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PAPER

Synthesis and characterization of silver(1) adducts supported solely by 1,3,5-triazapentadienyl ligands or by triazapentadienyl and other *N*-donors[†]

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Halogenated 1,3,5-triazapentadienyl ligands $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-, [N\{(CF_3)C(C_6F_5)N\}_2]^-$ and $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]^-$, alone or in combination with other *N*-donors like CH_3CN, CH_3(CH_2)_2CN, and N(C_2H_5)_3, have been used in the stabilization of thermally stable, two-, three- or four-coordinate silver(1) adducts. X-Ray crystallographic analyses of $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n, \{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n, \{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n, \{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n, \{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n, nevealed the presence of bridging 1,3,5-triazapentadienyl ligands bonded to silver through terminal nitrogen atoms. These adducts are polymeric in the solid state. <math>[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]AgN(C_2H_3)_3$ is monomeric and features a 1,3,5-triazapentadienyl ligand bonded to Ag(1) in a κ^1 -fashion *via* only one of the terminal nitrogen atoms. The solid state structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ has also been reported and it forms polymeric chains *via* inter-molecular N-H··· N hydrogen-bonding.

Introduction

1,5-Diazapentadienyl ligands (also known as β-diketiminates, 1) are one of the most useful group of monoanionic, nitrogen-based ligands in chemistry. They have been utilized widely in coordination chemistry¹⁻¹⁰ and to isolate lowvalent and low-coordinate main group adducts,11-16 prepare homogeneous catalysts, as well as for modelling active sites of metalloenzymes.¹⁷⁻²⁹ In contrast, 1,3,5-triazapentadienyl ligands 2 (the trinitrogen analogues of 1,5-diazapentadienyl systems) have received relatively little attention.³⁰ This is probably because facile and general synthetic methods for their generation have been rather poorly developed. Recently, groups led by Siedle and Dias reported the synthesis of fluorinated 1,3,5-triazapentadienes like $[N\{(C_3F_7)C(Ph)N\}_2]H$ (3) and $[N{(C_3F_7)C(Dipp)N}_2]H$ (4, where Dipp = 2,6-Prⁱ₂C₆H₃).³¹⁻³³ These molecules have easily ionizable NH hydrogen atoms and their conjugate bases have three basic nitrogen sites for metal ion coordination. The ligand backbones are also fairly flexible, and usually adopt W- or U-shaped conformations. Recent work also shows that they are useful in the isolation of coinage metal adducts like $[N{(C_3F_7)C(Dipp)N}_2]CuCO,^{32}$ $C_6H_3N_2$]Au(C_2H_4).³⁵

Over the last few years, we have been involved in the study of polyhalogenated ligands including those of 1,3,5-



triazapentadienes and their coinage metal (Cu, Ag, Au) complexes.³²⁻³⁷ For example, we have used fluorinated ligands like $[HB(3,5-(CF_3)_2Pz)_3]^-$ to stabilize rare organometallic complexes of silver(I) such as Ag-CO,³⁸ Ag-C₂H₂, and Ag-C₂H₄ adducts.³⁹ Some of those silver(I) adducts show promising catalytic properties (e.g., C-H and C-halogen bond activation)40-44 and antimicrobial activity,45-47 and serve as useful ligand transfer agents.48 Our preliminary work involving fluorinated 1,3,5-triazapentadienyl ligands in silver led to three monomeric silver(I) complexes (CH₃CN)Ag[N{(C_3F_7)C(Dipp)N}₂], (Bu^tNC)- $Ag[N\{(C_3F_7)C(Dipp)N\}_2]$, and $[N\{(C_3F_7)C(Dipp)N\}_2]Ag(PPh_3)$.³³ The isolation and antimicrobial properties of fluorinated ligands like $[N{(C_3F_7)C(C_6F_5)N}_2]H$ and their silver adducts were described in a recent patent.47 In addition, Siedle and co-workers also described the use of triazapentadienyl ligands to isolate silver adducts $[N{(C_3F_7)C(Ph)N}_2]Ag$ and $[N\{(C_3F_7)C(Ph)N\}_2][Ag(diphos)]$ but no structural data were reported.49 In this paper, we describe the use of halogenated

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1,3,5-triazapentadienyl ligands, $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$ (5) and $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]^-$ (6) to stabilize monomeric and polymeric silver(1) complexes featuring silver sites supported solely by 1,3,5-triazapentadienyl ligands or only by nitrogen-donor ligands. We also demonstrate the rich diversity of coordination modes of 1,3,5-triazapentadienyl ligands by providing examples of a triazapentadienyl ligand acting as a bridging ligand and as a κ^1 donor *via* one of the terminal nitrogen atoms.



For comparison, silver(I) complexes of 1,5-diazapentadienyl ligands are also rare as they are often light and heat sensitive, challenging to isolate, and decompose producing metallic silver. Shimokawa and Itoh reported the first 1,5-diazapentadienyl silver adducts, and the 1,5-diazapentadienyl ligand dimerization products resulting from silver(I) mediated redox chemistry (silver adduct decomposition).⁵⁰ Daugulis described several isolable monomeric silver 1,5-diazapentadienyl adducts including $[HC{(CF_3)C(3,5-(CF_3)_2C_6H_3)N}_2]Ag(C_2H_4).^{51}$

Results and discussion

 $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ and $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]H$ were synthesized as described previously using three equivalents of triethylamine and two equivalents of the corresponding aniline per equivalent of perfluoro-5-aza-4-nonene.^{35,36,47} These molecules are white to pale yellow solids and soluble in ethers or halogenated and polar solvents like CH_2Cl_2 , DMSO or acetone but only sparingly soluble in *n*-hexane. We also investigated the solid state structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ (Fig. 1). It crystallizes in the $P2_1/c$ space group with three independent $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ units in the asymmetric unit. It features a twisted, W-shaped (approaching an S-shape) NCNCN triazapentadiene ligand 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. $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ forms polymeric chains *via* intermolecular $NH \cdots N$ hydrogen bonding (Fig. 1). Such intermolecular $NH \cdots N$ bonds and polymeric chains have been observed for $[N\{(CF_3)C(C_6F_5)N\}_2]H$ and $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]H$.³⁵ $[N\{(C_3F_7)C(Dipp)N\}_2]H$ molecules (bearing much bulkier *N*-aryl groups) however do not form such intermolecular $NH \cdots N$ bonds but pack forming layers of hydrocarbon and fluorocarbon domains.^{33,35}

