Inorg. Chem. **2006**, *45*, 8859–8861

Inorganic Chemistry
Communication

Syntheses of Highly Fluorinated 1,3,5-Triazapentadienyl Ligands and Their Use in the Isolation of Copper(I)–Carbonyl and Copper(I)–Ethylene Complexes

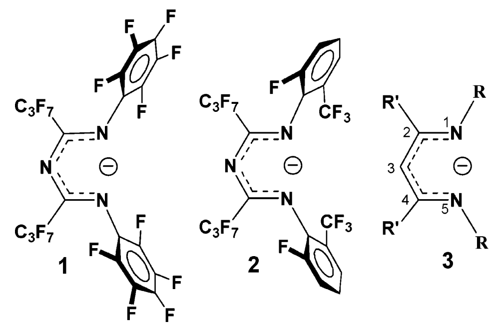
H. V. Rasika Dias,* Shreeyukta Singh, and Jaime A. Flores

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019

Received September 13, 2006

Fully fluorinated triazapentadienyl ligand $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ and the related $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ have been synthesized in good yield via a convenient route and used in the isolation of three- and four-coordinate copper(I)–carbon monoxide complexes. They show fairly high ν_{CO} values (>2100 cm^{-1}), indicating the presence of electron-poor Cu sites. The copper(I)–ethylene adduct $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$, featuring a three-coordinate Cu site, has also been synthesized using $[N\{(C_3F_7)C(C_6F_5)N\}_2]CuNCCH_3$ and C_2H_4.

Highly fluorinated ligands are of significant interest in metal coordination chemistry because they commonly improve the thermal stability, oxidative resistance, volatility, and fluorocarbon solubility of metal adducts.[1] This paper describes the chemistry of two such ligands of the 1,3,5-triazapentadienyl family.[2–8] In particular, we report a convenient route to the synthesis of the first *fully fluorinated* $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ ligand (**1**) and the related highly fluorinated analogue $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ (**2**). These 1,3,5-triazapentadienyl ligands are also closely related to the very popular 1,5-diazapentadienyl (also known as β-diketiminate, **3**) ligands.[9] However, perfluorinated ligands of the latter group have not been reported yet.[10,11]



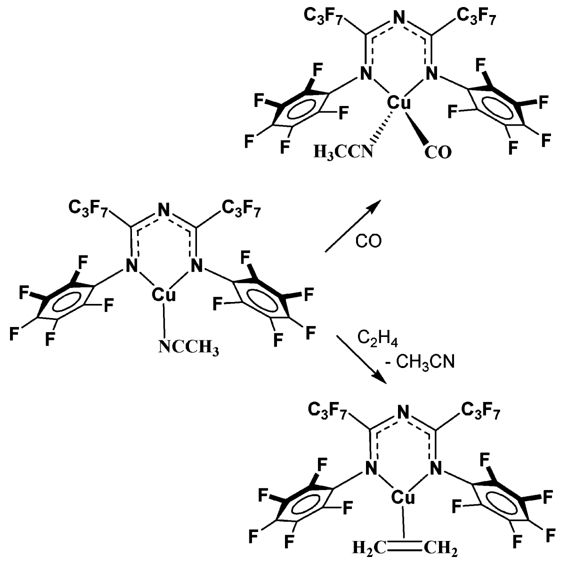
We also show that polyfluorinated $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ are good ligands for the stabilization of carbon monoxide and ethylene adducts of Cu. Structurally characterized Cu−CO and Cu−C_2H_4 adducts of 1,3,5-triazapentadienyl or 1,5-diazapentadienyl supporting ligands are rare. $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$[12] and $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$[4] are the only such examples in the literature.

* To whom correspondence should be addressed. E-mail: dias@uta.edu.

