I) oxide as the copper source. The synthetic route to **10** is outlined in Figure 3.

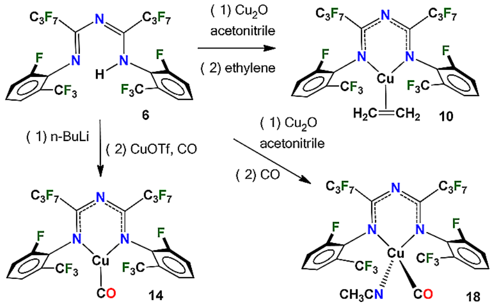

Figure 3. Synthesis of copper(I) ethylene and copper(I) carbonyl adducts of $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$.[22].

Compounds **9** and **10** are also thermally stable solids. The ^{13}C and ^1H NMR signals of copper(I)-coordinated ethylene in **9** and **10** and the corresponding resonances for several other adducts are summarized in Table 1. Compounds **7**−**10** show significant upfield shifts (or shifts toward lower frequency) relative to the free ethylene chemical shift values. For example, ^{13}C and ^1H NMR peaks of free ethylene appear at δ 123.3 and 5.40 ppm, respectively.[1]

Table 1. NMR Spectroscopic Data for Selected Copper Ethylene Complexes[a]

compd	$\delta(^1H)$ (ppm)	$\delta(^{13}C)$ (ppm)	ref
$[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**7**)	3.51	85.4	this work
$[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**8**)	3.68	87.6	this work
$[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (**9**)	3.48	85.3	this work
$[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (**10**)	3.59	85.2	this work
$[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ (**2**)	3.86	86.1	22
$[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (**13**)	3.37	86.0	8
$[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ (**11**)	2.91 (C_6D_6)	74.7	38
$[^tBu_2P(Me_3SiN)_2]Cu(C_2H_4)$ (**12**)	3.63 (at 223 K)	73.0 (C_6D_6)	41

[a] ^1H NMR data were acquired in $CDCl_3$ unless otherwise noted; ^{13}C NMR data have been reported in the same solvent. ^{13}C and ^1H NMR peaks of free ethylene appear at δ 123.3 and 5.40 ppm, respectively.

The upfield shift of ethylene has been linked to the metal→ethylene π back-bonding component, which creates a shielding effect.[33−37] In general, a survey of structurally authenticated Cu(I) monoethylene adducts (which also include cationic species) shows that their ethylene ^{13}C resonance appears in the range δ 89.5−73.0 ppm.[1] The ethylene carbon resonance in copper ethylene adducts **7**−**10** (δ 85.2−87.6 ppm, Table 1) appear at the higher chemical shift end of the spectrum, thus pointing to the presence of a relatively acidic and a poorly back-bonding metal site. This is not surprising, considering the weakly donating nature of triazapentadienyl ligands on **7**−**10** bearing fluoroalkyl and nitro groups. For comparison, the adduct $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ (**11**),[38]

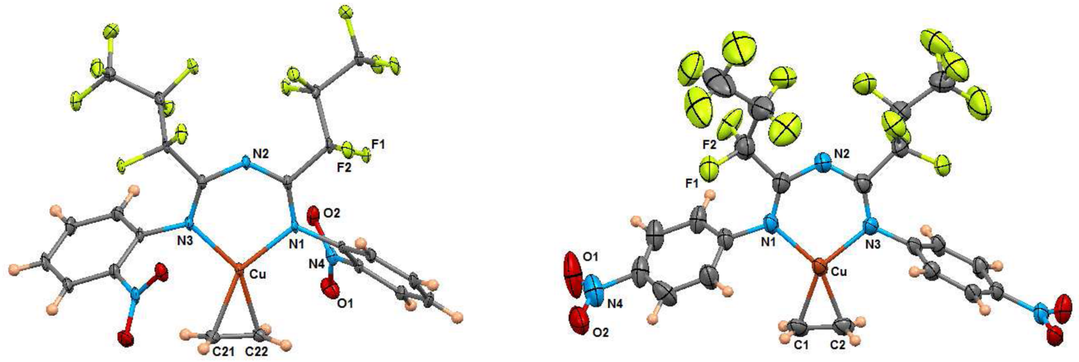

Figure 4. ORTEP diagrams of (left) $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**7**) and (right) $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**8**) (thermal ellipsoids set at 40% probability).

