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Synthesis and Molecular Structure of [{(HBpz$_3$)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]BF$_4$ (Hpz = Pyrazole), a Heterotrinuclear Rh$_2$Ag Compound with Square-Planar Silver(I)

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Reaction of [(HBpz$_3$)RhCl$_2$(PPh$_3$)] (Hpz = pyrazole) with silver salts AgA (A = BF$_4$, NO$_3$, SbF$_6$) affords the unexpected heterotrinuclear compounds [{(HBpz$_3$)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]A (A = BF$_4$ **(1)**, NO$_3$ **(2)**, SbF$_6$ **(3)**). The compounds have been fully characterized by IR, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy and FAB$^+$ mass spectrometry. The solid structure of compound **1** was determined by single-crystal X-ray diffraction. The cation consists of two (HBpz$_3$)RhCl$_2$(PPh$_3$) units bonded to a silver atom through two double μ-Cl bridges in an unusual distorted square-planar arrangement.

Introduction

Silver salt metathesis is the widely preferred method of halide abstraction to generate transition-metal fragments with vacant sites which are excellent intermediates for preparative organometallic synthesis and catalytic processes. By treating a labile transition-metal halide with silver salts of weak coordinating anions (AgA; A = ClO$_4$, BF$_4$, PF$_6$, SbF$_6$, CF$_3$SO$_3$, CB$_{11}$H$_{12}$, etc.), either complexes with coordinated anions (QA; Q = transition-metal complex cation) or cationic solvent complexes ([QS]A) could be obtained.[1] The latter are commonly prepared in donor solvents, and in fact, such type of donors very often shift to the right the equilibrium depicted in eq 1. Because both anion and solvent molecules are good leaving groups these metallic compounds are highly reactive.

$$\mathrm{QA} \overset{\mathrm{S}}{\rightleftharpoons} [\mathrm{QS}]\mathrm{A} \qquad (1)$$

Despite the widespread use of this type of reaction, very little attention has been paid to the elucidation of its mechanism(s). In this context, a handful of reactions between transition-metal halides and silver salts that render a variety of silver-containing compounds with strongly different geometries have been reported.[2−7] It has been proved that some of them are intermediates in the silver salt metathesis reactions,[2,3,6] making it clear this reaction is more complex than simple S$_N$1 or S$_N$2 processes.[3] Thus, Mattson and Graham studied[2] the mechanism of halide abstraction from [(η^5-C$_5$H$_5$)Fe(CO)$_2$I] by AgBF$_4$, and from solution spectroscopic measurements, they proposed the formation of the silver adduct “(η^5-C$_5$H$_5$)(CO)$_2$Fe(μ-I)Ag” with an iodide bridge between the two metals, comparable to the carboranes [(η^5-C$_5$H$_5$)(CO)$_2$Fe(μ-X)Ag(CB$_{11}$H$_{12}$)] obtained by Reed et al.[3] by treating the corresponding iron halides with Ag[CB$_{11}$H$_{12}$]. Mayer et al.[4] reported the crystal structure of the Re$_2$Ag compound [{TpRe(NTol)(Ph)I}$_2$Ag]PF$_6$ [Tp = hydrotris(1-pyrazolyl)borate], with an I−Ag−I group bridging the two rhenium moieties, prepared by treating [TpRe(NTol)-

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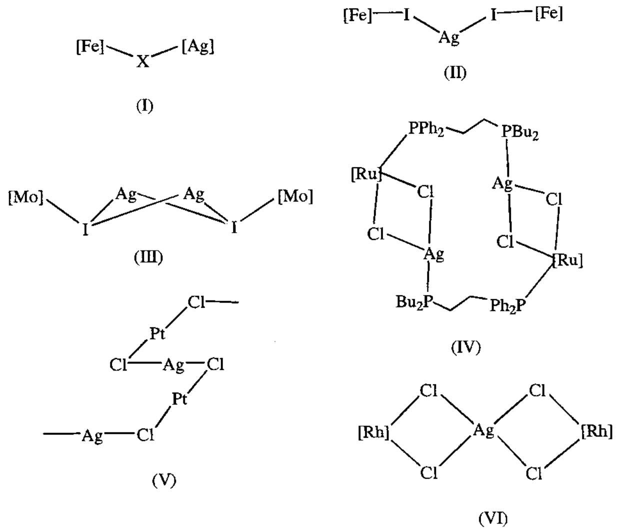
Chart 1. [a]



[a] [M] represents a metal fragment (see the text).

