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Syntheses and Spectroscopic and Structural Characterization of Silver(I) Complexes Containing Tertiary Phosphines and Hydrotris(pyrazol-1-yl)-, Hydrotris(4-bromopyrazol-1-yl)-, Hydrotris(3,5-dimethypyrazol-1-yl)-, and Hydrotris(3-methyl-2-thioxo-1-imidazolyl)borates

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(Trialkyl- and (triarylphosphine)silver(I) derivatives containing anionic tris(1*H*-pyrazol-1-yl)borates were prepared from AgX (X = CF_3SO_3 or NO_3), PR_3 (R = phenyl, benzyl, cyclohexyl, 2,4,6-trimethylphenyl, or *o*-, *m*-, and *p*-tolyl) or $PMePh_2$, and M[HB(pz)$_3$] [M = K or Na; pzH = pyrazole in general; in detail, pyrazole (PzH), 3,5-dimethylpyrazole (3,5-Me_2PzH), or 4-bromopyrazole (4-BrPzH)] and characterized through analytical and spectral (IR; ^{1}H, ^{13}C, and ^{31}P NMR) measurements. These air stable, light-sensitive complexes are not electrolytes in CH_2Cl_2 and acetone. In these solvents they decompose even with strict exclusion of oxygen and light. The solid-state structures show that the silver atom adopts a distorted tetrahedral geometry. Crystal data with Mo Kα (λ = 0.710 70 Å) at 293 K: [HB(Pz)$_3$]Ag(PPh$_3$), $C_{54}H_{50}Ag_2B_2N_{12}P_2$, a = 15.082(2) Å, b = 19.728(2) Å, c = 9.432(1) Å, α = 94.8(1)°, β = 107.4(1)°, γ = 87.8(1)°, triclinic, $P\bar{1}$, Z = 2; [HB(Pz)$_3$]Ag[P(*o*-tolyl)$_3$], $C_{30}H_{31}AgBN_6P$, a = 14.461(2) Å, b = 14.461(2) Å, c = 30.473(2) Å, α = 90°, β = 90°, γ = 120°, trigonal, $R\bar{3}$, Z = 6; [HB(Pz)$_3$]AgP(Bz)$_3$, $C_{30}H_{31}AgBN_6P$, a = 12.183(2) Å, b = 18.596(2) Å, c = 13.804(2) Å, β = 100.8(1)°, monoclinic, $P2_1/n$, Z = 4; [HB(3,5-Me$_2$Pz)$_3$]Ag[P(*p*-tolyl)$_3$], $C_{36}H_{41}AgBN_6P$, a = 34.839(3) Å, b = 10.375(2) Å, c = 10.203(2) Å, β = 90.8(1)°, monoclinic, $P2_1$/n, Z = 4. Crystal data with Cu Kα (λ = 1.5418 Å): [HB(4-BrPz)$_3$]AgPPh$_3$, $C_{27}H_{22}AgBBr_3N_6P_2$, a = 10.306(2) Å, b = 11.425(2) Å, c = 13.571(2) Å, α = 90.3(1)°, β = 107.0(1)°, γ = 91.4(1)°, triclinic, $P\bar{1}$, Z = 2. The anionic soft S_3-donor hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate (Tm) was synthesized as its potassium salt from the corresponding imidazole and KBH_4 in high yield. The potassium complex KTm was used as ligand transfer agent in the preparation of the silver(I) derivatives [(Tm)Ag]$_n$ and (Tm)Ag(PPh$_3$). The S-donor 1-methylimidazolyl-2-thione (Hmimt) reacts with [HB(3,5-Me$_2$Pz)$_3$]Ag(PPh$_3$), yielding the derivative [HB(3,5-Me$_2$Pz)$_3$](Hmimt)AgPPh$_3$ in which the [HB(3,5-Me$_2$Pz)$_3$]$^-$ acts likely as bidentate N_2-donor.

Introduction

The poly(pyrazol-1-yl)borates are a family of chelating agents, designed and first synthesized by Trofimenko,[1] of considerable interest for a variety of applications: they are able to improve the activity of certain metal-catalyzed reactions[2,3] and are know to be suited for stabilizing monomeric organyl and hydrido main group compounds and for building bioinorganic models.[4,5]

The donor properties of the anionic poly(pyrazol-1-yl)borate ligands $[H_{4-n}B(Pz)_n]^-$ (PzH = pyrazole, n = 2, 3, or 4) have been extensively investigated.[6] Several Zn^{II},[7] Cd^{II},[8] Hg^{II},[9] RHg^{II},[10] $R_nSn^{IV}X_{4-n}$,[11] and transition metal derivatives[12] have

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(1) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842.

(2) (a) Churchill, M. R.; De Boer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051. (b) Bruce, M. I.; Ostazewsky, A. P. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

(3) (a) Ruggiero, C. E.; Carrier, S. M.; Antholine, W. E.; Whitaker, J. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 11825. (b) Carrier, S. M.; Ruggiero, C. E.; Tolman, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 4407.

(4) (a) Ruggiero, C. E.; Carrier, S. M.; Tolman, W. B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 895.

(5) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711.

(6) (a) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99. (b) Trofimenko, S. *Acc. Chem. Res* **1971**, *4*, 17. (c) Trofimenko, S. *Chem. Rev. (Washington, D.C.)* **1972**, *72*, 497. (d) Shaver, A. *J. Organomet. Chem. Libr.* **1977**, *3*, 157. (e) Trofimenko, S. *Progr. Inorg. Chem.* **1986**, *34*, 115. (f) Trofimenko, S. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 943.

(7) Gioia Lobbia, G.; Bovio, B.; Santini, C.; Pettinari, C.; Marchetti, F. *Polyhedron* **1997**, *16*, 671.

(8) (a) Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1993**, *32*, 5217. Lipton, A. S.; Mason, S. S.; Reger, D. L.; Ellis, P. D. *J. Am. Chem. Soc.* **1994**, *116*, 10812.

(9) Gioia Lobbia, G.; Bonati, F.; Cecchi, P.; Pettinari, C. *Gazz. Chim. Ital.* **1991**, *121*, 355.

(10) Gioia Lobbia, G.; Cecchi, P.; Pettinari, C.; Cingolani, A. *Gazz. Chim. Ital.* **1991**, *123*, 641.

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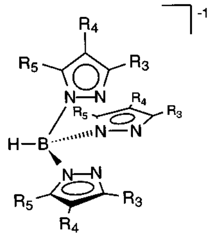

$HB(Pz)_3]^-$: $R_3 = R_4 = R_5 = H$
$HB(3,5\text{-}Me_2Pz)_3]^-$: $R_3 = R_5 = Me; R_4 = H$
$HB(4\text{-}BrPz)_3]^-$: $R_3 = R_5 = H; R_4 = Br$

Figure 1. General structure of the tris(pyrazol-1-yl)borato donors employed in this work.

been previously synthesized and structurally characterized, and it has been previously observed that the steric and electronic properties can be easily modified by changing the number of pyrazolate groups and the substituents thereon or at the B-center. In this class of versatile ligands, the tris(pyrazol-1-yl)borates, $[HB(Pz)_3]$, are the ones most widely used: they form complexes with metal ions throughout the periodic table. These complexes display a diversity of structural types, and several reviews on this topic have been published.[6] A vast majority of these studies involves the investigations of the relationship between structure and reactivity in metal tris(pyrazol-1-yl)borate complexes: for example, it has been noted that the substitutions on the pyrazole ring have strong effects on the nuclearity, geometry, spectroscopic properties, and reactivity of their metal derivatives.[13]

Recently, silver(I) poly(pyrazol-1-yl)borates derivatives have received great interest;[14] however the majority of these studies involves the use of polyfluorinated tris(pyrazol-1-yl)borate ligands,[15] while the chemistry of the unsubstituted $[HB(Pz)_3]^-$, or its alkyl- and aryl-substituted analogue systems, e.g. $[HB(3,5\text{-}Me_2Pz)_3]^-$, $[HB(3,5\text{-}Ph_2Pz)_3]^-$, $[HB(4\text{-}BrPz)_3]^-$, and $[HB(4\text{-}Br\text{-}3\text{-}MePz)_3]^-$ remain largely unexplored. In fact, in the literature[16] there are only a few formulations for simple Ag(I) complexes containing tris(pyrazol-1-yl)borates and tertiary phosphine, based only on analytical data and room-temperature ^1H NMR spectroscopic characterization; however no conclusive data, such as those which would be provided by an X-ray crystallographic analysis, have been reported for these silver(I) complexes. Here we report full details of the synthesis and spectroscopic characterization of several new tris(pyrazol-1-yl)borate−Ag(I)−phosphine derivatives ($[HB(Pz)_3]$, $[HB(3,5\text{-}Me_2Pz)_3]$, and $[HB(4\text{-}BrPz)_3]$; Figure 1). We also report the crystal and molecular structure of [hydrotris(pyrazol-1-yl)borate]Ag(PPh_3), [hydrotris(pyrazol-1-yl)borate]Ag(P-*o*-tolyl$_3$), [hydrotris(pyrazol-1-yl)borate]Ag[P(Bz$_3$)], [hydrotris(3,5-dimethylpyrazol-1-yl)borate]Ag(P-*p*-tolyl$_3$), and [hydrotris(4-Br-pyrazol-1-yl)borate]Ag(PPh_3) and also a comparison with the structural data reported in the literature for some selected silver(I) derivatives containing poly(pyrazol-1-yl)borate donors.[15,17] All the spectroscopic and structural data are discussed on the basis of electronic, e.g. basicity,[18] and steric arguments, e.g. Tolman angles.[19]

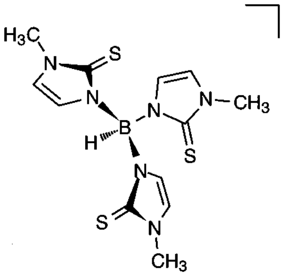

Figure 2. Structure of hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate, $(Tm)^-$.

This paper also reports an examination of the reactivity of $[HB(3,5\text{-}Me_2Pz)_3]Ag(PPh_3)$ and a comparison of the donating ability of $[HB(3,5\text{-}Me_2Pz)_3]$ with respect to that of the tris(azol-1-yl)borate S_3-donor (Tm) (Figure 2). This donor, a soft analogue of hydrotris(pyrazolyl)borate offers a different metal binding geometry with respect to that shown by $[HB(Pz)_3]$. To date only two compounds containing Tm have been synthesized: [20] in the zinc(II) bromide derivative Tm is coordinated in the anionic S_3-donor form, whereas the reaction between Tm and copper(I) chloride under a CO atmosphere failed, generating a complex consistent with the formation of [(Tm)Cu]. Here we report the interaction of Tm with Ag(I) acceptors.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. In some cases the reactions were protected from light by covering reaction vessels with aluminum foil. Concentration was always carried out in vacuo (water aspirator). The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in-house with a Carlo-Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHz for ^{13}C, and 121.4 MHz for ^{31}P). The electrical resistance of acetone solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The osmometric measurements were carried out at 40 °C over a range of concentrations with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed spectrophotometric grade chloroform. The results were reproducible to ±2%.

Preparations of Compounds. The donors $Na[HB(Pz)_3]$, $K[HB(Pz)_3]$, $K[HB(3,5\text{-}Me_2Pz)_3]$ and $K[HB(4\text{-}BrPz)_3]$ were prepared in accordance with the procedure reported in the literature.[21] KBH_4, $NaBH_4$, PR_3, $PMePh_2$, PzH, 3,5-Me_2PzH, 4-BrPzH, and Hmimt were purchased (Aldrich) and used as received.

