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Silver(I) Complexes of a Sterically Demanding Fluorinated Triazapentadienyl Ligand $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ (Dipp = 2,6-Diisopropylphenyl)

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Sterically demanding triazapentadiene $[N\{(C_3F_7)C(Dipp)N\}_2]H$ affords the isolation of thermally stable, two- and three-coordinate silver complexes. The free ligand $[N\{(C_3F_7)C(Dipp)N\}_2]H$ has a W-shaped ligand backbone in the solid state. $[N\{(C_3F_7)C(Dipp)N\}_2]H$ reacts with silver(I) oxide in acetonitrile leading to $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$. It features a two-coordinate silver center and a κ^1-coordinated triazapentadienyl ligand. This silver acetonitrile complex serves as an excellent precursor to obtain thermally stable, silver isocyanide *t*-BuNCAg$[N\{(C_3F_7)C(Dipp)N\}_2]$ and silver phosphine $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ adducts. IR spectroscopic data for the silver(I) isocyanide *t*-BuNCAg$[N\{(C_3F_7)C(Dipp)N\}_2]$ shows ν_{CN} at 2219 cm^{-1}. The silver ion coordinates to the triazapentadienyl ligand via the central nitrogen atom. The silver PPh_3 adduct, $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$, was synthesized by treating $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ with PPh_3. It displays relatively large Ag–P coupling in the ^{31}P NMR spectrum. The triazapentadienyl ligand in $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ acts as a chelating κ^2-donor. The Ag–P bond is relatively short (2.3487(10) Å).

Introduction

The chemistry of metal complexes containing fluorinated ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (**1**) is of significant interest.[1−6] Polyfluorinated ligands commonly improve the thermal stability, oxidative resistance, volatility, and fluorocarbon solubility of metal adducts. Some of the interesting complexes of silver(I) that have been isolated using fluorinated tris(pyrazolyl)borates include $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgL$, where L = CO, $CH_2{=}CH_2$, $HC{\equiv}CH$, NNNAd, and $NNC(CO_2Me)_2$.[7−9] The $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ is an example of a metal carbonyl where the bonding between the metal and the CO is essentially of σ-type (with little to no π-back-bonding).[10−12] Compounds such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ show useful catalytic properties as well. For example, it facilitates the carbene insertion to C−H and C−Cl bonds under mild conditions.[13,14]

Although silver(I) complexes of the related bis(pyrazolyl)borate ligands such as $[H_2B(3,5\text{-}(CF_3)_2Pz)_2]^-$ (**2**) are also of interest, they are generally less stable.[15−17] This is partly due to the relative ease of reducing silver(I) to metallic silver by

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[1] Thrasher, J. S.; Strauss, S. H. *Inorganic Fluorine Chemistry: Toward the 21st Century*; ACS Symposium Series 555; American Chemical Society: Washington, DC, 1994.

[2] Dias, H. V. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1996**, *15*, 2994−3003 and the references therein.

[3] Dias, H. V. R.; Goh, T. K. H. H. *Polyhedron* **2004**, *23*, 273−282.

[4] Fekl, U.; van Eldik, R.; Lovell, S.; Goldberg, K. I. *Organometallics* **2000**, *19*, 3535−3542 and the references therein.

[5] Hu, Z.; Williams, R. D.; Tran, D.; Spiro, T. G.; Gorun, S. M. *J. Am. Chem. Soc.* **2000**, *122*, 3556−3557.

[6] Lee, H.-J.; Brennessel, W. W.; Lessing, J. A.; Brucker, W. W.; Young, V. G., Jr.; Gorun, S. M. *Chem. Commun.* **2003**, 1576−1577.

[7] Dias, H. V. R.; Wang, Z.; Jin, W. *Inorg. Chem.* **1997**, *36*, 6205−6215.

[8] Dias, H. V. R.; Polach, S. A. *Inorg. Chem.* **2000**, *39*, 4676−4677.

[9] Dias, H. V. R.; Polach, S. A.; Goh, S.-K.; Archibong, E. F.; Marynick, D. S. *Inorg. Chem.* **2000**, *39*, 3894−3901.

[10] Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1995**, *117*, 11381−11382.

[11] Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 3687−3694.

[12] Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1−112.

[13] Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9270−9271.

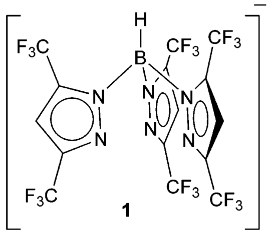
[14] Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. *Organometallics* **2004**, *23*, 1200−1202.

[15] Pettinari, C.; Cingolani, A.; Lobbia, G. G.; Marchetti, F.; Martini, D.; Pellei, M.; Pettinari, R.; Santini, C. *Polyhedron* **2004**, *23*, 451−469.

[16] Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College: London, 1999.

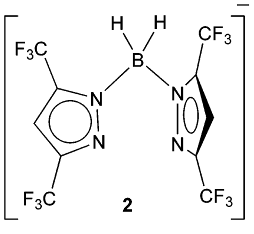
[17] Pettinari, C.; Santini, C. In *Comprehensive Coordination Chemistry II*; Elsevier Pergamon: New York, 2004; Vol. 1.

10.1021/ic0491231 CCC: $27.50



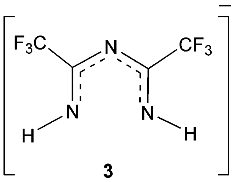
1

$[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$



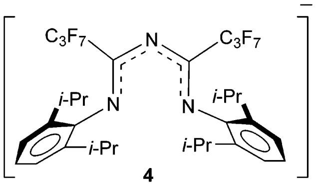
2

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



3

$[N\{(CF_3)C(H)N\}_2]^-$



4

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

the B−H moieties present in these ligands. As an alternative ligand without the problematic B−H moieties, we decided to examine the chemistry of the fluorinated triazapentadienyl systems.[18,19] They are both monoanionic, nitrogen-based donors capable of forming six-membered metallacycles upon coordination to metal ions. Very little is known about the coordination chemistry of triazapentadienyl ligands.[18−27] One reason may be the lack of versatile methods for the ligand synthesis.[18,28] Recently, a convenient route to fluoroalkylated triazapentadienes starting with $(C_4F_9)_3N$ appeared in the literature.[18] This method permits the synthesis of N-substituted molecules such as $[N\{(C_3F_7)C(Ph)N\}_2]H$. Several metal adducts of $[N\{(C_3F_7)C(Ph)N\}_2]^-$ are also known including the solid-state structures of $CH_3Hg[N\{(C_3F_7)C(Ph)N\}_2]$ and $[N\{(C_3F_7)C(Ph)N\}_2]_2Co$.[18−20] Early work involving fluorinated triazapentadienyl ligands concerns the use of $[N\{(CF_3)C(H)N\}_2]^-$ (**3**) as a ligand for few group 8−12 metal ions and for gallium.[21−25] Recently, we described the synthesis of a sterically demanding triazapentadienyl ligand $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ (Dipp = 2,6-diisopropylphenyl) and its copper(I) complexes in a communication.[29] IR data for $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ suggest that $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ is a fairly weak donor.

