Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 8569

www.rsc.org/dalton

PAPER

Silver(I) and copper(I) complexes supported by fully fluorinated 1,3,5-triazapentadienyl ligands†

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Received 28th March 2011, Accepted 9th June 2011
DOI: 10.1039/c1dt10524h

Synthesis of the perfluorinated 1,3,5-triazapentadiene $[N\{(CF_3)C(C_6F_5)N\}_2]H$ and the use of its conjugate base as a supporting ligand for the isolation of silver(I) and copper(I) complexes are reported. Some of the related chemistry involving $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ (that has bulkier $–C_3F_7$ groups on the 1,3,5-triazapentadienyl ligand backbone) is also presented. X-ray crystallographic data show a wide variety of structures ranging from intermolecular, hydrogen-bonded chain structure for $[N\{(CF_3)C(C_6F_5)N\}_2]H$ with a twisted W-shaped N_3C_2 core, monomeric $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ where the κ^1-bonded triazapentadienyl ligand bonding to the metal fragment *via* the central nitrogen atom, monomeric $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ that feature κ^1-bonded triazapentadienyl ligand bonding to the metal fragment *via* one of the terminal nitrogen atoms, to that of the monomeric $[N\{(CF_3)C(C_6F_5)N\}_2]Cu(CN^tBu)_2$ containing a κ^2-bonded triazapentadienyl ligand and a U-shaped NCNCN ligand backbone. The isocyanide adducts show relatively high ν_{CN} values in the IR spectra.

Introduction

Chelating systems such as β-diketones[1,2] and their nitrogen analogues, β-iminoketones and β-diketimines (1,5-diazapentadienes),[3–16] are some of the most ubiquitous ligands in chemistry. They have been utilized widely in coordination chemistry[17–20] and to prepare homogeneous catalysts[21–24] as well as for modeling active sites of metalloenzymes.[25–27] In contrast, the 1,3,5-triazapentadienes as trinitrogen analogues of 1,5-diazapentadienes have received relatively less attention.[28] This is probably because facile and general synthetic methods for their generation have been rather poorly developed. Reactions between the 1,3,5-triazapentadiene bearing electron-donor substituents and metal ions are also rare because free ligands are reactive and many of them are elusive in the free state.[29] Nevertheless, several neutral non-fluorinated triazapentadiene ligands and their mononuclear metal complexes, homo- or hetero-trinuclear clusters are known.[30–34] Direct metal–ligand reactions have been realized (thus far) only with thermally stable 1,3,5-triazapentadienes which usually bear strong electron withdrawing groups on the backbone C atoms (*e.g.* fluoroalkyls).[35–41] The anionic form of 1,3,5-triazapentadienes also offers an additional coordination site (compared to 1,5-diazapentadienyl systems) at the central nitrogen atom.[30,37,39,42–48] Moreover, the central nitrogen atom is also known to take part in facile acid–base equilibria,[46,49] thus providing pH sensing properties to their complexes.[50]

An area of research activity in our laboratories concerns the chemistry of fluorinated ligands including those of 1,3,5-triazapentadienes. 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.[51] We and others have reported the synthesis and use of several fluorinated 1,3,5-triazapentadienes including $[N\{(CF_3)C(H)N\}_2]H$,[43,52,53] $[N\{(C_3F_7)C(Ph)N\}_2]H$,[39] $[N\{(C_3F_7)C(Dipp)N\}_2]H$,[35,37] (Dipp = 2,6-$^iPr_2C_6H_3$), $[N\{(C_3F_7)C(Mes)N\}_2]H$[36] (Mes = 2,4,6-$Me_3C_6H_2$), $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$,[54] $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]H$[54] and $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]H$[55] (Fig. 1 a–g show the *N*-deprotonated form). These studies also show that metal adducts of 1,3,5-triazapentadienyl ligands display interesting solid-state structures and solution behavior and diverse coordination modes. For example, $[N\{(C_3F_7)C(Dipp)N\}_2]Ag(CN^tBu)$ features a κ^1-bonded $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ ligand with the silver(I) ion on the central nitrogen atom ligand with a W-shaped backbone (Fig. 2).[35] On the other hand, the silver and copper complexes $[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ [35] and $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(CH_3CN)$[37] have κ^2-bonded U-shaped ligand backbones. The $[N\{(C_3F_7)C(Ph)N\}_2]HgCH_3$ is believed to exist as two slowly inter-converting κ^1-bonded

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† CCDC reference numbers 818790–818795. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10524h

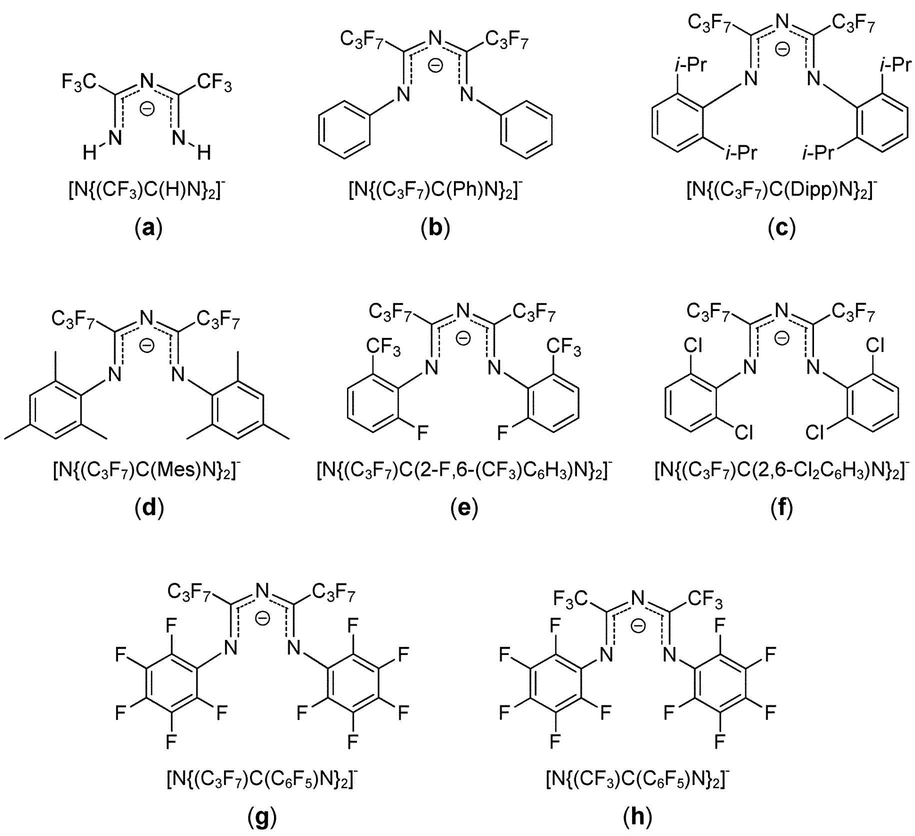


Fig. 1 A few examples of 1,3,5-triazapentadienyl ligands.

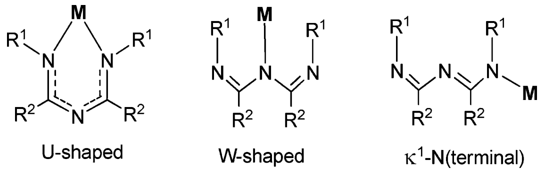


Fig. 2 Several coordination modes of 1,3,5-triazapentadienyl ligands.

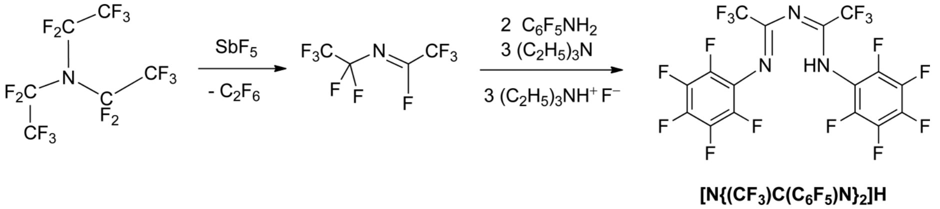
isomers in solution.[38] The solid state structure features a κ^1-bonded triazapentadienyl ligand with the mercury atom coordinating to the central nitrogen atom. Polyfluorinated 1,3,5-triazapentadienyls are good ligands for the stabilization of carbon monoxide and ethylene adducts of copper.[37,54] A rare gold(I) ethylene complex has also been isolated using $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]^-$ as the supporting ligand. $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Au(C_2H_4)$ features a U-shaped triazapentadienyl ligand backbone and a three-coordinate, trigonal gold center.[55]

Here we describe details of a new fluorinated 1,3,5-triazapentadienyl auxiliary ligand $[N\{(CF_3)C(C_6F_5)N\}_2]^-$ (Fig. 1h), and its copper(I) and silver(I) isocyanide and phosphine chemistry. For comparison, several copper and silver adducts of $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ (Fig. 1g, which features a longer fluoro-alkyl substituent on the backbone) are also reported.