Synthesis of Potassium Hydrotris(3-methy-2-thioxo-1-imidazolyl)borate, KTm. 1-Methyl-2-(3*H*)-imidazolinethione (Hmimt) (20.78 g; 0.182 mol) and finely divided KBH_4 (2.46 g; 46 mmol) were

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(11) Calogero, S.; Valle, G.; Gioia Lobbia, G.; Santini, C.; Cecchi, P.; Stievano, L. *J. Organomet. Chem.* **1996**, *526*, 269.
(12) Gioia Lobbia, G.; Pettinari, C.; Marchetti, F.; Bovio, B.; Cecchi, P. *Polyhedron* **1996**, *15*, 881.
(13) (a) Yoon, K.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 8414. (b) Curtis, M. D.; Shlu, K. B.; Butler, W. M. *Organometallics* **1983**, *2*, 1475.
(14) Amoroso, A. J.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Psillakis, E.; Ward, M. D. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1175.
(15) (a) Dias, H. V. R.; Lu, H.-L.; Ratcliff, R. E.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1975. (b) Dias, H. V. R.; Gorden, J. D. *Inorg. Chem.* **1996**, *35*, 318. (c) Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480. (d) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1995**, *117*, 11381. (e) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 267. (f) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317.
(16) (a) Bruce, M. I.; Walsh, J. D. *Aust. J. Chem.* **1979**, *32*, 2753. Salah, A.; Ashby, O. M.; Bruce, M. I.; Pederzolli, E. A.; Wallsh, J. D. *Aust. J. Chem.* **1979**, *32*, 1613.
(17) Bruce, M. I.; Walsh, J. D.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 956.
(18) (a) McAuliffe, C. A.; Levason, W. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979; p 202. (b) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716.
(19) Tolman, C. A. *Chem. Rev. (Washington, D.C.)* **1977**, *77*, 313.
(20) Garner, M.; Reglinski, J.; Cassidy, I.; Spicer, M. D.; Kennedy, A. R. *Chem. Commun.* **1996**, 1975.
(21) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

placed, together with a magnetic stirring bar, into a l-L single-necked flask equipped with a thermometer side arm. The flask was connected to a volumetric device and placed into an oil bath resting on a heating and stirring plate. The oil bath was heated to 150 °C and the mixture allowed to melt with stirring. Hydrogen evolution starts at this point. When about 120 mmol of H_2 had been evolved, the melt was cooled to about 30 °C and was then poured into 50 mL of stirred methanol. The solution was then filtered and concentrated under reduced pressure. Acetone (50 mL) was then added. The colorless precipitate obtained (11.71 g, 30 mmol) was filtered off and shown to be the compound potassium hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate (yield 65%), KTm (Figure 2). Mp: 225 °C dec. ^{1}H NMR [$(CD_3)_2SO$; δ]: 3.38 (s, 9H, C*H*$_3$), 6.40 (d, 3H, C*H*), 6.79 (d, 3H, C*H*). ^{13}C{^{1}H} NMR [$(CD_3)_2SO$; δ]: 33.6 (s, *C*H$_3$), 116.5 (s, *C*H), 120.8 (s, *C*H), 163.4 (s, C_{quat}). IR (cm^{-1}): 2465 (B−H). Anal. Calcd for $C_{12}H_{16}BN_6KS_3$: C, 36.9; H; 4.1; N, 21.5; S, 24.6. Found: C, 37.2; H, 4.3; N, 21.8; S, 24.9.

Synthesis of [HB(Pz)$_3$]Ag{PPh$_3$} (1). Method i. A mixture of Na[HB(Pz)$_3$] (0.24 g, 1 mmol) and $P(C_6H_5)_3$ (0.26 g, 1 mmol) in thf (30 mL) was added to $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (20 mL) at −70 °C. After the addition, the solution was stirred overnight at room temperature. The volatile materials were removed under reduced pressure, and the residue was extracted into benzene. Filtration through Celite followed by the removal of benzene from the filtrate gave **1**, which was recrystallized from benzene/ethyl acetate (1:1) (0.48 g, 0.83 mmol, yield 83%). Mp: 187 °C dec. ^{1}H NMR (CDCl$_3$; δ): 4.0−5.2 (br, 1H, B-*H*), 6.14 (t, 3H, 4-C*H*), 7.42 (d, 3H, 3 or 5-C*H*), 7.72 (d, 3H, 3 or 5-C*H*) 7.50−7.68 (m, 15H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 103.6 (s, 4-*C*H), 135.1 (s, 5-*C*H), 140.7 (s, 3-*C*H), 129.0 (d, ^3J(C,P) = 9.7 Hz, C_m); 130.5 (d, ^4J(C,P) = 1.2 Hz, C_p), 132.5 (d, ^1J(C,P) = 32.8 Hz, C_i); 133.9 d, ^2J(C,P) = 17.6 Hz, C_o). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 15.3 (br). ^{31}P{^{1}H} NMR (CDCl$_3$, 223 K; δ): 17.0 (dd, ^1J(P,^{107}Ag) = 607 Hz, ^1J(P,^{109}Ag) = 700 Hz). IR (cm^{-1}): 2451 w, 2401 w, 2392 w (BH). Anal. Calcd for $C_{27}H_{25}BN_6PAg$: C, 55.7; H; 4.3; N, 14.4. Found: C, 55.9; H, 4.4; N, 14.1.

Method ii. A mixture of KTp (0.34 g, 1 mmol) and $P(C_6H_5)_3$ (0.26 g, 1 mmol) in methanol (20 mL) was added to $AgNO_3$ (0.17 g, 1 mmol) in methanol (50 mL) at 25 °C. After 1 h the solvent was removed with a rotary evaporator. Ethyl acetate (50 mL) was added. The suspension was filtered, and the organic layer was dried on Na_2SO_4 and then filtered and concentrated under reduced pressure. A colorless precipitate was formed, which was filtered off, washed with methanol, and shown to be compound **1**.

Synthesis of [HB(Pz)$_3$]Ag[P(*o*-tolyl)$_3$] (2). Compound **2** was prepared similarly to compound **1**, by using K[HB(Pz)$_3$] (0.25 g, 1 mmol), P(*o*-tolyl)$_3$ (0.30 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (50 mL) at −70 °C. Compound **2** was recrystallized from benzene/ethyl acetate (1:1) (yield 75%). Mp: 180 °C dec. ^{1}H NMR (CDCl$_3$; δ): 2.52 (s, 9H, C*H*$_3$), 4.0−5.0 (br, 1H, B−*H*), 6.09 (t, 3H, 4-C*H*), 7.18 (d, 3H, 3 or 5-C*H*), 7.66 (d, 3H, 3 or 5-C*H*), 6.95 (t, 3H, C*H*), 7.10−7.60 (m, 9H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 22.5 (d, ^3J(C,P) = 18.0 Hz, *C*H$_3$), 104.3 (s, 4-*C*H), 127.1 (d, ^2J(C,P) = 5.9 Hz C_o), 130.8 (s, C_p), 131.9 (d, J(C,P) = 6.3 Hz, C_m); 133.6 (d, J(C,P) = 6.0 Hz, C_m), 135.9 (s, 5-*C*H) 141.0 (s, 3-*C*H) 143.3 (d, ^2J(C,P) = 17.8 Hz, C_o). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): −14.7 (d). ^{31}P{^{1}H} NMR (CDCl$_3$, 183 K; δ): −20.1 (dd, ^1J(P,^{107}Ag) = 598 Hz, ^1J(P,^{109}Ag) = 674 Hz). IR (cm^{-1}): 2437 m, 2403 w (BH). Anal. Calcd for $C_{30}H_{31}BN_6PAg$: C, 57.7; H; 5.0; N, 13.4. Found: C, 57.5; H, 5.0; N, 13.2.

Synthesis of [HB(Pz)$_3$]Ag[P(*m*-tolyl)$_3$] (3). Compound **3** was prepared similarly to compound **1**, by using K[HB(Pz)$_3$] (0.25 g, 1 mmol), P(*m*-tolyl)$_3$ (0.30 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (50 mL) at −70 °C. Compound **3** was recrystallized from benzene/ethyl acetate (1:1) (yield 65%). Mp: 194 °C dec. ^{1}H NMR (CDCl$_3$; δ): 2.36 (s, 9H, C*H*$_3$), 4.0−5.0 (br, 1H, B-*H*), 6.15 (t, 3H, 4-C*H*), 7.47 (d, 3H, 3 or 5-C*H*), 7.72 (d, 3H, 3 or 5-C*H*), 7.20−7.40-(m, 12H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 22.0 (s, *C*H$_3$), 104.1 (s, 4-*C*H), 129.2 (d, ^3J(C,P) = 10.0 Hz, C_m), 131.3 (d, ^2J(C,P) = 14.7 Hz, C_o), 131.8 (s, C_p), 133.0 (d, ^1J(C,P) = 32.3 Hz, C_i) 135.1 (d, ^2J(C,P) = 19.8 Hz, C_o); 135.7 (s, 5-*C*H), 139.2 (d, ^3J(C,P) = 10.9 Hz, C_m), 141.1 (s, 3-*C*H). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 17.4 (d). ^{31}P{^{1}H} NMR (CDCl$_3$, 253K; δ): −20.1 (dd, ^1J(P,^{107}Ag) = 612 Hz, ^1J(P,^{109}Ag) = 702 Hz). IR (cm^{-1}): 2445 m, 2401 w (BH). Anal. Calcd for $C_{30}H_{31}BN_6PAg$: C, 57.7; H; 5.0; N, 13.4. Found: C, 57.5; H, 5.1; N, 13.3.

Synthesis of [HB(Pz)$_3$]Ag[P(*p*-tolyl)$_3$] (4). Compound **4** was prepared similarly to compound **1**, by using K[HB(Pz)$_3$] (0.25 g, 1 mmol), P(*p*-tolyl)$_3$ (0.30 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (50 mL) at −70 °C. Compound **4** was recrystallized from benzene/ethyl acetate (1:1) (yield 71%). Mp: 126 °C dec. ^{1}H NMR (CDCl$_3$; δ): 2.40 (s, 9H, C*H*$_3$), 3.8−4.6 (br, 1H, B−*H*), 6.15 (t, 3H, 4-C*H*), 7.46 (d, 3H, 3 or 5-C*H*), 7.74 (d, 3H, 3 or 5-C*H*), 7.28 (d, 6H, C*H*), 7.44 (d, 6H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 21.4 (s, *C*H$_3$), 103.7 (s, 4-*C*H), 128.3 (s, C_p), 129.7 (d, ^3J(C,P) = 10.3 Hz,C_m), 133.8 (d, ^2J(C,P) = 17.6 Hz,C_o), 135.2 (s, 5-*C*H), 140.7 (s, 3-*C*H). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 14.6 (br). ^{31}P{^{1}H} NMR (CDCl$_3$, 253 K; δ): −14.7 (dd, ^1J(P,^{107}Ag) = 609 Hz, ^1J(P,^{109}Ag) = 700 Hz). IR (cm^{-1}): 2439 m, 2399 m, 2366 w (BH). Anal. Calcd for $C_{30}H_{31}BN_6PAg$: C, 57.7; H; 5.0; N, 13.4. Found: C, 57.8; H, 5.2; N, 13.2.

Synthesis of [HB(Pz)$_3$]Ag[P{(CH$_3$)$_3$C$_6$H$_2$}$_3$] (5). Compound **5** was prepared similarly to compound **1**, by using Na[HB(Pz)$_3$] (0.24 g, 1 mmol), trimesitylphosphine (0.39 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (50 mL) at −50 °C. Compound **5** was recrystallized from chlorofor*m*/*e*thyl acetate (1:1) (yield 73%). Mp: 166 °C dec. ^{1}H NMR(CDCl$_3$; δ): 2.20 (br, 18H, C*H*$_3$), 2.32 (s, 9H, C*H*$_3$), 6.05 (t, 3H, 4-C*H*), 7.03 (d, 3H, 3 or 5-C*H*), 7.62 (d, 3H, 3 or 5-C*H*), 6.86 (d, 6H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 21.5 (s, *C*H$_3$), 23.9 (d, ^3J(C,P) = 15.0 Hz, *C*H$_3$), 103.9 (s, 4-*C*H), 128.3 (s, C_p), 131.8 (d, J(C,P) = 6.2 Hz, C_m), 135.4 (s, 5-*C*H) 140.0 (s, 3-*C*H) 143.3 (d, ^2J(C,P) = 20.0 Hz, C_o). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): −26.9 (d). ^{31}P{^{1}H} NMR (CDCl$_3$, 253 K; δ): −26.9 (dd). ^{31}P{^{1}H} NMR (CDCl$_3$, 223 K; δ): −27.1 (dd, ^1J(P,^{107}Ag) = 602 Hz, ^1J(P,^{109}Ag) = 691 Hz), −29.1 (dd, ^1J(P,^{107}Ag) = 574 Hz, ^1J(P,^{109}Ag) = 662 Hz). IR (cm^{-1}): 2469 m (BH). Anal. Calcd for $C_{36}H_{43}BN_6PAg$: C, 61.0; H; 6.1; N, 11.9. Found: C, 61.2; H, 6.0; N, 12.0.