(Ph)I] with $AgPF_6$. Usón, Cotton, et al. published[5] the formation of a polymeric platinum−silver complex containing chloride bridges by reacting the anionic platinum complex $(NBu_4)_4[\mathit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ with $AgNO_3$ or $AgClO_4$, and very recently, Weller and co-workers,[6] have crystallographically characterized the adduct of the reaction between $[(\eta^5\text{-}C_5H_5)Mo(CO)_3I]$ and $Ag[CB_{11}H_{12}]$ as the Mo_2Ag_2 dimeric derivative $[(\eta^5\text{-}C_5H_5)Mo(CO)_3IAg(CB_{11}H_{12})]_2$ with an I−Ag−I−Ag central four-membered metallacycle bridging two $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ moieties. Finally, Werner et al.[7] have reported the characterization of a Ru_2Ag_2 compound, $[\{(p\text{-cym})RuAg(\mu\text{-}Cl)_2(\mu\text{-}P^1{}_{Ru},P^2{}_{Ag}\text{-}Ph_2P^1CH_2CH_2P^2\mathit{t}Bu_2)\}_2](PF_6)_2$ (cym = $MeC_6H_4\mathit{i}Pr$), resulting from the reaction of the dimer $[\{(p\text{-cym})RuCl\}_2(\mu\text{-}Cl)_2]$ with $Ph_2PCH_2CH_2P\mathit{t}Bu_2$ and $AgPF_6$. Its molecular structure revealed the presence of two $Ag(\mu\text{-}Cl)_2Ru$ groups connecting the two metals.

We believe it is worthwhile to point out the diversity of stoichiometries and structural motifs encountered in the resulting adducts (Chart 1). They range from heterodinuclear compounds with only one halide bridge (I) to the polymeric chloride bridged $[PtAg]_x$ derivatives (V) through heterotrinuclear complexes with an IAgI bridging group (II) and the dimeric tetranuclear Mo_2Ag_2 (III) and Ru_2Ag_2 (IV) structures.

On the other hand, we are interested in the preparation and characterization of solvate complexes of stoichiometry $[(\eta^5\text{-}C_5Me_5)M(AB^*)S]^{2+}$ (M = Rh, Ir; AB* = chiral chelate ligand; S = solvent molecule) and in their use as enantioselective catalysts in organic processes such as asymmetric hydrogen transfer[8] or enantioselective Diels−Alder[9] reactions. From a coordination point of view, protonated tris(pyrazolyl)borates are comparable to the ubiquitous cyclopentadienyl groups, although important differences between the two families of ligands actually exist.[10] With this in mind, we tried to extend our studies to rhodium tris(pyrazolyl)borate chemistry. Thus, we attempted the reaction of $[(HBpz_3)RhCl_2(PPh_3)]$ (pz = pyrazole)[11] with silver salts to create vacant sites able to further coordinate chiral auxiliaries. The outcome of the reaction was completely unexpected; a heterotrinuclear Rh_2Ag compound with the novel structural motif VI (Chart 1) was obtained instead. This structural disposition is noticeable in two respects: it presents a not previously reported $Rh(\mu\text{-}Cl)_2Ag(\mu\text{-}Cl)_2Rh$ core with four-coordinated silver, and the geometry around the silver is square-planar, a very rare structural feature in silver(I) chemistry.

In this paper, we present the preparation and spectroscopic characterization of the $[\{(HBpz_3)Rh(PPh_3)(\mu\text{-}Cl)_2\}_2Ag]^+$ cation obtained from the arrested silver halide metathesis reaction between $[(HBpz_3)RhCl_2(PPh_3)]$ and AgA (A = BF_4, SbF_6, NO_3). The solid-state molecular structure of the tetrafluoroborate derivative is also reported.

Experimental Section

All solvents were dried over appropriate drying agents, distilled under N_2, and degassed prior to use. All preparations have been carried out under nitrogen. The complex $[(HBpz_3)RhCl_2(PPh_3)]$ was prepared according to a literature procedure.[11] Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 1330 spectrophotometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian UNITY 300 spectrometer [299.9 (^1H), 121.4 (^{31}P), and 75.4 (^{13}C) MHz]. Chemical shifts are expressed in parts per million upfield from $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 in D_2O (^{31}P). FAB$^+$ mass spectra were recorded on a VG Autospec spectrometer.