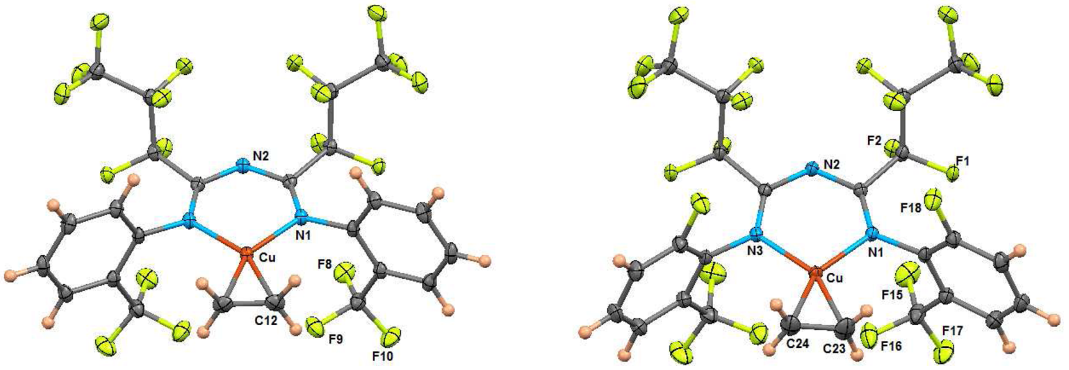

Figure 5. ORTEP diagrams of (left) $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (**9**) and (right) $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (**10**) (thermal ellipsoids set at 40% probability).

Table 2. X-ray Bond Distances (Å) and Bond Angles (deg) for Selected 1,3,5-Triazapentadienyl and 1,5-Diazapentadienyl Copper(I) Ethylene Complexes

compd	Cu−N (Å)	Cu−C (Å)	N−Cu−N (deg)	C−Cu−C (deg)	C═C (Å)	ref
$[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**7**)	1.953(2), 1.966(2)	2.021(3), 2.022(3)	96.78(9)	39.36(12)	1.361(4)	this work
$[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**8**)	1.955(5), 1.958(6)	2.027(8), 1.998(8)	96.4(2)	38.7(4)	1.332(12)	this work
$[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (**9**)	1.9509(16), 1.9509(16)	2.012(2), 2.012(2)	96.20(9)	39.34(13)	1.355(5)	this work
$[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (**10**)	1.9381(12), 1.9411(12)	1.9920(18), 2.0047(18)	96.64(5)	40.10(8)	1.370(3)	this work
$[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ (**2**)	1.946(2), 1.955(2)	2.010(3), 2.018(3)	96.66(9)	39.60(12)	1.364(4)	22
$[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (**13**)	1.9403(9), 1.9406(9)	1.9974(11), 2.0006(11)	95.55(4)	39.52(4)	1.3518(14)	8
$[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ (**11**)	1.908 (1), 1.917(2)	1.986(2), 1.992(2)	98.68(6)	40.13(9)	1.365(3)	38

which has a relatively electron-rich 1,5-diazapentadienyl ligand (and therefore, a relatively electron rich copper center), has its ethylene carbon resonance at δ 74.7 ppm. The ^{13}C chemical shift is a good indicator of a Cu−ethylene π-bonding interaction,[33−37] where weakly bound ethylene molecules usually show only a small upfield shift whereas metal adducts with strong σ/π bonds to ethylene (leading to "metallacyclopropane" type adducts) show a notable upfield shift (e.g., metal-bound ethylene carbon peaks appear at δ 104.9 ppm for $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ and δ 24.85 ppm for the N-heterocyclic carbene Ni(0) adduct $[Ni(^iPr_2Im)_2(C_2H_4)]$).[34,39,40]

The ^1H NMR signal of ethylene protons of copper(I) monoethylene adducts (which also include cationic species) have been observed in the range δ 5.22−2.92 ppm (cf., 5.40 ppm in $CDCl_3$ for free ethylene).[1] The ^1H NMR signal of copper(I)-coordinated ethylene in **7**−**10** was observed at δ 3.68−3.48 ppm. In these adducts, high upfield shifts relative to the free ethylene signal are very likely caused by *added* shielding contributions from the ring current effects of N-aryl groups flanking the ethylene moiety rather than just a result of Cu→ ethylene back-bonding.[1,7,21] For comparison, $[^tBu_2P(Me_3SiN)_2]Cu(C_2H_4)$ (**12**),[41] which has a relatively electron rich copper center and no flanking aryl groups, exhibits its ethylene proton signal at δ 3.63 ppm (in $CDCl_3$ at 223 K), which is similar to that observed in **7**−**10**, although they have very different ethylene carbon chemical shifts (δ 73.0 vs 85.2−87.6 ppm).

