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Syntheses and spectroscopic and structural characterization of silver(I) complexes containing tris(isobutyl)phosphine and poly(azol-1-yl)borates

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Abstract

Silver(I) derivatives $[Ag(L)(P^{i}Bu_{3})]$ (L = H₂B(tz)₂ (dihydrobis(1H-1,2,4-triazol-1-yl)borate), HB(tz)₃ (hydrotris(1H-1,2,4-triazol-1-yl)borate), Tp (hydrotris(1H-pyrazol-1-yl)borate), Tp^{Me} (hydrotris(3-methyl-1H-pyrazol-1-yl)borate), Tp^{Me} (hydrotris(4-bromo-1H-pyrazol-1-yl)borate), HB(tz)₃ (hydrotris(1H-1,2,4-benzotriazol-1-yl)borate), Tm (hydrotris(3-methyl-1-imidazolyl-2-thione)borate), pzTp (tetrakis(1H-pyrazol-1-yl)borate), pz⁰Tp^{Me} (tetrakis(3-methyl-1H-pyrazol-1-yl)borate) have been synthesized from the reaction of [Ag(NO₃)(PⁱBu₃)₂] with ML (M = Na or K) and characterized both in solution (¹H- and ³¹P{¹H} NMR, ESI MS spectroscopy, conductivity) and in the solid state (IR, single crystal X-ray structure analysis). These complexes are air-stable and light-sensitive and non-electrolytes in CH₂Cl₂ and acetone in which they slowly decompose, even with the strict exclusion of oxygen and light, yielding metallic silver and/or azolate (Az) species of formula [Ag(Az)(PⁱBu₃)], [Ag(Tp^{CF3})(PⁱBu₃)], [Ag{HB(btz)₃}(PⁱBu₃)], and [Ag(Tm)(PⁱBu₃)] show that the silver atom adopts a distorted tetrahedral coordination geometry.[Ag(L)(PPh₃)] can be easily obtained from the reaction of [Ag(L)(PⁱBu₃)] was recovered. ³¹P{¹H} NMR variable temperature NMR studies showed that in the pz⁰Tp^X derivatives the scorpionate ligand acts as a bidentate donor, whereas tridentate coordination is found for all tris(azolyl)borate derivatives, both in solution and in the solid state. ESI MS data suggest the existence in solution of species such as [Ag(PⁱBu₃)₂]⁺ upon dissociation of the L ligand, and also the formation of dimeric species of the form [Ag₂(L)(PⁱBu₃)₂]⁺.

Keywords: Scorpionates; Silver(I); Triorganophosphines; X-ray; ³¹P NMR; ESI MS

1. Introduction

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Since the first report of Trofimenko [1], poly(pyrazolyl)borates or scorpionate ligands [2], have been extensively employed as anionic σ -donor ligands in a wide variety of metal complexes [3]. These ligands are

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extremely versatile because the number of pyrazolate groups and the substituents thereon or at the B center can be readily modified in order to obtain ligands with different steric and/or electronic profiles. They have been extensively used to synthesize complexes of main and transition group metals and they are particularly useful for the synthesis of monomeric derivatives in which the coordination sphere of the metal can be carefully controlled [4–9]. Important modifications to poly(pyrazolyl)borates can be made by changing the substituents on the heterocyclic ring or also by replacement of the pyrazolyl rings with triazolyl [10], benzotriazolyl [11], imidazolyl [12,13], and methimazolyl moieties [14–21]. These replacements have led to new scorpionates able to bridge between different metal centers, yielding dimers or coordination polymers characterized by peculiar spectroscopic and structural features. Some of these new ligands are very promising for the synthesis of inorganic materials with inner cavities useful for the catalysis of organic reactions [22,23] or with collective magnetic phenomena for the design of molecular-based ferromagnets [24].

We have recently initiated an investigation into the structural and spectroscopic properties of mixed phosphine/N-donor derivatives of copper(I) [25], silver(I) [26–32] and gold(I) [33]. As a part of this study we have been interested in the exploration of complexes incorporating poly(azolyl)borate and phosphine ligands with different steric and electronic profiles. In our research concerning modifications of the poly(pyrazolyl)borate ligands in which the pyrazolyl rings are replaced by 1,2,4-triazolyl or imidazolyl rings, some interesting single-stranded silver(I) coordination polymers containing bridging poly(1-imidazolyl)borates have been reported [30].

We have also previously reported the substitution of triazole for pyrazole in poly(pyrazolyl)alkanes to form poly(triazolyl)alkanes such as the bis(1,2,4-triazolyl)alkane ligand, able to coordinate silver(I) salts through the nitrogen atoms, yielding two- and three-dimensional coordination polymers [34]. We have now extended this work to the investigation of different N- or S-donor *scorpionate* ligands with silver(I) salts in the presence of competitor phosphine ligands, in order to build new complexes with different solid state structure and properties. Here we describe the results of the interaction of various bis- and tris-(azolyl)borate ligands with AgNO₃ in the presence of the tris(isobutyl)phosphine coligand.

2. Experimental

2.1. Materials and methods

All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using stand-

ard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. All chemicals were purchased from Aldrich and used without further purification. Potassium dihydrobis(1H-1,2,4-triazol-1yl)borate K[H₂B(tz)₂], potassium hydrotris(1H-1,2,4-triazol-1-yl)borate K[HB(tz)₃] [25], sodium hydrotris(1Hpyrazol-1-yl)borate Na(Tp) [35], potassium hydrotris(3,5-dimethyl-1H-pyrazol-1-yl)borate K(Tp*) [35], hydrotris(3-methyl-1H-pyrazol-1-yl)borate sodium Na(Tp^{Me}), potassium tetrakis(1H-pyrazol-1-yl)borate K(pzTp) [35], potassium tetrakis(3-methyl-1H-pyrazol-1-yl)borate K(pz⁰TpMe) [35], sodium hydrotris(3-trifluoromethyl-1H-pyrazol-1-yl)borate Na(Tp^{CF3}) [36], hydrotris(4-bromo-1H-pyrazol-1-yl)borate potassium K(Tp^{4Br}) [37,38], potassium hydrotris(1H-1,2,4-benzotriazol-1-yl)borate, K[HB(btz)₃] [39] and potassium hydrotris(3-methy-1-imidazolyl-2-thione)borate, K(Tm) [26] were synthesized in accordance with literature methods. Elemental analyses (C, H, N, S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra (selected data are available as Supplementary material) were recorded from 4000 to 100 cm⁻¹ with a Perkin–Elmer System 2000 FT-IR instrument. ¹H, and ³¹P NMR spectra were recorded on a VXR-300 Varian spectrometer (300 MHz for ¹H, and 121.4 MHz for ³¹P). H chemical shifts are reported in ppm versus SiMe₄, P chemical shifts in ppm versus H_3PO_4 85%. The electrical conductances of the acetone, dichloromethane, DMSO and acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature. Positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/ml) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetone or acetonitrile. For the ESI-MS data, masses and intensities were compared to those calculated by using the IsoPro isotopic abundance simulator version 2.1 [40]; peaks containing silver(I) ions are identified as the centers of isotopic clusters.