Herein, we report the use of $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ (**4**) in silver chemistry. In particular, the synthesis, spectroscopic data, and the X-ray crystal structures of $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$, *t*-$BuNCAg[N\{(C_3F_7)C(Dipp)N\}_2]$, and $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ are reported. These molecules display two interesting modes of triazapentadienyl ligand coordination. Previous work on silver triazapentadienyl adducts has been limited to $[N\{(C_3F_7)C(Ph)N\}_2]Ag$ and $[(diphos)Ag][N\{(C_3F_7)C(Ph)N\}_2]$.[20] None of these silver complexes have been characterized structurally using X-ray diffraction.

Experimental Details

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were purchased from commercial sources, distilled from 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 a JEOL Eclipse 500 spectrometer (^1H, 500.16 MHz; ^{13}C, 125.78 MHz; ^{19}F, 470.62 MHz; ^{31}P, 202.47 MHz). Proton and carbon chemical shifts are reported in ppm versus Me_4Si. ^{19}F NMR chemical shifts were referenced relative to external $CFCl_3$, and ^{31}P NMR was referenced to external 85% H_3PO_4. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Ag_2O, PPh_3, *tert*-butyl isocyanide, and 2,6-diisopropylaniline were purchased from commercial sources. Perfluoro-5-aza-4-nonene was synthesized using the published procedure.[30] Elemental analyses were performed using a Perkin-Elmer model 2400 instrument.

$[N\{C_3F_7)C(Dipp)N\}_2]H$. Perfluoro-5-aza-4-nonene (10 g, 0.023 mol) was added dropwise to a solution of 2,6-diisopropylaniline (20.4 g, 0.115 mol) in ether (100 mL) at 0 °C. After addition, the solution was allowed to stir overnight at room temperature. The resulting mixture was filtered, and the filtrate was collected and washed first with 10% HCl and then twice with distilled water. The ether layer was separated and dried over $CaCl_2$. The solvent was removed under reduced pressure, and the resulting residue was recrystallized from hexane at room temperature to obtain colorless crystal of $[N\{C_3F_7)C(Dipp)N\}_2]H$ in 76% yield. *Although we have not attempted to confirm, spectroscopic data seem to indicate both the amino−imino and diimino forms of the ligand present in solution.* Mp: 88−90 °C. ^{19}F NMR ($CDCl_3$): δ −124.5 and −124.0 (AB multiplet, J_{AB} = 294 Hz, β-CF_2), −123.4 (s, β-CF_2), −123.1 (s, β-CF_2), −113.6 and −111.9 (AB multiplet, J_{AB} = 288 Hz, α-CF_2), −111.9 and −111.2 (AB multiplet, J_{AB} = 293 Hz, α-CF_2), −109.8 (d, J_{FF} = 9 Hz, α-CF_2), −80.2 (apparent triplet, J_{FF} = 12 Hz, 9 Hz, CF_3), −80.0 (apparent triplet, J_{FF} = 12 Hz, 9 Hz, CF_3). ^1H NMR ($CDCl_3$): δ 0.29−1.26 (nine separate d, $^3J_{HH}$ = 8.0 Hz, 24H, CH_3), 2.37−3.01 (four separate heptets, $^3J_{HH}$ = 8.0 Hz, 4H, C*H*), 6.29 (br s, 0.69H, NH), 6.81−7.28 (several multiplets, *m*- and *p*-Ar), 12.92 (br s, 0.19H, NH). ^1H NMR (C_6D_6): δ 0.49−1.32 (multiplet, 24H, CH_3), 2.31−3.10 (four separate heptets, $^3J_{HH}$ = 8.0 Hz, 4H, C*H*), 6.06 (br s, 0.88H, NH), 6.89−7.09 (several multiplets, *m*- and *p*-Ar), 13.27 (br s, 0.12H, NH); see Supporting Information for hard copies of the spectra. Anal. Calcd for $C_{32}H_{35}F_{14}N_3$: C, 52.82; H, 4.85; N, 5.78. Found: C, 52.70; H, 4.62; N, 5.61.

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(18) 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.

(19) Siedle, A. R.; Webb, R. J.; Brostrom, M.; Newmark, R. A.; Behr, F. E.; Young, V. G., Jr. *Organometallics* **2004**, *23*, 2281−2286.

(20) Siedle, A. R.; Webb, R. J.; Brostrom, M.; Chou, S.-H.; Weil, D. A.; Newmark, R. A.; Behr, F. E.; Young, V. G., Jr. *Inorg. Chem.* **2003**, *42*, 2596−2601.

(21) Brown, H. C.; Schuman, P. D. *J. Org. Chem.* **1963**, *28*, 1122−1127.

(22) 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.

(23) Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1994**, 3615−3620.

(24) Robinson, V.; Taylor, G. E.; Woodward, P.; Bruce, M. I.; Wallis, R. C. *J. Chem. Soc., Dalton Trans.* **1981**, 1169−1173.

(25) Aris, D. R.; Barker, J.; Phillips, P. R.; Alcock, N. W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1997**, 909−910.

(26) Guo, J.; Wong, W.-K.; Wong, W.-Y. *Eur. J. Inorg. Chem.* **2004**, 267−275.

(27) Barker, J.; Kilner, M.; Mahmoud, M. M.; Wallwork, S. C. *J. Chem. Soc., Dalton Trans.* **1989**, 837−841.

(28) Paciorek, K. J. L.; Nakahara, J. H.; Kratzer, R. H. *J. Fluorine Chem.* **1985**, *30*, 241−250.

(29) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 5786−5788.

(30) Siedle, A. R.; Webb, R. J.; Newmark, R. A.; Brostrom, M.; Weil, D. A.; Erickson, K.; Behr, F. E.; Young, V. G. *J. Fluorine Chem.* **2003**, *122*, 175−182.

$CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$. $[N\{C_3F_7)C(Dipp)N\}_2]H$ (0.63 g, 0.87 mmol) and Ag_2O (0.10 g, 0.43 mmol) were mixed in acetonitrile (50 mL) and refluxed for 12 h. The resulting mixture was filtered, and the filtrate was concentrated and cooled to −15 °C to obtain white crystals of $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$. Yield: 87%. Mp: ∼130 °C (dec). ^{19}F NMR ($CDCl_3$): δ −122.4 and −121.6 (AB multiplet, J_{AB} = 278 Hz, β-CF_2), −107.5 and −106.9 (AB multiplet, J_{AB} = 304 Hz, α-CF_2), −80.4 (s, CF_3). ^1H NMR ($CDCl_3$): δ 0.90 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 0.98 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.08 (d, $^3J_{HH}$ = 6.5 Hz, 6H, $CH(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.5 Hz, 6H, $CH(CH_3)_2$), 2.02 (s, 3H, CH_3CN), 2.83 (heptet, $^3J_{HH}$ = 7.0 Hz, 2H, $CH(CH_3)_2$), 2.89 (heptet, $^3J_{HH}$ = 6.5 Hz, 2H, $CH(CH_3)_2$), 6.90 (nonfirst-order t, 2H, *p*-Ar), 6.96 (d, $^3J_{HH}$ = 7.0 Hz, 2H, *m*-Ar), 7.03 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-Ar). Selected $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 1.9 (CH_3CN), 21.5 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$). 25.4 ($CH(CH_3)_2$), 27.8 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 116.6 (p-*C*Ar), 123.3 (m-*C*Ar), 138.0 (o-*C*Ar), 140.5 (*C*ipso), 149.9 (t, $^2J_{CF}$ = 23.0 Hz, N*C*N). Anal. Calcd for $C_{34}H_{37}F_{14}N_4Ag$: C, 46.64; H, 4.26; N, 6.40. Found: C, 47.22; H, 4.70; N, 6.21.

***t*-BuNCAg[N{(C₃F₇)C(Dipp)N}₂].** $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ (0.10 g, 0.12 mmol) was dissolved in hexane and treated with *tert*-butyl isocyanide (0.014 g, 0.11 mmol) at room temperature. The mixture stirred overnight, and the solution was concentrated and cooled to −15 °C to obtain colorless crystals. Yield: 85%. Mp: 89 °C. ^{19}F NMR ($CDCl_3$): δ −122.3 and −121.6 (AB multiplet, J_{AB} = 291 Hz, β-CF_2), −107.4 and −106.6 (AB multiplet, J_{AB} = 288 Hz, α-CF_2), −80.4 (s, CF_3). ^1H NMR ($CDCl_3$): δ 0.96 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.02 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.18 (d, $^3J_{HH}$ = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.44 (s, 9H, $C(CH_3)_3$), 2.86 (heptet, $^3J_{HH}$ = 7.0 Hz, 2H, $CH(CH_3)_2$), 2.90 (heptet, $^3J_{HH}$ = 7.0 Hz, 2H, $CH(CH_3)_2$), 6.92 (nonfirst-order t, 2H, *p*-Ar), 6.96 (d, $^3J_{HH}$ = 6.5 Hz, *m*-Ar), 7.06 (d, $^3J_{HH}$ = 7.0 Hz, *m*-Ar). IR (Nujol, cm^{-1}): 2219(CN). Anal. Calcd for $C_{37}H_{43}F_{14}N_4Ag$: C, 48.43; H, 4.72; N, 6.11. Found: C, 48.02; H, 4.36; N, 6.45.

$[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$. $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ (0.10 g, 0.12 mmol) was dissolved in hexane and treated with triphenylphosphine (0.03 g, 0.11 mmol) at room temperature. The mixture stirred overnight, and the solution was concentrated and cooled to −15 °C to obtain yellow crystals. Yield: 89%. Mp: 154−155 °C. ^{31}P NMR ($CDCl_3$): δ 17.3 ($^1J(^{107}Ag-^{31}P)$ = 616 Hz) and ($^1J(^{109}Ag-^{31}P)$ = 709 Hz). ^{19}F NMR ($CDCl_3$): δ −121.7 (s, β-CF_2), −104.4 (Apparent quartet, J_{FF} = 12, 8 Hz, α-CF_2), −80.4 (t, J_{FF} = 12 Hz, CF_3). ^1H NMR ($CDCl_3$): δ 0.75 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 3.23 (heptet, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 6.56−6.60 (m, 6H, *m*- and *p*-Ar), 7.02−7.29 (m, 15H, PPh). Selected $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.2 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 113.5 (*p*-*C*Ar), 125.4 (*m*-*C*Ar), 137.9 (*o*-*C*Ar), 145.3 (*C*ipso), 151.1 (t, $^2J_{CF}$ = 23.0 Hz, N*C*N). Anal. Calcd for $C_{50}H_{49}F_{14}N_3AgP$: C, 54.76; H, 4.50; N, 3.83. Found: C, 55.01; H, 4.22; N, 4.11.

X-ray Structure Determinations. A suitable crystal covered with a layer of hydrocarbon oil was selected and mounted with paratone-N oil on a cryo-loop and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å). The detector was placed at a distance of 5.995 cm from the crystal. The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multiscan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (version 6.14) software package. Some details of the data collection and refinement of $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$, *t*-BuNCAg[N{(C₃F₇)C(Dipp)N}₂], and $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ are given in Table 1. Selected bond distances and angles of these adducts as well as that of the free ligand are presented in Tables 2−5.