The X-ray structures of $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**7**), $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**8**), $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (**9**) and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (**10**) are illustrated in Figures 4 and 5. The key structural parameters are summarized in Table 2.

The basic features of **7**−**10** are similar to those observed for $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ (**2**; Figure 1)[22] and $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (**13**; Figure 6).[8] The 1,3,5-triazapentadienyl ligand coordinates to copper in a κ^2 fashion, although it is a versatile ligand that can adopt several different coordination modes.[28,30,42] Copper atoms have a trigonal-planar geometry. The N-aryl groups and CuN_3C_2 planes are fairly orthogonal to each other and flank the Cu ethylene moiety. Interestingly, trifluoromethyl groups on N-aryls of $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (**9**) occupy the same face of the CuN_3C_2 plane. $[N\{(C_3F_7)C(2\text{-F},6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (**10**) shows the same feature, while the nitro groups of $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (**7**) lie on opposite sides of the CuN_3C_2 plane. The ethylene groups adopt essentially a coplanar orientation with the 1,3,5-triazapentadienyl backbone (as is evident from small C_2Cu and CuN_2 dihedral angles, with the largest being 14.5° in **7**). These adducts show several intermolecular contacts such as H···F at less than 3 Å. Compound **8** also shows intermolecular Cu···O interactions at 2.84 Å between the copper center and nitro group of a neighboring molecule. The coplanar orientation of C_2Cu and CuN_2 facilitates enhanced interaction of the ethylene π^* orbital with the filled copper d orbitals.[38,43] We have observed a similar orientation in the adduct $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(3\text{-hexyne})$, in which calculations show that the coplanar N_2Cu and CuC_2 triangles are about 26 kJ/mol more stable compared to conformers with a 90° N_2Cu and CuC_2 dihedral angle.[44]

These adducts (except **8**, for which the crystal quality is not very satisfactory for detailed data analysis) show a small lengthening of C=C bond as a result of ethylene coordination to copper. For comparisons, the C=C bond length in free gaseous ethylene is estimated to be 1.3305(10) Å[45] while the corresponding distance from X-ray data is 1.313 Å.[1,46] Compounds **7**−**10** have weakly coordinating ligands and show slightly longer Cu−N bond distances in comparison to the corresponding distance of **11**, which has a relatively electron rich diazapentadienyl supporting ligand. The Cu−C distances are not significantly different (especially at the 3σ level of esd) for the compounds given in Table 2. Overall, NMR ethylene ^{13}C carbon resonance data (in solution at room temperature) and key structural parameters are similar in compounds **7**−**10**, and they are essentially identical with those observed even for **13**. Thus, these techniques are not sufficiently sensitive to detect effects of different substituents on N-aryl groups of the triazapentadienyl adducts given in Table 1. The ethylene proton chemical shifts, however, appear to have some correlation with the electron donating/withdrawing properties of the substituent on the aryl group, but this value is affected by aryl ring currents, which complicates the interpretation.

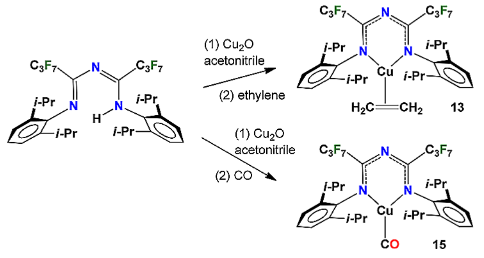

Figure 6. Preparation of $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ and $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$.[8,31]