Silver(I) salts $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n$ and $\{[N\{(C_3F_7) C(2,6-Cl_2C_6H_3)N_{2}]Ag_{n}$ were easily obtained by refluxing a mixture of the corresponding fluorinated ligand and Ag₂O in THF.47 In none of the cases was a silver mirror observed at the end of the reactions when the mixture was protected from light. $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n$ and $\{[N\{(C_3F_7)C(2,6 Cl_2C_6H_3N_2Ag_n$ are white solids. They are air and light stable for at least several days, and soluble in polar solvents like acetone, acetonitrile and DMSO but somewhat less soluble in halogenated or aromatic solvents. The X-ray crystal structure of $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n$ displays a linear polymer with the NCNCN ligand backbone in a slightly twisted Wshaped configuration while the two-coordinate silver sites are linear and bond to the terminal nitrogen atoms of the neighboring ligand units (Fig. 2). $[N\{(C_3F_7)C(C_6F_5)N\}_2]^{-1}$ therefore acts as a bidentate bridging ligand. To the best of our knowledge linear polymers featuring two-coordinate silver(I) in a linear geometry with nitrogen-based ligands are rare—one such case concerns a polymeric silver(1)-2pyrimidinolate complex.⁵² There is no significant difference in the N-Ag distances of this complex (2.117(3) Å and 2.114(3) Å), and those of the $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n$ (2.113(6) Å and 2.120(6) Å). {[HC{HC(Dipp)N}₂]Ag}₂ and $\{[NCC{HC(Dipp)N}_2]Ag\}_4$ involving bridging 1,5diazapentadienyl ligands are dimeric and tetrameric aggregates of the corresponding 1,5-diazapentadienylsilver(I) moiety and they have 2-coordinate silver sites and W-shaped NCCCN backbones.⁵⁰ We have also synthesized $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]$ Ag which presumably forms aggregates in the solid state. We have not been able to obtain X-ray quality crystals to confirm this assertion. However, the ESI-MS analysis of $[N{(C_3F_7)C(2,6 Cl_2C_6H_3N_2$]Ag shows signals assignable to different oligomers. As noted in the introduction section, $[N{(C_3F_7)C(Ph)N}_2]Ag$



Fig. 1 Molecular structure of $[N\{(C_3F_7)C(C_6F_5)N\}_2]H$ showing the atom numbering scheme and extended structure. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(1)-C(1) 1.347(4), N(2)-C(1) 1.274(4), N(2)-C(2) 1.368(4), N(3)-C(2) 1.269(4), N(1)-C(1)-N(2) 120.8(3), C(1)-N(2)-C(2) 130.6(3), N(2)-C(2)-N(3) 127.7(3).



Fig. 2 Molecular structure of $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n$ showing the atom numbering scheme and extended structure. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(3)–C(2) 1.298(9), C(2)–N(2) 1.318(10), N(2)–C(1) 1.327(10), C(1)–N(1) 1.278(10), N(1)–Ag 2.113(6), Ag–N(3a) 2.120(6), Ag–N(3)–C(2) 127.2(5), N(3)–C(2)–N(2) 124.4(7), C(2)–N(1) 131.7(7), N(2)–C(1)–N(1) 124.4(7), C(1)–N(1)–Ag 130.6(6), N(1)–Ag–N(3a) 174.7(2).

and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}CF_3C_6H_3)N\}_2]Ag$ are also known but structural data are not available.

Silver(I) acetonitrile adducts $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n$ and $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag(NCCH_3)\}_n$ were prepared by refluxing the corresponding triazapentadienes with Ag₂O in pure acetonitrile or a mixture of acetonitrile– THF. The products were obtained as dark oils initially but slowly crystallized upon standing in a ventilated hood. Loss of acetonitrile from $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n$ and $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag(NCCH_3)\}_n$ or prolonged exposure to light leads to some decomposition as is evident from the formation of black material on the walls of the sample container. These compounds are not soluble in *n*-hexane and slightly soluble in aromatic solvents or THF. They also decompose in halogenated solvents like CHCl₃ and CH₂Cl₂ over a period of several hours as is evident from the formation of a metallic silver mirror. The X-ray crystal structure of $\{[N\{(C_3F_7)C(C_6F_5)-N\}_2]Ag(NCCH_3)\}_n$ which exists as helical chains is illustrated in Fig. 3. It shows the presence of three-coordinate silver atoms (with almost T-shaped geometry, with an N1–Ag–N4 angle of 154.28(10)°) coordinated to the terminal nitrogen atoms of bridging, bidentate triazapentadienyl ligands. The third coordination site is occupied by an acetonitrile ligand which coordinates to silver at an angle (Ag–N–C angle = 160.4(3)°). The coordination of acetonitrile in a non-linear fashion may be a sign of a weak σ -donor type interaction. The NCNCN core of the triazapentadienyl ligand adopts a twisted S-shaped configuration.

Polymeric { $[N{(C_3F_7)C(2,6-Cl_2C_6H_3)N}_2]Ag(NCCH_3)$ }_n crystallizes in the P2₁/c space group with two different [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]Ag(NCCH₃) moieties in the asymmetric unit (one of those is shown in Fig. 4). The angle of acetonitrile coordination to Ag(1) is noticeably different in the two



Fig. 3 Molecular structure of $\{[N_{(C_3F_7)C(C_6F_5)N_2}]Ag(NCCH_3)\}_n$ showing the atom numbering scheme and extended structure. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(3)-C(2) 1.296(4), C(2)-N(2) 1.328(4), N(2)-C(1) 1.306(4), C(1)-N(1) 1.319(4), N(1)-Ag 2.191(3), Ag-N(3a) 2.436(3), Ag-N(4) 2.189(3), N(4)-C(21) 1.135(5), N(3)-C(2)-N(2) 131.8(3), C(2)-N(2)-C(1) 133.2(3), N(2)-C(1)-N(1) 124.7(3), N(1)-Ag-N(4) 154.28(10), N(1)-Ag-N(3a) 119.24(9), N(3a)-Ag-N(4) 86.24(10), Ag-N(4)-C(21) 160.4(3).