Table 1. X-ray Crystallographic Data for $LAgNCCH_3$, $LAgCNBu^t$, and $LAgPPh_3$ (L = $[N\{(C_3F_7)C(Dipp)N\}_2]$)

param	$LAgNCCH_3$	$LAgCNBu^t$	$LAgPPh_3$
formula	$C_{34}H_{37}AgF_{14}N_4$	$C_{37}H_{43}AgF_{14}N_4$	$C_{50}H_{49}AgF_{14}N_3P$
fw	875.55	917.62	1096.76
space group	$Pna2_1$	$Pca2_1$	$I4_1/a$
a, Å	18.4525(8)	23.111(3)	38.717(4)
b, Å	12.0836(5)	19.512(2)	38.717(4)
c, Å	16.6622(7)	18.112(2)	13.053(3)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	90	90	90
V, Å^3	3715.2(3)	8167.9(15)	19567(5)
Z	4	8	16
ρ_{calc}, g/cm^3	1.565	1.492	1.489
μ, mm^{-1}	0.643	0.589	0.536
λ, deg	0.710 73	0.710 73	0.710 73
T, K	100(2)	100(2)	100(2)
final R indices ($I > 2\sigma(I)$)	R1 = 0.0221 wR2 = 0.0550	R1 = 0.0540 wR2 = 0.1237	R1 = 0.0385 wR2 = 0.0904
R indices (all data)	R1 = 0.0231 wR2 = 0.0556	R1 = 0.0514 wR2 = 0.1210	R1 = 0.0568 wR2 = 0.1016

Results and Discussion

Synthesis of the triazapentadiene ligand $[N\{(C_3F_7)C(Dipp)N\}_2]H$ was described in a communication.[29] It can be obtained in good yield from the reaction of 2,6-diisopropylaniline with the perfluoro-5-aza-4-nonene ($C_3F_7CF{=}NC_4F_9$)[30] in ether. Colorless crystals of this molecule could be obtained from hexane at room temperature. Various solutions of pure $[N\{(C_3F_7)C(Dipp)N\}_2]H$ (e.g., in benzene, toluene, hexane, Et_2O, $CHCl_3$) are yellow-orange in color. Solid $[N\{(C_3F_7)C(Dipp)N\}_2]H$ prior to recrystallization also has a yellow color.

The room-temperature ^1H and ^{19}F NMR spectra of $[N\{(C_3F_7)C(Dipp)N\}_2]H$ are fairly complex. For example, the ^1H NMR spectrum (in $CDCl_3$ at room temperature) shows that signals due to the isopropyl $CH(CH_3)_2$ and $CH(CH_3)_2$ 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 and tautomers. Fluorinated triazapentadiene molecules with U- or W-shaped backbones are known in the solid state (vide infra).[19] The ^1H NMR spectrum $[N\{(C_3F_7)C(Dipp)N\}_2]H$ also shows two broad signals at δ 12.92 and 6.26 (in a 0.3:0.7 (±0.1) ratio). In C_6D_6, these two peaks are observed at δ 13.28 and 6.01 (0.2:0.8 (±0.1) ratio), respectively. These signals disappear upon the addition of a few drops of D_2O to the solution. Although we have not investigated NMR spectroscopic properties in detail, these two broad peaks may correspond to the NH protons of the two tautomers where the acidic proton is attached to the terminal nitrogen or to the central nitrogen atom. Rather complex NMR spectroscopic properties of $[N\{(C_3F_7)C(Ph)N\}_2]H$ as well as isomeric forms of $CH_3Hg[N\{(C_3F_7)C(Ph)N\}_2]$ in solution have been noted previously.[18−20] Interestingly, the related diaza-

Table 2. Selected Bond Distances (Å) and Angles (deg) for Triazapentadienes [N{(C$_3$F$_7$)C(Dipp)N}$_2$]H, [N{(C$_3$F$_7$)C(Mes)N}$_2$]H, and [N{(C$_3$F$_7$)C(Ph)N}$_2$]H, Triazapantadienyl Anion [N{(C$_3$F$_7$)C(Ph)N}$_2$]$^-$, and Diazapentadiene [HC{(CF$_3$)C(Dipp)N}$_2$]H[a]

param	[N{(C$_3$F$_7$)C(Dipp)N}$_2$]H	[N{(C$_3$F$_7$)C(Mes)N}$_2$]H	[N{(C$_3$F$_7$)C(Ph)N}$_2$]H	[N{(C$_3$F$_7$)C(Ph)N}$_2$]$^-$	[HC{(CF$_3$)C(Dipp)N}$_2$]H	
ref	this work	32	20	20	31	
conformatn	W	W	U	W	U	
N1−C1	1.3523(14)	1.357(5)	1.345(11)	1.297(6)	N1−C1	1.357(3)
C1−N2	1.2714(15)	1.269(4)	1.258(10)	1.337(6)	C1−CH	1.363(4)
N2−C2	1.3868(14)	1.370(5)	1.377(9)	1.336(5)	CH−C2	1.429(4)
C2−N3	1.2651(15)	1.281(5)	1.259(9)	1.288(5)	C2−N3	1.289(3)
N1−C1−N2	122.54(10)	119.0(4)	132.7(7)	130.0(4)	N1−C1−CH	124.2(2)
C1−N2−C2	129.08(10)	132.3(4)	131.8(6)	129.4(4)	C1−CH−C2	118.1(1)
N2−C2−N3	128.20(11)	127.0(4)	131.6(7)	129.6(4)	CH−C2−N3	121.3(2)

[a] Note that N2 = CH for [HC{(CF$_3$)C(Dipp)N}$_2$]H).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for CH$_3$CNAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$]

Ag−N(4)	2.1070(15)	N(3)−C(2)	1.2792(19)
Ag−N(2)	2.1605(13)	N(3)−C(21)	1.4251(19)
N(1)−C(1)	1.2761(19)	N(4)−C(33)	1.136(2)
N(1)−C(9)	1.424(2)	C(1)−C(3)	1.544(2)
N(2)−C(2)	1.3607(19)	C(2)−C(6)	1.544(2)
N(2)−C(1)	1.3740(19)	C(33)−C(34)	1.460(2)

N(4)−Ag−N(2)	177.33(6)	C(1)−N(1)−C(9)	121.56(13)
C(2)−N(2)−C(1)	126.76(13)	N(1)−C(1)−C(3)	111.01(13)
C(2)−N(2)−Ag	116.94(10)	N(2)−C(1)−C(3)	119.98(13)
C(1)−N(2)−Ag	116.29(10)	N(3)−C(2)−N(2)	128.18(14)
C(2)−N(3)−C(21)	122.26(13)	N(3)−C(2)−C(6)	110.32(12)
C(33)−N(4)−Ag	171.05(14)	N(2)−C(2)−C(6)	120.94(12)
N(1)−C(1)−N(2)	127.98(14)	N(4)−C(33)−C(34)	179.6(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *t*-BuNCAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$]