The CO stretching frequency of metal carbonyls is a useful tool to examine the effect of different ligands on a metal site.[47−49] We have reported $[N\{(C_3F_7)C(2\text{-F},6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$ (**14**; Figure 3) and $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ (**15**, Figure 6), and they show clearly different ν_{CO} values at 2128 and 2109 cm^{-1}, respectively (Figure 6).[22,31] The high ν_{CO} value for $[N\{(C_3F_7)C(2\text{-F},6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$ is a sign of poor Cu→CO back-donation resulting from the presence of a relatively acidic copper site and a weakly donating $[N\{(C_3F_7)C(2\text{-F},6\text{-}(CF_3)C_6H_3)N\}_2]^-$. For comparison, $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]CuCO$ (which is the CO analogue of **11**),[50] which has a nonfluorinated, relatively electron rich diazapentadienyl ligand, displays the CO stretch at a much lower value: ν_{CO} 2071 cm^{-1}. Our attempts to prepare Cu−CO adducts using $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]H$ (**3**) or $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$ (**4**), Cu_2O, and CO (via a route similar to those followed for **7** and **8**) were successful but resulted in $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (**16**) and $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (**17**), which also contain a molecule of acetonitrile on the copper center (Figure 2). The complete displacement of acetonitrile leading to the formation of three-coordinate ethylene adducts **7** and **8**, while acetonitrile is retained during the formation of **16** and **17** with four-coordinate copper sites may be primarily a result of steric effects. The η^2-bound ethylene occupies more space at copper(I) in comparison to an end-on-bound CO group. In fact, the complete displacement of acetonitrile by CO has been observed when bulkier triazapentadienyl ligands are present on copper, as in $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ (**15**; Figure 6).[31] We also note that both $[Cu(CO)_3]^+$ and $[Cu(CO)_4]^+$ are known among copper carbonyls, while only $[Cu(C_2H_4)_3]^+$ (but not $[Cu(C_2H_4)_4]^+$) has been reported thus far in the Cu(I) ethylene family.[1,51]

Compounds **16** and **17** have been characterized by several spectroscopic methods and by X-ray crystallography. The molecular structure of **17** is depicted in Figure 7. Although we

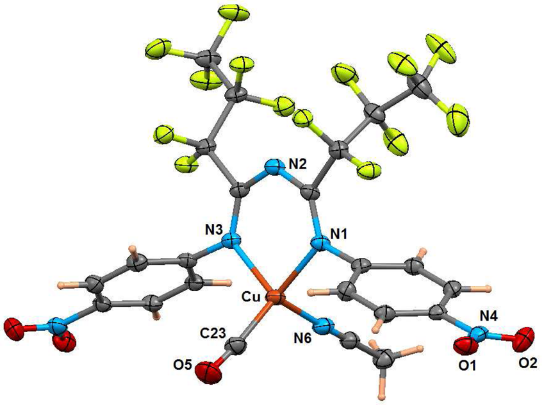

Figure 7. ORTEP diagram of $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (**17**) (thermal ellipsoids set at 40% probability). Selected bond lengths (Å) and angles (deg): Cu−N1 = 2.018(2), Cu−N3 = 2.018(2), Cu−N6 = 2.025(3), Cu−C23 = 1.832(3), N6−C21 = 1.139(4), O5−C23 = 1.123(4); N1−Cu−N3 = 92.37(9), N1−Cu−C23 = 120.94(12), N3−Cu−C23 = 113.46(12), N1−Cu−N6 = 104.56(10), N3−Cu−N6 = 105.30(9), C23−Cu−N6 = 116.73(12), Cu−N6−C21 = 176.8(2), Cu−C23−O5 = 174.5(3).

have solved the crystal structure of **16** (see the Supporting Information; which supports the identity as predicted from spectroscopic and analytical data), aryl groups and C_3F_7 suffer from positional disorder, affecting the overall quality. Both **16** and **17** feature pseudotetrahedral copper sites.

The Cu(I) carbonyl adducts **16** and **17** show a strong absorption band attributable to a CO stretch at 2106 and 2097 cm^{-1}, respectively. These values suggest relatively weak Cu→CO back-bonding and indicate the relatively weakly donating nature of the supporting ligands on copper. The corresponding signal in $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(CO)(NCCH_3)$ (**18**; Figure 3) is observed at a higher value, 2119 cm^{-1}, indicating the presence of an even more electron poor copper site. Thus, these findings suggest that $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ is a slightly weaker donor than $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]^-$ or $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]^-$. We are presently working on the isolation of related Cu(I) carbonyls without an acetonitrile ligand to obtain additional information about the donor properties of $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]^-$ or $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]^-$ and to see how they compare to those of ligands such as $[N\{(C_3F_7)C(Dipp)N\}_2]^-$.