$[\{(HBpz_3)Rh(PPh_3)(\mu\text{-}Cl)_2\}_2Ag]A$ (A = BF_4 (1), NO_3 (2), SbF_6 (3)). A solution of $[(HBpz_3)RhCl_2(PPh_3)]$ (194.7 mg, 0.3 mmol) in dichloromethane (10 mL) was treated with AgA (0.15 mmol) in methanol (5 mL) at room temperature and then was stirred for 1 h. Addition of 4 mL of methanol and concentration under reduced pressure led to the precipitation of a pale yellow solid which was recrystallized from dichloromethane−diethyl ether.

Data for 1. Yield: 184 mg, 83%. ^1H NMR (CD_2Cl_2): δ 8.03 (br s, 2H, H_3 of 2 pz), 7.77 (d, $^3J_{HH} = 2.2$ Hz, 4H, H_3 of 4 pz), 7.68 (m, 2H, H_5 of 2 pz), 7.51−7.35 (m, 30H, 6 C_6H_5), 6.67 (d, $^3J_{HH} = 2.2$ Hz, 4H, H_5 of 4 pz), 6.31 (pq, $^3J_{HH} = {}^4J_{PH} = 2.2$ Hz, 2H, H_4 of 2 pz), 5.92 (t, $^3J_{HH} = 2.2$ Hz, 4H, H_4 of 4 pz), 4.4−4.8 (br s, 2H, 2 BH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.5 (d, $^1J_{RhP} = 106.0$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.9 (s, C_3 of 4 pz), 142.1 (m, C_3 of 2 pz), 138.0 (s, C_5 of 4 pz), 136.1 (d, $J_{PC} = 4.2$ Hz, C_5 of 2 pz), 135.3 (d, $J_{PC} = 8.7$ Hz, $o\text{-}C_6H_5$), 132.2 (d, $J_{PC} = 3.2$ Hz,

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Table 1. Crystallographic Data for **1**

empirical formula	$C_{54}H_{50}AgB_3Cl_4F_4N_{12}P_2Rh_2$	Z	4
fw	1492.92	ρ_{calcd}, g cm^{-3}	1.645
space group	*C*2/*c* (no. 15)	λ, Å	0.71073
a, Å	24.329(4)	*T*, K	223
b, Å	10.3786(15)	μ(Mo Kα), mm^{-1}	1.153
c, Å	23.883(4)	R1[a]	0.0542, 0.1114
β, deg	91.262(15)	wR2[b]	0.1097, 0.1285
V, Å^3	6029.1(16)	GOF (F^2)	1.006, 1.022

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (3260 observed reflections, $I > 2\sigma(I)$). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

p-C_6H_5), 129.0 (d, $J_{PC} = 9.6$ Hz, *m*-C_6H_5), 126.6 (d, $^1J_{PC} = 51.6$ Hz *ipso*-C_6H_5), 107.7 (s, C_4 of 4 pz), 106.8 (d, $J_{PC} = 4.1$ Hz, C_4 of 2 pz). FAB$^+$ MS (*m*/*z*) (*m*-nitrobenzyl alcohol): 1406 (M$^+$, 25), 1370 (M$^+$ − Cl, 5). IR (Nujol, cm^{-1}): ν(BH) 2500 (m), ν(C=N) 1595 (m), ν(BF$_4$) 1050 (br s), 505 (s). Anal. Calcd for $C_{54}H_{50}N_{12}B_3P_2Cl_4F_4Rh_2Ag$: C, 43.45; H, 3.35; N, 11.25. Found: C, 43.25; H, 3.6; N, 11.0.

