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Communication

Copper(I) Complexes of Fluorinated Triazapentadienyl Ligands: Synthesis and Characterization of $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$ (Where L = $NCCH_3$, $CNBu^t$, CO; Dipp = 2,6-Diisopropylphenyl)

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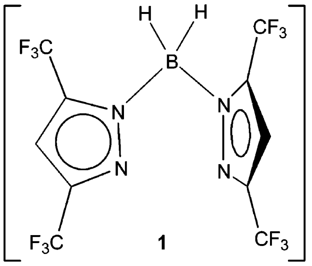
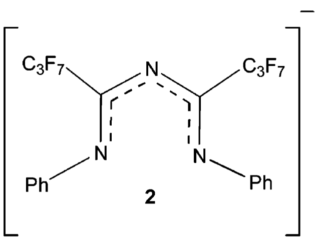
Sterically demanding triazapentadiene $[N\{(C_3F_7)C(Dipp)N\}_2]$ H has been synthesized in good yield. It features a W-shaped ligand backbone in the solid state. $[N\{(C_3F_7)C(Dipp)N\}_2]H$ reacts with copper(I) oxide in acetonitrile leading to $[N\{(C_3F_7)C(Dipp)N\}_2]$-$CuNCCH_3$. This copper adduct serves as an excellent precursor to obtain thermally stable $[N\{(C_3F_7)C(Dipp)N\}_2]CuCNBu^t$ and $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$. IR spectroscopic data of these copper(I) isocyanide ($\nu_{CN} = 2176$ cm^{-1}) and copper(I) carbonyl ($\nu_{CO} = 2109$ cm^{-1}) complexes indicate that the $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ ligand is a fairly weak donor.

Over the past few years, we have reported the chemistry of highly fluorinated ligands such as $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ (**1**) and $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$.[1−4] Their metal adducts display very interesting properties. For example, the copper(I) carbonyl and ethylene adducts, $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$[5] and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Cu(\eta^2\text{-}C_2H_4)$,[6] are air and thermally stable solids. Bis(pyrazolyl)borate complexes such as $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]Cu(2,4,6\text{-collidine})$ show rare blue luminescence.[7] Some of these copper(I) adducts also serve as excellent oxidation[8] and aziridination catalysts.[6]



1

$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$



2

$[N\{(C_3F_7)C(Ph)N\}_2]^-$

Fluorinated triazapentadienyl ligands[9] such as $[N\{(C_3F_7)C(Ph)N\}_2]^-$ (**2**) may be compared to bis(pyrazolyl)borates such as $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$. Both types are highly fluorinated, monoanionic, nitrogen based donors capable of forming six-membered metallacycles with metal ions. The coordination chemistry of triazapentadienyl ligands is therefore of comparative interest. Recently, Siedle et al. described a convenient route to these ligands starting with $(C_4F_9)_3N$.[9] Several metal adducts of $[N\{(C_3F_7)C(Ph)N\}_2]^-$ including copper(II) derivative $[N\{(C_3F_7)C(Ph)N\}_2]_2Cu$ were also described.[9,10] Other reports in this arena prior to their work concern the use of $[N\{(R)C(H)N\}_2]^-$ (R = fluoro alkyl) as a ligand for few late transition metal ions and gallium.[11] The scarcity of information on metal triazapentadienyl complexes and the interesting results we obtained using related fluorinated ligands prompted us to explore the metal coordination chemistry of fluorinated triazapentadienes in more detail.

In this paper, we report the synthesis of a sterically demanding, fluoroalkyl substituted, triazapentadiene ligand $[N\{(C_3F_7)C(Dipp)N\}_2]H$ (where Dipp = 2,6-diisopropylphenyl), and its utility in copper(I) chemistry. The triazapentadiene $[N\{(C_3F_7)C(Dipp)N\}_2]H$ can be obtained in 76% yield from the reaction of 2,6-diisopropylaniline with the perfluoro-5-aza-4-nonene ($C_3F_7{-}CF{=}N{-}C_4F_9$)[9] in ether (see Supporting Information).[12] It is a colorless, crystalline solid. The room

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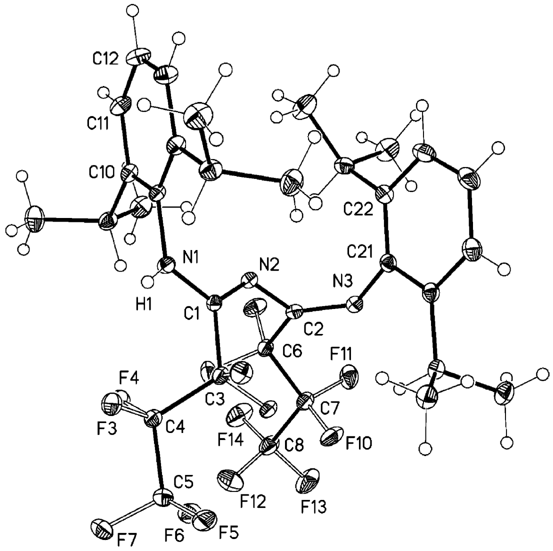