(1) Thrasher, J. S.; Strauss, S. H. *Inorganic Fluorine Chemistry: Toward the 21st Century*; ACS Symposium Series 555; American Chemical Society: Washington, DC, 1994. Fekl, U.; van Eldik, R.; Lovell, S.; Goldberg, K. I. *Organometallics* **2000**, *19*, 3535−3542 and references cited therein.
(2) Siedle, A. R.; Webb, R. J.; Behr, F. E.; Newmark, R. A.; Weil, D. A.; Erickson, K.; Naujok, R.; Brostrom, M.; Mueller, M.; Chou, S.-H.; Young, V. G., Jr. *Inorg. Chem.* **2003**, *42*, 932−934.
(3) Siedle, A. R.; Webb, R. J.; Brostrom, M.; Newmark, R. A.; Behr, F. E.; Young, V. G., Jr. *Organometallics* **2004**, *23*, 2281−2286.
(4) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 5786−5788.
(5) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 7396−7402.
(6) Dias, H. V. R.; Singh, S.; Cundari, T. R. Angew. *Chem., Int. Ed.* **2005**, *44*, 4907−4910.
(7) Dias, H. V. R.; Singh, S. *Dalton Trans.* **2006**, 1995−2000.
(8) Other examples of fluorinated 1,3,5-triazapentadienyl systems: Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1994**, 3615−3620. Bottrill, M.; Goddard, R.; Green, M.; Hughes, R. P.; Lloyd, M. K.; Taylor, S. H.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 1150−1155. Aris, D. R.; Barker, J.; Phillips, P. R.; Alcock, N. W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1997**, 909−910. Robinson, V.; Taylor, G. E.; Woodward, P.; Bruce, M. I.; Wallis, R. C. *J. Chem. Soc., Dalton Trans.* **1981**, 1169−1173. Brown, H. C.; Schuman, P. D. *J. Org. Chem.* **1963**, *28*, 1122−1227.
(9) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066.
(10) Examples of partially fluorinated 1,5-diazapentadienyl systems: Bottrill, M.; Goddard, R.; Green, M.; Hughes, R. P.; Lloyd, M. K.; Taylor, S. H.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 1150−1155. Shreider, V. A. *Inorg. Chim. Acta* **1982**, *64*, L101−L103. Sharma, R. K.; Singh, Y.; Rai, A. K. *Main Group Met. Chem.* **2000**, *23*, 777−780. Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909−3916. Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafe, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton Trans.* **2003**, 1083−1093. Sharma, R. K.; Sharma, R. K.; Rai, A. K.; Singh, Y. *Main Group Met. Chem.* **2003**, *26*, 59−65. Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2005**, *24*, 6250−6259. Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Dalton Trans.* **2005**, 273−277. Vidovic, D.; Jones, J. N.; Moore, J. A.; Cowley, A. H. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2888−2892. Vidovic, D.; Moore, J. A.; Jones, J. N.; Cowley, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 4566−4567. Tang, L.-M.; Duan, Y.-Q.; Li, X.-F.; Li, Y.-S. *J. Organomet. Chem.* **2006**, *691*, 2023−2030. Yang, Z.; Zhu, H.; Ma, X.; Chai, J.; Roesky, H. W.; He, C.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem.* **2006**, *45*, 1823−1827. Chiong, H. A.; Daugulis, O. *Organometallics* **2006**, *25*, 4054−4057.
(11) For Cu−CO complexes based on fluorinated 1,5-diazapentadienyl ligands, see: Laitar, D. S.; Mathison, C. J. N.; Davis, W. M.; Sadighi, J. P. *Inorg. Chem.* **2003**, *42*, 7354−7356.
(12) Dai, X.; Warren, T. H. *Chem. Commun.* **2001**, 1998−1999.