Overall, we have reported the synthesis of easily isolable copper(I) ethylene adducts supported by 1,3,5-triazapentadienyl ligands with fluoroalkyl groups on the ligand backbone and nitro or fluorine substituents on the N-aryl groups. The ethylene carbon chemical shift in the ^{13}C NMR and key structural parameters around copper are very similar for adducts **7−10**. They all feature trigonal-planar copper sites and κ^2-bonded, U-shaped triazapentadienyl ligands. The Cu(I) carbonyl adducts **16** and **17** have pseudotetrahedral copper sites with copper bonded to an acetonitrile, CO, and the chelating triazapentadienyl ligand. A comparison of CO stretching frequencies suggests that $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ is a weaker donor than $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]^-$ or $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]^-$. Considering the catalytic activity displayed by $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$, adducts **7−10** may also effectively mediate carbene and nitrene transfer chemistry.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a drybox. Solvents were purchased from commercial sources, purified by using an Innovative Technology SPS-400 PureSolv solvent drying system or by distilling over conventional drying agents, and degassed by the freeze−pump−thaw method twice prior to use. Glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on JEOL Eclipse 500 spectrometer (^1H, 500.16 MHz; ^{13}C, 125.77 MHz; ^{19}F, 470.62 MHz). Proton and carbon chemical shifts are reported in ppm versus Me_4Si. ^{19}F NMR chemical shifts were referenced relative to external $CFCl_3$. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer. Elemental analyses were performed using a Perkin-Elmer Series II CHNS/O analyzer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. All materials were obtained from commercial vendors, with the exception of perfluoro-5-aza-4-nonene[52] and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$, which were synthesized by using published procedures.[22,24]

$[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]H$ (3). Perfluoro-5-aza-4-nonene (10.00 g, 23.0 mmol) was added dropwise to a mixture of triethylamine (9.70 mL, 69.3 mmol) and *o*-nitroaniline (6.40 g, 46.2 mmol) in ether (250 mL) at 0 °C. The solution was then stirred overnight. The resulting mixture was washed with 6 M HCl (64 mL) solution in an ice bath. The ether layer was then separated after filtration and washed with deionized water, and ether was removed under reduced pressure. The resulting material was dispersed in deionized water at 70 °C and filtered hot. The residue was collected and dried under reduced pressure overnight. It was recrystallized from hexane to give yellow crystals of $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]H$. Yield: 5.90 g (39%). Mp: 108−109 °C. ^{19}F NMR ($CDCl_3$): δ −80.02 (br, CF_3), −113.74 to −116.69 (m, α-CF_2), 123.99 (br, β-CF_2), −125.53 (br, β-CF_2). ^1H NMR ($CDCl_3$): δ 10.89 (br, 1H, N*H*), 8.35 (br, 1H, *H*-Ar), 8.30 (br, 1H, *H*-Ar), 7.96 (br, 1H, *H*-Ar), 7.78 (br, 1H, *H*-Ar), 7.53 (br, 1H, *H*-Ar), 7.37 (br, 1H, *H*-Ar), 7.22 (br, 1H, *H*-Ar), 6.99 (br, 1H, *H*-Ar), Anal. Calcd for $C_{20}H_9F_{14}N_5O_4$: C, 37.00; H, 1.40; N, 10.79. Found: C, 36.91; H, 1.25; N, 10.91.

$[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$ (4). Perfluoro-5-aza-4-nonene (2.50 g, 5.8 mmol) was added dropwise to a mixture of triethylamine (2.42 mL, 17.3 mmol) and *p*-nitroaniline (1.59 g, 11.5 mmol) in ether at 0 °C. The solution was then stirred overnight. The mixture was washed with 6 M HCl (25 mL) solution. The ether layer was then separated after filtration and washed with deionized water, and the ether was removed under reduced pressure. The obtained material was dispersed in deionized water at 70 °C and filtered, and the residue was collected and dried using reduced pressure. It was then recrystallized from hexane to give crystals of $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$. Yield: 1.50 g (40%). Mp: 143−145 °C. ^{19}F NMR ($CDCl_3$): δ −79.9 (apparent triplet, *J* = 12.4 Hz, 7.3 Hz, CF_3), −80.2 (apparent triplet, *J* = 11.0 Hz, 7.3 Hz, CF_3), −115.32 (br, α-CF_2), −116.53 (s, α-CF_2), −124.44 (br, β-CF_2), −126.07 (br, β-CF_2). ^1H NMR ($CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H, *H*-Ar), 8.18 (d, *J* = 8.4 Hz, 2H, *H*-Ar), 7.43 (d, *J* = 8.4 Hz, 2H, *H*-Ar), 7.23 (br, 1H, N*H*), 6.99 (d, *J* = 8.4 Hz, 2H, C_6H_4). Anal. Calcd for $C_{20}H_9F_{14}N_5O_4$: C, 37.00; H, 1.40; N, 10.79. Found: 36.92; H, 1.38; N, 10.72.