Figure 1. Molecular structures of $[N\{(C_3F_7)C(Dipp)N\}_2]H$. Selected bond distances (Å) and angles (deg): N(1)−C(1) 1.3523(14), N(1)−C(9) 1.4419(14), N(2)−C(1) 1.2714(15), N(2)−C(2) 1.3868(14), N(3)−C(2) 1.2651(15), N(3)−C(21) 1.4366(15), C(1)−C(3) 1.5417(15), C(2)−C(6) 1.5382(16); C(1)−N(1)−C(9) 124.11(10), C(1)−N(2)−C(2) 129.08(10), C(2)−N(3)−C(21) 119.90(10), N(2)−C(1)−N(1) 122.54(10), N(2)−C(1)−C(3) 125.37(10), N(1)−C(1)−C(3) 112.05(9), N(3)−C(2)−N(2) 128.20(11), N(3)−C(2)−C(6) 116.09(10), N(2)−C(2)−C(6) 114.55(9).

temperature ^{1}H and ^{19}F NMR spectra of $[N\{(C_3F_7)C(Dipp)N\}_2]H$ in $CDCl_3$ are fairly complex. For example, the ^{1}H NMR signals due to the isopropyl $CH(C\mathit{H}_3)_2$ and $C\mathit{H}(CH_3)_2$ protons appear as nine sets of doublets and four sets of multiplets, respectively. This is likely a result of hindered rotation of the aryl groups at room temperature, as well as due to the presence of relatively rigid conformational isomers (e.g., molecules with U- or W-shaped backbones).[10] The X-ray crystal structure of $[N\{(C_3F_7)C(Dipp)N\}_2]H$ is illustrated in Figure 1. It crystallizes in the form where the acidic proton is bonded to one of the terminal nitrogen atoms. The backbone adopts a W-shaped configuration.

The copper(I) acetonitrile complex $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ is synthesized by treating the free ligand with copper(I) oxide in acetonitrile.[13] It can be isolated as an orange, crystalline product. Solid samples and acetonitrile solutions of $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ can be handled in air for short periods without any apparent signs of decomposition. The ^{1}H NMR spectrum of $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ in $CDCl_3$ shows just two sets of doublets for $CH(C\mathit{H}_3)_2$ and a septet for $C\mathit{H}(CH_3)_2$. This is in sharp contrast to the complex spectrum observed for the free ligand. $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ crystallizes in the $P2_12_12_1$ space group with three chemically similar, crystallographically independent molecules in the crystal lattice (Figure 2). The triazapentadienyl ligand acts as a chelating, bidentate donor toward copper(I). The copper center adopts trigonal planar geometry. The average Cu−N(CCH$_3$) bond length of 1.867(3) Å is similar to the corresponding distance of 1.860(3) Å observed for the nonfluorinated diazapentadieneyl complex $[PhC\{HC(Dipp)N\}_2]CuNCCH_3$.[14]

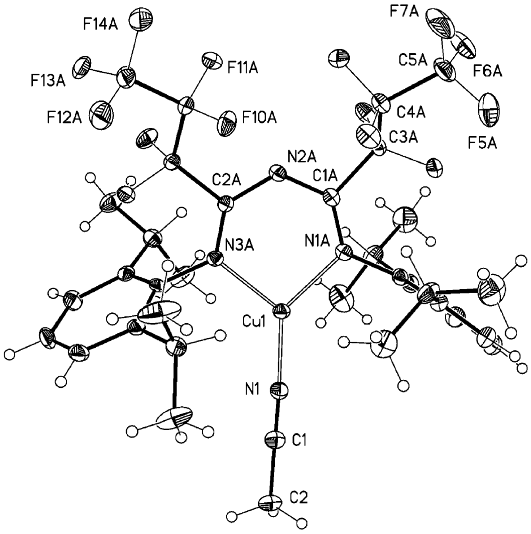

Figure 2. Molecular structure of $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$. Only one of the three molecules in the asymmetric unit is shown. Selected bond distances (Å) and angles (deg): Cu(1)−N(1) 1.864(3), Cu(1)−N(1A) 1.957(3), Cu(1)−N(3A) 1.964(2), N(1)−Cu(1)−N(1A) 135.53(11), N(1)−Cu(1)−N(3A) 128.36(11), N(1A)−Cu(1)−N(3A) 95.74(10), C(1)−N(1)−Cu(1) 171.5(3), N(1)−C(1)−C(2) 178.0(4).