Results and discussion

$[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) was synthesized in good yield by the reaction of $C_6F_5NH_2$, perfluoro-3-aza-2-pentene (prepared using $N(C_2F_5)_3$ and SbF_5 and used directly), and triethylamine (Scheme 1).[56,57]

It is a colorless crystalline solid. The most challenging aspect is the synthesis and handling of perfluoro-3-aza-2-pentene due to its high volatility. The room temperature ^{19}F NMR spectrum of $[N\{(CF_3)C(C_6F_5)N\}_2]H$ is somewhat complex which is normal for fluorinated 1,3,5-triazapentadienenes. For example, it displays three resonances corresponding to $-CF_3$ groups. This is



Scheme 1 Synthesis of the ligand $[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**).

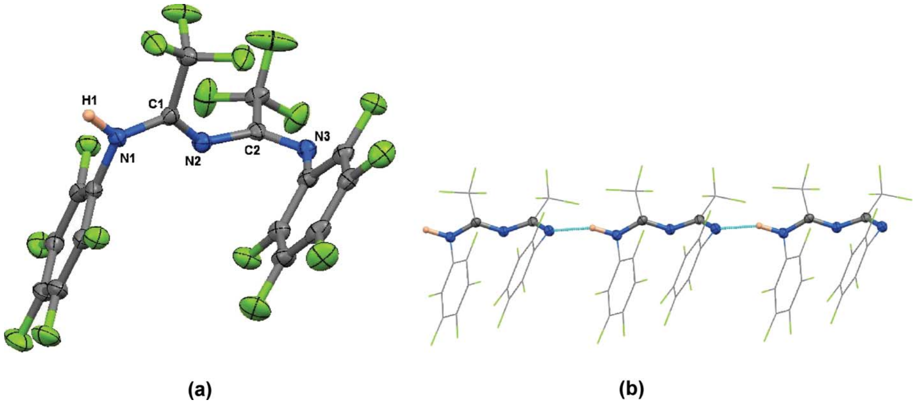


Fig. 3 Two views showing the molecular structure and atom numbering scheme of $[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) and extended structure formation *via* inter-molecular H-bonding. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.338(3), N(2)–C(1) 1.269(3), N(2)–C(2) 1.361(3), N(3)–C(2) 1.273(3), N(1)–C(1)–N(2) 122.7(2), C(1)–N(2)–C(2) 133.1(2), N(2)–C(2)–N(3) 128.7(2).

presumably due to the presence of relatively rigid conformational isomers and tautomers in solution.

X-ray crystal structure of $[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) is depicted in Fig. 3. It has a twisted, non-planar, W-shaped (which is approaching an S-shape with two F_3C-CN(central) planes at 88.1°) NCNCN triazapentadiene backbone. The proton is located on one of the terminal nitrogen atoms and the HNCNCN backbone displays long-short-long-short C–N bonds consistent with this observation. The crystal packing diagram shows the existence of NH···N hydrogen bonds (Fig. 3b) between neighboring molecules leading to a polymeric chain structure. X-ray structures of $[N\{(C_3F_7)C(Dipp)N\}_2]H$, $[N\{(C_3F_7)C(Mes)N\}_2]H$ (shows polymorphs), $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]H$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ have been reported previously.[36,37,55,58] All these fluorinated 1,3,5-triazapentadienes feature non-planar, distorted W-shaped triazapentadienyl ligand backbones. $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]H$, and one of the polymorphs of $[N\{(C_3F_7)C(Mes)N\}_2]H$, and $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ show aggregation *via* inter-molecular NH···N hydrogen bonding.

The *tert*-butyl isocyanide complexes of silver $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**2**) and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**3**) were synthesized by first treating the corresponding triazapentadiene with Ag_2O at an elevated temperature followed by the addition of CN^{t}Bu to the resulting product. The stoichiometry of the compound was not affected by reducing (to 1 equivalent) or increasing (>2 equivalents) the amount of the relevant isocyanide. $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ are air stable solids. They show good solubility in chloroform and CH_2Cl_2. Crystals of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**3**) were obtained by slow diffusion of hexane into a solution of the compound in CH_2Cl_2 while $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**2**) was recrystallized from $CHCl_3$–diethyl ether at room temperature. The ^{19}F NMR spectrum of $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ shows one singlet assignable to CF_3 in contrast to the complex ^{19}F NMR spectrum observed for the free ligand. $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ also displays a relatively less complex ^{19}F NMR spectrum compared to that of the free ligand $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$.

Strong signals in the IR spectra of (**2**) and (**3**) at 2214 cm^{-1} and 2211 cm^{-1}, respectively, indicate the presence of the CN^{t}Bu moiety in the product. The ν_{CN} bands show a significant increase in frequency as a result of coordination to the silver(I) centers. $[N\{(C_3F_7)C(Dipp)N\}_2]Ag(CN^tBu)$ is known and it also displays a ν_{CN} band at a fairly high wave number 2219 cm^{-1} (see Table 1).

The ν_{CN} bands in (**2**) and (**3**) show a shift of about 75 cm^{-1} as a result of coordination to the silver(I) center (ν_{CN} of free

Table 1 Selected Ag(I)–CN^{t}Bu complexes of tris(pyrazolyl)borates and 1,3,5-triazapentadienyl ligands and some of their structural and spectroscopic parameters

Complex	ν_{CN}/cm^{-1}	Ag–C/Å	Ag–N/Å	Ref.
$[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**2**)	2214	2.088(3) 2.095(3)	2.445(2)	This work
$[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**3**)	2211	2.113(4) 2.109(4)	2.415(3)	This work
$[N\{(C_3F_7)C(Dipp)N\}_2]Ag(CN^tBu)$	2219	2.046(5)	2.179(3)	35
$[HB(3,5\text{-}(CF_3)_2pz)_3]Ag(CN^tBu)$	2214	2.059(4)	2.349(3) 2.390(3) 2.387(3)	59
$[HB(3,5\text{-}(CH_3)_2pz)_3]Ag(CN^tBu)$	2178	2.05(1)	2.271(9) 2.36(1) 2.38(1)	60
$[HB(3,5\text{-}(Ph)_2pz)_3]Ag(CN^tBu)$	2185	2.08(1)	2.319(7) 2.363(7) 2.321(7)	60

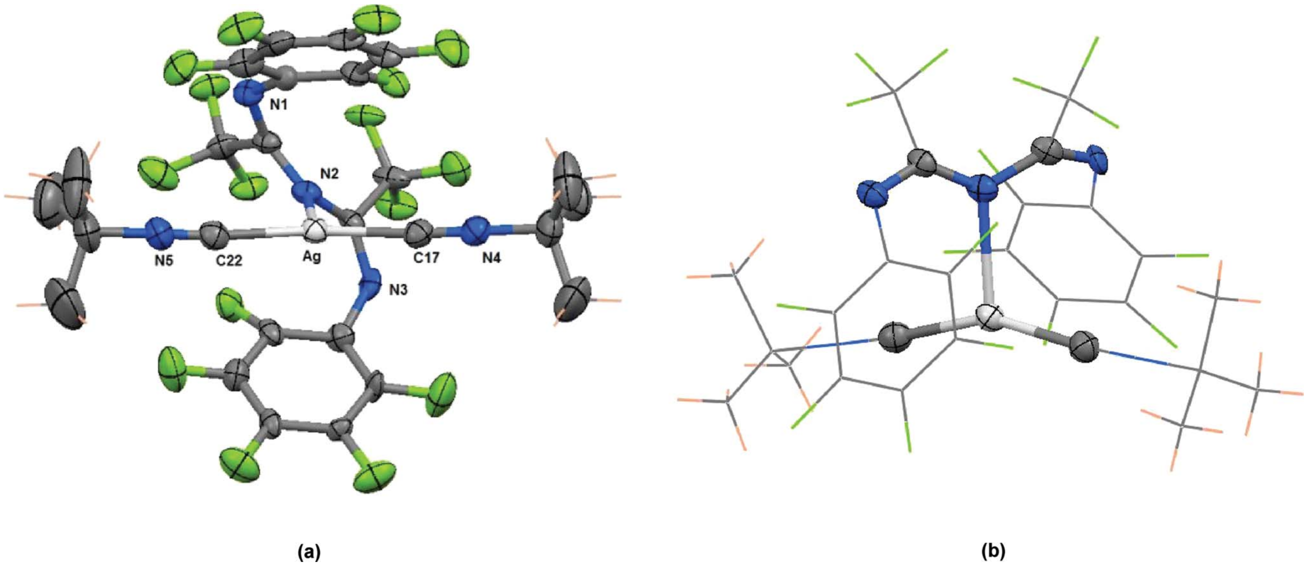


Fig. 4 Molecular structure of [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$ (**2**) ([N{(CF$_3$)C(C$_6$F$_5$)N}$_2$] moiety is disordered over two positions and only the major component is shown for clarity) and a view showing the triazapentadienyl ligand backbone. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ag–N(2) 2.445(2), Ag–C(17) 2.088(3), Ag–C(22) 2.095(3), N(5)–C(22) 1.125(4), N(4)–C(17) 1.144(4), C(17)–Ag–C(22) 154.56(13), N(2)–Ag–C(17) 102.42(11), N(2)–Ag–C(22) 102.78(11), Ag–C(17)–N(4) 173.7(3), Ag–C(22)–N(5) 174.3(3).