2.2. Syntheses

2.2.1. $[Ag(NO_3)(P^iBu_3)_2]$

P'Bu₃ (0.809 g, 4.0 mmol) was added at room temperature, under an atmosphere of dry oxygen-free dinitrogen, to an anhydrous THF solution (20 ml) of AgNO₃ (0.338 g, 2.0 mmol). After the addition, the solution was stirred under an atmosphere of dry oxygen-free dinitrogen for 24 h and subsequently the solvent was removed with a rotary evaporator. *n*-hexane (30 ml) was added; a brown precipitate was formed, which was filtered off and washed with *n*-hexane to give complex [Ag(NO₃)(PⁱBu₃)₂] as a colorless micro-crystalline solid in 85% yield, m.p. 73–76 °C. ¹H NMR (CDCl₃, 293 K): δ 0.99 (sbr, 6H, CH₂CH–(CH₃)₂), 1.58 (sbr, 2H, CH₂CH–(CH₃)₂), 1.81 (br, 1H, CH₂CH–(CH₃)₂). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –13.64 (dd, ¹J(³¹P, ¹⁰⁷Ag) = 480 Hz, ¹J(³¹P, ¹⁰⁹Ag) = 554 Hz). IR (nujol, cm⁻¹): 812s (NO₃). ESI MS (+): 511 [100] [Ag(PⁱBu₃)₂]⁺. (–) 62.2 [90] (NO₃)⁻, 230.9 [100] [Ag(NO₃)₂]⁻. Anal. Calc. for C₂₄H₅₄AgNP₂O₃: C, 50.2; H, 9.5; N, 2.4. Found: C, 49.8; H, 9.8; N, 2.3%.

2.2.2. $[Ag\{H_2B(tz)_2\}(P^iBu_3)]$ (1)

 $K[H_2B(tz)_2]$ (0.188 g, 1.0 mmol) was added at room temperature to a methanol solution (30 ml) of [Ag- $(NO_3)(P'Bu_3)_2$ (0.574 g, 1.0 mmol). After the addition, the solution was stirred for 2 h and subsequently the solvent was removed with a rotary evaporator. Chloroform (30 ml) was added. The suspension was filtered and the solution was concentrated under reduced pressure. Diethyl ether (30 ml) and *n*-hexane (20 ml) were then added; a colorless precipitate was formed, which was filtered off and washed with diethyl ether/n-hexane. Recrystallization from chloroform/methanol (1:2) gave complex 1 as a colorless micro-crystalline solid in 78%yield, m.p. 104–107 °C. ¹H NMR (CDCl₃, 293 K): δ 1.12 (d, 18H, CH₂CH-(CH₃)₂), 1.63 (pt, 6H, CH₂CH-(CH₃)₂), 1.90 (m, 3H, CH₂CH-(CH₃)₂), 7.86 (s, 2H, 5-CH), 8.14 (s, 2H, 3-CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -14.69 (br); ³¹P{¹H} NMR (CDCl₃, 218 K): δ $-15.3 \text{ (dd, } {}^{1}J({}^{31}\text{P}, {}^{107}\text{Ag}) = 626 \text{ Hz}, {}^{1}J({}^{31}\text{P}, {}^{109}\text{Ag}) = 721$ Hz). IR (nujol, cm⁻¹): 2418s (BH). Anal. Calc. for C₁₆H₃₃AgBN₆P: C, 41.9; H, 7.2; N, 18.3. Found: C, 42.3; H, 7.6; N, 18.0%. Silver(I) derivatives [Ag(scorpionate)($P^{i}Bu_{3}$)] have been synthesized from the reaction of $[Ag(NO_3)(P'Bu_3)_2]$ with sodium or potassium scorpionate salts and characterized both in solution and in the solid state.

2.2.3. $[Ag\{HB(tz)_3\}(P^{t}Bu_3)]$ (2)

K[HB(tz)₃] (0.255 g, 1.0 mmol) was added at room temperature to a methanol solution (30 ml) of [Ag- $(NO_3)(P^iBu_3)_2$] (0.574 g, 1.0 mmol). After the addition, the solution was stirred for 2 h. and subsequently the solvent was removed with a rotary evaporator. Chloroform (30 ml) was added. The suspension was filtered and the solution was concentrated under reduced pressure. Diethyl ether (30 ml) was added; a yellow precipitate was formed, which was filtered off and washed with diethyl ether/n-hexane. Re-crystallization from methanol/CHCl₃ (2:1) gave complex 2 as a colorless microcrystalline solid in 44% yield, m.p. 119-122 °C. ¹H NMR (CDCl₃, 293 K): δ 1.10 (d, 18H, CH₂CH-(CH₃)₂), 1.66 (pt, 6H, CH₂CH–(CH₃)₂), 1.95 (m, 3H, CH₂CH₋(CH₃)₂), 7.89 (s, 3H, 5-CH), 8.27 (s, 3H, 3-CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -12.31 (dd, ${}^{1}J({}^{31}P, {}^{107}Ag) = 629$ Hz, ${}^{1}J({}^{31}P, {}^{109}Ag) = 716$ Hz); ³¹P{¹H} NMR (CDCl₃, 218 K): δ -10.9 (dd, ¹J(³¹P, 107 Ag)=624 Hz, $^{1}J(^{31}$ P, 109 Ag)=719 Hz). IR (nujol, cm⁻¹): 2483m (BH). Anal. Calc. for C₁₈H₃₄AgBN₉P:

C, 41.1; H, 6.5; N, 24.0. Found: C, 41.5; H, 6.8; N, 23.5%.

2.2.4. $[Ag\{Tp\}(P^{i}Bu_{3})]$ (3)

Compound **3** was prepared similarly to compound **1**, by using Na(Tp) (0.236 g, 1 mmol) and $[Ag(NO_3)(P^{i-}Bu_3)_2]$ (0.574 g, 1.0 mmol); it was re-crystallized from methanol/CHCl₃ (2:1) to give complex **3** as a colorless micro-crystalline grey solid in 75% yield, m.p. 119–122 °C. ¹H NMR (CDCl₃, 293 K): δ 1.11 (d, 18H, CH₂CH–(CH₃)₂), 1.61 (pt, 6H, CH₂CH–(CH₃)₂), 1.98 (m, 3H, CH₂CH–(CH₃)₂), 6.10 (t, 3H, 4-CH), 7.43 (d, 3H, 5-CH), 7.65 (d, 3H, 3-CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –11.22 (d, ¹J(³¹P, Ag)=629 Hz; ³¹P{¹H} NMR (CDCl₃, 218 K): δ –8.72 (d, ¹J(³¹P, Ag)=636 Hz). IR (nujol, cm⁻¹): 2457s (BH). ESI MS (+): 511 [100] [Ag(PⁱBu₃)₂]⁺, 833.7 [90] [Ag₂{Tp}(PⁱBu₃)₂]⁺; (-) 231.9 [20] {Tp}⁻. Anal. Calc. for C₂₁H₃₇AgBN₆P: C, 48.2; H, 7.1; N, 16.1. Found: C, 48.4; H, 7.5; N, 15.8%.