$[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]H$ (5). Perfluoro-5-aza-4-nonene (4.6 mmol) was added dropwise to a mixture of triethylamine (1.38 mL, 13.8 mmol) and aniline (9.2 mmol) in ether (100 mL), at 0 °C. After addition the solution was stirred overnight at room temperature. A nitrogen atmosphere was not necessary after this point during this ligand synthesis. The mixture was then filtered, and the filtrate was collected and washed first with 10% HCl and then twice with deionized water. The ether layer was separated and dried over $CaCl_2$ or Na_2SO_4. The solvent was removed under reduced pressure to give $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]H$. Pentane was added to the yellow oily product and the mixture cooled to −20 °C to give transparent squares upon standing after several days. Yield: 1.76 g (55%). Mp: 53−56 °C. ^{19}F NMR ($CDCl_3$): δ −61.23 (s, 3F, CF_3), −61.43 (s, 3F, CF_3), −80.14 (t, *J* = 8.7 Hz, 10.9 Hz, 3F, *o*-CF_3), −80.41 (t, *J* = 8.7 Hz, 3F, *o*-CF_3), −114.34 and −116.04 (br, 4F, α-CF_3), −123.76, −124.71, and −126.17 (s, 4F, β-CF_2). ^1H NMR ($CDCl_3$): δ 7.68 (apparent doublet, *J* = 7.8 Hz, 1H, *H*-Ar), 7.61 to 7.55 (m, 2H, *H*-Ar), 7.45 to 7.40 (apparent doublet, 2H, *H*-Ar), 7.37 (t, *J* = 7.5 Hz, 1H, *H*-Ar), 7.16 (t, *J* = 7.5 Hz, 1H, *H*-Ar), 7.05 (br, 1H, N*H*), 6.87 (d, 1H, *J* = 8.3 Hz, *o*-Ar). Anal. Calcd for $C_{22}H_9F_{20}N_3$: C, 38.00; H, 1.30; N, 6.04. Found: C, 37.54; H, 1.30; N, 5.86.

$[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (7). $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]H$ (0.20 g, 0.28 mmol) and Cu_2O (0.03 g, 0.20 mmol) were added to acetonitrile (20 mL) and refluxed for 12 h. The resulting solution was filtered through a bed of Celite. The filtrate was collected, and the solvent was removed under reduced pressure. Dichloromethane (3 mL) was added, ethylene (1 atm) was passed through for 2 min, and the mixture was stirred at room temperature for 5 h. Later hexane (3 mL) was added to the solution, ethylene was then passed through again, and the mixture was kept at −20 °C to give red crystals of $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$. Yield: 0.12 g (58%). Mp: 74−82 °C dec. ^{19}F NMR ($CDCl_3$): δ −80.21 (apparent triplet, *J* = 10.9 Hz, 9.5 Hz, CF_3), −80.28 (apparent triplet, *J* = 9.5 Hz, 9.6 Hz, CF_3), −106.56 (apparent quartet, *J* = 9.1 Hz, α-CF_2), −106.83 (apparent quartet, *J* = 9.1 Hz, α-CF_2), −123.35 (d, *J* = 13.6 Hz, β-CF_2). ^1H NMR ($CDCl_3$): δ 8.08 (d, *J* = 7.6 Hz, 2H, *H*-Ar), 7.64−7.61 (m, 2H, *H*-Ar), 7.32 (t, *J* = 7.6 Hz, 2H, *H*-Ar), 7.19 (d, *J* = 7.6 Hz, 2H, *H*-Ar), 3.51 (s, 4H, C_2H_4), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ selected peaks 85.4 (s, C_2H_4). Anal. Calcd for $C_{22}H_{12}F_{14}N_5O_4Cu$: C, 35.71; H, 1.63; N, 9.47. Found: C, 34.86; H 1.05; N 9.66.