CN^{t}Bu = 2138 cm^{-1}).[61] For comparison, the ν_{CN} bands of highly electron deficient tris(pyrazolyl)borates or 1,3,5-triazapentadienyl ligands show a shift of the same order of magnitude. Complexes with more electron rich metal sites display the ν_{CN} bands at a relatively low frequency (see Table 1).

X-ray data show that [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$ (**2**) crystallizes in the *P*2$_1$/*c* space group and features a distorted W-shaped N$_3$C$_2$ core of the [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]$^-$ ligand (which is disordered over two positions at a 56 : 44 occupancy ratio) that coordinates to a Ag(CN^{t}Bu)$_2$ moiety in a κ^1-fashion *via* the central N-atom (Fig. 4). The three-coordinate silver center adopts a distorted trigonal planar (almost T-like) geometry with a large C22–Ag–C17 angle of 154.56(13)°. [N{(C$_3$F$_7$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$ (**3**) crystallizes in *P*2$_1$/*c* space group with three independent [N{(C$_3$F$_7$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$ molecules in the asymmetric unit (Fig. 5). Except for the disorder, the basic structural features are similar to those observed for [N{(CF$_3$)-C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$. [N{(C$_3$F$_7$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$ features relatively smaller C–Ag–C angles (141.01(17)°, 142.36(16)° and 147.94(15)° for the three independent molecules). As observed in [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$ and [N{(C$_3$F$_7$)C(C$_6$F$_5$)N}$_2$]Ag(CN^{t}Bu)$_2$, previously reported [N{(C$_3$F$_7$)C(Dipp)N}$_2$]Ag(CN^{t}Bu) also displays a κ^1-bonded (*via* central N) 1,3,5-triazapentadienyl moiety. [N{(C$_3$F$_7$)C-(Dipp)N}$_2$]Ag(CN^{t}Bu) is however a mono-isocyanide complex and has a two-coordinate, linear silver center.[35] It has a significantly shorter Ag–N bond perhaps due to the lower coordination number at silver (Table 1).

1,3,5-Triazapentadienyl ligands also allow us to stabilize di(*tert*-butyl isocyanide) adducts of copper(I). For example, [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Cu(CN^{t}Bu)$_2$ (**4**) can be obtained quite easily using [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]H, Cu$_2$O and CN^{t}Bu. The stoichiometry of the compound was not affected by reducing (to 1 equivalent) or increasing (>2 equivalents) the amount of the relevant isocyanide. Compound (**4**) displays a strong IR band at 2175 cm^{-1} (and a shoulder at 2193 cm^{-1}) that can be assigned to the C≡N stretch. This is similar to the ν_{CN} value observed for [N{(C$_3$F$_7$)C(Dipp)N}$_2$]Cu(CN^{t}Bu) (see Table 2). The related copper(I) complexes (see above) have relatively high CN stretching frequencies.

The IR stretching bands corresponding to the of *tert*-butyl isocyanide derivatives of 1,3,5-triazapentadienyl ligands appear as strong peaks at about 2175 cm^{-1} at frequencies significantly higher than the ν_{CN} value observed for the free *tert*-butyl isocyanide, in accordance with the occurrence of a primarily σ-bond between the metal and the isocyanide.[65] They are also higher than the corresponding values for [B(pz)$_4$]Cu(CN^{t}Bu) and [HB(pz)$_3$]Cu(CN^{t}Bu) as a direct result of the increased Lewis acidity of the copper center due to the presence of the weakly donating ligands while they are of the same order of magnitude of complexes containing poly(pyrazolyl)borate ligands bearing electron withdrawing substituents (Table 2). A number of other Cu(I) complexes containing the bis(isocyanide)copper(I) fragment are also known in the literature.[66–69]

X-ray crystal structure of [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Cu(CN^{t}Bu)$_2$ (**4**) is illustrated in Fig. 6. In contrast to [N{(CF$_3$)C(C$_6$F$_5$)-N}$_2$]Ag(CN^{t}Bu)$_2$, [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Cu(CN^{t}Bu)$_2$ features a U-shaped [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]$^-$ ligand backbone that coordinates to copper(I) in a κ^2-fashion *via* the two terminal N-atoms. The copper atom adopts a tetrahedral geometry with a C–Cu–C angle of 125.01(7)°. Although [N{(C$_3$F$_7$)C(Dipp)N}$_2$]Cu(CN^{t}Bu) is known and believed to contain a κ^2-bonded triazapentadienyl moiety based on spectroscopic data, the structural data are not-available for comparison.

The silver(I) phosphine complex [N{(CF$_3$)C(C$_6$F$_5$)-N}$_2$]Ag(PPh$_3$)$_2$ (**5**) was synthesized by the reaction of [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]H and Ag$_2$O in acetonitrile at reflux temperature for 16 h. Removal of solvent yielded a yellow solid, presumably [N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]Ag(CH$_3$CN)$_2$.

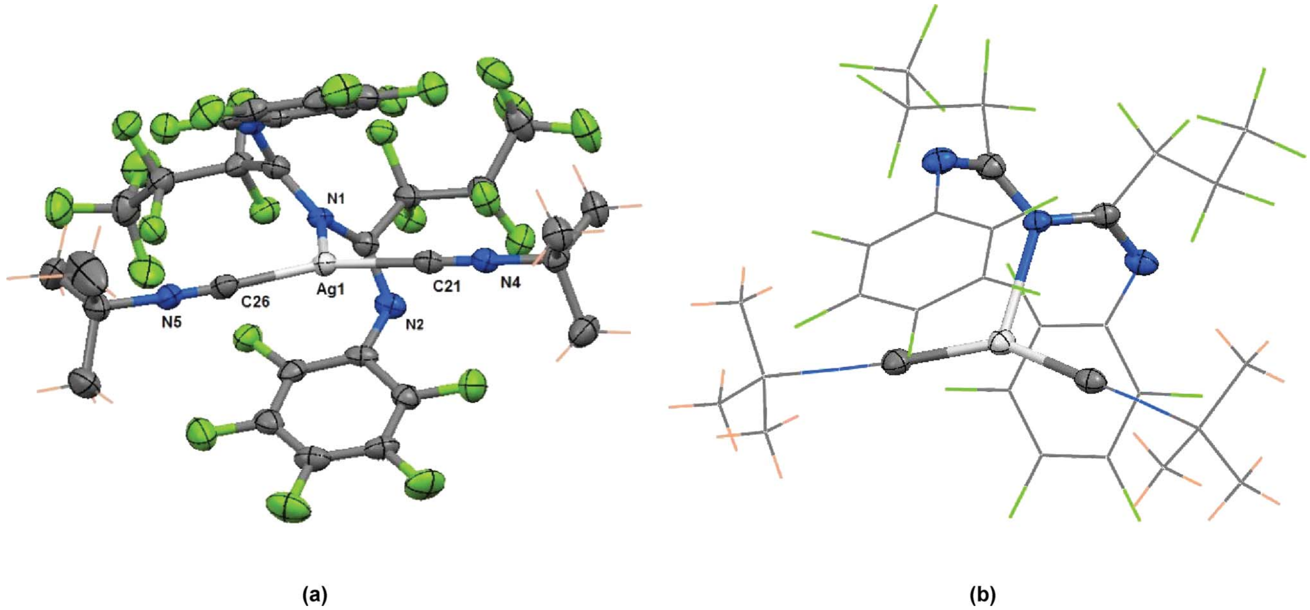


Fig. 5 Molecular structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**3**) and a view showing the triazapentadienyl ligand backbone. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.415(3), Ag(1)–C(21) 2.113(4), Ag(1)–C(26) 2.109(4), N(4)–C(21) 1.142(5), N(5)–C(26) 1.135(5), N(1)–Ag(1)–C(21) 104.37(12), N(1)–Ag(1)–C(26) 107.68(13), C(21)–Ag(1)–C(26) 147.94(15), Ag(1)–C(21)–N(4) 179.0(3), Ag(1)–C(26)–N(5) 176.8(3).