Data for 2. Yield: 142.5 mg, 65%. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.03 (d, $^3J_{HH} = 2.0$ Hz, 2H, H$_3$ of 2 pz), 7.79 (d, $^3J_{HH} = 2.2$ Hz, 4H, H$_3$ of 4 pz), 7.69 (m, 2H, H$_5$ of 2 pz), 7.55−7.33 (m, 30H, 6 C_6H_5), 6.72 (br s, 4H, H$_5$ of 4 pz), 6.32 (pq, $^3J_{HH} = {}^4J_{PH} = 2.2$ Hz, 2H, H$_4$ of 2 pz), 5.94 (t, $^3J_{HH} = 2.2$ Hz, 4H, H$_4$ of 4 pz), 4.4−4.8 (br s, 2H, 2 BH). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 18.2 (d, $^1J_{RhP} = 105.6$ Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 144.5 (s, C$_3$ of 4 pz), 142.1 (m, C$_3$ of 2 pz), 137.6 (s, C$_5$ of 4 pz), 135.5 (d, $J_{PC} = 8.6$ Hz, *o*-C_6H_5), 134.3 (m, C$_5$ of 2 pz), 129.6 (d, $J_{PC} = 3.2$ Hz, *p*-C_6H_5), 128.7 (d, $J_{PC} = 10.6$ Hz, *m*-C_6H_5), 127.7 (d, $^1J_{CP} = 50.9$ Hz *ipso*-C_6H_5), 107.2 (s, C$_4$ of 4 pz), 106.6 (d, $J_{PC} = 4.5$ Hz, C$_4$ of 2 pz). FAB$^+$ MS (*m*/*z*) (*m*-nitrobenzyl alcohol): 1406 (M$^+$, 33), 1370 (M$^+$ − Cl, 7). IR (Nujol, cm^{-1}): ν(BH) 2510 (m), ν(C=N) 1595 (m), ν(NO$_3$) 1285 (s). Anal. Calcd for $C_{54}H_{50}N_{13}AgB_2P_2Cl_4O_3Rh_2$: C, 44.2; H, 3.4; N, 12.4 Found: C, 43.35; H, 3.6; N, 12.5.

Data for 3. Yield: 180.0 mg, 73%. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.00 (br s, 2H, H$_3$ of 2 pz), 7.82 (d, $^3J_{HH} = 2.4$ Hz, 4H, H$_3$ of 4 pz), 7.72 (m, 2H, H$_5$ of 2 pz), 7.55−7.35 (m, 30H, 6 C_6H_5), 6.76 (d, $^3J_{HH} = 2.2$ Hz, 4H, H$_5$ of 4 pz), 6.35 (pq, $^3J_{HH} = {}^4J_{PH} = 2.2$ Hz, 2H, H$_4$ of 2 pz), 5.98 (t, $^3J_{HH} = 2.2$ Hz, 4H, H$_4$ of 4 pz), 4.4−4.8 (br s, 2H, 2 BH). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 18.1 (d, $^1J_{RhP} = 103.7$ Hz). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 144.8 (s, C$_3$ of 4 pz), 142.1 (m, C$_3$ of 2 pz), 137.8 (s, C$_5$ of 4 pz), 135.8 (d, J_{PC}= 3.0 Hz, C$_5$ of 2 pz), 135.4 (d, $J_{PC} = 8.6$ Hz, *o*-C_6H_5), 132.0 (br s, *p*-C_6H_5), 128.9 (d, $J_{PC} = 10.6$ Hz, *m*-C_6H_5), 127.2 (d, $^1J_{CP} = 51.4$ Hz *ipso*-C_6H_5), 107.5 (s, C$_4$ of 4 pz), 106.7 (d, $J_{PC} = 4.0$ Hz, C$_4$ of 2 pz). FAB$^+$ MS (*m*/*z*) (*m*-nitrobenzyl alcohol): 1406 (M$^+$, 20). IR (Nujol, cm^{-1}): ν(BH) 2510 (m), ν(C=N) 1600 (m), ν(SbF$_6$) 285 (m). Anal. Calcd for $C_{54}H_{50}N_{12}AgB_2P_2Cl_4F_6Rh_2Sb$: C, 39.5; H, 3.05; N, 10.2. Found: C, 40.0; H, 3.2; N, 10.3.

X-ray Structure Determination for 1 (Table 1). A yellow prismatic block (0.36 × 0.11 × 0.06 mm) was used for data collection. Intensity measurements were made using a Stoe AED-2 diffractometer with Mo Kα radiation. A total of 10598 reflections were collected ($2\theta = 3.3$−50°; $\omega/2\theta$ scans); of these 5329 were unique ($R_{int} = 0.0819$). A ϕ-scan absorption correction was applied[12] with minimum/maximum transmission factors 0.667/0.732. The structure was solved by Patterson and difference Fourier methods, and refined using SHELXTL (weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.0567P)^2$, where $P = [\max(F_o^2 + 2F_c^2)]/3$).[13] All non-hydrogen atoms of the cation were refined anisotropically; the BF$_4$ anion was observed severely disordered and was eventually modeled with two disordered moieties. Hydrogen atoms were included in calculated positions and refined with a positional riding model and a free thermal parameter for each atom. Atomic scattering factors were taken from a standard source.[14] The largest peak and hole were 1.37 and −0.71 e Å^{-3}.