2.2.5. $[Ag\{Tp^{Me}\}(P^{i}Bu_{3})]$ (4)

Compound 4 was prepared similarly to compound 1, by using Na[HB(3-Mepz)₃] (0.278 g, 1 mmol) and [Ag-(NO₃)(PⁱBu₃)₂] (0.574 g, 1.0 mmol); it was re-crystallized from CHCl₃/n-hexane (1:1) to give complex 4 as a colorless micro-crystalline solid in 76% yield, m.p. 151-154 °C. ¹H NMR (CDCl₃, 293 K): δ 1.04, 1.08 (dbr, 18H, CH₂CH-(CH₃)₂), 1.60 (br, 6H, CH₂CH-(CH₃)₂), 1.90 (mbr, 3H, CH₂CH-(CH₃)₂), 2.24 (s, 9H, 3-CH₃), 5.86 (d, 3H, 4-CH), 7.50 (d, 3H, 5-CH); ¹H NMR (CDCl₃, 223 K): δ 1.00, 1.08 (d, 18H, CH₂CH-(CH₃)₂), 1.60 (br, 6H, CH₂CH–(CH₃)₂), 1.95 (mbr, 3H, CH₂CH– (CH₃)₂), 2.22 (s, 9H, 3-CH₃), 5.87 (d, 3H, 4-CH), 7.51 (d, 3H, 5-CH). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃, 293 K): δ 107 Ag) = 590 ${}^{1}J({}^{31}P,$ Hz, $^{1}J(^{31}P.$ -18.74(dd, 109 Ag) = 680 Hz); 31 P{¹H} NMR (CDCl₃, 218 K): δ $^{1}J(^{31}P, ^{107}Ag) = 591$ -23.12 (dd, Hz, $^{1}J(^{31}\mathrm{P},$ ¹⁰⁹Ag)=681 Hz). IR (nujol, cm⁻¹): 2409m (BH). Anal. Calc. for C₂₄H₄₃AgBN₆P: C, 51.0; H, 7.7; N, 14.9. Found: C, 49.6; H, 8.0; N, 14.5%.

2.2.6. $[Ag \{Tp^{CF3}\}(P^{i}Bu_{3})]$ (5)

Compound 5 was prepared similarly to compound 1, by using Na(Tp^{CF3}) (0.440 g, 1 mmol) and $[Ag(NO_3)(P^{i-1})]$ Bu₃)₂] (0.574 g, 1.0 mmol); it was re-crystallized from $CHCl_3$ /methanol (1:1) to give complex 5 as a colorless micro-crystalline solid in 65% yield, m.p. 125-129 °C. ¹H NMR (CDCl₃, 293 K): δ 0.99, 1.10 (d, 18H, CH₂CH-(CH₃)₂), 1.55, 1.60 (d, 6H, CH₂CH-(CH₃)₂), 1.84, 2.11 (mbr, 3H, CH₂CH-(CH₃)₂), 6.42 (d, 3H, 4-CH), 7.66 (d, 3H, 5-CH). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃, 293 K): $\delta -17.25$ (dd, ${}^{1}J({}^{31}P, {}^{107}Ag) = 654$ Hz, ${}^{1}J({}^{107}Ag) = 654$ Hz, 109 Ag) = 749 Hz); 31 P{ 1 H} NMR (CDCl₃, 218 K): δ ${}^{1}J({}^{31}P, {}^{107}Ag) = 649 Hz,$ -24.01 (dd, $^{1}J(^{31}\text{P}.$ 109 Ag)=746 Hz). IR (nujol, cm⁻¹): 2457s (BH). ESI MS (+): 511 [100] $[Ag(P^{i}Bu_{3})_{2}]^{+}$, 1038 [20]

 $\begin{array}{l} [Ag_2\{Tp^{CF3}\}(P^iBu_3)_2]^+; \ (-) \ 417 \ [10] \ \{Tp^{CF3}\}^-, 434 \ [40] \\ [Ag\{NO_3\}_2(P^iBu_3)]^-. \ Anal. \ Calc. \ for \ C_{24}H_{34}AgBF_9N_6P: \\ C, \ 39.6; \ H, \ 4.7; \ N, \ 11.6. \ Found: \ C, \ 40.3; \ H, \ 5.0; \ N, \\ 11.2\%. \end{array}$

2.2.7. $[Ag\{Tp^{4Br}\}(P^{i}Bu_{3})]$ (6)

Compound **6** was prepared similarly to compound **1**, by using K(Tp^{4Br}) (0.488 g, 1 mmol), and [Ag(NO₃)(P^{*i*}-Bu₃)₂] (0.574 g, 1.0 mmol); it was re-crystallized from CHCl₃/methanol (1:1) to give complex **6** as a colorless micro-crystalline solid in 73% yield, m.p. 215–217 °C. ¹H NMR (CDCl₃, 293 K): δ 1.12 (d, 18H, CH₂CH– (CH₃)₂), 1.61 (pt, 6H, CH₂CH–(CH₃)₂), 1.96 (m, 3H, CH₂CH–(CH₃)₂), 7.36 (s, 3H, 5-CH), 7.63 (s, 3H, 3-CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –12.36 (dd, ¹J(³¹P, ¹⁰⁷Ag)=614 Hz, ¹J(³¹P, ¹⁰⁹Ag)=707 Hz); ³¹P{¹H} NMR (CDCl₃, 218 K): δ –10.74 (dd, ¹J(³¹P, ¹⁰⁷Ag)=613 Hz, ¹J(³¹P, ¹⁰⁹Ag)=708 Hz). IR (nujol, cm⁻¹): 2413m (BH). *Anal.* Calc. for C₂₁H₃₄AgBBr₃N₆P: C, 33.2; H, 4.5; N, 11.1. Found: C, 33.3; H, 4.8; N, 11.0%.

2.2.8. $[Ag{Tp*}(P^{i}Bu_{3})]$ (7)

Compound 7 was prepared similarly to compound 1, by using K[HB(3,5-Me₂Pz)₃] (0.336 g, 1 mmol), and $[Ag(NO_3)(P^iBu_3)_2]$ (0.574 g, 1.0 mmol); it was recrystallized from CHCl₃/methanol (1:1) to give complex 7 as a colorless micro-crystalline solid in 47% yield, m.p. 174–178 °C. ¹H NMR (CDCl₃, 293 K): δ 1.06, 1.12 (d, 18H, CH₂CH–(CH₃)₂), 1.53, 1.67 (pt, 6H, CH₂CH– (CH₃)₂), 1.90–2.05 (mc, 3H, CH₂CH–(CH₃)₂), 2.19 (s, 9H, CH₃), 2.37 (s, 9H, CH₃), 5.66 (s, 3H, 4-CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ -19.75 (dd, ¹J(³¹P, $^{107}Ag = 585$ Hz, $^{1}J(^{31}P, ^{109}Ag) = 675$ Hz); $^{31}P\{^{1}H\}$ NMR (CDCl₃, 218 K): δ -24.90 (dd, ¹J(³¹P, ¹⁰⁷Ag)=586 Hz, ¹J(³¹P, ¹⁰⁹Ag)=677 Hz). IR (nujol, cm^{-1}): 2516m (BH). 511 [100] $[Ag(P^{i}Bu_{3})_{2}]^{+}$, 917 [80] $[Ag_{2}{Tp*}(P^{i}Bu_{3})_{2}]^{+}; (-) 417 [10] {Tp}^{CF3}^{-},434 [40]$ $[Ag\{NO_3\}_2(P^iBu_3)]^-$. Anal. Calc. for $C_{27}H_{49}AgBN_6P$: C, 53.4; H, 8.1; N, 13.8. Found: C, 53.0; H, 8.3; N, 13.5%.