Table 2 Selected Cu(I)—CN^tBu complexes of poly(pyrazolyl)borates and 1,3,5-triazapentadienyl ligands and some of their structural and spectroscopic parameters

Complex	ν_{CN}/cm^{-1}	Cu–C/Å	Cu–N/Å	Ref.
$[N\{(CF_3)C(C_6F_5)N\}_2]Cu(CN^tBu)_2$ (**4**)	2175, 2193sh	1.9162(18) 1.9078(18)	2.0653(14) 2.0712(14)	This work
$[N\{(C_3F_7)C(Dipp)N\}_2]Cu(CN^tBu)$	2176	—	—	37
$[HB(3,5\text{-}(CF_3)_2pz)_3]Cu(CN^tBu)$	2196	1.827(6)	2.072(5) 2.093(4) 2.093(4)	62
$[H_3B(5\text{-}(CF_3)pz)]Cu(CN^tBu)_2$	2179	—	—	63
$[H_3B(3\text{-}(NO_2)pz)]Cu(CN^tBu)_2$	2178	—	—	61
$[H_2B(3\text{-}(NO_2)pz)_2]Cu(CN^tBu)_2$	2166, 2190sh	1.926(2) 1.903(2)	2.121(2) 2.129(2)	61
$[HB(3\text{-}(NO_2)pz)_3]Cu(CN^tBu)$	2162	—	—	61
$[H_2B(3\text{-}(CF_3)pz)_2]Cu(CN^tBu)_2$	2161, 2182sh	1.914(2) 1.9308(19)	2.0606(16) 2.0840(17)	63
$\{[H_2B(3,5\text{-}(CF_3)_2pz)_2]Cu(CN^tBu)\}_2$	2196	1.855(3)	2.018(3) 2.014(3)	62
$[HB(pz)_3]Cu(CN^tBu)$	2155	—	—	64
$[B(pz)_4]Cu(CN^tBu)$	2140	—	—	64

The product was dissolved in diethyl ether and 2 eq. of triphenylphosphine were added to the solution. After solvent removal, a pale yellow solid was obtained. The compound showed good solubility in chloroform and CH_2Cl_2. Similar to $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ or $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$, $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ did not show signs of decomposition after prolonged exposure to light. It was stable in air for at least 60 days. Crystals of compound (**5**) were obtained by slow diffusion of hexane into a solution of the compound in CH_2Cl_2 after 16 h as colorless plates. ^{31}P NMR spectrum of (**5**) in $CDCl_3$ at 293 K displayed a broad singlet at δ 10.79 but gave rise to an overlapping doublet of doublets at 218 K revealing the coupling to the two silver isotopes ($^1J(^{107}Ag–^{31}P) = 425$ Hz, $^1J(^{109}Ag–^{31}P) = 486$ Hz). The observed Ag–P coupling constants are in the range of the Ag–P couplings (from 300 to 500 Hz) typical of various silver diphosphine complexes (see Table 3). 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.

The X-ray molecular structure of crystalline $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**5**) is illustrated in Fig. 7. The NCNCN core adopts a twisted W-shaped conformation, as previously found for $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$. $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ also has a κ^1-bonded triazapentadienyl moiety. However, in contrast to $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**2**), the $[N\{(CF_3)C(C_6F_5)N\}_2]^-$ ligand in $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**5**) coordinates to silver(I) *via* one of the terminal N-atoms. Existence of such a coordination mode was proposed for $[N\{(C_3F_7)C(Ph)N\}_2]AuPPh_3$ but no

Table 3 Selected Ag(I)–PPh_3 complexes of poly(pyrazolyl)borates and 1,3,5-triazapentadienyl ligands and some of their structural and spectroscopic parameters

Complex	^{31}P NMR/δ (ppm)	Ag–P/Å	Ag–N/Å	Ref.
$[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$	17.3 dd (298 K) $^1J(^{107}Ag–^{31}P) = 616$ Hz $^1J(^{109}Ag–^{31}P) = 709$ Hz	2.3487(10)	2.250(3) 2.252(3)	35
$[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**5**)	10.31 dd (218 K) $^1J(^{107}Ag–^{31}P) = 425$ Hz $^1J(^{109}Ag–^{31}P) = 486$ Hz	2.4308(7) 2.4406(7)	2.321(2)	This work
$[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_3$ (**6**)	6.39 d (218 K) $^1J(Ag–^{31}P) = 232$ Hz	—	—	This work
$[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**7**)	10.8 d (298 K) $^1J(Ag–^{31}P) = 365$ Hz	2.4464(6) 2.4514(6)	2.3849(19)	This work
$[H_2B(pz)_2]Ag(PPh_3)_2$[a]	5.4 dd (183 K) $^1J(^{107}Ag–^{31}P) = 361$ Hz $^1J(^{109}Ag–^{31}P) = 414$ Hz	2.4256(9), 2.461(1) 2.5049(9), 2.484(1)	2.326(3), 2.295(2) 2.360(3), 2.323(2)	71
$[H_2B(3,5\text{-}Me_2pz)_2]Ag(PPh_3)_2$	3.37 d (223 K) $^1J(Ag–^{31}P) = 301$ Hz	—	—	71
$[H_2B(tz)_2]Ag(PPh_3)_2$	7.44 dd (223 K) $^1J(^{107}Ag–^{31}P) = 383$ Hz $^1J(^{109}Ag–^{31}P) = 439$ Hz	2.4329(8) 2.4344(8)	2.297(3) 2.425(3)	72
$[H_2B(btz)_2]Ag(PPh_3)_2$	7.40 dd (223 K) $^1J(^{107}Ag–^{31}P) = 300$ Hz $^1J(^{109}Ag–^{31}P) = 332$ Hz	—	—	73
$[B(pz)_4]Ag(PPh_3)_2$	6.1 br (223 K)	2.4265(6) 2.5342(7)	2.319(2) 2.364(2)	74
$[H_2B(3\text{-}(NO_2)pz)_2]Ag(PPh_3)_2$	11.53 d (223 K) $^1J(Ag–^{31}P) = 455$ Hz	2.4138(6) 2.4641(6)	2.3970(17) 2.5661(19)	75
$[H_2B(3\text{-}(CF_3)pz)_2]Ag(PPh_3)_2$[b]	4.16 dd (193 K) $^1J(^{107}Ag–^{31}P) = 281$ Hz $^1J(^{109}Ag–^{31}P) = 323$ Hz 8.57 dd (193 K) $^1J(^{107}Ag–^{31}P) = 404$ Hz $^1J(^{109}Ag–^{31}P) = 465$ Hz 16.66 dd (193 K) $^1J(^{107}Ag–^{31}P) = 638$ Hz $^1J(^{109}Ag–^{31}P) = 733$ Hz	—	—	75
$[H_3B(5\text{-}(CF_3)pz)]Ag(PPh_3)_2$	9.31 d (223 K) $^1J(Ag–^{31}P) = 417$ Hz	2.4285(10) 2.4736(10)	2.335(3)	76
$[HB(btz)_3]Ag(PPh_3)_3$[c]	6.36 d (218 K) $^1J(Ag–^{31}P) = 405$ Hz 16.04 d (218 K) $^1J(Ag–^{31}P) = 701$ Hz	2.5458(4) 2.5592(6) 2.5256(6)	2.403(1)	73

[a] Dinuclear complex. [b] In the ^{31}P NMR spectrum double doublets are observed at 223 K with coupling constants typical of tri-, di- and mono-phosphine species, suggesting the occurrence of dissociative equilibria. [c] In the ^{31}P NMR spectrum doublets are observed at 223 K with coupling constants, $^1J(Ag–^{31}P)$, of 405 and 701 Hz, typical of di- and mono-phosphine species, respectively, suggesting the occurrence of dissociative equilibria.

structural data were reported.[38] The silver atom in (**5**) is three coordinate and adopts an essentially trigonal planar geometry (sum of the angles at Ag = 356.8°) with P–Ag–P angle of 129.11(2)°.