Ag(1)−C(33)	2.046(5)	N(4)−C(33)	1.164(6)
Ag(1)−N(2)	2.179(3)	N(4)−C(34)	1.455(6)
Ag(2)−C(70)	2.026(5)	N(5)−C(38)	1.278(5)
Ag(2)−N(6)	2.156(3)	N(5)−C(46)	1.421(5)
N(1)−C(1)	1.289(5)	N(6)−C(38)	1.368(5)
N(1)−C(9)	1.440(5)	N(6)−C(39)	1.370(5)
N(2)−C(2)	1.366(5)	N(7)−C(39)	1.272(5)
N(2)−C(1)	1.380(5)	N(7)−C(58)	1.434(5)
N(3)−C(2)	1.273(5)	N(8)−C(70)	1.155(7)
N(3)−C(21)	1.434(5)		

C(33)−Ag(1)−N(2)	175.31(15)	C(33)−N(4)−C(34)	176.9(5)
C(70)−Ag(2)−N(6)	175.31(17)	C(38)−N(5)−C(46)	122.1(3)
C(1)−N(1)−C(9)	121.1(3)	C(38)−N(6)−C(39)	127.3(3)
C(2)−N(2)−C(1)	127.2(3)	C(38)−N(6)−Ag(2)	117.8(2)
C(2)−N(2)−Ag(1)	117.6(2)	C(39)−N(6)−Ag(2)	114.9(2)
C(1)−N(2)−Ag(1)	115.0(3)	C(39)−N(7)−C(58)	121.4(3)
C(2)−N(3)−C(21)	121.3(3)	N(1)−C(1)−N(2)	127.2(4)
N(1)−C(1)−C(3)	111.0(3)	N(4)−C(34)−C(36)	106.5(4)
N(2)−C(1)−C(3)	121.0(3)	N(5)−C(38)−N(6)	127.3(3)
N(3)−C(2)−N(2)	127.7(3)	N(5)−C(38)−C(40)	110.4(3)
N(3)−C(2)−C(6)	110.3(3)	N(6)−C(38)−C(40)	121.7(3)
N(2)−C(2)−C(6)	121.2(3)	N(7)−C(39)−N(6)	128.0(3)
C(10)−C(9)−N(1)	116.8(3)	N(7)−C(39)−C(43)	110.5(3)
C(14)−C(9)−N(1)	121.5(4)	N(6)−C(39)−C(43)	120.4(3)
C(26)−C(21)−N(3)	122.0(3)	C(51)−C(46)−N(5)	121.7(4)
C(22)−C(21)−N(3)	116.6(3)	N(5)−C(46)−C(47)	117.1(3)
N(4)−C(33)−Ag(1)	175.7(4)	C(59)−C(58)−N(7)	122.5(4)
N(4)−C(34)−C(35)	107.6(4)	C(63)−C(58)−N(7)	116.0(3)
N(4)−C(34)−C(37)	107.0(4)	N(8)−C(70)−Ag(2)	177.5(4)

pentadiene [HC{(CF$_3$)C(Dipp)N}$_2$]H shows a fairly simple ^{1}H NMR spectrum with just two sets of doublets for CH-(CH_3)$_2$ and a septet for CH(CH$_3$)$_2$.[31]

The X-ray crystal structure of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]H is illustrated in Figure 1. It crystallizes in the form where acidic proton is bonded to one of the terminal nitrogen atoms. This proton (H1 on N1) was located from the difference map and refined freely. There are no inter- or intramolecular close contacts between H1 and the other nitrogen atoms. The closest contact is with one of the fluorines of the β-CF$_2$ moiety (H1···F3 distance = 2.43 Å). The backbone of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]H adopts a W-shaped configuration.

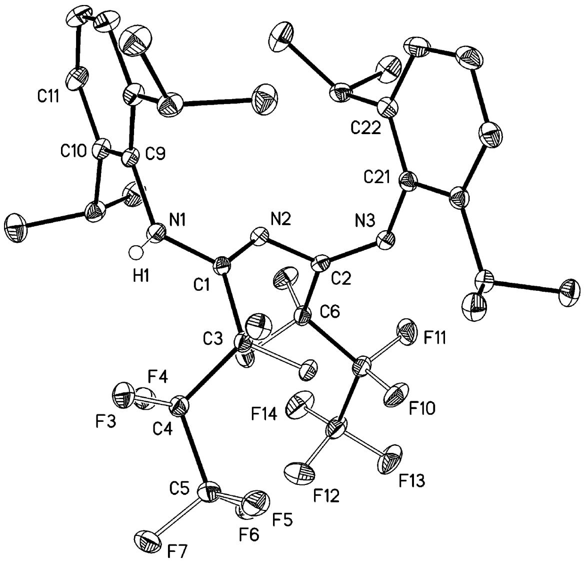

Figure 1. Crystal structure of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]H illustrating the W-shaped conformation. (All hydrogen atoms except the one on nitrogen have been omitted for clarity.)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [N{(C$_3$F$_7$)C(Dipp)N}$_2$]AgPPh$_3$

Ag−N(3)	2.250(3)	N(1)−C(9)	1.446(4)
Ag−N(1)	2.252(3)	N(2)−C(2)	1.345(4)
Ag−P	2.3487(10)	N(2)−C(1)	1.350(4)
P−C(33)	1.824(3)	N(3)−C(2)	1.301(4)
P−C(39)	1.827(4)	N(3)−C(21)	1.445(4)
P−C(45)	1.832(4)	C(1)−C(3)	1.550(5)
N(1)−C(1)	1.299(4)	C(2)−C(6)	1.558(5)

N(3)−Ag−N(1)	85.81(10)	C(33)−P−C(45)	104.59(16)
N(3)−Ag−P	141.61(7)	C(39)−P−C(45)	103.37(16)
N(1)−Ag−P	132.55(7)	C(33)−P−Ag	113.06(11)
C(33)−P−C(39)	105.23(16)	C(39)−P−Ag	116.41(12)
C(45)−P−Ag	112.99(12)	C(14)−C(9)−N(1)	119.3(3)
C(1)−N(1)−C(9)	125.2(3)	N(1)−C(1)−N(2)	130.0(3)
C(1)−N(1)−Ag	122.1(2)	N(1)−C(1)−C(3)	124.4(3)
C(9)−N(1)−Ag	112.1(2)	N(2)−C(1)−C(3)	105.6(3)
C(2)−N(2)−C(1)	127.7(3)	N(3)−C(2)−N(2)	130.1(3)
C(2)−N(3)−C(21)	123.7(3)	N(3)−C(2)−C(6)	123.7(3)
C(2)−N(3)−Ag	121.9(2)	N(2)−C(2)−C(6)	106.2(3)
C(21)−N(3)−Ag	114.3(2)	C(26)−C(21)−N(3)	119.8(3)
C(10)−C(9)−N(1)	118.4(3)	C(22)−C(21)−N(3)	118.4(3)