10.1021/ic061739y CCC: $33.50
Published on Web 10/07/2006

Scheme 1. Cu−CO and Cu−C_2H_4 Complexes of $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$



$[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ was prepared by the reaction of $C_6F_5NH_2$, $C_3F_7CF{=}NC_4F_9$, and triethylamine in a 2:1:3 molar ratio. It was isolated as a colorless crystalline solid in good yield. It is soluble in solvents such as toluene, tetrahydrofuran (THF), CH_2Cl_2, and Et_2O and sparingly soluble in hexane. Earlier, we and others reported the synthesis of triazapentadienes such as $[N\{(C_3F_7)C(R)N\}_2]H$ (e.g., R = Dipp, Ph) from the reaction of excess primary amines with $C_3F_7CF{=}NC_4F_9$.[2,4,6] However, this route did not give satisfactory results for the triazapentadienes such as $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$. This is perhaps due to the low basicity of $C_6F_5NH_2$. In any event, the new procedure we describe here is more *economical* and better suited for various triazapentadienes involving electron-deficient primary amines. $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$ was also synthesized using the newer method involving triethylamine.

Treatment of $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ with Cu_2O in CH_3CN serves as a cheaper and more convenient route to introduce a Cu ion into the ligand system. The resulting $[N\{(C_3F_7)C(C_6F_5)N\}_2]CuNCCH_3$ is a useful precursor for various other Cu-containing derivatives. For example, the reaction of $[N\{(C_3F_7)C(C_6F_5)N\}_2]CuNCCH_3$ with carbon monoxide (1 atm) in CH_2Cl_2 leads to $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(NCCH_3)$ (Scheme 1). Interestingly, CH_3CN remains bonded to the Cu^I site in the carbonyl adduct, as is evident from the spectroscopic and X-ray crystallographic data (vide infra). $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(CO)(NCCH_3)$ was also prepared from a similar route, and it also retains CH_3CN. In contrast, $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ was obtained free of CH_3CN.[4] However, the triazapentadienyl ligand in this adduct is more electron-rich and has sterically demanding substituents on both the 2 and 6 positions of the *N*-aryl groups.

The X-ray structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(NCCH_3)$ (Figure 1) shows that the Cu center is four-coordinate and adopts a pseudotetrahedral geometry. The triazapentadienyl ligand binds to the metal center in a κ^2 fashion. The Cu−C−O moiety is essentially linear with an angle of 176.68(16)°. The Cu−C distance is 1.8333(17) Å.

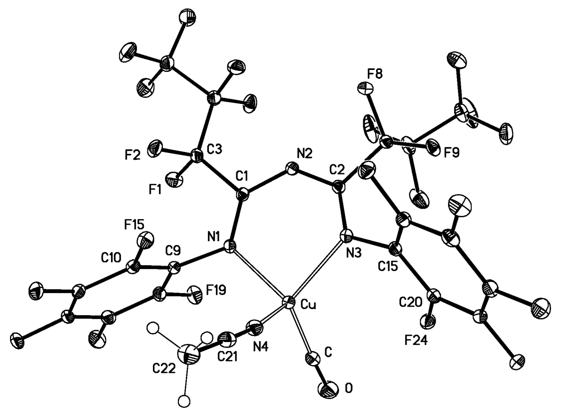
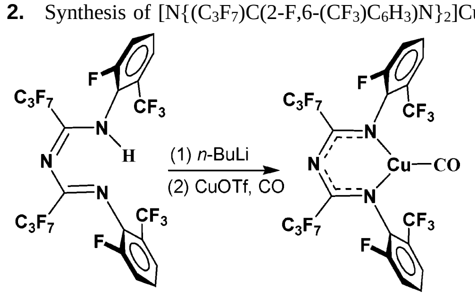


Figure 1. Molecular structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(NCCH_3)$. Selected bond lengths (Å) and angles (deg): Cu−C 1.8333(17), Cu−N4 2.0183(14), Cu−N1 2.0232(12), Cu−N3 2.0499(12), O−C 1.124(2); N1−Cu−N3 91.04(5), O−C−Cu 176.68(16).

Scheme 2. Synthesis of $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$



$[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(CO)(NCCH_3)$ also features a four-coordinate Cu center (see the Supporting Information). The Cu−C distance and Cu−C−O angle are 1.844(4) Å and 177.1(4)°, respectively.