Recently a gold(I) diketiminato complex, $[HC\{(CF_3)C(R)N\}_2]Au(PPh_3)$ ($R = 3,5\text{-}C_6H_3(CF_3)_2$) was reported, adopting a κ^1-bonded 1,5-diazapentadienyl moiety; by contrast, the analogous complex $[HC\{(CF_3)C(R)N\}_2]Cu(PPh_3)_2$ adopts the expected chelate structure with a κ^2-bonded 1,5-diazapentadienyl moiety.[70]

Interestingly, during the repeated synthesis of $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**5**), we observed that it is possible to obtain $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_3$ (**6**) by varying the phosphine to silver ratio. Although we have managed to isolate and characterize $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_3$ (**6**) using spectroscopic methods, it is difficult to propose the triazapentadienyl ligand coordination mode solely based on spectroscopic data. The ^{31}P NMR spectrum of (**6**) in $CDCl_3$ at 293 K displayed a broad singlet at δ 6.71 but gave rise to a doublet at 218 K with a coupling constant $^1J(Ag–^{31}P)$ of 232 Hz, in accordance with a $AgNP_3$ coordination core. The observed Ag–P coupling constant is at the lower end of the Ag–P couplings of various other silver phosphine complexes (see Table 3).

For comparison to compound (**5**) we have also synthesized and investigated the structural features of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**7**). This was also the product we isolated from a reaction containing 1 : 1 molar ratio of Ag:PPh_3 (rather than 1 : 2). $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**7**) features a twisted, S-shaped triazapentadienyl NCNCN core. It also coordinates to silver(I) *via* one of the terminal nitrogen atoms (Fig. 8). The three-coordinate silver center in (**7**) adopts a trigonal planar geometry (sum of the angles at Ag = 358.4°) with P–Ag–P angle of 128.81(2)°. The X-ray crystal structure

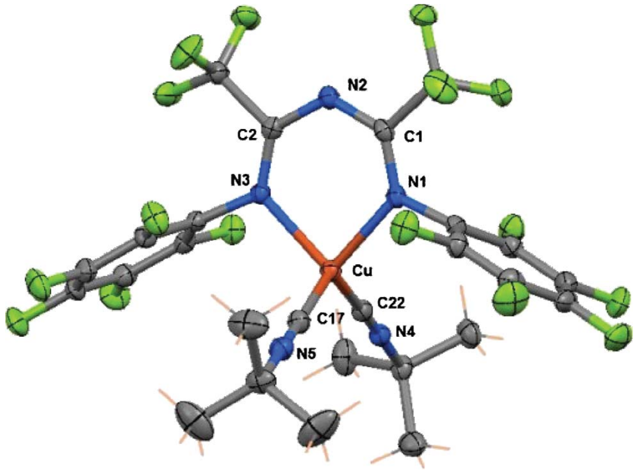


Fig. 6 Molecular structure of $[\text{N}\{(\text{CF}_3)\text{C}(\text{C}_6\text{F}_5)\text{N}\}_2]\text{Cu}(\text{CN}^t\text{Bu})_2$ (**4**). Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Cu–N(1) 2.0653(14), Cu–N(3) 2.0712(14), Cu–C(17) 1.9162(18), Cu–C(22) 1.9078(18), N(1)–Cu–N(3) 87.66(6), N(1)–Cu–C(22) 112.91(6), N(1)–Cu–C(17) 106.22(6), N(3)–Cu–C(22) 110.36(6), N(3)–Cu–C(17) 108.28(7), C(17)–Cu–C(22) 125.01(7).

of $[\text{N}\{(\text{C}_3\text{F}_7)\text{C}(\text{Dipp})\text{N}\}_2]\text{AgPPh}_3$ was reported earlier.[35] It also has a three-coordinate, trigonal planar silver center. The triazapentadienyl ligand in $[\text{N}\{(\text{C}_3\text{F}_7)\text{C}(\text{Dipp})\text{N}\}_2]\text{AgPPh}_3$ however acts as κ^2-donor.

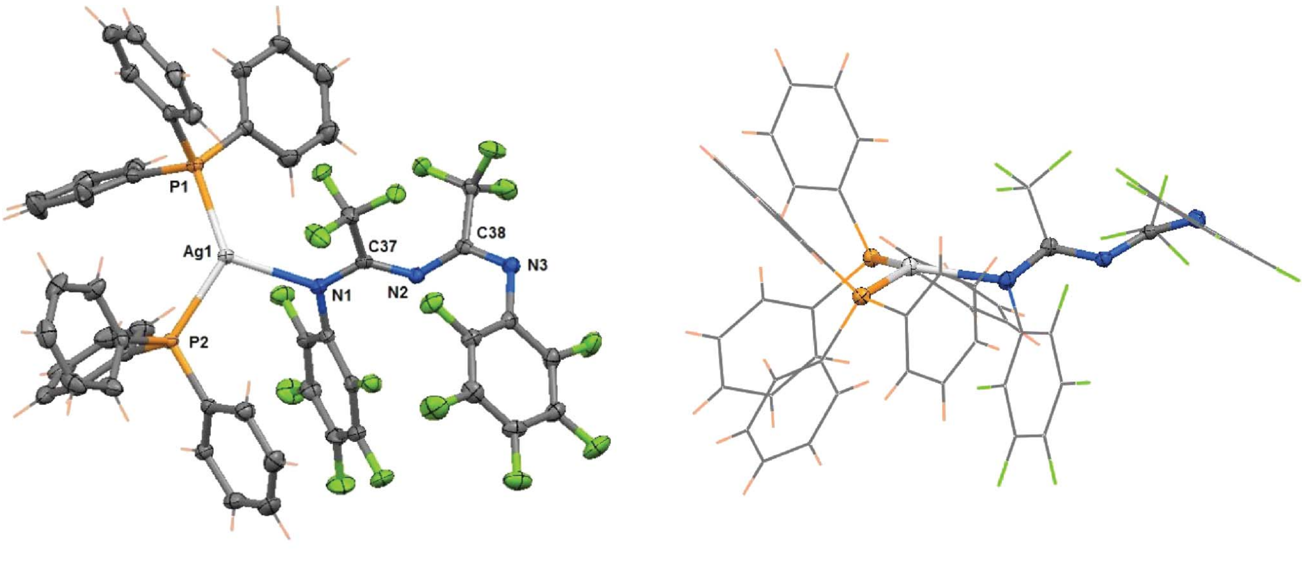
Coordination properties of fluorinated $[\text{N}\{(\text{R}^2)\text{C}(\text{R}^1)\text{N}\}_2]^-$ also merit some comments. This work and prior reports show that they bind to metal ions in several different fashions (*e.g.*, κ^1-N(central), κ^1-N(terminal), or κ^2-N(terminal) with W- or U-shaped (sometimes with significant twisting or S-shaped) ligand conformers). We have reported that the two lowest energy conformations found for the $[\text{N}\{(\text{C}_3\text{F}_7)\text{C}(\text{Dipp})\text{N}\}_2]^-$ at the PM3 level of theory are U-shaped and W-shaped.[77] The U-shaped conformer is only 0.1 kcal mol^{-1} lower in energy than the W-shaped conformer pointing to essentially degenerate structures. Furthermore, the HOMO is more or less evenly distributed among the three N atoms of either the W- or U-conformer of the anionic ligand. Calculated Mulliken charges of the U and W conformers are –0.2 for the terminal nitrogens and –0.4 for the central nitrogen. Thus, fluorinated $[\text{N}\{(\text{R}^2)\text{C}(\text{R}^1)\text{N}\}_2]^-$ systems are an interesting class of highly flexible supporting ligands and they seem to adapt easily by changing the coordination mode to satisfy the steric-electronic demands of the coordinating fragment. More detailed studies are presently underway to understand the ligands coordination modes and to see whether we can predict the observed structures using computational methods.

In summary, we report the synthesis of $[\text{N}\{(\text{CF}_3)\text{C}(\text{C}_6\text{F}_5)\text{N}\}_2]\text{H}$ (**1**) and the use of its conjugate base as a supporting ligand for the isolation of silver(I) and copper(I) complexes. Some of the related chemistry involving the $[\text{N}\{(\text{C}_3\text{F}_7)\text{C}(\text{C}_6\text{F}_5)\text{N}\}_2]^-$ is also presented. X-ray crystallographic data show an interesting array of coordination modes and triazapentadienyl ligand backbone conformations, and demonstrate the ability of triazapentadienyl supporting ligands to adopt their mode of coordination based on the requirements of the metal fragment.