Fig. 4 Molecular structure of $[N{(C_3F_7)C(2,6-Cl_2C_6H_3)N}_2]Ag(NCCH_3)$ showing the atom numbering scheme and extended structure. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(3)-C(2) 1.304(5), C(2)-N(2) 1.321(5), N(2)-C(1) 1.324(5), C(1)-N(1) 1.307(5), N(1)-Ag(1) 2.178(3), Ag(1)-N(4) 2.350(5), Ag(1)-N(3a) 2.227(3), N(4)-C(21) 1.158(8), N(3)-C(2)-N(2) 124.8(4), C(2)-N(2)-N(1) 131.6(3), N(2)-C(1)-N(1) 125.1(3), C(1)-N(1)-Ag(1) 136.5(3), N(1)-Ag(1)-N(3a) 150.28(12), N(1)-Ag(1)-N(4) 118.52(14), N(3a)-Ag(1)-N(4) 90.69(14), Ag(1)-N(4)-C(21) 150.9(6).

units with Ag–N–C angles of 132.9(5)° and 150.9(6)°, respectively. The triazapentadienyl ligand backbones adopt twisted W-shaped configurations. Three-coordinate silver atoms feature distorted T-shaped geometry and coordinate to the terminal nitrogen atoms of bridging, bidentate triazapentadienyl ligands. The third coordination site is occupied by an acetonitrile ligand.

 $\{[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2\}_n$ which has the smaller $-CF_3$ group on the triazapentadienyl ligand backbone was synthesized using $[N\{(CF_3)C(C_6F_5)\}_2]H$ and Ag_2O in a mixture of acetonitrile and THF. Removal of the solvent yielded an oily material which solidified upon standing. $\{[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2\}_n$ showed good solubility in chloroform and CH_2Cl_2 . Colorless rod shaped crystals of $\{[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2\}_n$ were obtained by slow diffusion of hexane into a solution of the compound in CH_2Cl_2 at room temperature (some product decomposition was also observed during the recrystallization leaving black material on the wall of the container). The crystals were stable in air for several minutes, but prolonged exposure to light turned the crystals dark brown.

The X-ray data of $\{[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2\}_n$ (Fig. 5) show that the asymmetric unit contains two moieties of $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2$. The overall structure is a polymer, featuring tetrahedral silver sites linked by bridging bidentate triazapentadienyl ligands. The NCNCN core adopts a helical configuration. Each silver atom is coordinated to two acetonitrile molecules with Ag–N–C angles ranging from 150.1(2)° to 170.7(2)°. The Ag(NCCH_3)_2 moiety is flanked by the two –CF₃ groups of the triazapentadienyl ligands. Interestingly, $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n$, which has larger –C₃F₇ substituents on the triazapentadienyl ligand backbone, crystallizes as a mono-acetonitrile adduct rather than a di-acetonitrile system. This is probably the result of a steric effect caused by the bulkier –C₃F₇ substituents preventing the coordination of an additional acetonitrile molecule to the silver.

We also reported a mono-acetonitrile silver(I) complex $(CH_3CN)Ag[N\{(C_3F_7)C(Dipp)N\}_2]$ bearing larger aryl groups on the triazapentadienyl terminal nitrogen atoms and $-C_3F_7$ substituents on the ligand backbone carbons.³³ It is a monomer



Fig. 5 Molecular structure of $\{[N\{(CF_3)C(C_6F_3)N\}_2]Ag(NCCH_3)_2\}_n$ showing the atom numbering scheme. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ag(1a)–N(8) 2.382(2), N(6)–Ag(2) 2.429(2), Ag(2)–N(9) 2.311(2), N(9)–C(37) 1.134(3), Ag(2)–N(10) 2.364(2), N(10)–C(39) 1.125(4), Ag(2)–N(3) 2.397(2), N(1)–Ag(1) 2.4404(19), Ag(1)–N(4) 2.294(2), Ag(1)–N(5) 2.318(3), N(4)–C(17) 1.138(3), N(5)–C(19) 1.136(4), N(3)–Ag(2)–N(10) 102.66(8), N(3)–Ag(2)–N(9) 135.33(8), N(3)–Ag(2)–N(6) 92.53(7), N(9)–Ag(2)– N(10) 96.52(9), N(9)–Ag(2)–N(6) 104.60(8), N(6)–Ag(2)–N(10) 131.00(8), N(1)–Ag(1)–N(5) 117.68(8), N(1)–Ag(1)–N(8a) 98.19(7), N(1)–Ag(1)–N(4) 108.23(8), N(5)–Ag(1)–N(8a) 105.95(8), N(5)–Ag(1)– N(4) 103.14(9), N(4)–Ag(1)–N(8a) 124.74(8), Ag(2)–N(9)–C(37) 170.7(2), Ag(2)–N(10)–C(39) 150.1(2), Ag(1)–N(5)–C(19) 160.6(2), Ag(1)–N(4)–C(17) 164.6(2).

and shows a very different triazapentadienyl ligand coordination mode in which the central nitrogen atom binds to silver (which is two-coordinate) in a κ^1 -fashion (Scheme 1).

We have also synthesized $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$ which has a relatively large ligand, butyronitrile. The X-ray structure of $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$ is depicted in Fig. 6. It is also a polymeric adduct with three-coordinate, distorted T-shaped silver sites. In contrast to $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag(NCCH_3)\}_n$, but as observed for $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n$, the larger N–Ag–N angle (155.62°) at the silver atom in



Fig. 6 Molecular structure of $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$ showing the atom numbering scheme and extended structure. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(3)-C(2) 1.313(3), C(2)-N(2) 1.315(3), N(2)-C(1) 1.329(3), C(1)-N(1) 1.299(3), N(1)-Ag 2.437(2), Ag-N(3a) 2.181(2), Ag-N(4) 2.169(2), N(4)-C(21) 1.147(4), N(3)-C(2)-N(2) 125.2(2), C(2)-N(2)-C(1)134.9(2), N(2)-C(1)-N(1) 132.7(2), C(1)-N(1)-Ag 131.72(17), N(1)-Ag-N(4) 87.87(8), N(1)-Ag-N(3a) 116.41(8), N(3a)-Ag-N(4) 155.62(8), Ag-N(4)-C(21) 170.2(2).