Three-coordinate $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$ can be synthesized using a different route involving the Li salt $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Li$, CuOTf, and carbon monoxide (1 atm) in THF (Scheme 2). $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$ crystallizes in the $P2_1/n$ space group with two chemically similar molecules in the asymmetric unit (the relative orientation of the C_3F_7 groups is the only key difference between the two). It features a trigonal-planar Cu site (Figure 2) and a linear Cu−CO moiety as in $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$.

The IR spectra show that the ν_{CO} bands of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(NCCH_3)$ and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(CO)(NCCH_3)$ appear at 2108 and 2119 cm^{-1}, respectively. Three-coordinate $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$ has a much higher ν_{CO} at 2128 cm^{-1}. Thus, the CH_3CN ligand in these molecules seems to reduce the acidity at the Cu site. However, ν_{CO} values of all of these adducts are fairly high and closer to that of the free carbon monoxide (2143 cm^{-1}), indicating the weakly donating nature of the polyfluorinated triazapentadienyl ligands and the presence of acidic Cu sites with poor Cu → CO π back-bonding. The ν_{CO} data of three-coordinate 1,3,5-triazapentadienyl and 1,5-diazapentadienyl Cu−CO adducts (*albeit* limited) indicate that triazapentadienyl ligands are weaker donors (see the Supporting Information, Table S9).

We have also synthesized a copper(I)−ethylene adduct of the 1,3,5-triazapentadienyl family. Treatment of $[N\{(C_3F_7)C-$

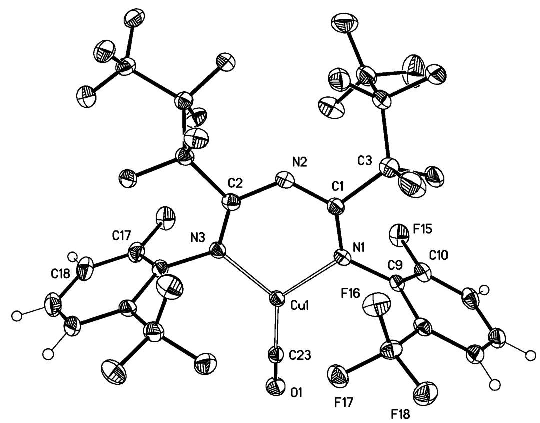


Figure 2. Molecular structure of $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$. Selected bond lengths (Å) and angles (deg) of molecule **1**: Cu1−C23 1.813(5), Cu1−N3 1.956(3), Cu1−N1 1.962(3); N3−Cu1−N1 95.74(14), O1−C23−Cu1 178.4(4). Selected bond lengths (Å) and angles (deg) of molecule **2**: Cu2−C46 1.818(5), Cu2−N6 1.952(3), Cu2−N4 1.959(3); N6−Cu2−N4 96.00(14), O2−C46−Cu2 178.3(4).

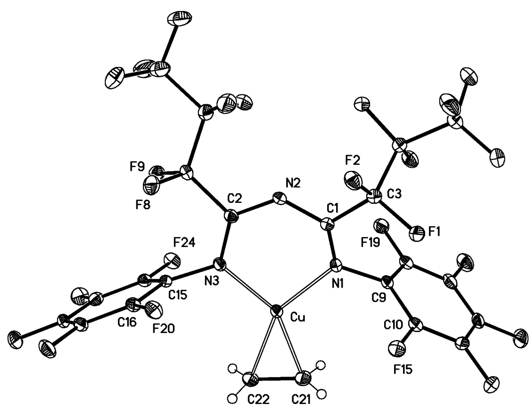


Figure 3. Molecular structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$. Selected bond lengths (Å) and angles (deg): Cu−N3 1.946(2), Cu−N1 1.955(2), Cu−C21 2.010(3), Cu−C22 2.018(3), C21−C22 1.364(4); N3−Cu−N1 96.66(9).