$[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ (8). $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$ (0.30 g, 0.46 mmol) and Cu_2O (0.04 g, 0.28 mmol) were added to acetonitrile (25 mL) and refluxed for 12 h. The resulting solution was filtered through a bed of Celite. The filtrate was collected, and the solvent was removed under reduced pressure. Dichloromethane (3 mL) was added to it, ethylene was passed through for 2 min, and the mixture was stirred at room temperature for 5 h. Later hexane (3 mL) was added to the solution, ethylene was then passed through again, and the mixture was kept at −20 °C to give red crystals of $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$. Yield: 0.11 g (32%). Mp: 155 °C dec. ^{19}F NMR ($CDCl_3$): δ −80.2 (apparent triplet, J = 11.0 Hz, 11.0 Hz, CF_3), −104.04 (apparent quartet, J = 9.8 Hz, α-CF_2), −123.23 (br, β-CF_2). ^1H NMR ($CDCl_3$): δ 8.24 (d, J = 8.4 Hz, 4H, H-Ar), 7.13 (d, J = 9.2 Hz, 4H, H-Ar), 3.68 (s, 4H, C_2H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ selected peaks 87.6 (s, C_2H_4). Anal. Calcd for $C_{22}H_{12}F_{14}N_5O_4Cu$: C, 35.71; H, 1.63; N, 9.47. Found: C, 35.54; H, 1.44; N, 9.56.

$[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ (9). $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]H$ (0.25 g, 0.36 mmol) and Cu_2O (0.03 g, 0.22 mmol) were mixed in acetonitrile (15 mL) and refluxed at 90 °C overnight. The solution was filtered and concentrated to give an oily mixture. It was then dissolved in 5 mL of CH_2Cl_2/n-hexane (1/1), and the solution was saturated with ethylene and cooled to −20 °C. Yellow square rods of $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ appeared overnight at 5 °C. Yield: 0.21 g (75%). Mp: darkened at 85 °C, melted at 94−98 °C. ^{19}F NMR ($CDCl_3$): δ −60.14 (broad, 3F, o-CF_3), −60.41 (broad, 3F, o-CF_3), −80.30 (overlapped triplets, J = 10.2 Hz, 6F, CF_3), −104.26 to −108.51 (m, 4F, α-CF_2), −122.94 (s, 2F, β-CF_2), −123.78 (d, J = 10.9 Hz, 2F, β-CF_2). ^1H NMR ($CDCl_3$): δ 7.62 (d, J = 7.9 Hz, 2H, H-Ar), 7.50 (t, J = 6.9 Hz, 2H, H-Ar), 7.23 (t, 2H, H-Ar), 7.03 (d, J = 7.9 Hz, 2H, H-Ar) 3.48 (s, 4H, C_2H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): selected δ 85.3 (s, C_2H_4). Anal. Calcd for $C_{24}H_{12}N_3F_{20}Cu$: C, 36.68; H, 1.54; N, 5.35. Found: C, 36.68; H, 1.62; N, 5.30.

$[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(C_2H_4)$ (10). $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$ (0.25 g, 0.34 mmol), Cu_2O (0.03 g, 0.21 mmol), acetonitrile (5 mL), and THF (10 mL) were stirred overnight at 80 °C. The solution was cooled, filtered, and concentrated to give an oily mixture. It was dissolved in 5 mL of CH_2Cl_2/n-hexane (1/3), and ethylene was bubbled through for 2 min. The resulting solution was left to crystallize at −20 °C to afford yellow hexagons overnight. Yield: 0.25 g (90%). Mp: 102 °C dec. ^{19}F NMR ($CDCl_3$): δ −60.17 (s, 6F, o-CF_3), −80.59 (t, J = 9.8 Hz, 6F, CF_3), −106.40 and −109.30 (AB multiplet, J_{AB} = 279.5 Hz, 4F, α-CF_2), −121.51 (s, 2F, o-F), −123.20 (s, 4F, β-CF_2). ^1H NMR ($CDCl_3$): δ 7.44 (d, J = 7.8 Hz, 2H, m-Ar), 7.34−7.21 (m, 4H, m- and p-Ar), 3.59 (s, 4H, C_2H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): selected δ 85.2 (s, C_2H_4). Anal. Calcd for $C_{24}H_{10}F_{22}N_3Cu$ (contains 0.1 equiv of $NCCH_3$): C, 35.19; H, 1.26; N, 5.26. Found: C, 34.70; H, 1.40; N, 5.92.