 $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$ results from the coordination of one of the terminal nitrogen atoms of the triazapentadienyl ligand and the nitrile nitrogen center. The Ag–N(nitrile) distances in $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCCH_3)\}_n$ and $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$ are similar at 2.189(3) Å and 2.169(2) Å, respectively. The corresponding values for $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag(NCCH_3)\}_n$ are significantly larger at 2.350(5) Å and 2.535(5) Å (two molecules). For comparison, the Ag-N distances of the tricoordinated species $(PPh_3)_2Ag(NCCH_3)$ and and tetracoordinated [Ag(NCCH₃)₄]BF₄ are 2.321(2) Å and 2.266 Å, respectively.^{53,54}

It should be noted that, in contrast to the formation of nitrile adducts described above, silver adducts prepared using fluorinated triazapentadienes with Ag_2O in either THF or THF–toluene or by using lithium salts of the triazapentadienyl ligands and $AgSbF_6$ in

THF did not produce THF or toluene coordinated complexes. A different coordination mode of the fluorinated triazapentadienvl ligand was observed when $N(C_2H_5)_3$ was used as the additional N-donor. Reaction of $[N{(C_3F_7)C(2,6-Cl_2C_6H_3)N}_2]H$ with Ag₂O in the presence of triethylamine gave $[N{(C_3F_7)C(2,6 Cl_2C_6H_3N_2]AgN(C_2H_5)_3$. The X-ray data of $[N\{(C_3F_7)C(2,6 Cl_2C_6H_3N_2AgN(C_2H_5)_3$ revealed the presence of a monomeric structure and a two-coordinate silver center with a slightly bent N-Ag-N angle of 169.86(8)° (Fig. 7). There are two intra-molecular Ag...F contacts at 2.892 and 3.083 Å (cf. sum of the van der Waals radii of Ag and F = 3.19 Å) on the wider side of the N-Ag-N angle, perhaps causing this slight distortion. The $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]^-$ ligand binds to silver in a $\kappa^1\text{-}$ fashion via one of the terminal N-atoms. ¹⁹F NMR analysis in $CDCl_3$ indicated that the $-C_3F_7$ chains sit in different chemical environments in solution at room temperature. The NCNCN core adopts a distorted W-shaped configuration. The triethylamine ligand forms an umbrella-like covering over the silver(I) atom. The N-Ag-N(C_2H_5)₃ distances are 2.1170(19) Å and 2.163(2) Å, respectively. The X-ray crystal structures of silver(I) $N(C_2H_5)_3$ complexes are not available for comparison. Monomeric metal adducts with κ^1 -coordinated side-bonded 1,5-diazapentadienyl ligands have not been reported to our knowledge. One of the isomers of $[N{(C_3F_7)C(Ph)N}_2]$ HgMe is believed to feature a sidebonded 1,3,5-triazapentadienyl ligand in solution.55

Conclusions

Overall, we report the isolation and full characterization of a series of silver(I) adducts supported solely by 1,3,5-triazapentadienyl ligands or by triazapentadineyl and other nitrogen donors like acetonitrile, butyronitrile and triethylamine. The polymeric salts $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag\}_n$ and $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag\}_n$ show high air and light stability for days. We also described the first structures of bridging, bidentate triazapentadienyl systems as well as a rare side bonded κ^1 -coordination



Fig. 7 Molecular structure of $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3F_5)N\}_2]AgN(C_2H_5)_3$ showing the atom numbering scheme and the conformation of the ligand backbone. Thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): N(3)-C(2) 1.279(3), C(2)-N(2) 1.353(3), N(2)-C(1) 1.292(3), C(1)-N(1) 1.327(3), N(1)-Ag 2.1170(19), Ag-N(4) 2.163(2), N(3)-C(2)-N(2) 127.8(2), C(2)-N(2)-C(1) 133.7(2), N(2)-C(1)-N(1) 123.8(2), C(1)-N(1)-Ag 129.15(16), N(1)-Ag-N(4) 169.86(8).

of a triazapentadienyl ligand (Scheme 1). In these adducts, the triazapentadienyl ligands use terminal nitrogen atoms for metal ion coordination. In contrast, (MeCN)Ag[N{ $(C_3F_7)C(Dipp)N$ }_2] shows metal coordination *via* the central nitrogen atom of the triazapentadienyl ligand. We are currently exploring the ligand transfer chemistry and catalytic properties of silver-triazapentadienyl systems.

Experimental

General procedures

All manipulations were carried out under an inert atmosphere of purified nitrogen using standard Schlenk techniques. Reactions involving silver(I) starting materials were performed in flasks covered with aluminium foil (to protect from light). 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 in CDCl₃ at 25 °C on JEOL Eclipse 500 and 300 spectrometers (1H: 500.16 MHz, 300.53 MHz and 19F: 470.62 MHz, 282.78 MHz). Proton chemical shifts are reported in ppm versus Me₄Si. ¹⁹F NMR chemical shifts were referenced relative to external CFCl₃. Elemental analyses were performed using a Perkin Elmer Series II CHNS/O analyzer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Silver(I) oxide, triethylamine and butyronitrile were purchased from commercial sources. $[N{(C_3F_7)C(C_6F_5)N}_2]H$, $[N{(C_3F_7)C(2,6 Cl_2C_6H_3N_2$]H and $[N\{(CF_3)C(C_6F_5)N\}_2]$ H were prepared as described previously.31,35,47

 $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag\}_n$. $[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)-N\}_2]H$ (1 eq.) and silver(1) oxide (0.75 eq., 50% excess) were refluxed in THF for 12 h. The solution was filtered over a bed of Celite and the solvent was evaporated to dryness. The residue was washed with *n*-hexane, decanted and pumped dry to afford $\{[N\{(C_3F_7)C(2,6-Cl_2C_6H_3)N\}_2]Ag\}_n$ as a white solid. Small

needles were obtained by slow evaporation from a solution in acetone–toluene. Yield: 41%. ESI–MS: m/z 802, 804 (Ag–L·H⁺); 908, 910 (Ag–L·Ag⁺); 1497, 1499 (H–L–Ag–L·H⁺); 1603, 1605 (Ag–L–Ag–L·H⁺); 2298, 2300 (H–L–Ag–L-Ag–L·H⁺); 2404, 2406 (Ag–L–Ag–L–Ag–L·H⁺). M.p.: 220–225 °C (dec.). ¹⁹F NMR (470.62 MHz, DMSO-d₆, 25 °C): δ –79.5 (t, J_{FF} = 8.6 Hz, 6F, CF₃), –111.2 (s, 4F, CF₂), –123.9 (s, 4F, CF₂). ¹H NMR (500.16 MHz, DMSO-d₆, 25 °C): δ 7.20 (br, 4H, *m*-Ar), 6.85 (br, 2H, *p*-Ar). Anal. calcd for C₂₀H₆Cl₄F₁₄N₃Ag C, 29.88; H, 0.75; N, 5.23; found C, 30.47; H, 1.06; N, 5.19%.