Experimental

Materials and general methods

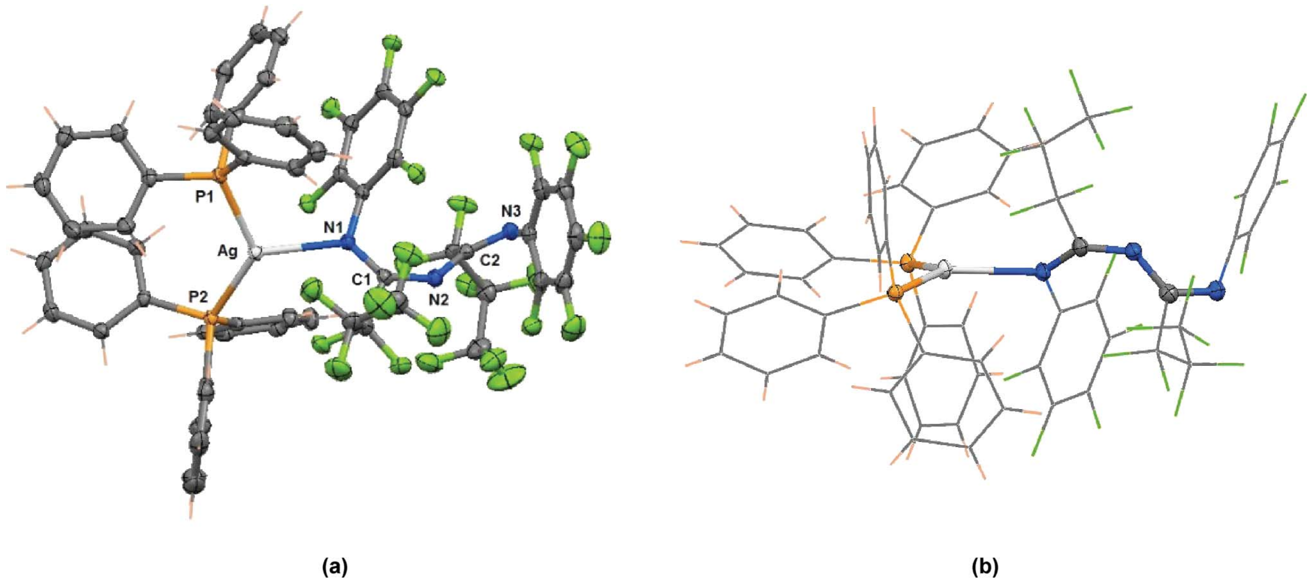
All syntheses and handling were carried out under an atmosphere of dry dinitrogen, using standard Schlenk techniques or in a glove



(a)

(b)

Fig. 7 Molecular structure of $[\text{N}\{(\text{CF}_3)\text{C}(\text{C}_6\text{F}_5)\text{N}\}_2]\text{Ag}(\text{PPh}_3)_2$ (**5**) and a view showing the triazapentadienyl ligand backbone. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.321(2), Ag(1)–P(1) 2.4308(7), Ag(1)–P(2) 2.4406(7), N(1)–C(37) 1.316(3), N(2)–C(38) 1.354(3), N(3)–C(38) 1.283(3), Ag(1)–N(1)–C(37) 127.53(17), N(1)–Ag(1)–P(1) 121.80(6), N(1)–Ag(1)–P(2) 105.94(5), P(1)–Ag(1)–P(2) 129.11(2), N(2)–C(38)–N(3) 127.6(2).



(a)

(b)

Fig. 8 Molecular structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (**7**) and a view showing the triazapentadienyl ligand backbone. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ag–N(1) 2.3849(19), Ag–P(1) 2.4464(6), Ag–P(2) 2.4514(6), N(1)–C(1) 1.322(3), N(2)–C(1) 1.305(3), N(2)–C(2) 1.341(3), N(3)–C(2) 1.287(3), N(1)–Ag–P(1) 122.53(5), N(1)–Ag–P(2)107.02(5), P(1)–Ag–P(2) 128.81(2), Ag–N(1)–C(1) 129.27(15), N(1)–C(1)–N(2) 134.5(2), C(1)–N(2)–C(2) 132.1(2), N(2)–C(2)–N(3) 127.9(2).

box. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer SPECTRUM ONE System. FT-IR instrument accessorised with a single reflection ATR unit (universal diamond ATR top-plate). IR annotations used: br = broad, m = medium, s = strong, sbr = strong broad, sh = shoulder, w = weak. ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on an Oxford-400 Varian spectrometer (400.4 MHz for ^1H, 376.8 MHz for ^{19}F and 162.1 MHz for ^{31}P). Chemical shifts, in ppm, for ^1H NMR spectra are relative to internal Me_4Si. ^{19}F NMR chemical shifts were referenced relative to external $CFCl_3$. ^{31}P NMR chemical shifts were referenced to a 85% H_3PO_4 standard. The ^{31}P NMR spectroscopic data were accumulated with ^1H decoupling. NMR annotations used: br = broad, d = doublet, dd = double doublet, m = multiplet, s = singlet, sbr = broad singlet, t = triplet, tt = triple triplet. Electrospray mass spectra (ESI MS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using a methanol mobile phase. The compounds were added to reagent grade methanol to give solutions of approximate concentration 0.1 mM. These solutions were injected (1 μL) into the spectrometer *via* a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 μL min^{-1}, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 V and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in this ESI MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the IsoPro 3.0 computer program. All reagents were purchased from Aldrich and used without further purification. $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ was synthesized using the method reported in the literature.[54]

Synthesis of $[N\{(CF_3)C(C_6F_5)N\}_2]H$ (1)

Perfluoro-3-aza-2-pentene was prepared under a nitrogen atmosphere by dropwise addition of $N(C_2F_5)_3$ (15.0 g, 40.4 mmol) to SbF_5 (10.0 g, 46.1 mol) which was pre-heated at 55 °C in a 50 mL three-neck flask while stirring vigorously.[56] The temperature was raised to 60 °C to distill off the product as quickly as it was formed (this is important because, based on our experience, the product yield suffers significantly if it is left in the crude mixture) through a short pass condenser cooled at −10 °C and collected in a 50 mL pear shape flask cooled at −78 °C. Yield: 5.01 g, (53%). This volatile compound was used immediately in the next step (or stored at −20 °C). Perfluoro-3-aza-2-pentene (5.4 g, 23.0 mmol) was added dropwise (which is also a challenging task due to the high volatility of perfluoro-3-aza-2-pentene) to a mixture of triethylamine (3.5 mL, 34.5 mmol) and perfluoroaniline (4.2 g, 23 mmol) in ether 100 mL at −5 °C (salt–ice–water bath). 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 at 5 °C, first with 5% HCl and then twice with deionized water. The ether layer was separated and dried over anhydrous $CaCl_2$ or Na_2SO_4. The solvent was removed at reduced pressure to obtain $[N\{(CF_3)C(C_6F_5)N\}_2]H$ as a colorless solid. Yield: 8.06 g (65%). Mp: 130–140 °C. IR (cm^{-1}): 3142 w, 2992 w, 2914 w (CH); 1716 s, 1639 m, 1500 s, 1463 m, 1443 w, 1369 w, 1327 m, 1312 m, 1202 s, 1171 m, 1133 m, 1196 s, 993 s, 979 sh, 932 m, 812 m, 789 w, 755 m, 740 w, 719 m, 702 m. ^1H NMR ($CDCl_3$, 293 K): δ 7.67 (s, 1H, N*H*). ^1H NMR (DMSO-d^6, 293 K): δ 11.97 (s, 1H, N*H*).^{19}F NMR ($CDCl_3$, 293 K): δ −69.44, −71.24 and −74.81 (s, 6F, CF_3), −143.51 (d, *J* = 15.2 Hz, C*F*), −144.67, −148.23 and −150.67 (sbr, C*F*), −152.58 (t, *J* = 21.7 Hz, C*F*), −159.44 and −159.96 (sbr, C*F*), −160.36 (t, *J* = 21.7 Hz, C*F*), −162.67 (sbr, C*F*). ^{19}F NMR (DMSO-d^6, 293 K): δ −69.51, −73.64 and −75.10 (s, 6F, CF_3), −145.17 (d, J = 19.5 Hz, CF), −148.28 (sbr, CF), −154.49 (t, J = 23.8 Hz, CF), −161.93 (t, J = 23.8 Hz, CF), −164.32 (sbr, CF). ESI MS (major negative-ions, CH_3OH), m/z (%): 538 (100) $[N\{(CF_3)C(C_6F_5)N\}_2]^-$. Anal. Calcd. for $C_{16}HF_{16}N_3$: C, 35.64; H, 0.19; N, 7.79%. Found: C, 35.30; H, 0.23; N, 7.62%.