Synthesis of [HB(Pz)$_3$]Ag[P(Bz)$_3$] (6). Compound **6** was prepared similarly to compound **1**, by using Na[HB(Pz)$_3$] (0.24 g, 1 mmol), tribenzylphosphine (0.30 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (50 mL) at −70 °C. Compound **6** was recrystallized from chlorofor*m*/*e*thyl acetate (1:1) (yield 65%). Mp: 140 °C dec. ^{1}H NMR (CDCl$_3$; δ): 3.08 (pq, 6H, C*H*$_2$), 4.7−5.3 (br, 1H, B−*H*) 6.09 (t, 3H, 4-C*H*), 7.05 (d, 3H, 3 or 5-C*H*), 7.67 (d, 3H, 3 or 5-C*H*), 7.20(br, 15H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 34.6 (d, ^1J(C,P) = 9.1 Hz, *C*H$_2$), 103.2 (s, 4-*C*H), 126.8 (d, ^5J(C,P) = 3.0 Hz, C_p), 128.9 (d, ^4J(C,P) = 2.0 Hz, C_m), 129.6 (d, ^3J(C,P) = 6.0 Hz, C_o) 134.8 (s, *5-C*H) 140.5 (s, 3-*C*H). ^{31}P{^{1}H} NMR (CDCl$_3$, 293K; δ): 15.4 (dd). ^{31}P{^{1}H} NMR (CDCl$_3$, 253 K; δ): 15.4 (dd, ^1J(P,^{107}Ag) = 626 Hz, ^1J(P,^{109}Ag) = 712 Hz). IR (cm^{-1}): 2457 m (BH). Anal. Calcd for $C_{30}H_{31}BN_6PAg$: C, 57.7; H; 5.0; N, 13.4. Found: C, 57.5; H, 5.2; N, 13.3.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag(PPh$_3$) (7). Compound **7** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), $P(C_6H_5)_3$ (0.26 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (50 mL) at −60 °C. Compound **7** was recrystallized from benzene (yield 86%). Mp: 258−263 °C. ^{1}H NMR (CDCl$_3$; δ): 4.4−5.2 (br, 1H, B−*H*), 1.85 (s, 9H, C*H*$_3$) 2.40 (s, 9H, C*H*$_3$) 5.67 (s, 3H, 4-C*H*), 7.40, 7.64 (br, 15H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.0 (s, *C*H$_3$), 14.3 (s, *C*H$_3$), 104.1 (s, 4-*C*H), 144.0 (s, 5-*C*CH$_3$), 147.4 (s, 3-*C*CH$_3$), 128.9 (d, ^3J(C,P) = 9.7 Hz, C_m); 130.2 (d, ^4J(C,P) = 1.2 Hz, C_p), 134.1(d, ^2J(C,P) = 17.7 Hz, C_o). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 17.9 (dd, ^1J(P,^{107}Ag) = 576 Hz, ^1J(P,^{109}Ag) = 665 Hz). IR (cm^{-1}): 2508 m (BH). Anal. Calcd for $C_{33}H_{37}BN_6PAg$: C, 59.5; H; 5.6; N, 12.6. Found: C, 59.9; H, 5.7; N, 12.9.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag[P(*o*-tolyl)$_3$] (8). Compound **8** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), P(*o*-tolyl)$_3$ (0.30 g, 1 mmol), and $Ag(CF_3SO_3)$ (0.26 g, 1 mmol) in thf (60 mL) at −70 °C. Compound **8** was recrystallized from benzene/ethyl acetate (1:1) (yield 91%). Mp: 150 °C dec. ^{1}H NMR(CDCl$_3$; δ): 4.0−5.0 (br, 1H, B−*H*), 1.60 (s, 9H, C*H*$_3$), 2.40 (s, 9H, C*H*$_3$), 2.68 (s, 9H, C*H*$_3$), 5.63 (s, 3H, 4-C*H*), 6.85 (t, 3H, C*H*), 7.30−7.50 (m, 9H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.1 (s, *C*H$_3$), 13.4 (s, *C*H$_3$), 22.4 (d, ^3J(C,P) = 20.3 Hz, *C*H$_3$), 104.3 (s, 4-*C*H), 126.5 (d, J(C,P) = 4.9 Hz, C_m), 128.3 (s, C_p), 130.1 (s br, C_m), 131.4 (s br, C_o), 132.8 (s br, C_o), 143.4 (s, 5-*C*CH$_3$), 147.3 (s, 3-*C*CH$_3$). ^{31}P{^{1}H}

NMR (CDCl$_3$, 293K; δ): −15.5 (d), (CDCl$_3$, 293 K; δ): −16.3 (dd), ^1J(P,^{107}Ag) = 559 Hz, ^1J(P,^{109}Ag) = 646 Hz. IR (cm^{-1}): 2484 m (BH). Anal. Calcd for $C_{36}H_{43}BN_6PAg$: C, 61.0; H; 6.1; N, 11.9. Found: C, 61.1; H, 6.3; N, 11.8.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag[P(*m*-tolyl)$_3$] (9). Compound **9** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), P(*m*-tolyl)$_3$ (0.30 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (80 mL) at −70 °C. Compound **9** was recrystallized from benzene/ethyl acetate (1:1) (yield 70%). Mp: 140 °C dec. ^{1}H NMR (CDCl$_3$; δ): 4.2−5.3 (br, 1H, B−*H*), 1.86 (s, 9H, C*H*$_3$), 2.40 (s, 9H, C*H*$_3$), 2.36 (s, 9H, C*H*$_3$), 5.68 (s, 3H, 4-C*H*), 7.20−7.50 (mc, 12H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.6 (s, *C*H$_3$), 14.8 (s, *C*H$_3$), 22.0 (s, *C*H$_3$), 104.6 (s, 4-*C*H), 129.1 (d, ^3J(C,P) = 10.4 Hz, C_m), 131.5 (s, C_p), 131.8 (d, *J*(C,P) = 17.2 Hz, C_o), 135.0 (d, ^2J(C,P) = 17.9 Hz, C_o), 134.0 (d, ^1J(C,P) = 30.5 Hz, C_i), 139.0 (d, *J*(C,P) = 10.1 Hz, C_m-CH$_3$), 144.5 (s, 5-*C*CH$_3$), 147.9 (s, 3-*C*CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 17.9 (dd, ^1J(P,^{107}Ag) = 581 Hz, ^1J(P,^{109}Ag) = 669 Hz). IR (cm^{-1}): 2504 m (BH). Anal. Calcd for $C_{36}H_{43}BN_6PAg$: C, 61.0; H; 6.1; N, 11.9. Found: C, 61.3; H, 6.3; N, 11.7.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag[P(*p*-tolyl)$_3$] (10). Compound **10** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), P(*p*-tolyl)$_3$ (0.30 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (70 mL) at −70 °C. Compound **10** was recrystallized from benzene/ethyl acetate (1:1) (yield 67%). Mp: 150 °C dec. ^{1}H NMR (CDCl$_3$; δ): 4.0−5.0 (br, 1H, B−*H*), 1.86 (s, 9H, C*H*$_3$), 2.37 (s, 9H, C*H*$_3$), 2.38 (s, 9H, C*H*$_3$), 5.65 (s, 3H, 4-C*H*), 7.18 (d, 6H, C*H*), 7.37−7.52 (mc, 6H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.6 (s, *C*H$_3$), 14.9 (s, *C*H$_3$), 21.9 (s, *C*H$_3$), 104.6 (s, 4-*C*H),130.1 (d, ^3J(C,P) = 10.5 Hz, C_m), 131.0 (d, ^1J(C,P) = 32.0 Hz, C_i), 134.5 (d, ^2J(C,P) = 19.8 Hz, C_o), 140.8 (s, C_p), 144.6 (s, 5-*C*CH$_3$), 147.9 (s, 3-*C*CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 15.6 (dd, ^1J(P,^{107}Ag) = 586 Hz, ^1J(P,^{109}Ag) = 674 Hz). IR (cm^{-1}): 2504 m (BH). Anal. Calcd for $C_{36}H_{43}BN_6PAg$: C, 61.0; H; 6.1; N, 11.9. Found: C, 60.8; H, 6.2; N, 11.6.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag[P{(CH$_3$)$_3$C$_6$H$_2$}$_3$] (11). Compound **11** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), trimesitylphosphine (0.39 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (40 mL) at −50 °C. Compound **1** was recrystallized from benzene (yield 80%). Mp: 180 °C dec. ^{1}H NMR (CDCl$_3$; δ): 4.0−5.2 (br, 1H, B−*H*), 5.55 (s, 3H, 4-C*H*); the signals of the methyls due to the pyrazole moiety are indistinguishable from those of the substituents of phosphine (we observed six sharp singlets at 1.46, 1.83, 1.90, 2.26, 2.30, and 2.70 ppm, respectively and one broad one at 2.05 ppm); 6.54 (s, 4H, C*H*), 6.86 (s, 2H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 12.8 (s, *C*H$_3$), 13.6 (s, *C*H$_3$) 21.3 (s, *C*H$_3$), 23.1 (br, *C*H$_3$), 24.1 (br, *C*H$_3$), 25.2 (s, *C*H$_3$), 104.4 (s, 4-*C*H), 128.5 (s, C_p), 131.8 (d, ^3J(C,P) = 14.5 Hz, C_m), 130.3, 131.4, 139.6, 140.8 (br, $C_i + C_o + C_m$), 144.6 (s, 5-*C*H) 147.1 (s, 3-*C*H). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): −24.4 (dd, ^1J(P,^{107}Ag) = 539 Hz, ^1J(P,^{109}Ag) = 622 Hz). IR (cm^{-1}): 2504 m (BH). Anal. Calcd for $C_{42}H_{55}BN_6PAg$: C, 63.6; H; 7.0; N, 10.6. Found: C, 63.5; H, 7.3; N, 10.3.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag(PMePh$_2$) (12). Compound **12** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), PCH$_3$(C$_6$H$_5$)$_2$ (0.20 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (60 mL) at −70 °C. Compound **12** was recrystallized from benzene (yield 64%). Mp: 150 °C dec. ^{1}H NMR (CDCl$_3$; δ): 4.0 (br, 1H, B−*H*), 2.05 (s, 3H, C*H*$_3$), 2.40 (s, 9H, C*H*$_3$), 5.67 (s, 3H, 4-C*H*), 7.42 (m, 6H, CH) 7.70 (m, 4H, CH). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.0 (s, *C*H$_3$), 14.6 (s, *C*H$_3$), 15.4 (d, ^1J(C,P) = 15.8 Hz, *C*H$_3$), 104.0 (s, 4-*C*H), 128.8 (d, ^3J(C,P) = 10.4 Hz, C_m); 130.1 (d, ^4J(C,P) = 1.2 Hz, C_p), 132.7(d, ^2J(C,P) = 17.1 Hz, C_o), 144.0 (s, 5-*C*CH$_3$), 147.1 (s, 3-*C*CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293K; δ): −4.2 (d). ^{31}P{^{1}H} NMR (CDCl$_3$, 183 K; δ): −3.6 (dd), ^1J(P,^{107}Ag) = 595 Hz, ^1J(P,^{109}Ag) = 686 Hz). IR (cm^{-1}): 2506 m (BH). Anal. Calcd for $C_{28}H_{35}BN_6PAg$: C, 55.6; H; 5.8; N, 13.9. Found: C, 56.0; H, 5.7; N, 13.6.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag[P(benzyl)$_3$] (13). Compound **13** was prepared similarly to compound **1**, by using K[HB(3,5-Me$_2$Pz)$_3$] (0.34 g, 1 mmol), tribenzylphosphine (0.30 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (50 mL) at −70 °C. Compound **13** was recrystallized from benzene (yield 74%). Mp: 173 °C dec. ^{1}H NMR (CDCl$_3$; δ): 1.60 (s, 9H, C*H*$_3$), 2.40 (s, 9H, C*H*$_3$), 3.08 (pq, 6H, C*H*$_2$), 4.5 (br, 1H, B−*H*), 5.62 (s, 3H, 4-C*H*), 7.30 (br, 15H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.2 (s, *C*H$_3$), 14.0 (s, *C*H$_3$) 35.3 (br, *C*H$_2$), 103.8 (s, 4-CH), 126.8 (d, ^5J(C,P) = 2.5 Hz, C_p), 128.9 (d, ^4J(C,P) = 1.8 Hz, C_m), 129.6 (d, ^3J(C,P) = 20.6 Hz, C_o), 134.8 (s, C_i), 143.8 (s, 5-*C*CH$_3$), 146.8 (s, 3-*C*CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 8.6 (dd, ^1J(P,^{107}Ag) = 599 Hz, ^1J(P,^{109}Ag) = 691 Hz). IR (cm^{-1}): 2496 m (BH). Anal. Calcd for $C_{36}H_{43}BN_6PAg$: C, 61.0; H; 6.1; N, 11.9. Found: C, 60.8; H, 6.3; N, 11.6.