{[N{(C_3F_7)C(C_6F_5)N}₂]Ag(NCCH₃)}_n. [N{(C_3F_7)C(C_6F_5)N}₂]-H (0.5 g, 0.68 mmol), Ag₂O (0.09 g, 0.41 mmol), acetonitrile 10 mL and THF 20 mL were heated at 75 °C for 12 h in an oil bath. The solution was filtered over a bed of Celite and concentrated. Transparent needles are obtained after three days by slow evaporation at room temperature. Yield: 58%. M.p. 120–125 °C (dec). ¹⁹F NMR (282.78 MHz, DMSO-d₆, 25 °C): δ -80.1 (t, $J_{FF} = 8.7$ Hz, 6F, CF_3), -113.5 (s, 4F, CF_2), -125.4 (s, 4F, CF_2), -149.0 (d, $J_{FF} = 19.5$ Hz, 4F, CF), -166.5 (t, $J_{FF} = 19.5$ Hz, 21.7 Hz, 4F, CF), -167.6 (t, $J_{FF} = 21.7$ Hz, 23.8 Hz, 2F, CF). ¹H NMR (300.53 MHz, DMSO-d₆, 25 °C): δ 2.05 (s, 3H, CH₃CN). Anal. calcd for C₂₂H₃F₂₄N₄Ag C, 29.79; H, 0.34; N, 6.32; found C, 29.04; H, 0.22; N, 6.93%.

{[N{(CF₃)C(C₆F₅)}₂]Ag(NCCH₃)₂}_n. [N{(CF₃)C(C₆F₅)}₂]H (0.100 g, 0.185 mmol) was added to a suspension of Ag₂O (0.032 g, 0.14 mmol) in a mixture of acetonitrile (5 mL) and THF (10 mL); the mixture was refluxed for 16 h. The solution was filtered over a bed of Celite and the solvent was removed from the filtrate under reduced pressure to leave light yellow crystalline solid. The solid was dissolved in minimum amount of CH₂Cl₂ and layered with hexanes to obtain colorless crystals. Yield: 90.6%. M.p. 100 °C (dec.), ¹⁹F NMR (DMSO-d₆, 293 K): δ –71.9 (s, CF₃), –150.9 (s, CF), –168.4 (t, J_{FF} = 22.0 Hz, CF), –169.6 (t, J_{FF} = 22.0 Hz, CF). ¹H NMR (CDCl₃, 293 K): 2.05 (s, CH₃). Anal. calcd for C_{17.6}H_{2.4}AgF_{1.6}N_{3.8}: C, 31.14; H, 0.36; N, 7.84%; found: C, 30.70; H, 0.36; N, 7.90%. {[N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]Ag(NCCH₃)}_{*n*}. [N{(C₃F₇)C-(2,6-Cl₂C₆H₃)N}₂]H (0.25 g, 0.36 mmol) and Ag₂O (0.04 g, 0.18 mmol) were heated at 90 °C for 12 h in acetonitrile 20 mL. The solution was filtered over a bed of Celite and concentrated until an oily residue was obtained. This was dissolved in CH₂Cl₂, filtered and left to evaporate at air at room temperature. Crystals were observed after 24 h. Yield: 39%. M. p. 242–250 °C (dec.). ¹⁹F NMR (282.78 MHz, DMSO-d₆, 25 °C): δ –79.6 (t, J_{FF} = 8.7 Hz, 10.8 Hz, 6F, CF₃), –111.4 (s, 4F, CF₂), –124.0 (s, 4F, CF₂). ¹H NMR (300.53 MHz, DMSO-d₆, 25 °C): δ 7.18 (d, ³ J_{HH} = 8.3 Hz, 4H, *m*-Ar), 6.82 (t, ³ J_{HH} = 7.9, 2H, *p*-Ar), 2.08 (s, NCCH₃). Anal. calcd for C₂₂H₉Cl₄F₁₄N₄Ag C, 31.27; H, 1.07; N, 6.63; found C, 31.24; H, 1.17; N, 6.49%.

 $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$. $[N\{(C_3F_7)C(C_6F_5)-$ N₂]H (0.5 g, 0.68 mmol), Ag₂O (0.09 g, 0.41 mmol), butyronitrile (6 mL, 67.7 mmol) and THF 20 mL were stirred for 12 h at 75 °C. Once cooled the reaction mixture was filtered and concentrated up to 2 mL. It was left to crystallize in darkness by slow evaporation at room temperature. Transparent plates are obtained after one week (0.47 g, 76%). M.p. 150-152 °C (dec). ¹⁹F NMR (282.78 MHz, DMSO-d₆, 25 °C): δ -79.9 (s, 6F, CF₃), -113.3 (s, 4F, CF₂), -125.3 (s, 4F, CF₂), -149.0 (d, $J_{FF} = 19.5$ Hz, 4F, CF), -166.3 (t, $J_{FF} =$ 21.7 Hz, 4F, CF), -167.4 (t, $J_{FF} = 23.8$ Hz, 21.7 Hz, 2F, CF). ¹⁹F NMR (470.62 MHz, C₆D₆, 25 °C): δ -80.3 (t, 8.6 Hz, 6F, CF_3), -112.4 (m, J_{FF} = 734.2, 4F, CF_2), -124.4 (m, J_{FF} = 394.4 Hz, 4F, CF₂), -147.8 (broad, 4F, CF), -164.4 (apparent triplet, J_{FF} = 23.0 Hz, 20.2 Hz, 2F, CF), -165.2 (apparent triplet, $J_{\text{FF}} = 17.3$ Hz, 23.0 Hz, 4F, CF). ¹H NMR (500.16 MHz, C₆D₆, 25 °C): δ 1.35 (t, ${}^{3}J_{\rm HH} = 6.9$ Hz, 2H, α -CH₂), 0.94 (m, 2H, β -CH₂), 0.55 (t, ${}^{3}J_{\rm HH} =$ 7.3 Hz, 3H, CH_3). Anal. calcd for $C_{24}H_7F_{24}N_4AgC$, 31.50; H, 0.77; N, 6.12; found C, 32.47; H, 1.08; N, 5.98%.