2.2.9. $[Ag\{HB(btz)_3\}(P^iBu_3)]$ (8)

Compound **8** was prepared similarly to compound **1**, by using K[HB(btz)₃] (0405 g, 1 mmol), and [Ag(NO₃)-(P^{*i*}Bu₃)₂] (0.574 g, 1.0 mmol); it was re-crystallized from CHCl₃/methanol (1:2) to give complex **8** as a colorless micro-crystalline solid in 92% yield, m.p. 177–181 °C. ¹H NMR (CDCl₃, 293 K): δ 1.16 (d, 18H, CH₂CH– (CH₃)₂), 1.77 (br, 6H, CH₂CH–(CH₃)₂), 2.13 (br, 3H, CH₂CH–(CH₃)₂), 7.26–8.08 (mc, 12H, CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –15.19 (dd, ¹J(³¹P, ¹⁰⁷Ag)=659 Hz, ¹J(³¹P, ¹⁰⁹Ag)=748 Hz); ³¹P{¹H} NMR (CDCl₃, 218 K): δ –18.87 (dd, ¹J(³¹P, ¹⁰⁷Ag)=653 Hz, ¹J(³¹P, ¹⁰⁹Ag)=754 Hz). IR (nujol, cm⁻¹): 2477m (BH). *Anal.* Calc. for C₃₀H₄₀AgBN₉P: C, 53.3; H, 6.0; N, 18.6. Found: C, 53.0; H, 6.2; N, 18.3%.

2.2.10. $[Ag\{Tm\}(P^{t}Bu_{3})]$ (9)

Compound **9** was prepared similarly to compound **1**, by using KTm (0.390 g, 1 mmol), and $[Ag(NO_3)(P^{i}Bu_3)_2]$ (0.574 g, 1.0 mmol); it was re-crystallized from CHCl₃/ methanol (1:2) to give complex **9** as a colorless microcrystalline solid in 92% yield, m.p. 185–188 °C. ¹H NMR (CDCl₃, 293 K): δ 1.03 (d, 18H, CH₂CH– (CH₃)₂), 1.51 (pt, 6H, CH₂CH–(CH₃)₂), 1.94 (m, 3H, CH₂CH–(CH₃)₂), 3.60 (s, 9H, CH₃), 6.67 (d, 3H, CH), 6.77 (d, 3H, CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –15.34 (d, ¹J(³¹P, Ag)=529 Hz); ³¹P{¹H} NMR (CDCl₃, 218 K): δ –23.56 (dd, ¹J(³¹P, ¹⁰⁷Ag)=460 Hz, ¹J(³¹P, ¹⁰⁹Ag)=530 Hz). IR (nujol, cm⁻¹): 2379m (BH). ESI MS (+): 769 (45) [Ag₂{Tm}(PⁱBu₃)]⁺. Anal. Calc. for C₂₄H₄₃AgBN₆PS₃: C, 43.6; H, 6.5; N, 12.7; S, 14.7. Found: C, 43.2; H, 7.2; N, 12.4; S, 14.4%.

2.2.11. $[\{B(pz)_4\}Ag(P^iBu_3)]$ (10)

Compound 10 was prepared similarly to compound 1, by using K[B(pz)₄] (0.319 g, 1 mmol) and [(PⁱBu₃)Ag-NO₃] (0.574 g, 1.0 mmol); it was re-crystallized from $CHCl_3/n$ -hexane (1:1) to give complex 10 as a colorless micro-crystalline solid in 63% yield, m.p. 98-100 °C. ¹H NMR (CDCl₃, 293 K): δ 1.04, 1.10 (d, 18H, CH₂CH-(CH₃)₂), 1.50 (pt, 6H, CH₂CH-(CH₃)₂), 1.79 (br, 3H, CH₂CH-(CH₃)₂), 6.22 (t, 4H, 4-CH), 7.09 (d, 4H, 3- or 5-CH), 7.63 (d, 4H, 3- or 5-CH). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃, 293 K): δ -10.5 (dbr); ³¹P{¹H} NMR (CDCl₃, 218 K): δ -9.98 (dd, ${}^{1}J({}^{31}P, {}^{107}Ag) = 618$ Hz, 109 Ag)=713 $^{1}J(^{31}\mathrm{P},$ Hz). Anal. Calc. for C₂₄H₃₉AgBN₈P: C, 48.9; H, 6.7; N, 19.0. Found: C, 49.2; H, 7.0; N, 18.8%.

2.2.12. $[\{B(3-Mepz)_4\}Ag(P^iBu_3)]$ (11)

Compound **11** was prepared similarly to compound **1**, by using K[B(3-Mepz)₄] (0.374 g, 1 mmol) and [(P^{*i*} Bu₃)AgNO₃] (0.574 g, 1.0 mmol); it was re-crystallized from CHCl₃/*n*-hexane (1:1) to give complex **11** as a colorless micro-crystalline solid in 72% yield, m.p. 117–120 °C. ¹H NMR (CDCl₃, 293 K): δ 1.02 (d, 18H, CH₂CH– (CH₃)₂), 1.51 (pt, 6H, CH₂CH–(CH₃)₂), 1.73 (m, 3H, CH₂CH–(CH₃)₂), 2.28 (s, 9H, CH₃), 5.95 (d, 4H, 4-CH), 7.03 (d, 4H, 5-CH). ³¹P{¹H} NMR (CDCl₃, 293 K): δ –14.58 (dd, ¹J(³¹P, ¹⁰⁷Ag)=616 Hz, ¹J(³¹P, ¹⁰⁹Ag)=702 Hz); ³¹P{¹H} NMR (CDCl₃, 218 K): δ –16.42 (dd, ¹J(³¹P, ¹⁰⁷Ag)=610 Hz, ¹J(³¹P, ¹⁰⁹Ag)=704 Hz). Anal. Calc. for C₂₈H₄₇AgBN₈P: C, 52.1; H, 7.3; N, 17.4. Found: C, 51.7; H, 7.5; N, 17.0%.