Copper acetonitrile adducts are useful precursors for various copper containing derivatives. For example, the copper(I) isocyanide complex $[N\{(C_3F_7)C(Dipp)N\}_2]CuCNBu^t$ could be obtained by reacting $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ with *tert*-butyl isocyanide.[15] The ^{1}H NMR data corresponding to the triazapentadienyl moiety of $[N\{(C_3F_7)C(Dipp)N\}_2]CuCNBu^t$ are similar to those observed for the acetonitrile adduct $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$, suggesting the presence of a κ^2-coordinated ligand. A singlet at δ 1.33 in the ^{1}H NMR spectrum corresponding to the *tert*-butyl group protons, as well as a strong absorption band in the IR spectrum at 2176 cm^{-1} (compared to ν_{CN} of free $CNBu^t = 2138$ cm^{-1}), indicates the formation of the expected copper isocyanide adduct. The ν_{CN} band shows a shift of about 38 cm^{-1} as a result of coordination to the copper(I) center. For comparison, the ν_{CN} bands of $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCNBu^t$ and $\{[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCNBu^t\}_2$ appear at a much higher value (2196 cm^{-1}).[16] Complexes with more electron rich metal sites as in $[HB(Pz)_3]CuCNBu^t$ display the ν_{CN} band at a relatively low frequency (2155 cm^{-1}).[17]

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(12) $[N\{C_3F_7)C(Dipp)N\}_2]H$: yield (76%), mp 88−90 °C.

(13) $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$: yield (69%), mp 89 °C. ^{19}F NMR ($CDCl_3$, 25 °C): δ −122.5 (s, β-CF_2), −106.5 (apparent quartet, J_{FF} = 12, 8 Hz, α-CF_2), −80.3 (apparent triplet J_{FF} = 12, 8 Hz, CF_3). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.10 (d, $^3J_{HH}$ = 5.0 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.23 (d, $^3J_{HH}$ = 10.5 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.74 (s, 3H, $NCC\mathit{H}_3$), 3.03 (heptet, $^3J_{HH}$ = 6.7 Hz, 4H, $C\mathit{H}(CH_3)_2$), 7.04 (m, 6H, m- and p-Ar).

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(15) $[N\{(C_3F_7)C(Dipp)N\}_2]CuCNBu^t$: yield (88%), mp 92 °C. ^{19}F NMR ($CDCl_3$, 25 °C): δ −122.6 (s, β-CF_2), −106.2 (s, α-CF_2), −80.2 (s, CF_3). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.12 (d, $^3J_{HH}$ = 6.5 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.22 (d, $^3J_{HH}$ = 6.5 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.33 (s, 9H, Bu^t), 3.02 (heptet, $^3J_{HH}$ = 6.5 Hz, 4H, $C\mathit{H}(CH_3)$), 7.05 (m, 6H, m- and p-Ar). IR (KBr, cm^{-1}): 2176 (CN).

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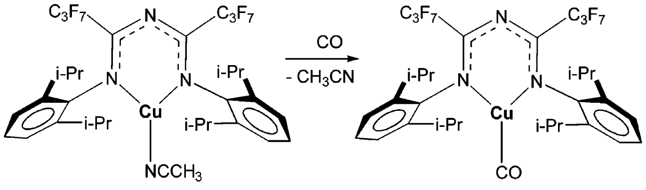
The copper(I) carbonyl complex could be obtained either by treating $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ with CO or from a reaction between $[N\{(C_3F_7)C(Dipp)N\}_2]Li$ and CuOTf in the presence of CO.[18] It is a thermally stable, pale yellow solid. $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ can be handled in air for a few minutes without any apparent signs of decomposition. $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ displays a strong absorption band in the IR at 2109 cm^{-1}.



$[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ **$[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$**

We have used IR data of copper carbonyl adducts extensively to assess the donor properties of fluorinated tris(pyrazolyl)borate ligands.[19] This high ν_{CO} suggests that the $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ ligand is a fairly weak donor. It is also a much weaker donor compared to the comparatively substituted diazapentadineyl ligands such as $[HC\{(CF_3)C(3,5\text{-}(Me)_2Ph)N\}_2]^-$ as evident from the CO stretching frequency of $[HC\{(CF_3)C(3,5\text{-}(Me)_2Ph)N\}_2]CuCO$ which appears at 2097 cm^{-1}.[20] For comparison, copper(I) carbonyl adducts of the fluorinated tris(pyrazolyl)borate ligands $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ show CO stretching frequency bands at 2103 and 2137 cm^{-1}, respectively.[19]