Synthesis of $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (2)

$[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) (0.270 g, 0.50 mmol) was added to a suspension of Ag_2O (0.058 g, 0.25 mmol) in acetonitrile (25 mL); the mixture was refluxed for 12 h. The solvent was removed under vacuum, the resulting residue was dissolved in chloroform (25 mL) and *tert*-butyl isocyanide (0.083 g, 1.00 mmol) was added at room temperature. The mixture stirred overnight and the solvent was removed under vacuum to afford a grey solid in 52% yield. The crude complex $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (**2**) was dissolved in $CHCl_3$–diethyl ether (1 : 4) solution and crystals suitable for X-ray diffraction analysis were obtained at room temperature. M.p. 116 °C. IR (cm^{-1}): 2996 w (CH); 2214 s (C≡N); 1747 w, 1650 w, 1626 w; 1558 s, 1498 sbr, 1440 m, 1377 m, 1309 w, 1190 s, 1160 s, 1140 s, 1131 s, 1123 s, 1104 s, 994 s, 980 s, 913 m, 845 w, 725 s, 712 m. ^1H NMR ($CDCl_3$, 293 K): δ 1.51 (s, CCH_3). ^{19}F NMR ($CDCl_3$, 293 K): δ −69.56 (s, CF_3), −146.85 (sbr, CF), −163.92 (t, J = 21.5 Hz, CF), −164.6 (t, J = 20.5 Hz, CF). ESI MS (major posive-ions, CH_3OH), m/z (%): 274 (100) $[Ag(CN^tBu)_2]^+$, 920 (50) $[[N\{(CF_3)C(C_6F_5)N\}_2]AgCN^tBu + AgCN^tBu]^+$. ESI MS (major negative-ions, CH_3OH), m/z (%): 538 (100) $[N\{(CF_3)C(C_6F_5)N\}_2]^-$, 1184 (30) $[[N\{(CF_3)C(C_6F_5)N\}_2]_2Ag]^-$. Anal. Calcd. for $C_{26}H_{18}AgF_{16}N_5$: C, 38.44; H, 2.23; N, 8.62%. Found: C, 38.03; H, 1.98; N, 8.43%.

Synthesis of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (3)

$[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ (0.200 g, 0.271 mmol) and Ag_2O (0.047 g, 0.203 mmol, 50% excess) were mixed in THF and refluxed for 16 h. The solution was filtered over a bed of Celite and *tert*-butyl isocyanide (0.10 mL, 0.88 mmol) was added to the filtrate. The solvent was removed under vacuum to leave light yellow solid. The solid was dissolved in minimum amount of dichloromethane and layered with hexane to obtain colorless prismatic crystals (the mixture first formed a yellow oil at the bottom of the flask, but eventually formed crystals.) Yield: 0.240 g (88%). M.p. 60–65 °C. IR (cm^{-1}): 3000 w, 2947 w (CH); 2211 s (C≡N); 1558 sbr, 1513 sbr, 1437 s, 1399 s, 1378 m, 1344 s, 1306 m, 1235 sbr, 1123 s, 1072 m, 1002 s, 982 s, 910 w, 838 s, 747 m, 709 w, 657 m. ^1H NMR ($CDCl_3$, 293 K): δ 1.49 (s, CCH_3). ^{19}F NMR ($CDCl_3$, 293 K): δ −83.6 (t, J = 11.0 Hz, CF_3), −111.2 and −117.8 (AB multiplet, J_{AB} = 271.5 Hz, α-CF_2), −125.9 and −128.3 (AB multiplet, J_{AB} = 286.1 Hz, β-CF_2), −149.7 (s, CF), −167.2 (t, J = 22 Hz, CF), −167.6 (t, J = 22 Hz, CF). Anal. Calcd. for $C_{30}H_{18}AgF_{24}N_5$: C, 35.59; H, 1.79; N, 6.92%. Found: C, 35.39; H, 1.40; N, 6.85%.

Synthesis of $[N\{(CF_3)C(C_6F_5)N\}_2]Cu(CN^tBu)_2$ (4)

$[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) (0.270 g, 0.50 mmol) was added to a suspension of Cu_2O (0.036 g, 0.25 mmol) in acetonitrile (25 mL); the mixture was refluxed for 12 h. The solvent was removed under vacuum, the resulting residue was dissolved in dichloromethane (25 mL) and *tert*-butyl isocyanide (0.083 g, 1.00 mmol) was added at room temperature. The mixture stirred overnight and the solvent was removed under vacuum to afford a green–brown solid in 55% yield. The crude complex $[N\{(CF_3)C(C_6F_5)N\}_2]Cu(CN^tBu)_2$ (**4**) was dissolved in $CHCl_3$–diethyl ether (1 : 4) solution and a single crystal suitable for X-ray diffraction analysis was obtained at room temperature. M.p. 136–137 °C. IR (cm^{-1}): 2993 w (CH); 2193 sh, 2175 s (C≡N); 1599 m, 1506 s, 1498 m, 1469 m, 1416 w, 1374 w, 1339 w, 1306 w, 1222 sh, 1193 s, 1153 m, 1112 m, 1025 w, 987 s, 906 w, 842 m, 809 w, 768 w, 753 w, 730 w, 706 w. ^1H NMR ($CDCl_3$, 293 K): δ 1.43 (s, CCH_3). ^{19}F NMR ($CDCl_3$, 293 K): δ −68.42 (s, CF_3), −150.26 (sbr, CF), −162.92 (br, CF), −164.48 (sbr, CF). ESI MS

Table 4 Crystal data and summary of data collection and refinement

Formula	$[N\{(CF_3)C(C_6F_5)$-$N\}_2]H$ (**1**)	$[N\{(CF_3)C(C_6F_5)$-$N\}_2]Ag(CN^tBu)_2$ (**2**	$[N\{(C_3F_7)C(C_6F_5)$-$N\}_2]Ag(CN^tBu)_2$ (**3**)	$[N\{(CF_3)C(C_6F_5)$-$N\}_2]Cu(CN^tBu)_2$ (**4**)	$[N\{(CF_3)C(C_6F_5)$-$N\}_2]Ag(PPh_3)_2$ (**5**)	$[N\{(C_3F_7)C(C_6F_5)$-$N\}_2]Ag(PPh_3)_2$ (**7**)
FW	539.20	812.32	3037.09	767.99	1170.60	1370.64
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$
Cell dimensions	a = 7.660(2) Å	a = 19.9480(8) Å	a = 15.6234(19) Å	a = 20.3464(14) Å	a = 11.3585(9) Å	a = 11.3132(4) Å
	b = 7.236(2) Å	b = 11.4960(5) Å	b = 19.773(2) Å	b = 16.8298(12) Å	b = 16.9513(14) Å	b = 13.4430(5) Å
	c = 31.921(9) Å	c = 13.2404(5) Å	c = 35.489(4) Å	c = 19.7746(14) Å	c = 24.725(2) Å	c = 18.4935(7) Å
	α = 90°	α = 90°	α = 90°	α = 90°	α = 90°	α = 75.796(1)°
	β = 90.188(3)°	β = 90.466(1)°	β = 96.133(2)°	β = 115.546(1)°	β = 93.422(1)°	β = 77.788(1)°
	γ = 90°	γ = 90°	γ = 90°	γ = 90°	γ = 90°	γ = 86.892(1)°
V (Å^3)	1769.2(2)	3036.2(2)	10900(2)	6109.4(7)	4752.1(7)	2664.86(17)
Z	4	4	4	8	4	2
d_c (g cm^{-3})	2.024	1.777	1.851	1.670	1.636	1.708
μ (mm^{-1})	0.241	0.789	0.710	0.840	0.596	0.566
F(000)	1048	1600	5952	3056	2336	1360
θ range (°)	1.28 to 26.50	2.04 to 26.00	1.18 to 28.37	1.64 to 26.50	1.46 to 28.29	1.71 to 26.00
Reflns collected	15 226	24 060	107 229	24 961	46 428	21 671
R_{int} (ind reflns)	0.0263(3666)	0.0375(5963)	0.0452 (27199)	0.0263(6320)	0.0544(11784)	0.0213(10405)
Data/restr/params	3666/0/321	5963/23/676	27199/30/1639	6320/0/439	11784/0/667	10405/0/775
GOF on F^2	1.033	1.138	1.047	1.049	1.025	1.041
R_1 [$I > 2\sigma(I)$]/all data	0.0455/0.0475	0.0374/0.0402	0.0571/0.0765	0.0320/0.0367	0.0420/0.0648	0.0342/0.0393
wR_2 [$I > 2\sigma(I)$]/all data	0.1185/0.1202	0.0951/0.0971	0.1455/0.1612	0.0810/0.0845	0.0903/0.1006	0.0869/0.0901

(major positive-ions, CH_3OH), *m*/*z* (%): 230 (100) $[Cu(CN^tBu)_2]^+$, 831 (30) $[[N\{(CF_3)C(C_6F_5)N\}_2]CuCN^tBu + CuCN^tBu]^+$. ESI MS (major negative-ions, CH_3OH), *m*/*z* (%): 538 (100) $[N\{(CF_3)C(C_6F_5)N\}_2]^-$, 1140 (50) $[[N\{(CF_3)C(C_6F_5)N\}_2]_2Cu]^-$. Anal. Calcd. for $C_{26}H_{18}CuF_{16}N_5$: C, 40.66; H, 2.36; N, 9.12%. Found: C, 40.50; H, 2.22; N, 8.97%.