2.3. Structure determinations

Full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω -scans;

Table 1 Crystal/refinement data

Compound	3 ^b	4	5	8	9
Formula	C ₂₁ H ₃₇ AgBN ₆ P	C24H43AgBN6P	C24H34AgBF9N6P	C30H40AgBN9P	C24H43AgBN9PS3
M _r (Da)	523.2	565.3	727.2	676.4	661.5
Crystal system	monoclinic	monoclinic	monoclinic	cubic	rhombohedral
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	Pa3 (No. 205)	$R\bar{3}$ (No. 148) ^a
a (Å)	8.5920(5)	13.199(2)	15.864(2)	18.877(2)	15.121(1)
b (Å)	17.245(1)	11.978(2)	9.877(1)		
c (Å)	17.340(1)	18.200(2)	60.410(8)		23.360(2)
β (°)	94.524(1)	91.435(2)	93.963(2)		
$V(Å^3)$	2561	2876	9443	6740	4626
$D_{\text{calc}} (\text{gcm}^{-3}) (Z (\text{f.u.}))$	$1.35_7(4)$	1.30 ₅ (4)	1.53_4 (12)	$1.33_{6}(8)$	$1.42_{5}(6)$
$\mu_{\rm Mo} \ ({\rm mm}^{-1})$	0.87	0.78	0.77	0.68	0.93
Specimen (mm)	0.36×0.20×0.17	$0.34 \times 0.08 \times 0.06$	0.16×0.06×0.05	0.25×0.15×0.12	0.24×0.22×0.18
T _{min/max}	0.86	0.86	0.90	0.90	0.87
$2\theta_{\rm max}$ (°)	75	58	53	70	
Nt	51030	13350	87447	59 530	32145
$N(R_{\rm int})$	13245 (0.025)	3369 (0.029)	19296 (0.075)	2858 (0.038)	4536 (0.029)
No	10178	3160	13813	2317	3951
R	0.029	0.032	0.073	0.035	0.029
R _w	0.086	0.044	0.10	0.056	0.041

^a Hexagonal setting.

^b Refinement on F^2 .

monochromatic Mo K α radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction, $N_{\rm o}$ with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the nonhydrogen atoms, $(x, y, z, U_{iso})_{H}$ included constrained at estimates. Conventional residuals R, R_w on |F| are quoted at convergence (weights: $(\sigma^2(F) + 0.0004F^2)^{-1})$, neutral atom complex scattering factors being employed within the XTAL 3.7 program system [41]. Pertinent results are given in Tables 1 and 2 and Fig. 1, the latter showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms where shown having arbitrary radii of 0.1 Å. In 5, considerable disorder is evident, all modelled in terms of pairs of components of site occupancies set at 0.5 after trial refinement for the *i*-butyl groups of molecule 1 (presumably concerted) by inversion of the secondary carbons, and CF_3 groups 113, 123, by rotation about the C-C(ring) pendant. The very long primitive axis presented some difficulty in data acquisition.

3. Results and discussion

3.1. Syntheses and spectroscopy

An excess of $P^{i}Bu_{3}$ reacts with AgNO₃ under an atmosphere of dry oxygen-free dinitrogen yielding [Ag-(NO₃)($P^{i}Bu_{3}$)₂] in high yields. Further, no other compounds were identified in the reaction mixture also when a large excess of the P-donor was employed. From the

interaction of one equivalent of $[Ag(NO_3)(P'Bu_3)_2]$ freshly prepared with one equivalent of $K(H_nB(tz)_{4-n})$ (n=1 or 2), $M(Tp^x)$ (M=Na or K; Tp=Tp, Tp*, Tp^{Me}, Tp^{CF3}, Tp^{4Br}), $M(pz^0Tp^x)$ (M=Na or K, $pz^0Tp^x=pzTp$ or $pz^0Tp^{Me})$, K(Tm) and $K(HB(btz)_3)$ in organic solvents at room temperature, complexes 1–11 have been obtained in high yield (Eq. 1)

$$\begin{split} & [\operatorname{Ag}(\operatorname{NO}_3)(\operatorname{P}^i\operatorname{Bu}_3)_2] + \operatorname{ML} \\ & \to [\operatorname{Ag}(\operatorname{L})(\operatorname{P}^i\operatorname{Bu}_3)] + \operatorname{M}(\operatorname{NO}_3) + \operatorname{P}^i\operatorname{Bu}_3 \end{split} \tag{1}$$

The derivatives $[Ag(NO_3)(P^iBu_3)_2]$ and 1–11 show good solubility in chlorinated solvents, but are insoluble in diethyl ether, aliphatic and aromatic hydrocarbons. They are non-electrolytes in acetone, acetonitrile, DMSO and CH₂Cl₂ solution. In the former solvent the conductivity values are always less than 2.0 Ω^{-1} cm²mol⁻¹. They are air-stable and somewhat light-sensitive. With exception of 1, 2, 8, 10 and 11 the chloroform solutions of the scorpionate complexes often rapidly darken, even with strict exclusion of oxygen and light. In complexes 3–7 containing Tp^x ligands, this is presumably due to the strong reducing power of the borate anion (retaining one hydrogen in the Tp derivatives) which immediately converts the complex into metallic silver, in accordance with the following Eq. 2:

$$2[\operatorname{Ag}(\operatorname{Tp})(\operatorname{P'}\operatorname{Bu}_3)] \to \operatorname{H}_2 + 2\operatorname{Ag} + [\operatorname{B}(\operatorname{pz})_3]_2 + 2\operatorname{P'}\operatorname{Bu}_3$$
(2)

In some cases colorless powders were recovered from the chloroform solutions of 3–7. These have been preliminarily identified as a mixture of $[Ag(pz^x)(P^iBu_3)_n]$ and $[Ag(P^iBu_3)_n(Hpz^x)(NO_3)]$ complexes (n=1 or 2;

Table 2
Selected molecular geometries

Cpd/mol	4	5	5/1,2,3	9	10 ^a
Distances (Å)					
Ag–P	2.3469(3)	2.345(1)	2.378(2), 2.380(2), 2.391(2)	2.3783(6)	2.4035(6)
Ag-N(12)	2.379(1)	2.431(5)	2.475(6), 2.424(7), 2.423(6)	2.432(2)	2.5953(3)
Ag-N(22)	2.348(1)	2.298(5)	2.393(6), 2.407(6), 2.433(6)		
Ag-N(32)	2.361(1)	2.415(5)	2.410(6), 2.458(7), 2.460(6)		
$\delta Ag(1)^{b}$	0.250(3)	1.350(9)	0.28(1), 0.55(2), 0.52(1)	0.014(3)	2.337(3)
$\delta Ag(2)$	0.059(3)	0.118(10)	0.04(1), 0.17(1), 0.43(2)		
$\delta Ag(3)$	0.282(3)	0.250(10)	0.03(1), 0.43(1), 0.38(2)		
Angles (°)					
P-Ag-N(12)	113.82(3)	123.4(1)	128.2(1), 131.1(2), 133.6(1)	132.83(4)	118.19(1)
P-Ag-N(22)	128.38(3)	135.8(1)	131.3(2), 133.4(2), 133.3(2)		
P-Ag-N(32)	129.60(3)	131.4(1)	134.1(2), 129.9(2), 128.4(2)		
N(12)-Ag-N(22)	84.09(4)	81.3(2)	82.2(2), 81.2(2), 80.1(2)	78.86(6)	99.51(1)
N(12)-Ag-N(32)	79.99(4)	84.0(2)	80.2(2), 81.1(2), 79.2(2)		
N(22)-Ag-N(32)	82.45(4)	82.5(2)	81.4(2), 80.3(2), 82.0(2)		
N(11)-B-N(21)	110.4(1)	112.6(5)	110.6(6), 111.8(7), 111.6(7)	109.0(2)	112.6(1)
N(11)-B-N(31)	110.8(1)	108.2(5)	111.3(6), 110.8(6), 110.4(7)		
N(21)-B-N(31)	110.1(1)	110.6(5)	111.5(6), 108.3(6), 110.4(7)		
Torsion angles (°)					
N(trans)-Ag-P-C(111)	161.55(6)	163.7(3)	-158.3(7)/166.9(5), 164.5(4), -171.7(3)	$-1.4(1)^{c}$	-164.18(6)
N(trans)-Ag-P-C(211)	170.58(6)	169.4(3)	-162.8(6)/168.1(6), 166.9(4), -165.6(4)		
N(trans)-Ag-P-C(311)	162.37(6)	173.3(3)	-155.6(6)/170.0(6), 167.8(5), -165.5(3)		
Ag-P-C(111)-C(112)	43.8(1)	52.0(6)	-56(2)/57(1), 49.8(9), -49.7(7)	28.5(2)	-31.9(4)
Ag-P-C(211)-C(212)	31.0(1)	50.0(4)	-55(1)/53(1), 52.6(8), -47.1(6)		
Ag-P-C(311)-C(312)	61.7(1)	51.2(5)	-56(2)/54(1), 50.6(11), -61.2(6)		
P-C(111)-C(112)-H(112)	41	42	-50/34, 42, -45	-56	46
P-C(211)-C(212)-H(212)	-53	39	-47/36, 44, 29		
P-C(311)-C(312)-H(312)	54	45	-32/35, 46, -35		