 Table 1
 Crystallographic data

[N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]AgN(C₂H₅)₃. [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]H (0.5 g, 0.72 mmol), Ag₂O (0.083 g, 0.36 mmol) and triethylamine (0.1 mL, 0.72 mmol) were refluxed in THF for 12 h in an oil bath. The solution was filtered over a bed of Celite and concentrated. Yellow cubes grew at -20 °C after 2 days. Yield: 56%. M. p. 125–127 °C (dec.). ¹⁹F NMR (470.62 MHz, CDCl₃, 25 °C): δ –80.0 and –80.4 (s, 6F, CF₃), –109.5 (s, CF₂), –122.8 and –124.9 (s, CF₂). ¹H NMR (500.16 MHz, CDCl₃, 25 °C): δ 7.32 to 7.17 (multiplet, 4H, *m*-Ar), 6.95 to 6.84 (multiplet, 2H, *p*-Ar), 2.06 (br, 6H, CH₂CH₃), 0.87 (br, 9H, CH₂CH₃). Anal. calcd for C₂₆H₂₁Cl₄F₁₄N₄Ag C, 34.50; H, 2.34; N, 6.19; found C, 34.58; H, 2.29; N, 6.17

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 K α fine-focus sealed tube ($\lambda = 0.71073$ Å). The data frames were integrated with the Bruker SAINT-Plus software package. 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. X-Ray files in cif-format are available as supporting information,† and crystallographic data are summarized in Table 1.

 $[N{(C_3F_7)C(C_6F_5)N}_2]H$. Crystallized in space group P_{2_1}/c with three independent $[N{(C_3F_7)C(C_6F_5)N}_2]H$ molecules in the asymmetric unit. The hydrogens on N-atoms were located and refined. The fluorine atoms of one of the C_2F_3 molecules show

Compound	$[N\{(C_3F_7)C-(C_6F_5)N\}_2]H$	$\{[N\{(C_3F_7)C-(C_6F_5)N\}_2]Ag\}_n$	$ \begin{split} &\{ [N\{(C_3F_7)\text{-}\\ &C(C_6F_5)N\}_2]\text{-}\\ &Ag(NCCH_3)\}_n \end{split} $	$ \{ [N\{(C_3F_7)-C(2,6-Cl_2C_6H_3)-N\}_2] Ag(NCCH_3) \}_n $	$ \{ [N\{(CF_3)C-\\(C_6F_5)N\}_2]-\\Ag(NCCH_3)_2 \}_n $	$ \{ [N\{(C_3F_7)C-(C_6F_5)N\}_2] - Ag(NCC_3H_7) \}_n $	$ [N\{(C_3F_7)C-\\(2,6\text{-}Cl_2C_6H_3)-\\N\}_2]AgN(C_2H_5)_3 $
Formula FW Temperature (K) Crystal system Space group Cell dimensions	$C_{20}HF_{24}N_3$ 739.24 100(2) Monoclinic P2(1)/c $a = 19.7349(8) \text{ Å}$ $b = 17.2001(7) \text{ Å}$ $c = 21.5731(8) \text{ Å}$ $\alpha = 90^{\circ}$ $\beta = 94.326(1)^{\circ}$	$\begin{array}{l} C_{20} AgF_{24} N_3 \\ 846.10 \\ 100(2) \\ Monoclinic \\ P2(1)/n \\ a = 12.2939(6) \text{ Å} \\ b = 14.3955(6) \text{ Å} \\ c = 14.8014(7) \text{ Å} \\ \alpha = 90^{\circ} \\ \beta = 103.430(1)^{\circ} \end{array}$	$\begin{array}{l} C_{22}H_3AgF_{24}N_4\\ 887.15\\ 100(2)\\ Monoclinic\\ P2(1)/n\\ a=10.1781(6) \text{ Å}\\ b=14.2903(8) \text{ Å}\\ c=18.6323(10) \text{ Å}\\ \alpha=90^\circ\\ \beta=93.876(1)^\circ\end{array}$	$C_{22}H_9AgCl_4F_{14}N_4$ 845.00 100(2) Monoclinic P2(1)/c a = 20.1753(12) Å b = 16.8846(10) Å c = 18.9949(11) Å $\alpha = 90^{\circ}$ $\beta = 116.350(1)^{\circ}$	$\begin{array}{l} C_{20}H_6AgF_{16}N_5\\ 728.17\\ 100(2)\\ Triclinic\\ P\bar{I}\\ a=9.5740(9) \text{ Å}\\ b=13.1644(12) \text{ Å}\\ c=19.7396(18) \text{ Å}\\ \alpha=84.958(1)^{\circ}\\ \beta=89.652(1)^{\circ} \end{array}$	$C_{24}H_7AgF_{24}N_4$ 915.21 100(2) Orthorhombic P2(1)2(1)2(1) $a = 10.5771(6)$ Å $b = 14.5688(9)$ Å $c = 18.7937(11)$ Å $\alpha = 90^{\circ}$ $\beta = 90^{\circ}$	$\begin{array}{l} C_{26}H_{21}AgC_{14}F_{14}N_{4}\\ 905.14\\ 100(2)\\ Monoclinic\\ P2(1)/n\\ a=11.0348(7) \text{ Å}\\ b=26.8261(17) \text{ Å}\\ c=11.6999(7) \text{ Å}\\ \alpha=90^{\circ}\\ \beta=105.503(1)^{\circ} \end{array}$
$V(\text{\AA})^3$	$\gamma = 90^{\circ}$ 7302.0(5)	$\gamma = 90^{\circ}$ 2547.9(2) 4	$\gamma = 90^{\circ}$ 2703.8(3) 4	$\gamma = 90^{\circ}$ 5798.3(6) 8	$\gamma = 71.234(1)^{\circ}$ 2345.9(4) 4	$\gamma = 90^{\circ}$ 2896.0(3) 4	$\gamma = 90^{\circ}$ 3337.4(4)
$\begin{aligned} & \mathcal{L} \\ & \mathcal{d}_{calcd} (g \text{ cm}^{-3}) \\ & \mathcal{A}bs \text{ coeff (mm}^{-1}) \\ & F (000) \\ & \theta \text{ range (}^{\circ}) \\ & $	12 2.017 0.251 4296 1.57 to 26.00 58302 0.0294(14338) 14338/72/1299 1.017 0.0677/0.0758	2.206 0.987 1616 2.00 to 25.50 18231 0.0325(4734) 4734/24/454 1.197 0.0736/0.0799	2.179 0.936 1704 1.80 to 26.00 20097 0.0291(5273) 5273/31/483 1.039 0.0316/0.0364	8 1.936 1.177 3280 1.70 to 26.00 40248 0.0355(11119) 11119/0/813 1.039 0.0451/0.0572	2.062 1.009 1408 1.64 to 26.50 20452 0.0202(9670) 9670/0/761 1.039 0.0310/0.0356	2.099 0.878 1768 1.77 to 26.00 22557 0.0273 (5674) 5674/30/501 1.068 0.0228/0.0551	1.801 1.029 1784 2.06 to 28.28 29716 0.0291(8016) 8016/48/458 1.026 0.0369/0.0458
$wR2 [I > 2\sigma(I)]/$ all data	0.1837/0.1921	0.1930/0.1979	0.0726/0.0796	0.1113/0.1212	0.0748/0.0783	0.0233/0.0554	0.0878/0.0933