Synthesis of $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (5)

$[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) (0.270 g, 0.50 mmol) was added to a suspension of Ag_2O (0.058 g, 0.25 mmol) in acetonitrile (25 mL); the mixture was refluxed for 12 h. The solvent was removed under vacuum, the resulting residue was dissolved in diethyl ether (25 mL) and triphenylphosphine (0.262 g, 1.0 mmol) was added at room temperature. The mixture was stirred overnight and the solvent was removed under vacuum to obtain a solid that was recrystallized with *n*-hexane to afford a pale yellow solid in 90% yield. Crystals suitable for X-ray diffraction analysis were obtained after 16 h as colorless plates by slow diffusion of hexane into a solution of the compound in CH_2Cl_2. M.p. 139–141 °C. IR (cm^{-1}): 3057 w (CH); 1594 br; 1499 s, 1488 sh (C=C + C=N); 1436 m, 1332 w, 1307 w, 1234 m, 1194 m, 1141 m, 1094 m, 1026 w, 978 s, 917 m, 847 w, 785 w, 742 s, 690 s. ^1H NMR ($CDCl_3$, 293 K): 7.17–7.43 (m, PPh_3). ^{19}F NMR ($CDCl_3$, 293 K): δ −70.05 (s, CF_3), −148.58 (sbr, CF), −164.76 (sbr, CF), −165.39 (sbr, CF). ^{31}P NMR ($CDCl_3$, 293 K): δ 10.79 (sbr). ^{31}P NMR ($CDCl_3$, 218 K): δ 10.31 (dd, $^1J(^{107}Ag–^{31}P) = 425$ Hz, $^1J(^{109}Ag–^{31}P) = 486$ Hz). ESI MS (major positive-ions, CH_3OH), *m*/*z* (%): 632 (100) $[Ag(PPh_3)_2]^+$. ESI MS (major negative-ions, CH_3OH), *m*/*z* (%): 538 (100) $[N\{(CF_3)C(C_6F_5)N\}_2]^-$. Anal. Calcd. for $C_{52}H_{30}AgF_{16}N_3P_2$: C, 53.35; H, 2.58; N, 3.59%. Found: C, 53.76; H, 2.38; N, 3.41%.

Synthesis of $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_3$ (6)

$[N\{(CF_3)C(C_6F_5)N\}_2]H$ (**1**) (0.270 g, 0.50 mmol) was added to a suspension of Ag_2O (0.058 g, 0.25 mmol) in acetonitrile (25 mL); the mixture was refluxed for 12 h. The solvent was removed under vacuum, the resulting residue was dissolved in diethyl ether (25 mL) and triphenylphosphine (0.393 g, 1.5 mmol) was added at room temperature. The mixture was stirred overnight and the solvent was removed under vacuum to obtain a gray solid that was recrystallized with *n*-hexane to afford a light gray solid in 85% yield. M.p. 149–150 °C. IR (cm^{-1}): 3064 w (CH); 1768 w, 1655 w, 1580 m; 1509 sh, 1497 s, 1479 m, 1435 s, 1348 m, 1305 m, 1245 m, 1198 m, 1161 w, 1136 m, 1081 m, 1026 m, 992 s, 867 m, 840 m, 783 m, 743 s, 691 s. ^1H NMR ($CDCl_3$, 293 K): 7.00–7.37 (m, PPh_3). ^{19}F NMR ($CDCl_3$, 293 K): δ −70.77 (s, CF_3), −149.02 (sbr, CF), −166.60 (t, J = 21.5 Hz, CF), −167.27 (sbr, CF). ^{31}P NMR ($CDCl_3$, 293 K): δ 6.71 (sbr). ^{31}P NMR ($CDCl_3$, 218 K): δ 6.39 (d, $^1J(Ag–^{31}P) = 232$ Hz). ESI MS (major positive-ions, CH_3OH), *m*/*z* (%): 632 (100) $[Ag(PPh_3)_2]^+$. ESI MS (major negative-ions, CH_3OH), *m*/*z* (%): 538 (100) $[N\{(CF_3)C(C_6F_5)N\}_2]^-$. Anal. Calcd. for $C_{70}H_{45}AgF_{16}N_3P_3$: C, 58.68; H, 3.17; N, 2.93%. Found: C, 58.86; H, 3.09; N, 2.73%.

Synthesis of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (7)

$[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ (1.0 g, 1.4 mmol), Ag_2O (0.16 g, 0.7 mmol), triethylamine (0.2 mL, 1.4 mmol) and THF (20 mL) were stirred at 75 °C for 16 h. The mixture was filtered over a bed of Celite and the filtrate added dropwise over a solution of triphenylphosphine (0.73 g, 2.8 mmol) in *n*-hexane (30 mL) at room temperature. It was left to stir for 12 h. The solution was then filtered and concentrated up to 2 mL. Transparent square rods of $[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ crystallized at room temperature after 16 h. Yield: 1.40 g (73%). M.p. 153–154 °C. ^1H NMR (C_6D_6): δ 7.13 (d, J = 7.1 Hz, 6H, *o*-Ar), 6.96 (tt, ^3J = 7.3 Hz, ^4J = 2.2 Hz, 3H, *p*-Ar), 6.9 (t, ^3J = 7.5 Hz, 6H, *m*-Ar). ^{19}F NMR (C_6D_6): δ −80.07 (t, J = 8.3 Hz, 6F, CF_3), −114.17 and −113.11 (AB multiplet, J = 264.1 Hz, 4F, α-CF_3), −124.61 (s, 2F, β-CF_2), −124.71 (s, 2F, β-CF_2), −147.92 (d, J = 15.1 Hz, 4F, CF), −163.73 (t, J = 19.3 Hz, 2F, CF), −164.44 (t, J = 21.2 Hz, 4F, CF). ^{31}P NMR (C_6D_6): δ 10.8 (d, $^1J(Ag–^{31}P) = 365$ Hz). Anal. Calcd for $C_{56}H_{30}F_{24}N_3P_2Ag$: C, 49.07; H, 2.21; N, 3.07%. Found: C, 48.40; H, 2.15; N, 3.12%.

X-ray data collection and structure determinations

Suitable crystals covered with a layer of paratone-N oil, were selected and mounted within 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 = 0.71073 Å).[78] The data frames were integrated with the Bruker SAINT-Plus software package.[79] Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package.[80] Crystallographic data are summarized in Table 4.

$[N\{(CF_3)C(C_6F_5)N\}_2]H$ (1). Crystallized in space group $P2_1/n$. All the non-hydrogen atoms were refined anisotropically. The N-hydrogen atom was located from the difference map, included and refined. All other hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons. The structure was refined using the TWIN command with a twin ratio of 76 : 24.

$[N\{(CF_3)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (2). Crystallized in space group $P2_1/c$. All the non-hydrogen atoms were refined anisotropically except for C5 (carbon atom from C_6F_6). The ISOR command was used to refine C26 anisotropically. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons. The molecule demonstrated positional disorder in the "$[N\{(CF_3)C(C_6F_5)N\}_2]$" fragment over two positions which was modeled successfully and the occupancies were refined to a ratio of 56 : 44.

$[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(CN^tBu)_2$ (3). Crystallized in space group $P2_1/c$. Three independent molecules are present in the asymmetric unit. All the non-hydrogen atoms were refined anisotropically. The ISOR command was used to refine atoms C67, C68, F56, F58, and F62.

$[N\{(CF_3)C(C_6F_5)N\}_2]Cu(CN^tBu)_2$ (4). Crystallized in space group $C2/c$. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons.

$[N\{(CF_3)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (5). Crystallized in space group $P2_1/n$. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons.

$[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(PPh_3)_2$ (7). Crystallized in space group $P\bar{1}$. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons. Individual C_3F_7 groups were not disordered and refined well without further restraints.

Acknowledgements

This work was financially supported by MIUR (PRIN 20078EWK9B). We are grateful to CIRCMSB (Consorzio Interuniversitario di Ricerca in Chimica dei Metalli nei Sistemi Biologici). Support by the National Science Foundation (CHE-0845321 to H.V.R.D) and the Robert A. Welch Foundation (Grant Y-1289 to H.V.R.D) are also gratefully acknowledged. The NSF (CHE-0840509) is thanked for providing funds to upgrade the NMR spectrometer at UT Arlington used in this work. The X-ray crystallography was performed in the Center for Nanostructured Materials (CNM) at the University of Texas at Arlington.

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