Results and Discussion

At room temperature the compound [(HBpz$_3$)RhCl$_2$(PPh$_3$)], in dichloromethane, reacts with AgBF$_4$, in methanol (2:1 molar ratio), to give [{(HBpz$_3$)Rh(PPh$_3$)(μ-Cl)$_2$}$_2$Ag]BF$_4$ (**1**) in 83% yield (eq 2).

$$2[\mathrm{HBpz_3)Rh(PPh_3)Cl_2} + \mathrm{AgA} \xrightleftharpoons{\mathrm{CH_2Cl_2/MeOH}} [\{(\mathrm{HBpz_3})\mathrm{Rh(PPh_3)}(\mu\text{-}\mathrm{Cl_2}]\}_2\mathrm{Ag}]\mathrm{A} \quad \mathrm{A} = \mathrm{BF_4}\ (\mathbf{1}),\ \mathrm{NO_3}\ (\mathbf{2}),\ \mathrm{SbF_6}\ (\mathbf{3}) \tag{2}$$

No precipitation of AgCl was observed after several days from the dichloromethane solution even when an additional 1 equiv of AgBF$_4$ was added. The solid isolated is yellow, air-stable, and slightly soluble in dichloromethane or acetone. It has been fully characterized by elemental analyses, IR, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy, FAB$^+$ MS spectrometry, and X-ray diffraction methods. The IR spectrum in Nujol shows two bands at ca. 1100 and 520 cm^{-1} characteristic of the uncoordinated BF$_4^-$ anion and a medium-intensity ν(BH) band at 2500 cm^{-1} typical of trihapto HBpz$_3$ ligands.[15] The NMR spectra do not show important changes with respect to the starting compound [(HBpz$_3$)RhCl$_2$(PPh$_3$)]. In the ^{1}H and ^{13}C{^{1}H} NMR spectra the pyrazolyl rings give rise to two sets of resonances in a 2:1 ratio. All the proton resonances of the pyrazolyl rings, except that of the H$_3$ protons of the pyrazolyl group trans to the PPh$_3$ ligand (0.1 ppm upfield shifted), are downfield shifted about 0.1−0.2 ppm. Inspection of the molecular structure of **1** (see below) shows that H$_3$ protons could be shielded by the ring current of a phenyl group of the PPh$_3$ coordinated to the second rhodium atom. In the ^{13}C{^{1}H} NMR spectra, small J_{PC} couplings (ca. 4 Hz) are observed for the pyrazolyl carbons of the ring trans to the phosphine. ^{31}P{^{1}H} NMR indicates the chemical equivalence of the two phosphorus nuclei showing a doublet centered at 18.2 ppm with a coupling constant of 106.0 Hz, usual for $^1J_{RhP}$ couplings in octahedral Rh(III) compounds. The elemental analyses are consistent with the proposed stoichiometry, and the most significant FAB$^+$ MS peak appears at *m*/*z* = 1406, with an isotopic distribution corresponding to that of the (HBpz$_3$)$_2$Rh$_2$(PPh$_3$)$_2$Cl$_4$Ag$^+$ fragment. All these data are consistent with a dinuclear structure with two {Rh(HBpz$_3$)-

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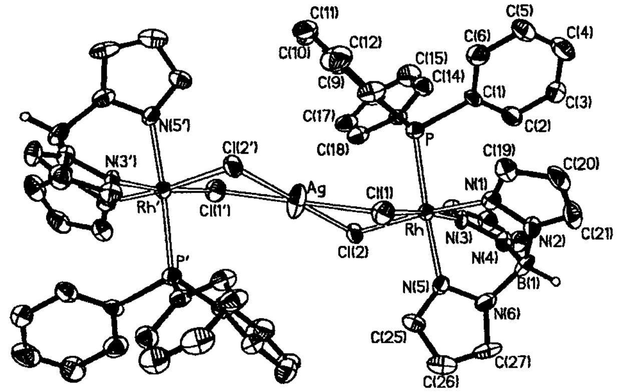