$[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (16). $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]H$ (0.56 g, 0.86 mmol) and Cu_2O (0.06 g, 0.43 mmol) were added to acetonitrile, and the mixture was refluxed for 14 h. The resulting solution was filtered through a bed of Celite. The filtrate was collected, and the solvent was removed under reduced pressure. CH_2Cl_2 (3 mL) was added to it, CO was passed through for 4 min, and the mixture was stirred at room temperature for 5 h. Later hexane (5 mL) was added to the solution, CO was then passed through again, and the mixture was kept at −20 °C to give orange crystals of $[N\{(C_3F_7)C(2\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$. Yield: 0.32 g (47%). Mp: 65 °C −71 °C dec. ^{19}F NMR ($CDCl_3$): δ −80.29 (br, CF_3), −106.32 to −106.49 (m, α-CF_2), −123.16 to −123.29 (m, β-CF_2). ^1H NMR ($CDCl_3$): δ 8.05 (d, J = 7.7 Hz, 2H, Ar), 7.59 (br, 2H, Ar), 7.29 (t, J = 7.0 Hz, 2H, Ar), 7.20 (d, J = 7.0 Hz, 2H, Ar), 1.20 (s, 3H, $NCCH_3$). Anal. Calcd for $C_{23}H_{11}F_{14}N_6O_5Cu$: C, 35.38; H, 1.42; N, 10.76. Found: C, 34.75, H 1.33; N 10.50. IR (KBr, cm^{-1}), selected peak: 2106 (CO).

$[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ (17). $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]H$ (0.50 g, 0.77 mmol) and Cu_2O (0.06 g, 0.43 mmol) were added to acetonitrile and refluxed for 14 h. The resulting solution was filtered through a bed of Celite. The filtrate was collected, and the solvent was removed under reduced pressure. CH_2Cl_2 (3 mL) was added to it, CO was passed through for 4 min, and the mixture was stirred at room temperature for 5 h. Later hexane (5 mL) was added to the solution, CO was then passed through again, and the mixture was kept at −20 °C to give orange crystals of $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(CO)(NCCH_3)$ Yield: 0.25 g (41%). Mp: 126 °C −130 °C dec. ^{19}F NMR ($CDCl_3$): δ −80.23 (apparent triplet, J = 11 Hz, CF_3), −104.00 (br, α-CF_2), −123.15 (br, β-CF_2), ^1H NMR ($CDCl_3$): δ 8.19 (d, J = 8.6 Hz, 4H, Ar), 7.13 (d, J = 8.6 Hz, 4H, Ar), 2.05 (s, 3H, $NCCH_3$), Anal. Calcd for $C_{23}H_{11}F_{14}N_6O_5Cu$: C, 35.38; H, 1.42; N, 10.76. Found: C, 34.43; H, 1.36; N, 10.51. IR (KBr, cm^{-1}): selected peak 2097 (CO).

X-ray Crystallographic Data. Diffraction data were collected at T = 100(2) K. The data sets were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensity data were processed using the Saint Plus program. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14).[53] Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using XL. Absorption corrections were applied by using SADABS. Except for hydrogen atoms on the ethylene moiety, other hydrogen atoms were included at calculated positions and refined in a riding manner along with the attached carbons. Hydrogen atoms on ethylene were located in the difference Fourier maps and refined freely. $[N\{(C_3F_7)C(2\text{-}(CF_3)C_6H_4)N\}_2]Cu(C_2H_4)$ crystallized in the space group $P2_1/m$, and the molecule sits on a mirror plane containing N2, Cu, and the ethylene centroid (for a Z value of 2). The crystal of $[N\{(C_3F_7)C(4\text{-}(NO_2)C_6H_4)N\}_2]Cu(C_2H_4)$ diffracted poorly. It also displays disorder of C_3F_7 moieties, as is evident from the relatively high thermal parameters. A summary of the refinement details and the results are given in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving X-ray crystallographic data for **7**−**10** and **17** and the molecular structure and X-ray data for **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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