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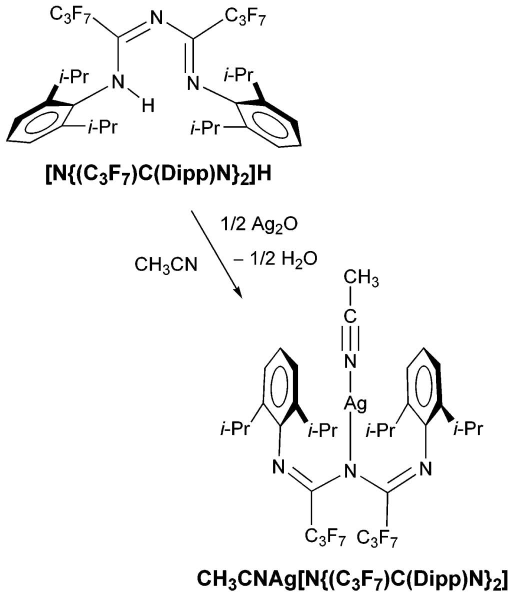
(31) Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafe, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton Trans.* **2003**, 1083−1093.

The NCNCN moiety, however, is not planar. $[N\{(C_3F_7)C(Dipp)N\}_2]H$ shows a long−short−long−short C−N bond length pattern in the backbone (see Table 2) consistent with the localized proton on one of the terminal nitrogens (N1). A similar trend is observed for $[N\{(C_3F_7)C(Mes)N\}_2]H$ (where Mes = 2,4,6-trimethylphenyl)[32] and $[N\{(C_3F_7)C(Ph)N\}_2]H$.[20] One of these (i.e., $[N\{(C_3F_7)C(Ph)N\}_2]H$), however, features a U-shaped backbone. The closely related diazapentadine $[HC\{(CF_3)C(Dipp)N\}_2]H$ also shows bond distances consistent with amine and imine type nitrogen sites. In contrast to the triazapentadiene $[N\{(C_3F_7)C(Dipp)N\}_2]H$, the diazapentadiene $[HC\{(CF_3)C(Dipp)N\}_2]H$ crystallizes in the U-shaped conformation and features an intramolecular NH···N hydrogen bond.[31]



$[N\{(C_3F_7)C(Dipp)N\}_2]H$

$CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$

The silver(I) acetonitrile complex $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ was prepared by refluxing a mixture of silver oxide and $[N\{(C_3F_7)C(Dipp)N\}_2]H$ in acetonitrile for 12 h. It is a colorless solid with somewhat limited stability in most organic solvents at room temperature. $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ is stable in acetonitrile but decomposes in hexane or benzene over a period of several hours. In solvents such as CH_2Cl_2 or $CHCl_3$, a slow formation of a black solid could be observed within minutes. However, $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ survives even in chlorinated solvents long enough to obtain good NMR spectra or to perform reactions with other reagents (vide infra). The related $[N\{(C_3F_7)C(Ph)N\}_2]Ag$ has been obtained as an acetonitrile *free* solid following a similar route.[20] It is reported to be stable only in acetonitrile solutions or as a solid.

The ^{19}F NMR spectrum of $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ shows a singlet assignable to CF_3 and two AB multiplets corresponding to the α-CF_2 and β-CF_2 fluorines. This is in sharp contrast to the complex ^{19}F NMR spectrum observed for the free ligand. The ^1H NMR spectrum in $CDCl_3$ is also relatively simple. It displays four sets of doublets for $CH(CH_3)_2$ and two septets for $CH(CH_3)_2$. The NMR spectroscopic data for $[N\{(C_3F_7)C(Ph)N\}_2]Ag$ have not been reported. It is known to behave as a 1:1 electrolyte in acetonitrile.[20]

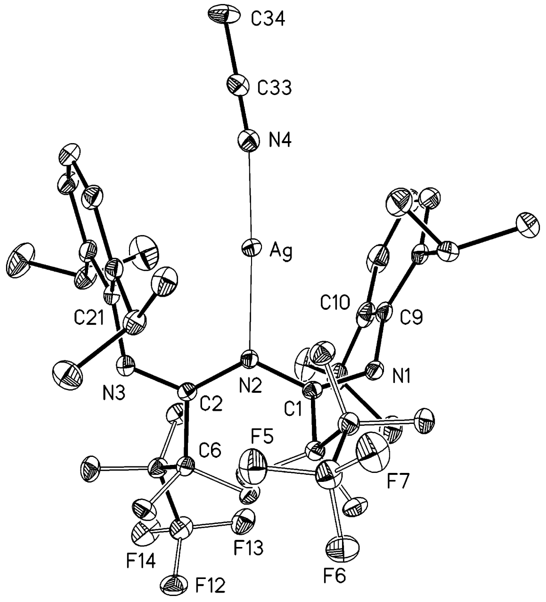


Figure 2. Crystal structure of $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$. (Hydrogen atoms have been omitted for clarity.)

The X-ray crystal structure of $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ shows that $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ acts as a κ^1-donor (Figure 2). Silver coordinates to the triazapentadienyl ligand via the central nitrogen atom and adopts a linear geometry. Ligand backbone features a W-shaped configuration with the two Dipp moieties flanking the silver ion. The closest Ag···C(aryl) distances are 2.892 Å (Ag···C9) and 2.844 Å (Ag···C21). These values are within the sum of van der Waals radii of silver and carbon atoms ($r_{vW}(Ag) + r_{vW}(C) = 3.42$ Å). The $Ag-N(CCH_3)$ distance of 2.1070(15) Å is not much different from the corresponding distances of two-coordinate species $(CF_3)_2FCAgNCCH_3$ (2.083(7) Å)[33] and four-coordinate silver adduct $[HB(3,5-(CF_3)_2Pz)_3]AgNCBu^t$ (2.120(4) Å).[7] Compounds with much longer Ag−N distances are also known, e.g., $(PPh_3)_2AgNCCH_3$ (2.321(2) Å)[34] and $[Ag(NCCH_3)_4]BF_4$ (2.266 Å).[35] The closely related copper analogue $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ has been reported.[29] It features a κ^2-bonded triazapentadienyl ligand and a three-coordinate copper center. The $Cu-N(CCH_3)$ bond length of 1.867(3) Å is, as expected, shorter than the $Ag-N(CCH_3)$ distance observed for the silver analogue $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$.