The X-ray structure of $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ shows that the copper center is three coordinate (Figure 3). The triazapentadienyl ligand binds to the metal center in a κ^2-fashion. The Cu−C−O moiety is essentially linear with the Cu−C−O angle of 178.3(2)°. The Cu−C distance is 1.782(2) Å. Copper carbonyl compounds such as this three-coordinate $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ are rare.[20−22] In most cases the CO ligand is highly labile or compounds decompose easily in air. For example, $[HC\{(CF_3)C(3,5\text{-}(Me)_2Ph)N\}_2]CuCO$ and even more fluorine rich $[HC\{(CF_3)C(3,5\text{-}(CF_3)_2Ph)N\}_2]CuCO$ (ν_{CO} = 2110 cm^{-1}) have not been obtained as thermally stable solids.[20] Thus far, we have not been able to isolate copper carbonyl adducts of the highly fluorinated bis(pyrazolyl)borate $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ either.

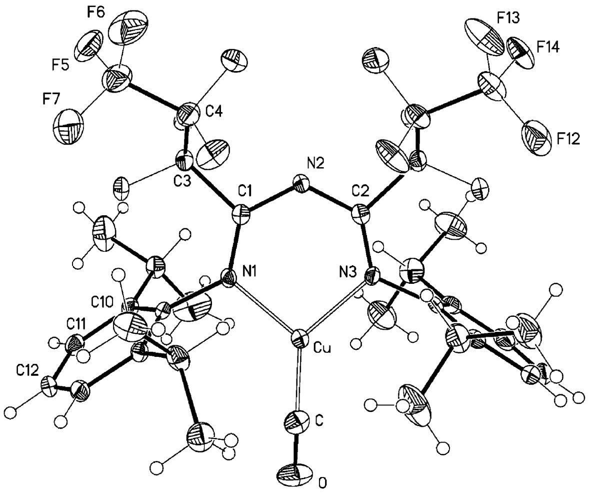


Figure 3. Molecular structure of $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$. Selected bond distances (Å) and angles (deg): C−O 1.138(2), C−Cu 1.782(2), Cu−N(3) 1.9391(15), Cu−N(1) 1.9410(15), C(1)−N(1) 1.303(2), C(1)−N(2) 1.338(2), C(1)−C(3) 1.546(3), C(2)−N(3) 1.301(2), C(2)−N(2) 1.335(2), C(2)−C(6) 1.551(3); O−C−Cu 178.3(2), N(1)−C(1)−N(2) 128.38(17), N(3)−C(2)−N(2) 129.20(17), C−Cu−N(3) 133.31(8), C−Cu−N(1) 130.51(8), N(3)−Cu−N(1) 96.16(6), C(1)−N(1)−C(9) 127.56(15), C(1)−N(1)−Cu 120.68(12), C(9)−N(1)−Cu 111.68(11), C(2)−N(2)−C(1) 125.11(17), C(2)−N(3)−C(21) 127.43(16), C(2)−N(3)−Cu 120.22(13), C(21)−N(3)−Cu 112.33(12).

Overall, we report the synthesis and structural characterization of the first triazapentadienyl complexes of copper(I). In contrast to the κ^1-coordinated $CH_3Hg[N\{(C_3F_7)C(Ph)N\}_2]$,[10] these adducts feature κ^2-coordinated triazapentadienyl moieties. The IR data of the copper carbonyl and isocyanide adducts indicate that the fluorinated ligands such as $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ are fairly weak donors. Further studies of the coordination chemistry of this interesting class of fluorinated ligands and the applications of their metal adducts are presently underway.

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Supporting Information Available: X-ray crystallographic data for $[N\{(C_3F_7)C(Dipp)N\}_2]H$ and $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$ (where L = $NCCH_3$ and CO) (CIF), and experimental details for free ligand and copper complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$: yield (65%), mp dec 80 °C. ^{19}F NMR ($CDCl_3$, 25 °C): δ −122.4 (s, β-CF_2), −106.2 (s, α-CF_2), −80.2 (s, CF_3). ^1H NMR ($CDCl_3$, 25 °C): δ 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH-(CH_3)$_2$), 1.28 (d, $^3J_{HH}$ = 7.0 Hz 12H, CH(CH_3)$_2$), 3.03 (heptet, $^3J_{HH}$ = 6.5 Hz, 4H, CH(CH$_3$)$_2$), 7.15 (m, 6H, m- and p-Ar). ^{13}C NMR ($CDCl_3$, 25 °C): δ selected peaks 152.2 (t, $^2J_{CF}$ = 23.0 Hz, NCN), 172.9 (s, CO). IR (Nujol, cm^{-1}): 2109 (CO).

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