^a For N(*n*2) read S; Ag–S–C(2) is 98.09(4)°.

^b δ Ag(*n*) is the deviation of the silver atom from ligand plane. ⁺Labelling of the C, H atoms may have more or less digits depending on the complexity of the structure.

² The *cis*-angle in an 'eclipsed' array.

Hpz^x = a generic pyrazole), presumably due to breaking of the B–N bond in the scorpionate ligand and consequent coordination of the azole or of the azolate to the silver metal center.

The infrared spectra of 1–11 (available as Supporting information) show all the bands required by the presence of the organic nitrogen donor and of the P'Bu₃ ligand. In all compounds we found the v(CH) of the heterocyclic ring above 3100 cm^{-1} , the breathing of the heterocyclic rings in the range 1600–1500 cm^{-1} , and finally the B-N stretching vibration as a band of medium intensity at ca. 1400 cm⁻¹. In the Tp* derivative 7 the B-H stretching appears as a single peak at ca. 2500 cm⁻¹, suggesting symmetric κ^3 -hapticity [42] of the ligand (Fig. 2), whereas a closer examination of the spectra of 3 and 6 reveals a medium absorption at ca. 2450 cm⁻¹ and the presence of other weaker absorptions at ca. 2400 cm^{-1} , in keeping with the existence of independent molecules in the solid state, perhaps also containing the scorpionate ligand in a less symmetric tripodal chelating fashion (see Section 3.2). In the spectrum of $[Ag(NO_3)(P^iBu_3)_2]$ the separation between v_1

and v_4 is ca. 80 cm⁻¹, in accordance with a bidentate nitrato group. This has been confirmed by the presence of at least two broad bands in the overtones region at 2400–2300 and 1800–1700 cm⁻¹, typical of a bidentate O₂NO group [43].

In the far-IR spectra of all compounds a number of weak to medium bands in the region $300-100 \text{ cm}^{-1}$, absent in the spectra of the alkali metal scorpionate salt and of $[\text{Ag}(\text{NO}_3)(\text{P}^{i}\text{Bu}_3)_2]$, can be assigned to Ag–N and Ag–P vibrations in accordance with previous assignments. As expected in the far-IR spectrum of **9** we have found several bands due to v(C-S) coupled with v(Ag-S) bands at ca. 280 cm⁻¹, which suggest ligand thione S-donation [26].

In the ¹H NMR spectra of all compounds, recorded in CDCl₃ (see Section 2), the signals due to the tris-(iso-butyl)phosphine lie in the range 1.0–1.1 (multiplet due to the methyl), 1.7–2.0 (multiplet due to CH₂), 2.1–2.2 (multiplet due to CH), showing a pattern of signals and chemical shifts different from those found for free P^{*i*}Bu₃ and for [Ag(NO₃)(P^{*i*}Bu₃)₂], and suggesting the existence of the complexes in solution.







5



Fig. 1. Projections, normal to the (quasi-) 3 axes of 3, 4, 5 (three molecules), 8, 9.

The room temperature ¹H NMR spectra of the Tp^x , $H_2B(tz)_2$, $HB(tz)_3$, $HB(btz)_2$ and Tm exhibit similar signals for their azolyl groups also at low temperature, suggesting highly fluxional species with either a rocking motion of the $Ag(P^iBu_3)_2^+$ moieties between the two or three nitrogen or sulfur atoms of the scorpionate ligands,

or complete dissociation and reassociation of the azolyl nitrogens or sulfurs occurring rapidly at lower temperature; in fact, on cooling the CDCl₃ solutions to 193 K, no additional signals due to azolyl protons appeared [44].

The pz⁰Tp^{Me} derivative **11** shows a different behavior: at room temperature only one set of signals is found



Fig. 2. Symmetric κ^3 -hapticity of Tp in derivative 3.

for the protons of the four pyrazolyl groups, whereas from ca. 203 K each resonance type splits into three with 2/1/1 integrated intensity, indicating that these species are fluxional at room temperature, but not below 203 K. At this temperature two of the four pyrazolyl groups appear to be coordinated to silver in an N₂AgP trigonal environment (Fig. 3). In the case of the pzTp derivative **10** at 183 K very broad signals only were detected suggesting that fluxionality is almost lost at this temperature. The difference between **10** and **11** may be ascribed to the steric hindrance of the methyl groups in the pz⁰Tp^{Me} derivative **11**.

The ${}^{31}P$ NMR data for all compounds (chemical shifts, ${}^{109}Ag{-}^{31}P$ and ${}^{107}Ag{-}^{31}P$ coupling constants) in CDCl₃ solution have been reported in Section 2.

It should be noted that the free phosphine signal (ca. -43 ppm) appears upfield of the silver(I) complexes. $\Delta \delta({}^{31}\mathrm{P}) = \delta({}^{31}\mathrm{P}_{\text{complex}}) - \delta({}^{31}\mathrm{P}_{\text{ligand}}), \text{ the differences in}$ shift between $P^i B u_3$ and the silver complexes lie in the range 20-35 ppm. It is further worth noting that the shift is a function of the steric hindrance on the scorpionate ligands, the lower $\Delta\delta(^{31}P)$ values being found for the Tp^{Me}, Tp* and pz⁰Tp^{Me} complexes. The $\Delta \delta(^{31}P)$ is greater not only with respect to the values observed in the copper(I) complexes containing scorpionate and monodentate P-donor ligands [25,31,40], in which a weak bonding interaction has been hypothesized in solution, but is also greater with respect to those reported for other silver(I) phosphino species [26-30,32]. In contrast to previous observations all scorpionate compounds and $[Ag(NO_3)(P^{\prime}Bu_3)_2]$ exhibit at room temperature two doublets in which the separate coupling of ³¹P to the ¹⁰⁷Ag and ¹⁰⁹Ag are resolved, in accordance with a stopped or slow phosphine exchange process. The ${}^{1}J({}^{109}\text{Ag}{}^{-31}\text{P})$ and ${}^{1}J({}^{107}\text{Ag}{}^{-31}\text{P})$ coupling constants for $[Ag(NO_3)(P^iBu_3)_2]$ are smaller than those found for the monophosphine scorpionate complexes, as expected, and of the same order of magnitude of those reported for analogous silver(I) phosphino species [45,46].