Silver adducts such as $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ containing weakly coordinating fluorinated ligands are of significant interest because they serve as useful ligand transfer agents.[36] However, not many silver(I) complexes of monoanionic, nitrogen-based ligands are known in the literature. We have reported a number of such adducts involving the fluorinated, tridentate tris(pyrazolyl)borates and

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(32) Dias, H. V. R.; Singh, S. Unpublished results.

(33) Burch, R. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 5359−5360.

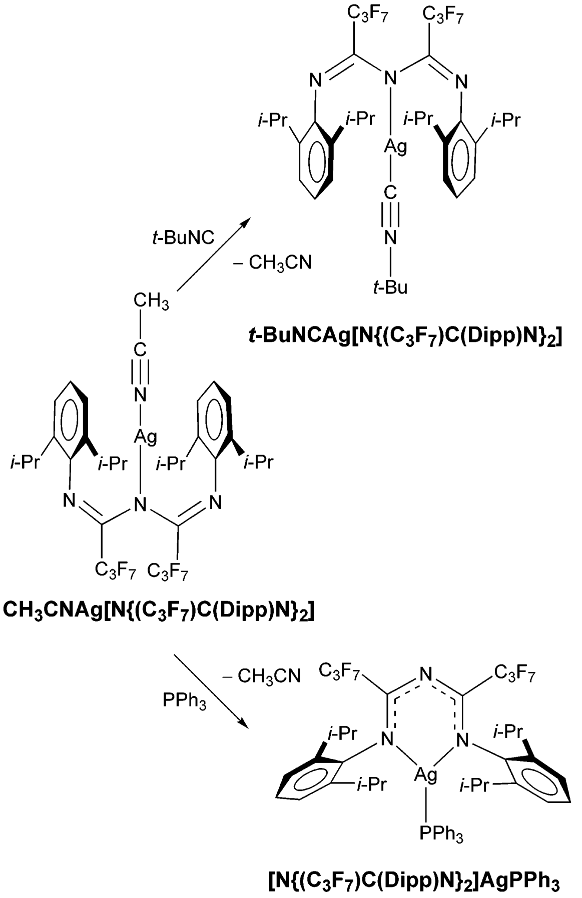
(34) Bachman, R. E.; Andretta, D. F. *Inorg. Chem.* **1998**, *37*, 5657−5663.

(35) Jones, P. G.; Bembenek, E. *Z. Kristallogr.* **1993**, *208*, 213−218.

(36) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942.

one example containing the bidentate, bis(pyrazolyl)borate.[7−10,13,14,37−42] [N{(C$_3$F$_7$)C(Ph)N}$_2$]Ag and [(diphos)-Ag][N{(C$_3$F$_7$)C(Ph)N}$_2$] are the only silver complexes reported for the triazapentadienyl family.[20]

CH$_3$CNAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$] may be used as a convenient starting material for other silver derivatives of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]$^-$. For example, CH$_3$CNAg[N{(C$_3$F$_7$)C-(Dipp)N}$_2$] reacts with *tert*-butyl isocyanide in hexane to yield *t*-BuNCAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$] in 85% yield. A strong signal in the IR spectrum at 2219 cm^{-1} indicates the presence of the CNBu^t moiety in the product. The ν_{CN} band shows a shift of about 78 cm^{-1} as a result of coordination to the silver(I) center (ν_{CN} of free CNBu^t = 2138 cm^{-1}). The ν_{CN} value is similar to that observed for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]-AgCNBu^t, which appears at 2214 cm^{-1}.[7] There are no isocyanide complexes of silver(I) bis(pyrazolyl)borates to our knowledge.[15] The related copper(I) triazapentadienyl complex, [N{(C$_3$F$_7$)C(Dipp)N}$_2$]CuCNBu^t, displays the ν_{CN} at a much lower value (2176 cm^{-1}).[29]



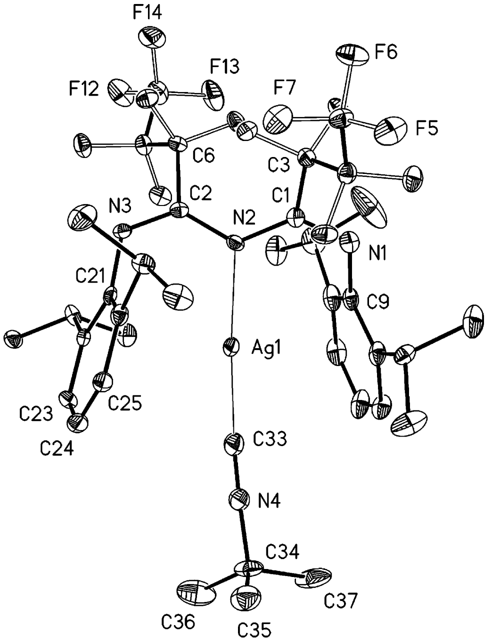


Figure 3. Crystal structure of *t*-BuNCAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$]. (One of the two molecules in the asymmetric unit is shown. Hydrogen atoms have been omitted for clarity.)

The ^{1}H NMR peaks corresponding to the triazapentadienyl moiety of *t*-BuNCAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$] are similar to those observed for the corresponding acetonitrile adduct. The X-ray crystal structure of *t*-BuNCAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$] (Figure 3) indeed reveals closely related structures. The isocyanide adduct crystallizes in the *Pca*2$_1$ space group with two molecules in the asymmetric unit. One of these shows minor rotational disorder of the *tert*-butyl moiety. As in the acetonitrile adduct, the triazapentadienyl ligand coordinates to silver atom in an κ^1-fashion via the central nitrogen atom. The Ag1−N2 distance is 2.179(3) Å (Ag2−N6 2.156(3) Å). The Ag−C distances (2.046(5), 2.026(5) Å) are in the typical range. For example, the related Ag−C distances of [HB-(3,5-(CF$_3$)$_2$Pz)$_3$]AgCNBu^t and [HB(3,5-(Ph)$_2$Pz)$_3$]AgCNBu^t are 2.059(4) and 2.063(5) Å, respectively.[7,43] The two aryl groups (Dipp groups) of the triazapentadienyl ligand sandwich the silver center. The closest Ag···C(aryl) separation is about 2.80 Å (e.g., Ag1···C21 = 2.802 Å, Ag2···C46 = 2.801 Å). The Ag−C−N moieties are essentially linear (175.7(4) and 177.5(4)°).