Synthesis of [HB(3,5-Me$_2$Pz)$_3$]Ag[P(cyclohexyl}$_3$] (14). To a stirred diethyl ether suspension of **7**, PCy$_3$ was added at room temperature. The clear solution obtained was then filtered, the volatile materials were removed under reduced pressure, and the residue was washed with petroleum ether/diethyl ether and filtered off to give compound **14** (yield 75%). Mp: 215 °C dec. ^{1}H NMR (CDCl$_3$; δ): 1.20−2.00 (br, 33H, C$_6$*H*$_{11}$), 2.18 (s, 9H, C*H*$_3$), 2.35 (s, 9H, C*H*$_3$), 5.66 (s, 3H, 4-C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 13.2 (s, *C*H$_3$), 14.9 (s, *C*H$_3$), 26.1 (s, *C*H$_2$), 27.5 (d, ^2J(C,P) = 10.9 Hz, CH$_2$), 31.6 (d, ^3J(C,P) = 4.9 Hz, *C*H$_2$), 32.5 (d, ^1J(C,P) = 11.5 Hz, *C*−H), 104.2 (s, 4-CH), 143.8 (s, 5-*C*CH$_3$); 147.1 (s, 3-*C*CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 36.6 (dd, ^1J(P,^{107}Ag) = 576.0 Hz, ^1J(P,^{109}Ag) = 664.5 Hz). IR (cm^{-1}): 2395 m (BH). Anal. Calcd for $C_{33}H_{55}BN_6PAg$: C, 57.9; H; 8.1; N, 12.3. Found: C, 58.1; H, 8.3; N, 12.4.

Synthesis of [HB(4-BrPz)$_3$]Ag(PPh$_3$) (15). Compound **15** was prepared similarly to compound **1**, by using K[HB(4-BrPz)$_3$] (0.48 g, 1 mmol), P(C$_6$H$_5$)$_3$ (0.26 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (20 mL) at −70 °C. Compound **15**, was recrystallized from benzene (yield 83%). Mp: 185−188 °C. ^{1}H NMR (CDCl$_3$; δ): 7.32 (d, 3H, 3- or 5-C*H*), 7.68 (d, 3H, 3- or 5-C*H*) 7.40−7.60 (br, 15H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 92.6 (s, 4-*C*Br), 129.6 (d, ^3J(C,P) = 10.2 Hz, C_m); 131.2 (s, C_p), 132.9(d, ^1J(C,P) = 32.7 Hz, C_i); 134.3 (d, ^2J(C,P) = 17.3 Hz, C_o), 136.0 (s, 5-*C*H), 141.8 (s, 3-*C*H). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 16.6 (br). ^{31}P{^{1}H} NMR (CDCl$_3$, 223 K; δ): 16.9 (dd, ^1J(P,^{107}Ag) = 612.7 Hz, ^1J(P,^{109}Ag) = 707.2 Hz). IR (cm^{-1}): 2466 m (BH). Anal. Calcd for $C_{27}H_{22}BBr_3N_6PAg$; C, 39.6; H; 2.7; N, 10.2. Found: C, 39.5; H, 2.8; N, 10.5.

Synthesis of [HB(4-BrPz)$_3$]Ag[P(Bz)$_3$] (16). Compound **16** was prepared similarly to compound **1**, by using K[HB(4-BrPz)$_3$] (0.48 g, 1 mmol), tribenzylphosphine (0.30 g, 1 mmol), and Ag(CF$_3$SO$_3$) (0.26 g, 1 mmol) in thf (60 mL) at −70 °C. Compound **16** was recrystallized from benzene (yield 74%). Mp: 198−202 °C. ^{1}H NMR (CDCl$_3$; δ): 3.08 (d, 6H, C*H*$_2$), 7.37 (s, 3H, 3- or 5-C*H*), 7.2−7.3 (br, 15H, C*H*), 7.60 (s, 3H, 3 or 5-C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$; δ): 35.0 (d, ^1J(C,P) = 9.3 Hz *C*H$_2$), 92.1 (s, 4-*C*Br), 127.5 (d, ^4J(C,P) = 2.8 Hz, C_m); 129.6 (s, C_p), 130.0 (d, ^3J(C,P) = 6.3 Hz, C_o); 134.9 (br, C_i), 135.6 (s, 5-*C*H), 141.6 (s, 3-*C*H). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 18.9 (d). ^{31}P{^{1}H} NMR (CDCl$_3$, 283 K; δ): 19.8 (dd, ^1J(P,^{107}Ag) = 629 Hz, ^1J(P,^{109}Ag) = 725 Hz). IR (cm^{-1}): 2469 m (BH). Anal. Calcd for $C_{30}H_{28}BBr_3N_6PAg$: C, 41.8; H; 3.3; N, 9.7. Found: C, 42.2; H, 3.3; N, 10.0.

Synthesis of [Hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate]-Ag(PPh$_3$) (17). A mixture of KTm (0.39 g, 1 mmol) and P(C$_6$H$_5$)$_3$ (0.26 g, 1 mmol) in thf (30 mL) was added to Ag(CH$_3$SO$_3$) (0.26 g, 1 mmol) in thf (20 mL) at 25 °C. After the addition, the solution was stirred overnight. The volatile materials were removed under reduced pressure, and the residue was extracted into chloroform. The suspension was filtered, and the solvent was removed. Diethyl ether was then added, and the colorless precipitate obtained was filtered off, washed, and shown to be TmAg(PPh$_3$) (**17**) (yield 70%). Mp: 142 °C dec. ^{1}H NMR (CDCl$_3$; δ): 3.61 (s, 3H, C*H*$_3$), 3.63 (s, 6H, C*H*$_3$); 6.64 (d, 3H, C*H*); 6.76 (d, 3H, C*H*), 7.35−7.50 (m, 15H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$): 30.9 (s, *C*H$_3$), 34.3 (s, *C*H$_3$), 114.7 (s, *C*H), 119.6 128.4 (d, ^2J(C,P) = 11.5 Hz, C_o); 131.9 (d, ^4J(C,P) = 3.0 Hz, C_p), 132.1 (d, ^3J(C,P) = 9.7 Hz, C_m). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K; δ): 8.4 (br). ^{31}P{^{1}H} NMR (CDCl$_3$, 213 K; δ): 10.2 (dd, ^1J(P,^{107}Ag) = 499 Hz, ^1J(P,^{109}Ag) = 576 Hz). IR (cm^{-1}): 2369 m (BH). Anal. Calcd for $C_{30}H_{31}BN_6PS_3Ag$: C, 50.0; H; 4.3; N, 11.6; S, 13.3. Found: C, 50.0; H, 4.4; N, 11.7; S, 13.5.

Synthesis of [Silver(I) hydrotris(3-methyl-2-thioxo-1-imidazolyl)-borate]$_n$ (18). Method i. To a stirred methanol solution (50 mL) of KTm (0.39 g, 1.0 mmol) was added AgNO$_3$ at room temperature. A colloidal precipitate was formed after 5 h. The mixture was then heated

Table 1. Crystal Data and Summary of Data Collection and Refinement Parameters for Compounds **1**, **2**, **6**, **10**, and **15**

	compound				
	1	**2**	**6**	**10**	**15**
formula	$C_{54}H_{50}Ag_2B_2N_6P_2$	$C_{30}H_{31}N_6BAgP$	$C_{30}H_{31}N_6BAgP$	$C_{36}H_{41}N_6BAgP$	$C_{27}H_{22}Br_3N_6BAgP$
fw	1166.3	625.3	625.3	707.4	820.0
space group	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	15.082(2)	14.461(2)	12.183(2)	34.839(3)	10.306(2)
b, Å	19.728(2)	14.461(2)	18.596(2)	10.375(2)	11.425(2)
c, Å	9.432(1)	30.473(2)	13.804(2)	10.203(2)	13.571(2)
α, deg	94.8(1)	90			90.3(1)
β, deg	107.4(1)	90	100.8(1)	90.8(1)	107.0(1)
γ, deg	87.8(1)	120°			91.4(1)
V, Å^3	2668(1)	5518(2)	3072(1)	3687(1)	1527.5(9)
Z	2	6	4	4	2
ρ(calcd), g/cm^3	1.45	1.15	1.35	1.27	1.78
μ, cm^{-1}	7.54	7.617	6.58	6.135	101.41
T, K	293	293	293	293	293
λ, Å	0.710 70	0.710 70	0.710 70	0.710 70	1.541 80
R, R_w[a]	0.034, 0.038	0.056, 0.069	0.041, 0.042	0.040, 0.045	0.086, 0.087

[a] $R = (\sum||F_o| - k|F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) for Compounds **1**, **2**, **6**, **10**, and **15**

$[HB(Pz)_3]Ag(PPh_3)$ (**1**)			
I			
Ag(1)−P(1)	2.336(3)	Ag(1)−N(3)	2.351(3)
Ag(1)−N(1)	2.325(4)	Ag(1)−N(5)	2.355(3)
II			
Ag(2)−P(2)	2.337(2)	Ag(2)−N(9)	2.374(3)
Ag(2)−N(7)	2.321(3)	Ag(2)−N(11)	2.340(4)
$[HB(Pz)_3]Ag[P(o\text{-tolyl}_3]$ (**2**)			
Ag(1)−P(1)	2.368(1)	Ag(1)−N(1)	2.357(3)
$[HB(Pz)_3]Ag[P(Bz)_3]$ (**6**)			
Ag(1)−P(1)	2.328(2)	Ag(1)−N(3)	2.383(4)
Ag(1)−N(1)	2.343(4)	Ag(1)−N(5)	2.357(4)
$HB(3,5\text{-}Me_2Pz)_3]Ag[P(p\text{-tolyl})_3]$ (**10**)			
Ag(1)−P(1)	2.332(2)	Ag(1)−N(3)	2.348(4)
Ag(1)−N(1)	2.292(3)	Ag(1)−N(5)	2.356(4)
$[HB(4\text{-}BrPz)_3]Ag(PPh_3)$ (**15**)			
Ag(1)−P(1)	2.345(3)	Ag(1)−N(3)	2.383(9)
Ag(1)−N(1)	2.446(8)	Ag(1)−N(5)	2.304(8)

to favor the formation of the precipitate. The solid obtained was then filtered off, washed with methanol, and shown to be $[(Tm)Ag]_n$ (**18**) (yield 70%). Mp: 220 °C dec. ^{1}H NMR[$(CD_3)_2SO$; δ]: 3.50 (s, 9H, C$\mathit{H_3}$); 6.70 (d, 3H, CH); 7.20 (d, 3H, CH). IR (cm^{-1}): 2433 m (BH), 1558 m (CN), 442 m (CS), 310 br, 270 m, 240 m (terminal Ag−S), 151 m, 132 m, 126 w (bridging Ag−S). Anal. Calcd for $C_{12}H_{16}BN_6S_3Ag$: C, 31.4; H; 3.5; N, 18.3; S, 20.9. Found: C, 31.4; H, 3.7; N, 17.9; S, 21.0.

Method ii. To a methanol solution of compound **7** (0.195 g, 0.5 mmol) was added KTm (0.195 g, 0.5 mmol). After a few minutes the solution became yellow. A colorless precipitate was formed which was filtered off, washed with methanol, and shown to be compound $[(Tm)Ag]_n$.

Synthesis of $[HB(3,5\text{-}Me_2Pz)_3]Ag(Hmimt)(PPh_3)$ (19). To a benzene solution of compound **7** (0.195 g, 0.5 mmol) was added 1-methyl-2-(3*H*)-imidazolinethione (Hmimt) (0.21 g; 1.82 mmol). After 2 days, the suspension was filtered and the residue obtained washed with *n*-hexane and diethyl ether and shown to be $\{[HB(3,5\text{-}Me_2Pz)_3]Ag(Hmimt)(PPh_3)\}$ (**19**) (yield 65%). Mp: 128 °C dec. ^{1}H NMR ($CDCl_3$; δ): 1.85 (s, 6H, C$\mathit{H_3}$), 2.30 (br, 6H, C$\mathit{H_3}$), 2.44 (s, 6H, C$\mathit{H_3}$), 3.63 (s, 3H, N−C$\mathit{H_3}$); 5.68 (s, 2H, 4-CH); 5.82 (s, 1H, 4-CH), 6.70 (d, 1H, CH); 6.73 (d, 1H, CH); 7.30−7.70 (br, 15H, CH). IR (cm^{-1}): 2433 m (BH). Anal. Calcd for $C_{37}H_{42}BN_8PSAg$: C, 56.9; H; 5.4; N, 14.4; S, 4.1. Found: C, 56.6; H, 5.6; N, 14.0; S, 4.4.