Figure 1. Molecular representation of the trinuclear cationic complex **1**. Primed atoms are related to the unprimed ones by the symmetry transformation $^1/_2 - x$, $^1/_2 - y$, $-z$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Rh−Cl(1)	2.354(2)	Rh−Cl(2)	2.3440(17)
Rh−P(1)	2.362(2)	Rh−N(1)	2.027(6)
Rh−N(3)	2.045(6)	Rh−N(5)	2.078(6)
Ag−Cl(1)	2.619(2)	Ag−Cl(2)	2.6588(19)
Cl(1)−Rh−Cl(2)	88.35(7)	Cl(2)−Rh−N(5)	88.67(16)
Cl(1)−Rh−P(1)	96.05(7)	P(1)−Rh−N(1)	92.61(17)
Cl(1)−Rh−N(1)	89.20(19)	P(1)−Rh−N(3)	90.64(18)
Cl(1)−Rh−N(3)	173.30(18)	P(1)−Rh−N(5)	176.09(17)
Cl(1)−Rh−N(5)	87.12(17)	N(1)−Rh−N(3)	90.8(2)
Cl(2)−Rh−P(1)	93.70(7)	N(1)−Rh−N(5)	85.1(2)
Cl(2)−Rh−N(1)	173.44(17)	N(3)−Rh−N(5)	86.2(2)
Cl(2)−Rh−N(3)	90.89(16)		
Cl(1)−Ag−Cl(2)	76.67(5)	Cl(1)−Ag−Cl(2′)[a]	103.33(5)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation $^1/_2 - x$, $^1/_2 - y$, $-z$.

$Cl_2(PPh_3)$} units bridged by chloride ligands to a silver(I) atom. To unequivocally determine the molecular structure of **1**, an X-ray diffraction study was undertaken (see below).

Compound **1** was also prepared in pure methanol and does not extrude AgCl even after being heated at 65 °C for 2 h in the presence of an excess of $AgBF_4$.

The nitrate (**2**) and hexafluoroantimonate (**3**) homologues were prepared similarly and present comparable spectroscopic parameters (see the Experimental Section).

Molecular Structure of 1. A view of the complex cation together with the atom labeling used is shown in Figure 1. As concluded from the spectroscopic measurements, the polynuclear cation consists of two $Rh(HBpz_3)Cl_2(PPh_3)$ units linked to a silver atom through two double μ-Cl bridges. The Rh···Ag separation, 3.6448(4) Å, excludes any direct intermetallic interaction.

The rhodium atoms complete octahedral coordinations considering the two bridging chlorides, the three nitrogens of a tridentate tris(pyrazolyl)borate, and the phosphorus atom of a triphenylphosphine ligand as donor atoms. However, the most striking structural feature of **1** concerns the peculiar coordination observed around the silver atom. Interestingly, the Ag center sits in a crystallographic inversion center which makes its environment slightly distorted square-planar. The distortion arises from the differences in the two Ag−Cl bond lengths (2.619(2) and 2.6588(19) Å) and in the Cl−Ag−Cl bond angles (76.67° and 103.33(5)°) (Table 2), the latter restricted by the formation of two four-membered metallocycles Ag−Cl−Rh−Cl. Although statistically different, both Ag−Cl bond distances are clearly in the range reported for Ag(I) complexes containing bridging chlorides (mean 2.650 Å)[16] or related complexes with the "$(\mu\text{-Cl})_2-Ag^I-(\mu\text{-Cl})_2$" moiety as in the *catena*-complexes $NBu_4[AgCl_2]$ and $[Si(acac)_3][AgCl_2]$ (2.586−2.689(3) Å).[17] However, in all these cases, as in most tetracoordinated Ag(I) complexes, the silver center exhibits tetrahedral coordination,[16] in clear contrast to the unusual square-planar arrangement observed in **1**. As far as we know, only three previous structures [the mononuclear $[(ADPO)_4Ag]^+$ complex,[18] the heterotrinuclear $[\{(NH_3)_5Co(\mu\text{-pyrazine})\}_2Ag(H_2O)_2]^+$ compound,[19] and the polymeric $[Ag_2(L^3)_2]_n$ [L^3 = 1,3-bis(dicyanomethylidene)indan]][20] have been described with a Ag(I) atom in a square-planar environment, and remarkably, in the two first cases, the silver atom occupies crystallographically constrained positions, C_4 and C_{2h}, respectively, which forces this particular coordination. Most likely the *identical* and *high steric* requirements of the two Rh complexes in **1** push the formation of the centrosymmetric arrangement around the silver center and, consequently, this uncommon square-planar coordination.

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Supporting Information Available: Full details of crystallographic data, hydrogen positional parameters, anisotropic displacement parameters, and a full list of bond distances and angles (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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