Fig. 3. The N₂AgP trigonal environment of compound 11.

The coupling constant values of **1–11** well fit into the correlation previously reported between ${}^{1}J({}^{109}\text{Ag}{-}^{31}\text{P})$ and ${}^{1}J({}^{107}\text{Ag}{-}^{31}\text{P})$ and the inverse of the cone angle of the phosphorous donor [26]. The values are not strongly dependent on the steric hindrance of the substituents on the scorpionate ligands, but are dependent on their electronic features, the highest values being found for the derivative containing the fluorinated ligand Tp^{CF3}.

We also tested the reactivity of compound $[Ag{Tp*}(P^{i}Bu_{3})]$ (7) toward PPh₃, monitoring the reaction both by ¹H and ³¹P NMR. When equimolar quantities of 7 and PPh₃ were mixed in CDCl₃, a mixture containing equimolar quantities of $[Ag{Tp*}(P^{i}Bu_{3})]$ and [Ag{Tp*}(PPh₃)] formed in accordance with complete redistribution of the TpAg moiety between the two P-donors. Interestingly, a large excess of PPh₃ reacts with 7 completely displacing $P'Bu_3$ and yielding $[Ag{Tp*}(PPh_3)]$ in quantitative yield. The full displacereaction does not take place ment when $[Ag{Tp*}(PPh_3)]$ reacts with excess of $P^{\prime}Bu_{3}$, $[Ag{Tp*}(PPh_3)]$ being the most abundant species isolated. Interestingly the reaction of $[Ag{Tp*}(P'Bu_3)]$ with $P(o-tolyl)_3$ does not take place either when a large excess of $P(o-tolyl)_3$ is employed.

The positive electrospray mass spectra of complexes 1–11 (the most relevant data are reported in Section 2) indicate that these derivatives generally undergo loss of the anionic scorpionate ligand, the $[Ag(P'Bu_3)_x]^+$ species being easily detected. The isotopic distribution of these species is in accord with the calculated composition. Some dimeric $[Ag_2(P'Bu_3)_2(\text{scorpionate})]^+$ species have been found in certain cases, their detection presumably being due to the different solubilities of the complexes in acetonitrile solution. The spectra are independent of the solvent employed, no adducts containing CH₃CN being detected at concentration 10^{-4} M.

Under our conditions in the solution containing Tp and Tp*, Tp^{Me} and Tp^{CF3} complexes, aggregates containing two silver atoms, two phosphines and one Tp^x dominate or are equivalent with adducts containing one silver atom and two phosphine donors, whereas all other ligands (Tm, pz^0Tp^x) in solution seem to favor aggregates containing only one silver center coordinated by two phosphine donors. In some cases oxidation of the phosphine is also evident. No fragments containing two positive charges have been detected. As previously reported by us the negative electrospray spectra are always dominated by the presence of molecular peaks due to $[NO_3]^-$, $[Ag(NO_3)_2]^-$, and $[Ag(NO_2)(NO_3)]^-$ [47].

3.2. Single crystal X-ray studies

The results of the single crystal X-ray studies are consistent with the formulations of **3**, **4**, **5**, **8** in terms of stoichiometry and connectivity as neutral molecular 1:1 silver(I) tris(azolyl)borate:tris(*i*-butyl)phosphine complexes, the silver in each case having a four-coordinate PAgN₃ environment, the tris(azolyl)borate behaving as an N, N', N''-tripod ligand through the three 2-nitrogen atoms of the three rings; in the case of 9, a similar array is found except that the three nitrogen atoms are supplanted by the three sulfur atoms at the 2-ring sites. In 8 and 9, the molecules lie disposed with their Ag-P bonds lying on crystallographic 3-axes, one third of the molecule comprising the asymmetric unit of the structure in each case. In 3 and 4, one, and in 5, three, complete molecules, devoid of crystallographic symmetry comprise the asymmetric unit. In all compounds the silver tris(azolyl)borate component has potential 3m symmetry, realized crystallographically in none, the rings canted to a greater or lesser degree from the incipient plane, the distortions evidenced also in the deviations of the silver atoms from each plane. In 9, where the donor capability of the sulfur has no coplanar imperative, the deviation is very large and the twist of the ligand plane away from the 3m ideal very considerable. With the phosphine ligand constant, Ag-P are rather variable, unsurprisingly so in the case of the $PAgS_3$ array of 9, where Ag-P is longest, 2.4035(6) Å. Ag-N in those species devoid of crystallographic symmetry, are much more variable, with concomitant variations within 'equivalent' P, N–Ag–N sets. (()N–B–N()) ranges from 109.0(2)° in 8 to 112.6(1)° in 9. Consideration of the C–P–Ag–N(S) torsions shows the immediate phosphorus substituents to be more nearly 'trans'-/staggered to a similar degree in all cases *except* 8 where they are 'cis'-/eclipsed. The P'Bu₃ array forms an 'umbrella' at that end of the molecule, |Ag-P-C((ln)1)-C((ln)2)| all being acute, range 28.5(2)-57(1)°. The subsequent P-C-C-H torsion in each string is also acute, but, depending on whether its sign is the same as or the opposite of, its associated Ag-P-C-C precursor, the tertiary hydrogen lies directed approximately parallel to the Ag-P axis and 'inward' and 'axial' toward the other ligand, or 'equatorial' with the three hydrogens presumably (see 5 below) concerted in direction in accord with quasi-3 symmetry. The former is found in 3 (two groups), 8 and 9, in situations where the azolyl rings have no 3 substituent (8) (there are no close interligand $H \cdots N$ contacts here which suggest themselves as drivers of the 'eclipsed' conformation) or where it is removed from the inner ambience by insertion of the sulfur (9). The other form ('equatorial') is found in 4 and 5, where CH_3 or CF_3 substituents are found at the 3positions of the aza rings, presumably exercising some interligand steric effect, also in one of the substituents in 3. 5 is complicated by disorder in some *i*-butyl substituents and CF₃ groups, most notably in molecule 1 where all *i*-butyl groups are disordered (presumably in concert) as if by inversion at the tertiary carbon. Anomalously in molecule 3, one of the tertiary hydrogens is 'axial'.

3.3. Conclusions

New silver tris(iso-butyl)phosphine derivatives containing different bis-, tris- and tetrakis-azolylborates (L) and also the S₃-donor ligand tris(imidazolyl-2-thione)borate Tm have been synthesized and fully characterized in the solid state and solution. The silver/ phosphine/scorpionate ratio is always 1:1:1, even with the N₂-donor $H_2B(tz)_2$, where silver atom is likely 3-coordinate. In all complexes containing the N₃- and S₃-donor ligands the silver atom is four-coordinated in a skewed tetrahedral coordination environment, whereas in the complex containing the pz⁰Tp^{Me} ligand, the silver is 3-coordinated, at least in solution, as indicated by NMR data. Most of the silver derivatives are quite light-sensitive and decompose both in chloroform and acetone solution, yielding metallic silver and/or azolate species. ESI-MS data indicate the formation in solution of species as $[Ag(P'Bu_3)_2]^+$ and $[Ag_2(L)(P'Bu_3)_2]^+$, which likely represent intermediates in the decomposition pattern.