Reaction of $[HB(3,5\text{-}Me_2Pz)_3]Ag(PPh_3)$ with 1,10-Phenanthroline. To a benzene solution of compound **7** (0.195 g, 0.5 mmol) was added 1,10-phenanthroline (0.18 g; 1.0 mmol). After 2 days, the suspension was filtered and the precipitate washed with *n*-hexane and diethyl ether and shown to be the starting derivative $[(PPh_3)AgTp^*]$ (**7**).

Reaction of $[HB(3,5\text{-}Me_2Pz)_3]Ag(PPh_3)$ with 1-Methylimidazole. To a benzene solution of compound **7** (0.195 g, 0.5 mmol) was added 1-methylimidazole (0.08 g; 1.0 mmol). After 2 days, the suspension was filtered and the precipitate washed with *n*-hexane and diethyl ether and shown to be the starting derivative $[(PPh_3)AgTp^*]$ (**7**).

X-ray Data Collection and Solution and Refinement of Structures. General Procedures. Crystal data and a summary of data collection parameters for compounds [hydrotris(pyrazol-1-yl)borate]Ag(PPh_3) (**1**), [hydrotris(pyrazol-1-yl)borate]Ag[P{*o*-tolyl}$_3$] (**2**), [hydrotris(pyrazol-1-yl)borate]Ag[PBz_3] (**6**), [hydrotris(3,5-dimethylpyrazol-1-yl)borate]Ag[P(*p*-tolyl)$_3$] (**10**), and [hydrotris(4-Br-pyrazol-1-yl)borate]Ag(PPh_3) (**15**) are summarized in Table 1. Data were collected on a Philips PW 1100 diffractometer by using Mo Kα radiation except for **15** which was collected by using Cu Kα radiation. Data were corrected for the Lorentz and polarization effects. The structures were solved by SHELXS 86 or SHELXL-93 direct methods.[22] Full-matrix least-squares refinement on F was computed and the function $\sum w[|F_o| - |F_c|]^2$ minimized. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated. In the phenyl moieties of the here reported molecular structures the observed average C−C bond distances and the C−C−C bond angles were 1.395(3) Å and 120.0(2)°, respectively. The molecules **1**, **2**, **6**, **10**, and **15** are discrete since no interatomic contacts are present. In all the structures here reported the weighted least-squares pyrazolate planes and the phenyl planes do not deviate significantly from planarity. Selected bond lengths and angles for **1**, **2**, **6**, **10**, and **15** are listed in Tables 2 and 3, respectively. The ORTEP plots of **1**, **2**, **6**, **10**, and **15** together with the numbering scheme are displayed in Figures 3, 4, 5, 6, and 7, respectively (the probability level of the thermal ellipsoids is 50%).

Results and Discussion

Synthesis. The interaction between a tertiary phosphine PR_3 or PRR'_2 (PPh_3, triphenylphosphine; (PBz_3), tribenzylphosphine; P(*o*-tolyl)$_3$, tri-*o*-tolylphosphine; P(*m*-tolyl)$_3$, tri-*m*-tolylphosphine; P(*p*-tolyl)$_3$, tri-*p*-tolylphosphine; $PMePh_2$, methyldiphenylphosphine; P(2,4,6-Me_3Ph)$_3$, tris(2,4,6-trimethylphenyl)phosphine), silver(I) trifluoromethanesulfonate, and potassium salts of the tris(pyrazol-1-yl)borates, $[HB(Pz)_3]$ (pzH = pyrazole, 3,5-dimethylpyrazole, or 4-bromopyrazole), in tetrahydrofuran at −70 °C or in methanol at room temperature readily gives

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(22) Sheldrich, G. M. SHELXS-86 and SHELXL-93 Programs for the automatic solution of crystal structure, Göttingen, Germany, 1990 and 1993.

Table 3. Selected Bond Angles (deg) for Compounds **1**, **2**, **6**, **10**, and **15**

$[HB(Pz)_3]Ag(PPh_3)$ (**1**)			
I			
N(3)−Ag(1)−N(5)	83.5(2)	Ag(1)−P(1)−C(10)	115.9(1)
N(1)−Ag(1)−N(5)	86.2(2)	Ag(1)−N(3)−C(6)	137.7(3)
N(1)−Ag(1)−N(3)	79.7(2)	Ag(1)−N(3)−N(4)	115.1(3)
P(1)−Ag(1)−N(5)	119.4(2)	Ag(1)−N(1)−C(3)	137.3(4)
P(1)−Ag(1)−N(3)	137.2(1)	Ag(1)−N(1)−N(2)	115.1(4)
P(1)−Ag(1)−N(1)	133.0(4)	Ag(1)−N(5)−C(9)	137.8(3)
Ag(1)−P(1)−C(22)	112.4(2)	Ag(1)−N(5)−N(6)	115.7(4)
Ag(1)−P(1)−C(16)	114.9(3)		
II			
N(9)−Ag(2)−N(11)	80.9(2)	Ag(2)−P(2)−C(37)	115.2(2)
N(7)−Ag(2)−N(11)	83.7(2)	Ag(2)−N(9)−C(33)	137.9(4)
N(7)−Ag(2)−N(9)	83.8(2)	Ag(2)−N(9)−N(10)	115.5(2)
P(2)−Ag(2)−N(11)	129.9(3)	Ag(2)−N(7)−C(30)	137.3(4)
P(2)−Ag(2)−N(9)	129.1(1)	Ag(2)−N(7)−N(8)	116.5(4)
P(2)−Ag(2)−N(7)	131.6(2)	Ag(2)−N(11)−C(36)	136.6(4)
Ag(2)−P(2)−C(49)	111.9(2)	Ag(2)−N(11)−N(12)	116.2(3)
Ag(2)−P(2)−C(43)	116.5(2)		
$[HB(Pz)_3]Ag[P(o\text{-tolyl}_3)]$ (**2**)			
N(1)−Ag(1)−N(13)	81.70(1)	Ag(1)−P(1)−C(4)	114.12(6)
P(1)−Ag(1)−N(1)	130.93(5)	Ag(1)−N(1)−C(3)	135.92(2)
P(1)−Ag(1)−N(1′)	130.95(3)	Ag(1)−N(1)−N(2)	116.52(5)
Ag(1)−P(1)−C(4')	114.14(6)	Ag(1)−N(1)−N(2′)	116.55(5)
$[HB(Pz)_3]Ag[P(Bz)_3]$ (**6**)			
N(3)−Ag(1)−N(5)	81.4(2)	N(1)−Ag(1)−N(5)	83.8(1)
N(1)−Ag(1)−N(3)	82.0(2)	P(1)−Ag(1)−N(5)	136.2(1)
P(1)−Ag(1)−N(3)	133.4(1)	P(1)−Ag(1)−N(1)	121.0(1)
Ag(1)−P(1)−C(24)	114.0(2)	Ag(1)−P(1)−C(17)	116.6(2)
Ag(1)−P(1)−C(10)	119.0(2)	Ag(1)−N(1)−N(2)	117.3(3)
Ag(1)−N(1)−C(3)	137.1(4)	Ag(1)−N(3)−N(4)	115.8(4)
Ag(1)−N(3)−C(4)	138.3(4)	Ag(1)−N(5)−N(6)	116.0(3)
Ag(1)−N(5)−C(7)	136.9(4)		
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(p\text{-tolyl})_3]$ (**10**)			
N(3)−Ag(1)−N(5)	83.8(1)	Ag(1)−P(1)−C(16)	114.6(1)
N(1)−Ag(1)−N(5)	84.9(1)	Ag(1)−N(3)−C(6)	133.7(4)
N(1)−Ag(1)−N(3)	82.5(2)	Ag(1)−N(1)−C(1)	136.2(3)
P(1)−Ag(1)−N(5)	129.8(1)	Ag(1)−N(5)−C(11)	133.4(3)
P(1)−Ag(1)−N(3)	131.0(1)	Ag(1)−N(3)−N(4)	112.3(3)
P(1)−Ag(1)−N(1)	128.0(1)	Ag(1)−N(5)−N(6)	113.7(3)
Ag(1)−P(1)−C(30)	113.0(2)	Ag(1)−N(1)−N(2)	115.8(3)
Ag(1)−P(1)−C(23)	114.3(1)		
$[HB(4\text{-}BrPz)_3]Ag(PPh_3)$ (**15**)			
N(3)−Ag(1)−N(5)	83.3(3)	N(1)−Ag(1)−N(5)	79.9(3)
N(1)−Ag(1)−N(3)	84.1(3)	P(1)−Ag(1)−N(5)	142.7(3)
P(1)−Ag(1)−N(3)	122.4(2)	P(1)−Ag(1)−N(1)	125.4(3)
Ag(1)−P(1)−C(22)	113.2(3)	Ag(1)−P(1)−C(16)	116.7(4)
Ag(1)−P(1)−C(10)	111.7(3)	Ag(1)−N(1)−N(2)	112.1(7)
Ag(1)−N(1)−C(1)	136.9(7)	Ag(1)−N(3)−N(4)	115.5(6)
Ag(1)−N(3)−C(4)	136.7(8)	Ag(1)−N(5)−N(6)	116.5(7)
Ag(1)−N(5)−C(7)	135.9(7)		

the complexes **1**−**13**, **15**, and **16** in high yield, in accordance with the general eqs 1 and 2.

$$PR_3 + AgCF_3SO_3 + M[HB(pz)_3] \xrightarrow{\text{thf}/-70\ °C} [HB(pz)_3]Ag(PR_3) + MCF_3SO_3 \quad (1)$$

1−13, 15, 16

$$PR_3 + AgNO_3 + M[HB(pz)_3] \xrightarrow[\text{r.t.}]{CH_3OH} [HB(pz)_3]Ag(PR_3) + MNO_3 \quad (2)$$

1−13, 15, 16

The tricyclohexylphosphine (PCy_3) interacts with $[HB(3,5\text{-}Me_2Pz)_3]AgPPh_3$ **(7)** completely displacing the PPh_3 from the Ag(I) center and yielding the complex $[HB(3,5\text{-}Me_2Pz)_3]AgP(Cy_3)$ **(14)**. The occurrence of this displacement reaction is due to greater basicity of PCy_3 with respect to PPh_3.

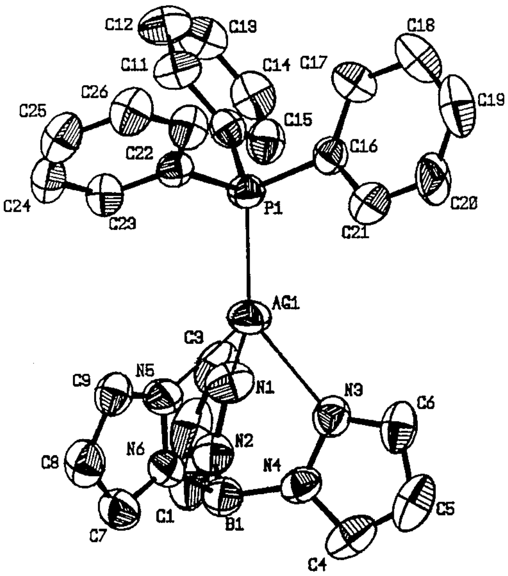

Figure 3. ORTEP drawing of the molecular structure of **1**, with H atoms omitted.