positional disorder. The disorder of the "CF₂" unit was modelled successfully with an occupancy ratio of 80:20. All the nonhydrogen atoms, except the minor occupancy fluorines (F3c and F4c) were refined anisotropically. The largest maximum (positive) residual density of 1.90 e Å⁻³ and minimum (negative) residual density of -0.92 e Å⁻³ were observed at 0.54 Å from F4c and 0.77 Å from F2b, respectively. We have repeated the data collection using a fresh crystal from a different batch but the residual densities did not change significantly.

 ${[N{(C_3F_7)C(C_6F_5)N}_2]Ag}_n$. Crystallized in space group P2₁/n. All the non-hydrogen atoms were refined with anisotropic displacement parameters.

 $\{[N_{\{(C_3F_7)C(C_6F_5)N_2]}Ag(NCCH_3)\}_n$. Crystallized in space group P2₁/n. Fluorine atoms of one of the C₂F₃ moieties show positional disorder. It was modelled successfully with an occupancy ratio of 72 : 28 for the fluorines of the CF₂ moiety and 76 : 24 for the fluorines of the CF₃ moiety. All the non-hydrogen atoms, except the minor occupancy fluorines were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

 $\{[N_{\{(C_3F_7)C(2,6-Cl_2C_6H_3)N_{2}]Ag(NCCH_3)\}_n$. Crystallized in space group P2₁/c with two independent $[N_{\{(C_3F_7)C(2,6-Cl_2C_6H_3)N_{2}]Ag(NCCH_3)}$ moieties in the asymmetric unit. All the non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

 $\{[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2\}_n$. Crystallized in space group $P\bar{I}$ with two $[N\{(CF_3)C(C_6F_5)N\}_2]Ag(NCCH_3)_2$ moieties in the asymmetric unit. All the non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

 $\{[N\{(C_3F_7)C(C_6F_5)N\}_2]Ag(NCC_3H_7)\}_n$. Crystallized in space group P2₁2₁2₁. Fluorine atoms of one of the C₂F₃ moieties show positional disorder. It was modelled successfully with an occupancy ratio of 71:29 for the fluorines of the CF₂ moiety and 71:29 for the fluorines of the CF₃ moiety. All the nonhydrogen atoms, except the minor occupancy fluorines were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

 $[N{(C_3F_7)C(2,6-Cl_2C_6H_3)N}_2]AgN(C_2H_5)_3$. Crystallized in space group P2₁/n. Fluorine atoms of one of the C₂F₃ moieties show positional disorder. It was modelled successfully with an occupancy ratio of 70:30 for the fluorines of the CF₂ moiety and 70:30 for the fluorines of the CF₃ moiety. The ethyl groups of N(C₂H₃)₃ were also disordered over two positions and were successfully modelled at a 58:42 occupancy ratio. All the non-hydrogen atoms except the carbons atoms of the ethyl groups were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