The Ag(I)−PPh$_3$ analogue could be obtained by treating CH$_3$CNAg[N{(C$_3$F$_7$)C(Dipp)N}$_2$] with 1 equiv of PPh$_3$. Interestingly, [N{(C$_3$F$_7$)C(Dipp)N}$_2$]AgPPh$_3$ has an κ^2-coordinated triazapentadienyl ligand (vide infra). The ^{19}F NMR data indicate that this compound has equivalent C$_3$F$_7$ groups. The ^{1}H NMR spectrum displays just two sets of doublets for CH(C*H*$_3$)$_2$ and a septet for C*H*(CH$_3$)$_2$. This pattern is similar to those observed for [N{(C$_3$F$_7$)C(Dipp)N}$_2$]-CuL (L = CO, NCCH$_3$, and CNBu^t) featuring a κ^2-bonded [N{(C$_3$F$_7$)C(Dipp)N}$_2$]$^-$ ligand.[29] Note however that the κ^1-coordinted silver(I) adducts described above display four sets of doublets for CH(C*H*$_3$)$_2$ and two septets for C*H*(CH$_3$)$_2$.

The ^{31}P NMR spectrum of [N{(C$_3$F$_7$)C(Dipp)N}$_2$]AgPPh$_3$ shows a superposition of two doublets arising from the

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(37) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3890−3893.

(38) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3724−3727.

(39) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, *41*, 3259−3268 and the references therein.

(40) Omary, M. A.; Rawashdeh-Omary, M. A.; Diyabalanage, H. V. K.; Dias, H. V. R. *Inorg. Chem.* **2003**, *42*, 8612−8614.

(41) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 267−268.

(42) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317−2328.

(43) Gioia Lobbia, G.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2000**, *298*, 146−153.

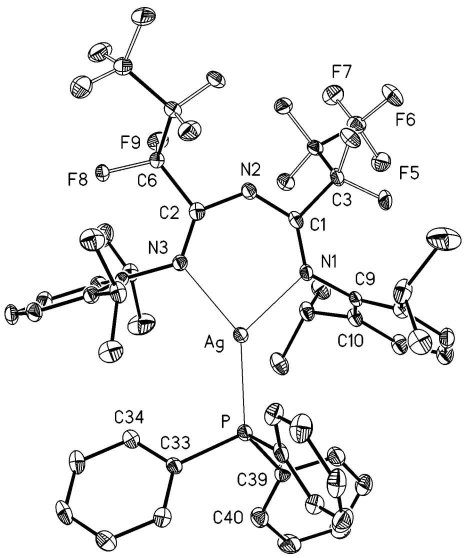

Figure 4. Crystal structure of $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$. (Hydrogen atoms have been omitted for clarity.)

$^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ coupling. The observed Ag−P coupling constants ($J(^{107}Ag-^{31}P) = 616$ Hz) and ($J(^{109}Ag-^{31}P) = 709$ Hz) are at the higher end of the Ag−P coupling of various other silver phosphine complexes (typical ^1J(Ag−P) constants range from 200 to 800 Hz).[44−46] The ratio of $J(^{109}Ag-^{31}P)/J(^{107}Ag-^{31}P)$ is in good agreement with the $^{109}Ag/^{107}Ag$ gyromagnetic ratio of 1.15. We have observed similar large ^1J(Ag−P) coupling in the tris(pyrazolyl)borate adduct, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgPPh_3$ (657.5 and 758.8 Hz).[42] The ^{31}P NMR spectrum of $[(diphos)Ag][N\{(C_3F_7)C(Ph)N\}_2]$ in $CDCl_3$ shows a broad doublet with much smaller ^1J(Ag−P) coupling (201 Hz). It primarily exists as a 1:1 electrolyte in acetonitrile.[20]

The X-ray crystal structure of $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ reveals the presence of a three-coordinate, trigonal planar silver center (Figure 4). The triazapentadienyl ligand acts as an κ^2-donor. The Ag−N bond distances are equivalent, and the U-shaped ligand backbone is essentially planar. The Dipp groups lie almost perpendicular to the triazapentadienyl plane (the aryls are twisted by about 83 and 84° from the NCNCN plane). The Ag−P distance of $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ is 2.3487(10) Å. This is at the shorter end of the typical $Ag-PPh_3$ distances (average Ag−P value of 27 silver triphenylphosphine complexes = 2.419 Å).[47] This suggests a strong Ag−P bonding interaction. The three-coordinate Ag(I) pyrazolate adduct $PPh_3Ag[3,5\text{-}(CF_3)_2Pz]_2AgPPh_3$ (2.350(1), 2.374(1) Å)[48] and the four-coordinate tris(pyrazolyl)borate complex $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgPPh_3$ (2.376(1) Å)[42] also have relatively short Ag−P bonds. A few bis(pyrazolyl)borato complexes of silver(I) containing phosphine ligands are known.[15]

Overall, we described the use of a bulky, fluoroalkyl-substituted, triazapentadieneyl ligand in silver(I) coordination chemistry. Compounds such as $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ may serve as good $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ transfer agents or as precursors for silver triazapentadienyl complexes. Silver adducts $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$ and $t\text{-}BuNCAg[N\{(C_3F_7)C(Dipp)N\}_2]$ feature κ^1-bonded triazapentadienyl ligands, whereas $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ has a chelating, κ^2-bonded ligand. The NCNCN backbone adopts either W- or U-shaped conformation. These adducts represent the first structurally characterized silver complexes of the triazapentadienyl family. We also note that, to the best of our knowledge, thermally stable silver(I) complexes of closely related diazapentadienyl (β-diketiminate) ligands have not been reported.[49] We are presently investigating the use of these triazapentadienyl silver adducts in various catalytic and ligand transfer applications.

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Supporting Information Available: X-ray crystallographic data for $CH_3CNAg[N\{(C_3F_7)C(Dipp)N\}_2]$, $t\text{-}BuNCAg[N\{(C_3F_7)C(Dipp)N\}_2]$, and $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ (CIF) and ^1H NMR spectra of $[N\{(C_3F_7)C(Dipp)N\}_2]H$ and selected regions showing the characteristic $(CH_3)_2CH$ resonances of the free ligand and silver complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386−6391.

(45) Szlyk, E.; Szymanska, I.; Surdykowski, A.; Glowiak, T.; Wojtczak, A.; Golinski, A. *Dalton Trans.* **2003**, 3404−3410.

(46) Baker, L. J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Steigelmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656−3662.

(47) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

(48) Dias, H. V. R.; Diyabalanage, H. V. K. Unpublished results.

(49) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066.