All the colorless compounds **1**−**16** decompose without melting. They are stable to air and somewhat light-sensitive, soluble in chlorinated solvents, acetone, DMSO, ethyl acetate, methanol, ethanol, and benzene, and insoluble in acetonitrile and water. They are stable in benzene, while in chloroform solution they rapidly darken, even with strict exclusion of oxygen and light: this is due to the strong reducing power of the borate anion retaining one hydrogen which immediately converts the complex into metallic silver,[23] in accordance with the following eq 3.

$$2PR_3Ag[HB(Pz)_3] \rightarrow H_2 + 2Ag + [B(Pz)_3]_2 + 2PR_3 \quad (3)$$

All the compounds are nonelectrolytes in acetone; however, in this solvent a nonionic dissociation such as that proposed in eq 4 cannot be excluded, also on the basis of vaporimetric

$$[HB(Pz)_3]Ag(PR_3) \xrightleftharpoons{(CH_3)_2CO} PR_3 + [HB(Pz)_3]Ag \quad (4)$$

molecular weight determination, r, the ratio between calculated (fw) and vaporimetric molecular weight (MW) being in the order of 0.70−0.80 at concentration 0.07% w/w. The derivative $[HB(3,5\text{-}Me_2Pz)_3]AgPPh_3$ (**7**) reacts in methanol solution with the soft potentially tridentate S_3-donor $(Tm)^-$ immediately yielding the complex $[(Tm)Ag]_n$ (**18**) in accordance with eq 5.

$$[HB(3,5\text{-}Me_2Pz)_3]AgPPh_3 + KTm \xrightarrow{CH_3OH} [(Tm)Ag]_n + PPh_3 + K[HB(3,5\text{-}Me_2Pz)_3] \quad (5)$$

Vaporimetric molecular weight determinations obtained using chloroform as a solvent (r is ca. 1.95 at concentration 0.04% w/w) suggested that this compound has a dinuclear structure. Also on the basis of ^1H NMR results (see below) we indicate for this complex the structure in Figure 8, where the two Ag(I) centers are tetracoordinate.

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[23] Gioia Lobbia, G.; Bonati, F.; Cecchi, P.; Pettinari, C. *Gazz. Chim. Ital.* **1991**, *121*, 355.

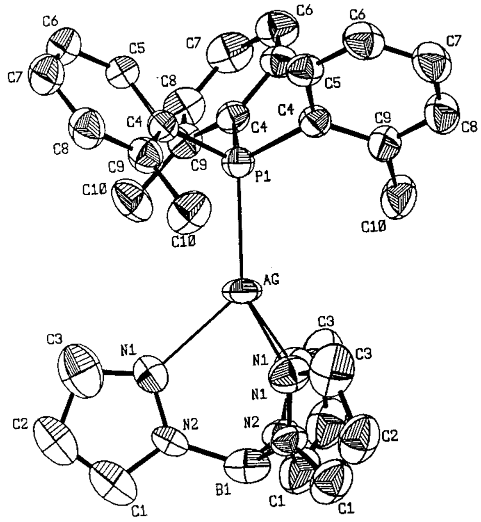

Figure 4. ORTEP drawing of the molecular structure of **2**, with H atoms omitted.

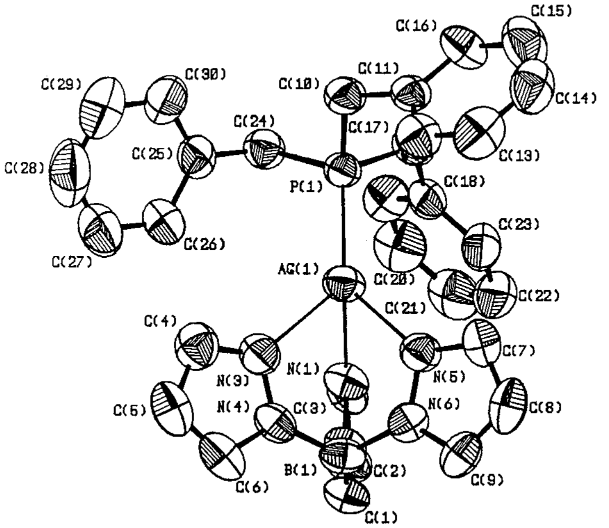

Figure 5. ORTEP drawing of the molecular structure of **6**, with H atoms omitted.

The substitution of the [HB(3,5-$Me_2Pz)_3$] in methanol with the anionic (Tm)$^-$, a donor with greater affinity for the soft cation Ag$^+$, is accompanied by the displacement from the metal center of the triphenylphosphine. This is likely due to the different metal binding geometry of (Tm)$^-$ with respect to [HB-(3,5-$Me_2Pz)_3$] and also to marked steric hindrance of the former donor. However the possibility of coexistence of (Tm)$^-$ on the Ag$^+$ cation, together with a phosphino group, is demonstrated by the successful synthesis of (Tm)AgPPh$_3$ (**17**) when thf as solvent and Ag(CF_3SO_3) and PPh$_3$ as starting materials were employed. The difference is likely based on relative solubility of compounds **17** and **18**: the phosphine-free product precipitates from methanol but not from thf.

The treatment of [HB(3,5-$Me_2Pz)_3$]AgPPh$_3$ (**7**) with 1-methyl-3-imidazolinethione (Hmimt) excess in benzene led to compound [HB(3,5-$Me_2Pz)_3$](Hmimt)Ag(PPh$_3$) (**19**) (Figure 9) in 70% yield, whereas the reaction of **7** with 1-methylimidazole or 1,10-phenanthroline was unsuccessful, the starting materials always being recovered.

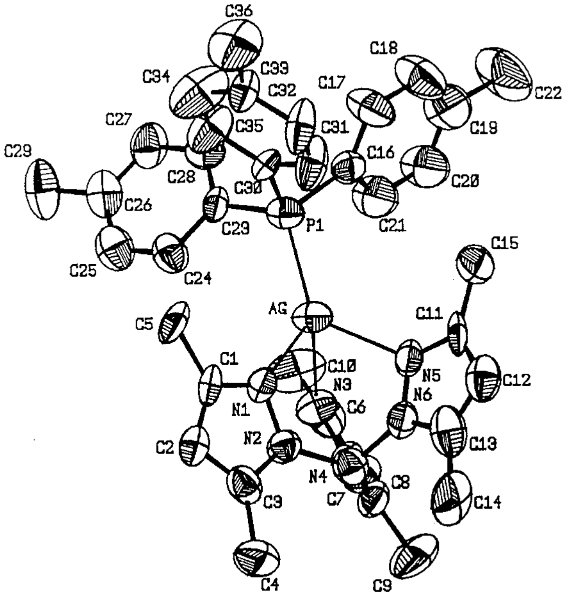

Figure 6. ORTEP drawing of the molecular structure of **10**, with H atoms omitted.

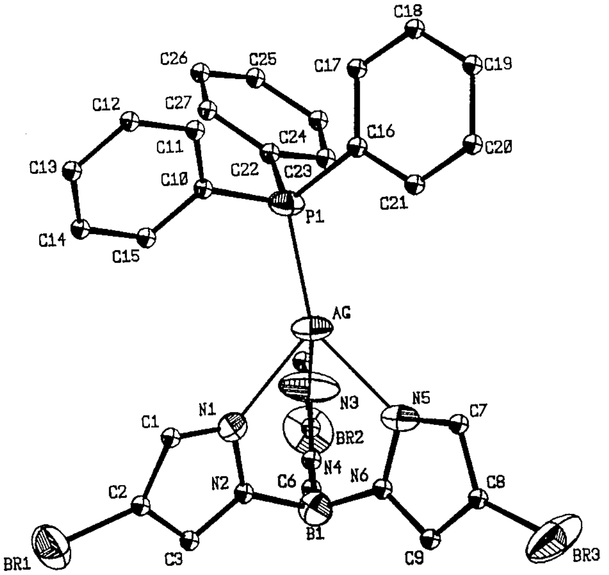

Figure 7. ORTEP drawing of the molecular structure of **15**, with H atoms omitted.

Spectroscopy. The infrared spectra (the most remarkable bands observed in the spectra of **1**−**19** and of the [tris-(hydropyrazol-1-yl)borato]potassium and -sodium compounds M[HB(Pz)$_3$] are available as Supporting Information) show all of the bands required by the presence of the organic nitrogen donor and phosphine ligand.

The spectra were recorded in Nujol mull and in chloroform solution. The latter spectra provide strong support for the identification of observations generally hidden under Nujol bands. No significant differences were found between the spectra carried out in chloroform solution and those in Nujol mull, thus suggesting again that the compounds are not dissociated in chlorinated solvents.

In the spectra of all the derivatives **1**−**19**, we found the ν(C−H) of the heterocyclic ring above 3100 cm^{-1}, the ν(C−H) of the stretching vibrations due to phenyl or benzyl groups at ca. 3080−3020 cm^{-1}, the "breathing" of the heterocyclic rings[24] and the $\nu(\mathrm{C}\underset{\cdot\cdot}{=}\mathrm{C})$ stretching vibrations of the triorganophosphino groups at ca. 1540−1500 and 1580−1610 cm^{-1}, respec-

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(24) Nieuwpoort, G.; Vos, J. G.; Groeneveld, W. L. *Inorg. Chim. Acta* **1978**, *29*, 117.

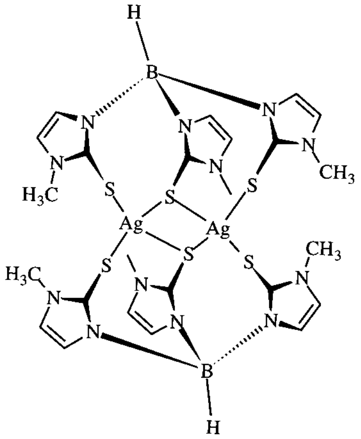

Figure 8. Structure proposed for the derivative **18**.

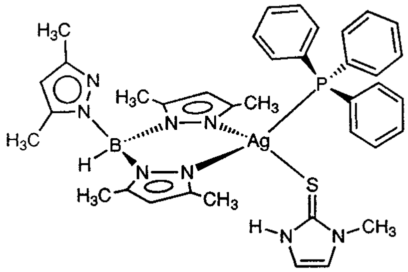

Figure 9. Structure proposed for the derivative **19**.

tively, and finally the B−N stretching vibration as a band of medium intensity at ca. 1400 cm^{-1}.[25]

In the spectrum of compound $[HB(3,5\text{-}Me_2Pz)_3](Hmimt)Ag(PPh_3)$ (**19**), we found a broad strong absorption in the range 3200−2800 cm^{-1}, characteristic of the ν(N−H) stretching vibration. This suggests that the donor (Hmimt) is coordinated to Ag(I) in the neutral S-donor fashion.[26]

In the derivatives of $[HB(3,5\text{-}Me_2Pz)_3]$ the B−H stretch generally appears as a single peak in the 2490−2510 cm^{-1} region, whereas a closer examination of the spectra of the derivative of $[HB(Pz)_3]$ reveals a medium absorption at ca. 2450 cm^{-1} and the presence of a second weaker absorption at ca. 2400 cm^{-1}. These bands are not significantly shifted upon coordination.

In the far-IR spectra of derivatives **1**−**5**, **7**−**13**, **15**−**17** and **19**, we assigned, on the basis of previous reports on silver(I) and copper(I) phosphino derivatives, the broad strong absorptions near 500 cm^{-1} and those at ca. 450−400 cm^{-1} to Whiffen's *y* and *t* vibrations, respectively.[27]

The IR spectrum of the complex **18** revealed the ν(C−N) shifted to higher frequencies with respect to the analogous bands in the potassium salts of Tm. In the far-IR region we also found several bands due to ν(C−S) coupled with ν(Ag−S) bands at ca. 280 cm^{-1} which suggest ligand thione S-donation. The absorptions found in the 200−150 cm^{-1} region are analogous to those reported for dinuclear S-bridged Cu(I), Ag(I), and Hg(II) derivatives.[28] In particular the absorptions at 150 and 130 cm^{-1} are assigned, in accordance with literature data, to the bridging ν(Ag−S) modes.[28a] Also on the basis of molecular weight determinations we hypothesized the dinuclear structure proposed in Figure 8. However, in absence of X-ray data we cannot exclude the possibility of tetranuclear or oligonuclear compound.

In addition to several absorptions characteristic of the azole ring system and of the starting silver(I) derivatives, there are some bands at ca. 350−250 cm^{-1}, similar to those described in the literature[29] for some metal(I) azolato derivatives, tentatively assigned to ν(Ag−N) vibrations and a band of medium or weak intensity at ca. 130 cm^{-1}, which is assigned to a ν(Ag−P) mode.[30]

The ^{31}P NMR data (chemical shifts, $^{109}Ag-^{31}P$ and $^{107}Ag-^{31}P$ coupling constants) in $CDCl_3$ solution of $[HB(Pz)_3]$, $[HB(3,5\text{-}Me_2Pz)_3]$, and $[HB(4\text{-}BrPz)_3]$ silver(I) complexes with phosphorus donor ligands confirm the stability of most of the complexes in this solvent.