$(C_6F_5)N\}_2]CuNCCH_3$ with ethylene (1 atm) in CH_2Cl_2 gave the corresponding $Cu-C_2H_4$ complex. The ^{1}H NMR spectrum of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ in C_6D_6 shows the ethylene signal at δ 3.27, which is significantly upfield-shifted relative to the corresponding peak of free ethylene (δ 5.24).[13] Related diazapentadienyl system $[HC\{(CH_3)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ (containing relatively electron-rich ligand) displays an ethylene signal at an even more shielded region, δ 2.91.[12] The treatment of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ with excess ethylene leads to the disappearance of the bound ethylene signal, indicating fast exchange with free ethylene on the NMR time scale. The ethylene C signal of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ in the $^{13}C\{^1H\}$ NMR spectrum is observed at δ 86.1. The corresponding peak in free ethylene appears at a much higher frequency (δ 123.5).[13]

The X-ray structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ (Figure 3) shows that the ethylene molecule coordinates to Cu^I in a typical η^2 fashion. The ethylene protons were located on the difference map and refined isotropically. The C═C bond distance of the coordinated ethylene (1.364(4) Å) is identical with that found in $[HC\{(CH_3)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ [1.365(3) Å][12] and marginally longer as compared to that of free ethylene [1.313 (exptl) and 1.333 (calcd) Å].[14,15] The N−Cu distances of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ [1.946(2) and 1.955(2) Å] are much shorter compared to those observed for $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(CH_3CN)$. This may be primarily a steric effect because the former has a three-coordinate metal site (vs a four-coordinate site in the latter). In fact, the Cu−N distances of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ are similar to those seen with three-coordinate $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$ featuring weakly donating ligands.

The stability of these Cu−CO and $Cu-C_2H_4$ adducts warrants some comment. $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(NCCH_3)$, $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$, and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ can be dried under reduced pressure without losing carbon monoxide or ethylene, but $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(CO)(NCCH_3)$ loses carbon monoxide somewhat easily under these conditions to give $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuNCCH_3$. The easy loss of a ligand (in this case, carbon monoxide) in the latter compound may be a steric effect of having a bulkier triazapentadienyl ligand. The reason for the retention of CH_3CN over carbon monoxide is less clear and may be the result of having a more acidic Cu center. The CH_2Cl_2 *solutions* of the Cu−CO adduct, and to a lesser degree the ethylene adduct, turn green with time when exposed to air. However, *solid* samples of these Cu−CO and $Cu-C_2H_4$ adducts can be handled in air for short periods without any apparent decomposition.

Overall, we describe the synthesis of two highly fluorinated, weakly donating, 1,3,5-triazapentadienyl ligands and their copper(I)−carbonyl and −ethylene complexes. $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$ do not have C−H bonds near the metal coordination site. Such ligands would be particularly suitable to support reactive metal complexes. Further studies of the coordination chemistry of these fully and partially fluorinated triazapentadienyl ligands and the catalytic applications of their metal adducts are presently underway.

Acknowledgment. This work has been supported by the Robert A. Welch Foundation (Grant Y-1289) and the National Science Foundation (Grant CHE 0314666). We are grateful to 3M for providing us with a sample of $N(C_4F_9)_3$.

Supporting Information Available: X-ray crystallographic data for $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(CO)(CH_3CN)$, $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]Cu(CO)(NCCH_3)$, $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]CuCO$, and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ and experimental details for free ligand and Cu complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061739Y

(13) Dias, H. V. R.; Lu, H.-L.; Kim, H.-J.; Polach, S. A.; Goh, T. K. H. H.; Browning, R. G.; Lovely, C. J. *Organometallics* **2002**, *21*, 1466−1473.
(14) Van Nes, G. J. H.; Vos, A. *Acta Crystallogr., Sect. B* **1979**, *35*, 2593−601.
(15) Krossing, I.; Reisinger, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 5725−5728 and references cited therein.