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Appendix A. Supporting materials

Selected IR data for all compounds 1–11. Five X-ray crystallographic files, in CIF format. full *cif.* depositions reside also with the Cambridge Crystallographic Data Centre, #236319-236323. Supplementary data associated with this article can be found, in the online version at 10.1016/j.ica.2004.06.020.

References

- [1] S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842.
- [2] C. Pettinari, C. Santini, Polypyrazolylborate and scorpionate ligands, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II. From Biology to Nanotechnology, vol. 1, 2004, p. 159 Ch. 1.10.
- [3] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligand, Imperial College Press, London, 1999.
- [4] G. Parkin, Adv. Inorg. Chem. 42 (1995) 291.
- [5] N. Kitajima, W.B. Tolman, Prog. Inorg. Chem. 43 (1995) 419.
- [6] I. Santos, N. Marques, New J. Chem. 19 (1995) 551.
- [7] D.L. Reger, Coord. Chem. Rev. 147 (1996) 571.
- [8] S. Trofimenko, Acc. Chem. Res. 4 (1971) 17.
- [9] S. Trofimenko, Chem. Rev. 93 (1993) 943.
- [10] C. Janiak, T.G. Scharmann, J.C. Green, R.P.G. Parkin, M.J. Kolm, E. Riedel, W. Mickler, J. Elguero, R.M. Claramunt, D. Sanz, Chem. Eur. J. 2 (1996) 992.

- [11] F.J. Lalor, S. Miller, N. Garvey, Polyhedron 9 (1990) 63.
- [12] S.A.A. Zaidi, T.A. Khan, Synth. React. Inorg. Met. Org. Chem. 14 (1984) 717.
- [13] C. Janiak, S. Temidzemir, C. Röhr, Z. Anorg. Allg. Chem. 626 (2000) 1265.
- [14] C. Kimblin, T. Hascall, G. Parkin, Inorg. Chem. 36 (1997) 5680.
- [15] R. Garcia, A. Domingos, A. Paulo, I. Santos, R. Alberto, Inorg. Chem. 41 (2002) 2422.
- [16] J. Reglinski, M. Garner, I.D. Cassidy, P.A. Slavin, M.D. Spicer, D.R. Armstrong, J. Chem. Soc., Dalton Trans. (1999) 2119.
- [17] C. Kimblin, B.M. Bridgewater, T. Hascall, G. Parkin, J. Chem. Soc., Dalton Trans. (2000) 891.
- [18] C. Santini, M. Pellei, G. Gioia Lobbia, C. Pettinari, A. Drozdov, S. Troyanov, Inorg. Chim. Acta 325 (2001) 20.
- [19] I. Cassidy, M. Garner, A.R. Kennedy, G.B.S. Potts, J. Reglinski, P.A. Slavin, M.D. Spicer, Eur. J. Inorg. Chem. (2002) 1235.
- [20] J.L. White, J.M. Tanski, D. Rabinovich, J. Chem. Soc., Dalton Trans. (2002) 2987.
- [21] S. Bakbak, C.D. Incarvito, A.L. Rheingold, D. Rabinovich, Inorg. Chem. 41 (2002) 998.
- [22] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. 116 (1994) 1151.
- [23] A.M.A. Ibrahim, T.M. Soliman, S.E.H. Etaiw, R.D. Fischer, J. Organomet. Chem. 468 (1994) 93.
- [24] G. De Munno, M. Julve, F. Nicolo, F. Lloret, J. Faus, R. Ruiz, E. Sinn, Angew. Chem. Int. Ed. Engl. 32 (1993) 613.
- [25] G. Gioia Lobbia, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, N. Somers, A.H. White, J. Chem. Soc., Dalton Trans. (2002) 2333.
- [26] C. Santini, G. Gioia Lobbia, C. Pettinari, M. Pellei, G. Valle, S. Calogero, Inorg. Chem. 37 (1998) 890.
- [27] C. Santini, G. Gioia Lobbia, M. Pellei, C. Pettinari, G. Valle, S. Calogero, Inorg. Chim. Acta 282 (1998) 1.
- [28] C. Santini, C. Pettinari, G. Gioia Lobbia, D. Leonesi, G. Valle, S. Calogero, Polyhedron 17 (1998) 3201.
- [29] Effendy, G. Gioia Lobbia, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1998) 2739.
- [30] Effendy, G. Gioia Lobbia, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (2001) 528.

- [31] M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, N. Somers, A.H. White, J. Chem. Soc., Dalton Trans. (2000) 3416.
- [32] Effendy, G. Gioia Lobbia, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, Inorg. Chim. Acta 315 (2001) 153.
- [33] G. Gioia Lobbia, J.V. Hanna, M. Pellei, C. Pettinari, C. Santini, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (2004) 951.
- [34] Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B.W. Skelton, A.H. White, Inorg. Chem. 42 (2003) 112.
- [35] S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170.
- [36] H.V.R. Dias, W. Jin, H.-J. Kim, H.-L. Lu, Inorg. Chem. 35 (1996) 2317.
- [37] S. Calogero, G. Valle, G. Gioia Lobbia, C. Santini, P. Cecchi, L. Stievano, J. Organomet. Chem. 526 (1996) 269.
- [38] M. Garner, J. Reglinski, I. Cassidy, M.D. Spicer, A.R. Kennedy, J. Chem. Soc., Chem. Commun. (1996) 1976.
- [39] G. Gioia Lobbia, M. Pellei, C. Pettinari, C. Santini, N. Somers, A.H. White, Inorg. Chim. Acta 333 (2002) 100.
- [40] M.W. Senko, IsoPro Isotopic Abundance Simulator, v.2.1, National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, NM.
- [41] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), The XTAL 3.7. System, University of Western Australia, 2001.
- [42] T.O. Northcutt, R.J. Lachicotte, W.D. Jones, Organometallics 17 (1998) 5148.
- [43] A.B.P. Lever, E. Mantovani, B.S. Ramaswamy, Can. J. Chem. 49 (1971) 1957.
- [44] (a) M.C. Keyes, V.G. Young Jr., W.B. Tolman, Organometallics 15 (1996) 4133;
 (b) S.M. Ng, C.P. Lau, M.-F. Fan, Z. Lin, Organometallics 18

(1999) 2484;

(c) S.M. Carrier, C.E. Ruggiero, R.P. Houser, W.B. Tolman, Inorg. Chem. 32 (1993) 4889.

- [45] E.L. Muetterties, C.W. Alegranti, J. Am. Chem. Soc. 94 (1972) 6386.
- [46] M. Barrow, H.-B. Burgi, M. Camalli, F. Caruso, E. Fischer, L.M. Venanzi, L. Zambonelli, Inorg. Chem. 22 (1983) 2356.
- [47] A. Cingolani, M. Pellei, C. Pettinari, C. Santini, Effendy, B.W. Skelton, A.H. White, Inorg. Chem. 47 (2002) 6633.