It should be noted (Table 4) that every free phosphine appears upfield of the corresponding silver(I) complexes. $\Delta\delta(^{31}P) = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$, the difference in shift between each free phosphine and corresponding silver(I) derivatives, is on the order of 9−12 ppm for $P(2,4,6\text{-}Me_3Ph)_3$, 14−15 ppm for $P(o\text{-tolyl})_3$, 21−23 ppm for PPh_3, 19−27 ppm for $P(Bz)_3$, 22−23 ppm for $P(m\text{-tolyl})_3$ and for $P(p\text{-tolyl})_3$, 23−24 ppm for $MePh_2P$, and finally 24.8 ppm for $P(Cy)_3$. It is worth noting that the shift is a function of the cone angle and basicity of the phosphine: for example, the small shift found in the derivatives of $P(2,4,6\text{-}Me_3Ph)_3$ suggests a weak Ag−P bond interaction.

The $\Delta\delta(^{31}P) = \delta(^{31}P_{Ag(I)complex}) - \delta^{31}P_{ligand})$ is greater with respect to that observed in analogous copper(I) tris(pyrazol-1-yl)borate complexes,[12,31] in which a weak bonding interaction has been hypothesized.

The detection of one broad signal only in the spectra at room temperature of compounds **1**−**4** is in accordance with the existence of a fast phosphine exchange process and/or of equilibria of dissociation of the phosphorus donors such as that proposed in Figure 10. The rate of this exchange is strongly dependent from the temperature, as expected. Whereas, at room temperature, all the other compounds show generally two doublets in which the separate couplings of ^{31}P to the ^{107}Ag and ^{109}Ag are resolved.[32]

We have found that a good correlation exists between the $^{1}J(Ag-^{31}P)$ coupling constant and the inverse of the cone angle of the phosphorus donor, and with the exception of the derivatives of $P(2,4,6\text{-}Me_3Ph)_3$, which is the more sterically hindered P-donor, and of PCy_3, which is the more basic one, we also noted that a good correlation exists between the $^{1}J(Ag-^{31}P)$ and the pK_a of the triorganophosphine. This indicates that the strength of the Ag−P bond increases with increasing donating ability of PR_3.

Finally, we have also observed that the coupling constant values are not strongly dependent on the nature of the anionic

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(25) Zaidi, S. A. A.; Khan, T. A.; Zaidi, S. R.; Siddiqi, Z. A. *Polyhedron* **1985**, *4*, 1163.

(26) (a) García Martínez, E.; Sanchéz Gonzaléz, A.; Casas, J. S.; Sordo, J.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1992**, *191*, 75. (b) García Martínez, E.; Sanchéz Gonzaléz, A.; Casas, J. S.; Sordo, J.; Valle, G.; Russo, U. *J. Organomet. Chem.* **1993**, *453*, 47.

(27) (a) Shobatake, K.; Postmus, C.; Ferraro, J. F.; Nakamoto, K. *Appl. Spectrosc.* **1969**, *23*, 12. (b) Bradbury, J.; Forest, K. P.; Nuttal, R. H.; Sharp, S. W. A. *Spectrochim. Acta* **1967**, *23*, 2701.

(28) (a) Bowmaker, G. A.; Dance, I. G.; Harris, R. K.; Henderson, W.; Laban, I.; Scudder, M. L.; Oh, S.-W. *J. Chem. Soc., Dalton Trans.* **1996**, 2381. (b) Raper, E. S.; Wilson, J. D.; Clegg, W. *Inorg. Chim. Acta* **1992**, *194*, 51. (c) Tallon, J.; Garcia-Vazquez, J. A.; Romero, J.; Louro, M. S.; Sousa, A.; Chen, Q.; Chang, Y.; Zubieta, J. *Polyhedron* **1995**, *14*, 2309. (d) Raper, E. S.; Creighton, J. R.; Robson, D.; Wilson, J. D.; Clegg, W.; Milne, A. *Inorg. Chim. Acta* **1988**, *143*, 95. (e) Raper, E. S.; Clegg, W. *Inorg. Chim. Acta* **1991**, *180*, 239.

(29) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; pp 201−220.

(30) Bowmaker, G. A.; Effendy; Hanna, J. V.; Healy, P. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1993**, 1387.

(31) Gioia Lobbia, G.; Pettinari, C.; Santini, C.; Colapietro, M.; Cecchi, P. *Polyhedron* **1997**, *16*, 207.

Table 4. Selected ^{31}P NMR ($CDCl_3$) Data for Derivatives 1−17

compd	no.	$\delta(^{31}P)$	$^1J(^{31}P-^{107}Ag)$	$^1J(^{31}P-^{109}Ag)$	$\Delta\delta(^{31}P)^a$
$[HB(pz)_3]Ag(PPh_3)$	**1**	17.0 dd (−50 °C)	607	700	23.0
$[HB(pz)_3]Ag[P(o\text{-tolyl})_3]$	**2**	−20.1 dd (−90 °C)	598	674	8.9
$[HB(pz)_3]Ag[P(m\text{-tolyl})_3]$	**3**	17.4 dd (−20 °C)	612	702	22.3
$[HB(pz)_3]Ag[P(p\text{-tolyl})_3]$	**4**	14.7 dd (−20 °C)	609	700	22.2
$[HB(pz)_3]Ag[P(mesyt)_3]$	**5**	−27.1 dd [3]^b (−50 °C)	602	691	8.9
		−29.1 dd [1]^b	574	662	6.9
$[HB(pz)_3]Ag[P(Bz)_3]$	**6**	15.4 dd (20 °C)	626	712	27.2
$[HB(3,5\text{-}Me_2Pz)_3]Ag(PPh_3)$	**7**	17.9 dd (20 °C)	576	665	23.9
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(o\text{-tolyl})_3]$	**8**	−16.3 dd (20 °C)	559	646	12.7
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(m\text{-tolyl})_3]$	**9**	17.9 dd (20 °C)	581	669	22.8
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(p\text{-tolyl})_3]$	**10**	15.6 dd (20 °C)	586	674	23.1
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(mesyt)_3]$	**11**	−24.4 dd (20 °C)	539	622	11.2
$[HB(3,5\text{-}Me_2Pz)_3]Ag(PMePh_2)$	**12**	−3.6 dd (20 °C)	595	686	24.4
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(Bz)_3]$	**13**	8.6 dd (20 °C)	599	691	19.6
$[HB(3,5\text{-}Me_2Pz)_3]Ag[P(Cy)_3]$	**14**	36.6 dd (20 °C)	576	664	24.8
$[HB(4\text{-}BrPz)_3]Ag(PPh_3)$	**15**	16.9 dd (−40 °C)	613	707	22.9
$[HB(4\text{-}BrPz)_3]Ag[P(Bz)_3]$	**16**	19.8 dd (20 °C)	629	725	30.8
$TmAg(PPh_3)$	**17**	10.1 dd (−70 °C)	537	449	16.1

^{a} $\Delta\delta(^{31}P) = \delta(^{31}P_{complex}) - \delta(^{31}P_{ligand})$. ^{b} Intensity ratio in square brackets.

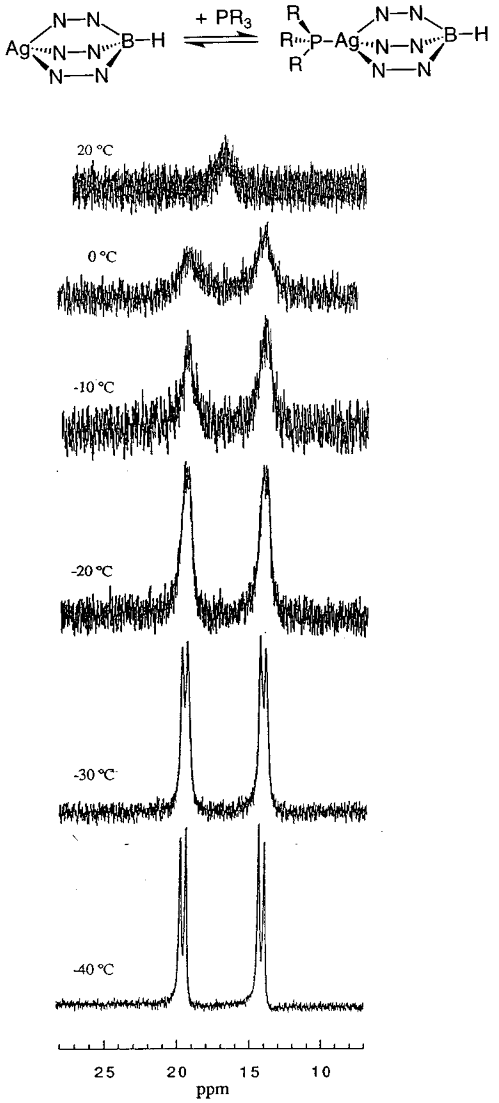

Figure 10. Variable-temperature ^{31}P NMR spectra for the derivative **15**.

tris(pyrazol-1-yl)borato donors, and there is no correlation between the $^1J(^{31}P-Ag)$ and the inverse of the pK_a of the azole: for example, in the series of (triphenylphosphine[tris(pyrazol-1-yl)borato]silver(I) derivatives, the highest values of $^1J(^{31}P-Ag)$ was found in $[HB(4\text{-}BrPz)_3]Ag(PPh_3)$ (pK_a of 4-BrPzH = 0.64), whereas the lowest was in $[HB(3,5\text{-}Me_2Pz)_3]Ag(PPh_3)$ (pK_a of 3,5-Me_2PzH = 4.12).[33]

The observed Ag−P coupling constant values are relatively higher than those reported for various other silver(I) phosphine complexes (typically $^1J(Ag-P)$ coupling constants in tetracoordinate silver complexes range from 200 to 500 Hz),[34] but in all the compounds **1**−**16** they are lower with respect to those reported for analogous polyfluorinated tris(pyrazol-1-yl)borate complexes.[15] In all the spectra, the ratio $^1J(^{109}Ag-^{31}P)/^1J(^{107}Ag-^{31}P)$ is consistent with the $^{109}Ag/^{107}Ag$ gyromagnetic ratio of 1.149.

The $\Delta\delta(^{31}P)$ observed for compound **17** is lower with respect to all the other triphenylphosphine complexes. The $\Delta\delta(^{31}P)$ is of the same order of magnitude of those indicated for tricoordinated Ag(I) triphenylphosphine complexes. In the ^1H and ^{13}C NMR spectrum of **17**, the multiplicity observed for the signals due to imidazole ring indicates a tricoordinate Ag(I) center (Scheme 1).

The ^1H and ^{13}C NMR spectra were obtained using chloroform as a solvent. They support the formulas proposed and show that our N_3-donors have not undergone any structural change upon coordination.

The resonance of the boron hydrogens was observed as a broad signal, in accordance with previous observations on compounds of this type. The resonance is probably broadened by interaction with the ^{11}B quadrupole ($I = ^3/_2$). The generally not negligible Δ (Δ = difference in chemical shift of a given magnetically equivalent nucleus in the anionic ligand with respect to its silver(I) phosphine derivative) suggests the existence of the complexes in weak donor solvents such as the chlorinated ones.

In the ^1H NMR spectra, as previously found in other poly(azol-1-yl)borate derivatives,[6−12] upfield resonances in the case of H(3), H(4), and $CH_3C(5)$ and downfield ones in the case of H(5) and $CH_3C(5)$ were detected. The shift is generally higher

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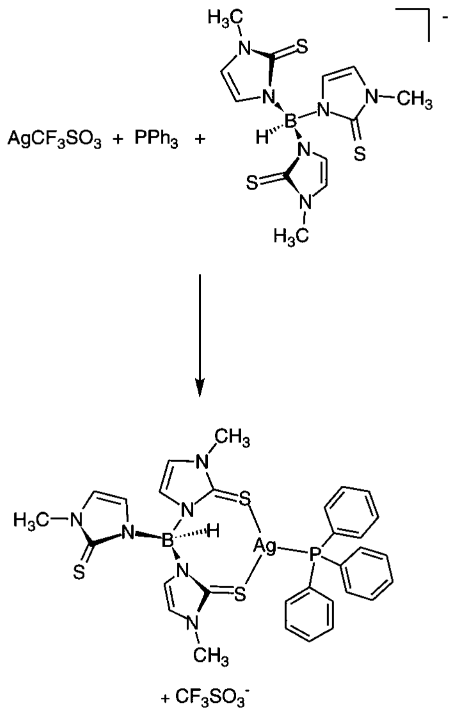
(32) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6388.
(33) Grimmett, M. R. Imidazoles and their benzo derivatives: (i) Structure. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R. and Rees, C. W., Eds. in Chief, and Potts, K. T., Ed.; Pergamon: Oxford, U.K., 1984; Vol. 5, Part 4A.
(34) (a) Kourkine, I. V.; Maslennikov, S. V.; Ditchfield, R.; Glueck, D. S.; Yap, C. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 6708. (b) Baker, L.-J.; Bowmaker, G. A.; Camp, D.; Effendy; Healy, P. C.; Schmidbaur, H.; Steigelmann, O.; White, A. H. *Inorg. Chem.* **1992**, *31*, 3656.