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References

- 1 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, 102, 3031–3066.
- 2 W. E. Piers and D. J. H. Elmslie, *Coord. Chem. Rev.*, 2002, 233–234, 131–155.
- 3 X. Dai and T. H. Warren, J. Am. Chem. Soc., 2004, 126, 10085-10094.
- 4 E. Kogut, H. L. Wienko, L. Zhang, D. E. Cordeau and T. H. Warren, J. Am. Chem. Soc., 2005, **127**, 11248–11249.
- 5 C. Ruspic, S. Nembenna, A. Hofmeister, J. Magull, S. Harder and H. W. Roesky, J. Am. Chem. Soc., 2006, 128, 15000–15004.
- 6 J. S. Thompson, A. Z. Bradley, K.-H. Park, K. D. Dobbs and W. Marshall, *Organometallics*, 2006, **25**, 2712–2714.
- 7 Z. J. Tonzetich, A. J. Jiang, R. R. Schrock and P. Mueller, Organometallics, 2006, 25, 4725–4727.
- 8 J. T. York, A. Llobet, C. J. Cramer and W. B. Tolman, J. Am. Chem. Soc., 2007, 129, 7990–7999.
- 9 H. Fan, D. Adhikari, A. A. Saleh, R. L. Clark, F. J. Zuno-Cruz, G. Sanchez-Cabrera, J. C. Huffman, M. Pink, D. J. Mindiola and M.-H. Baik, J. Am. Chem. Soc., 2008, 130, 17351–17361.
- 10 P. L. Holland, Acc. Chem. Res., 2008, 41, 905-914.
- 11 W. Clegg, S. J. Coles, E. K. Cope and F. S. Mair, Angew. Chem., Int. Ed., 1998, 37, 796–798.
- 12 C. E. Radzewich, L. A. Guzei and R. F. Jordan, J. Am. Chem. Soc., 1999, 121, 8673–8674.
- 13 Y. Cheng, P. B. Hitchcock, M. F. Lappert and M. Zhou, Chem. Commun., 2005, 752–754.
- 14 D. Vidovic, J. A. Moore, J. N. Jones and A. H. Cowley, J. Am. Chem. Soc., 2005, 127, 4566–4567.
- 15 D. Vidovic, M. Findlater, G. Reeske and A. H. Cowley, J. Organomet. Chem., 2007, 692, 5683–5686.
- 16 S. Nagendran and H. W. Roesky, Organometallics, 2008, 27, 457-492.
- 17 M. Cheng, E. B. Lobkovsky and G. W. Coates, J. Am. Chem. Soc., 1998, 120, 11018–11019.
- 18 C. E. Radzewich, M. P. Coles and R. F. Jordan, J. Am. Chem. Soc., 1998, 120, 9384–9385.
- 19 X. L. Dai and T. H. Warren, Chem. Commun., 2001, 1998-1999.
- 20 B. A. Jazdzewski, P. L. Holland, M. Pink, V. G. Young, D. J. E. Spencer and W. B. Tolman, *Inorg. Chem.*, 2001, **40**, 6097–6107.
- 21 J. Kim, J. W. Hwang, Y. Kim, Hyung M. Lee, Y. Han and Y. Do, J. Organomet. Chem., 2001, 620, 1–7.
- 22 B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, J. Chem. Soc., Dalton Trans., 2001, 2215–2224.
- 23 L. D. Amisal, X. L. Dai, R. A. Kinney, A. Krishnaswamy and T. H. Warren, *Inorg. Chem.*, 2004, **43**, 6537–6539.
- 24 Y. Li, L. Wang, H. Gao, F. Zhu and Q. Wu, *Appl. Organomet. Chem.*, 2006, 20, 436–442.
- 25 L. F. Sanchez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, Organometallics, 2006, 25, 1012–1020.
- 26 C. Shimokawa, J. Teraoka, Y. Tachi and S. Itoh, J. Inorg. Biochem., 2006, 100, 1118–1127.
- 27 Y. Yao, Z. Zhang, H. Peng, Y. Zhang, Q. Shen and J. Lin, *Inorg. Chem.*, 2006, 45, 2175–2183.
- 28 S. Hong, L. M. R. Hill, A. K. Gupta, B. D. Naab, J. B. Gilroy, R. G. Hicks, C. J. Cramer and W. B. Tolman, *Inorg. Chem.*, 2009, 48, 4514–4523.
- 29 F. Drouin, T. J. J. Whitehome and F. Schaper, *Dalton Trans.*, 2011, 40, 1396–1400.
- 30 M. N. Kopylovich and A. J. L. Pombeiro, Coord. Chem. Rev., 2011, 255, 339–355.

- 31 A. R. Siedle, R. J. Webb, F. E. Behr, R. A. Newmark, D. A. Weil, K. Erickson, R. Naujok, M. Brostrom, M. Mueller, S. H. Chou and V. G. Young, *Inorg. Chem.*, 2003, 42, 932–934.
- 32 H. V. R. Dias and S. Singh, Inorg. Chem., 2004, 43, 5786-5788.
- 33 H. V. R. Dias and S. Singh, Inorg. Chem., 2004, 43, 7396-7402.
- 34 J. A. Flores, V. Badarinarayana, S. Singh, C. J. Lovely and H. V. R. Dias, *Dalton Trans.*, 2009, 7648–7652.
- 35 J. A. Flores and H. V. R. Dias, Inorg. Chem., 2008, 47, 4448-4450.
- 36 H. V. R. Dias, S. Singh and J. A. Flores, *Inorg. Chem.*, 2006, 45, 8859– 8861.
- 37 H. V. R. Dias, J. A. Flores, J. Wu and P. Kroll, J. Am. Chem. Soc., 2009, 131, 11249–11255.
- 38 H. V. R. Dias and W. Jin, J. Am. Chem. Soc., 1995, 117, 11381-11382.
- 39 H. V. R. Dias, Z. Wang and W. Jin, *Inorg. Chem.*, 1997, **36**, 6205–6215.
- 40 H. V. R. Dias, R. G. Browning, S. A. Polach, H. V. K. Diyabalanage and C. J. Lovely, J. Am. Chem. Soc., 2003, 125, 9270–9271.
- 41 C. J. Lovely, R. G. Browning, V. Badarinarayana and H. V. R. Dias, *Tetrahedron Lett.*, 2005, 46, 2453–2455.
- 42 P. Krishnamoorthy, R. G. Browning, S. Singh, R. Sivappa, C. J. Lovely and H. V. R. Dias, *Chem. Commun.*, 2007, 731–733.
- 43 C. J. Lovely, J. A. Flores, X. F. Meng and H. V. R. Dias, *Synlett*, 2009, 129–132.

- 44 K. Rangan, M. Fianchini, S. Singh and H. V. R. Dias, *Inorg. Chim. Acta*, 2009, **362**, 4347–4352.
- 45 H. V. R. Dias, K. H. Bardorf, M. Fianchini, H. V. K. Diyabalanage, S. Carnahan, R. Mulcahy, A. Rabiee, K. Nelson and L. van Waasbergen, *J. Inorg. Biochem.*, 2006, **100**, 158–160.
- 46 L. van Waasbergen, I. Fajdetic, M. Fianchini and H. V. R. Dias, J. Inorg. Biochem., 2007, 101, 1180–1183.
- 47 H. V. R. Dias, L. van Waasbergen, J. A. Flores, *Polyhalogenated triazapentadiene compositions*, US Patent #7667077, 2010.
- 48 H. V. R. Dias and C. J. Lovely, Chem. Rev., 2008, 108, 3223-3238.
- 49 A. R. Siedle, R. J. Webb, M. Brostrom, S. H. Chou, D. A. Weil, R. A. Newmark, F. E. Behr and V. G. Young, *Inorg. Chem.*, 2003, 42, 2596–2601.
- 50 C. Shimokawa and S. Itoh, Inorg. Chem., 2005, 44, 3010-3012.
- 51 H. A. Chiong and O. Daugulis, Organometallics, 2006, 25, 4054-4057.
- 52 M. Quiros, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1994, 50, 1236–1239.
- 53 P. G. Jones and E. Bembenek, Z. Kristallogr., 1993, 208, 213–218.
- 54 R. E. Bachman and D. F. Andretta, *Inorg. Chem.*, 1998, **37**, 5657–5663.
- 55 A. R. Siedle, R. J. Webb, M. Brostrom, R. A. Newmark, F. E. Behr and V. G. Young, *Organometallics*, 2004, **23**, 2281–2286.