Scheme 1



in derivatives of [HB(3,5-Me$_2$Pz)$_3$] with respect to analogous derivatives of [HB(Pz)$_3$], and it is higher in derivatives containing P(*o*-tolyl)$_3$, (PBz)$_3$ and P(2,4,6-Me$_3$Ph)$_3$. The differences between complexes **1**−**6** and **7**−**14** are presumably steric in origin and arise from the nature of the boron-containing ligands. In fact, the [HB(3,5-Me$_2$Pz)$_3$] donor is sterically very demanding, the methyl groups nearest the metal-coordinated nitrogen interfering with the phosphine on silver(I). In the ^{1}H NMR spectrum of **19**, we found two different sets of signals for each magnetically equivalent nucleus of the tris(pyrazol-1-yl)borate donors. This pattern is different from that observed in copper−bis(triphenylphosphine) derivatives.[12] On the basis of previous reports, we hypothesized that the fast concomitant breaking and formation of the Ag−N bond, observed in derivatives **1**−**16** and in analogous copper(I) compounds,[12] is not operating in this case and that compound **19** has a structure such as that indicated in Figure 9, in which the donor [HB(3,5-Me$_2$Pz)$_3$] acts in the anionic bidentate fashion.

In the ^{13}C NMR spectra, we found that all the absorptions undergo only a slight displacement, in accordance with the trend previously observed for silver(I) compounds of poly(pyrazol-1-yl)alkanes.[35] In the derivatives **1**−**5**, **7**−**12**, **15**, and **17**, the restricted rotation of the aryl groups around the P−C bond axis due to the bulkiness of the two phosphine moieties, previously found in several bis(triarylphosphine)copper(I) derivatives,[36] is not observed. Whereas, the presence of a sharp doublet due to ipso carbon suggests equivalence of the phenyl rings due to free rotation around the P−C bonds.

Description of the Molecular Structure of [Hydrotris(pyrazol-1-yl)borate]Ag(PPh$_3$) (1). The cell content consists of four discrete molecules [HB(Pz)$_3$]Ag(PPh$_3$) distributed in two equivalent positions. The silver(I) atom (Figure 3) adopts a strongly distorted tetrahedral environment owing to the bulky PPh$_3$ and [HB(Pz)$_3$] groups: for example, in the coordination sphere the N−Ag−P angles range from 119.4(2) to 137.2(1)°, whereas the N−Ag−N angles range from 79.7(2) to 86.2(2)°. The Ag−P bond lengths are 2.336(3) and 2.337(2) Å. These values are shorter than the typical Ag−P distance observed for silver(I) triphenylphosphine complexes (average 2.419 Å for 27 compounds)[37] and are slightly shorter than those found in the analogous polyfluorinated derivatives. The Ag−N bond distances (2.351(3), 2.355(3), and 2.325(4) Å) are slightly shorter than those found in derivatives which involve a highly fluorinated “electron-poor system”.[15] Bond distances and angles within the [HB(Pz)$_3$] ligand do not differ greatly from those observed in other complexes containing this donor;[6,38] the following order of size of bond angles was observed:

$$\mathrm{Ag{-}N1{-}C3} > \mathrm{Ag{-}N1{-}N2}$$

$$\mathrm{N1{-}N2{-}C1} > \mathrm{N2{-}N1{-}C3}$$

$$\mathrm{N1{-}C3{-}C2} > \mathrm{N2{-}C1{-}C2}$$

The C−P−C angles (weighted average 104.0°) and the Ag−P−C (weighted average 114.45°) are comparable with the weighted value found in [HB(Pz)$_3$]Cu{PPh$_3$},[12] whereas the mean N−Ag−N (bite angles) and N−Ag−P are smaller and greater, respectively, than those found in the analogous copper complex.[12]

Description of the Molecular Structure of [Hydrotris(pyrazol-1-yl)borate]Ag[P(*o*-tolyl)$_3$] (2). The cell content consists of six discrete molecules. The atoms Ag, P(1), B(1), and related hydrogen atom (H1A), along the ternary axis, have a site occupancy factor $^1/_3$. The ligand arrangement around the silver(I) atom (Figure 4) is described as strongly distorted tetrahedral: in the coordination sphere, the N−Ag−N bond angle is 81.70(1)°, whereas P−Ag−N is 130.93°. There is no steric hindrance between the Ag atom and the methyl carbon C(10) or the pyrazolate carbon C(3), since the closest contacts are at 3.4834(11) or 3.4428(6) Å, respectively. Ag−P [2.368(1) Å) and Ag−N (2.357(3) Å] are comparable with the values found in [HB(Pz)$_3$]Ag(PPh$_3$) and are larger than the sum of the covalent radii of silver(I) and of the donor. The Ag−P−C angles [114.14(6)°] are of the same order of magnitude as the weighted average value found in [HB(Pz)$_3$]Ag{PPh$_3$}.

Description of the Molecular Structure of [Hydrotris(pyrazol-1-yl)borate]Ag[P(Bz)$_3$] (6). The cell content consists of four discrete molecules [HB(Pz)$_3$]Ag[P(Bz)$_3$]. The ligand arrangement around the silver(I) atom (Figure 5) is described as strongly distorted tetrahedral owing to the bulky P(Bz)$_3$ and [HB(Pz)$_3$] groups: for example in the coordination sphere the N−Ag−N bond angles range from 81.4(2) to 83.8(1)° and P−Ag−N from 121.0(1) to 136.2(1)°. The Ag−P (2.328(2) Å) and Ag−N (2.343(4), 2.383(4) and 2.357(4) Å) are comparable with the values found in [HB(Pz)$_3$]Ag(PPh$_3$) and are larger than the sum of the covalent radii of silver(I) and of the donor. The Ag−P−C angles [weighted average 116.5(2)°] are larger than the weighted average value found in [HB(Pz)$_3$]Ag(PPh$_3$). This is likely due to greater steric hindrance of P(Bz)$_3$ (cone angle = 165°) with respect to PPh$_3$ (cone angle = 145°). The steric hindrance of P(Bz)$_3$ also produces a decrease of the N−Ag−N bite angles. In this compound, the N−Ag−N

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(35) Pettinari, C.; Gioia Lobbia, G.; Sclavi, G.; Leonesi, D.; Colapietro, M.; Portalone, G. *Polyhedron* **1995**, *14*, 1709.

(36) Pettinari, C.; Marchetti, F.; Polimante, R.; Cingolani, A.; Portalone, G.; Colapietro, M. *Inorg. Chim. Acta* **1996**, *249*, 215.

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

(38) (a) Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1994**, *33*, 1803. (b) Reger, D. L.; Ding, Y. *Organometallics* **1993**, *12*, 4485. (c) Cowley, A. H.; Carrano, C. J.; Geerts, R. L.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277.

weighted average angles are smaller than those found in [HB(Pz)$_3$]Ag(PPh$_3$). It is also of interest to compare the present structure of **6** with that of **1**: although the differences in the angles are slight, it may be noted that the increase in N−Ag−P values for **6** is consistent with a consequent decrease of the N−Ag−N one. This, taken together with the C−P−C increase, depicts a situation in which the bulky (Bz)$_3$PAg^I moiety demands more space and slightly compresses the [HB(Pz)$_3$].

Description of the Molecular Structure of [Hydrotris(3,5-dimethylpyrazol-1-yl)borate]Ag[P(*p*-tolyl)$_3$] (10). The cell content consists of four discrete molecules [HB(3,5-Me$_2$Pz)$_3$]-Ag[P(*p*-tolyl)$_3$]. The silver(I) atom (Figure 6) adopts a strongly distorted tetrahedral environment owing to the bulky P(*p*-tolyl)$_3$ and [HB(3,5-Me$_2$Pz)$_3$] groups: for example, in the coordination sphere the N−Ag−P angles range from 129.8(2) to 131.0(1)°, whereas the N−Ag−N angles range from 82.5(2) to 84.9(2)°. The Ag−P and Ag−N bond distances are of the same order of magnitude as those found in [HB(Pz)$_3$]Ag{PPh$_3$}: this suggests that the steric hindrance and the basicity of the tris(pyrazol-1-yl)borate has effected only a small perturbation on the molecular parameters of the coordination environment of silver(I).

The C−P−C angles [weighted average 104.6(2)°] and the Ag−P−C [weighted average 114.0(2)°] are comparable with the weighted values found in [HB(Pz)$_3$]Ag(PPh$_3$). The greater difference between the structure of **1** and that of **10** is in the distortion, suffered by [HB(3,5-Me$_2$Pz)$_3$] ligand upon coordination, which involves rotations about B−N (ring bonds). The dihedral angles between the pyrazolate planes of **10** are significantly different with respect to those observed in **1** and also with respect to those reported in previous mononuclear structures having [HB(Pz)$_3$] ligands of approximately C_{3v} local symmetry.[38]

Description of the Molecular Structure of [Hydrotris(4-bromopyrazol-1-yl)borate]Ag(PPh$_3$) (**15**). The cell contains two discrete molecules [HB(4-BrPz)$_3$]Ag(PPh$_3$). The coordination around the Ag site is described as strongly tetrahedral (Figure 7) distorted with bond angles P−Ag−N in the range from 122.4(2) to 142.7(3)° and bond lengths Ag−P(1) 2.345(3), Ag−N(1) 2.446(8), Ag−N(3) 2.383(9), and Ag−N(5) 2.304(8) Å. It is of interest to compare the present structure of **15** with the previously obtained one of [HB(Pz)$_3$]Ag(PPh$_3$) (**1**): beside the N−Ag−N, Ag−P−C, and C−P−C angles which are similar and underscore the homogeneity of the silver(I) derivatives, the Ag−N bond lengths and the P−Ag−N bond angles show a different trend. Three different values have been found in both cases: this is likely due to different coordinating ability of [HB(4-BrPz)$_3$] with respect to [HB(Pz)$_3$], as previously observed in organotin(IV) complexes.

The P−C bond lengths (1.808(9), 1.813(7), and 1.816(8) Å) are not different from the P−C bond length in the free phosphine (1.807(5) Å).[39] This may be attributed to the absence of π-back-bonding interactions.

Conclusions

We have prepared and characterized a series of silver(I) phosphine complexes of tris(azol-1-yl)borates and used X-ray crystallography and NMR spectroscopy to examine how the ligand properties of [HB(Pz)$_3$] are dependent on the cone angle and basicity of the triaryl- and trialkylphosphines. We have found that the behavior in solution is very different from that in solid state: for example comparison of the Ag−N bond lengths in the structures solved here suggests that bonding of [HB(Pz)$_3$] to the AgPR$_3^+$ fragment is similar despite the steric and electronic differences of the supporting ligands. On the other hand, the magnitude of the Ag−^{31}P coupling constant and the ^{31}P chemical shift indicate that the structure and stability of complexes in solution is strongly dependent on the Tolman cone angle and pK_a of PR$_3$.

It has been noted that it is possible to displace trialkyl- and triarylphosphines from the Ag^I center with a more basic P-donor but not with a neutral N-donor mono- (imidazole) or bidentate (1,10-phenanthroline) ligand, even if more basic than PR$_3$. The monodentate neutral S-donor (Hmimt) is able to coordinate the [HB(Pz)$_3$]Ag(PR$_3$) complexes yielding a complex in which the tris(pyrazol-1-yl)borate donor acts in the anionic bidentate fashion. The anionic S$_3$-donor hydrotris(3-methy-1-imidazolyl-2-thione)borate (Tm), which is more basic and has a strong affinity for the soft Ag^I cation, is able not only to coordinate the [AgPPh$_3$]$^+$ cation but also to displace the [HB(3,5-Me$_2$Pz)$_3$] and PPh$_3$ from [HB(3,5-Me$_2$Pz)$_3$]Ag(PPh$_3$), yielding the dinuclear tetracoordinate complex AgTm. However, more structural and spectroscopic studies, including other tertiary phosphines, bidentate diphosphines and different anionic and neutral donors, will be required to see whether these results are general and to develop the coordination chemistry of poly(azol-1-yl)-borato donors with respect to the Ag^I metal center.

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Supporting Information Available: Five X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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(39) (a) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1987**, *26*, 1941 and references therein. (b) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.