Inorg. Chem. **2002**, *41*, 1870–1875

Synthesis of Tris- and Tetrakis(pyrazol-1-yl)borate Gold(III) Complexes. Crystal Structures of [Au{κ^2-*N*,*N*′-BH(Pz)$_3$}Cl$_2$] (pz = Pyrazol-1-yl) and [Au{κ^2-*N*,*N*′-B(Pz)$_4$}(κ^2-*C*,*N*-C$_6$H$_4$CH$_2$NMe$_2$-2)]ClO$_4$·CHCl$_3$

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Received October 5, 2001

Na[BH(pz)$_3$] and Na[AuCl$_4$]·2H$_2$O react in water (1:1) to give [Au{κ^2-*N*,*N*′-BH(pz)$_3$}Cl$_2$] (**1**) or, in the presence of NaClO$_4$ (2:1:1), the cationic complex [Au{κ^2-*N*,*N*′-BH(pz)$_3$}$_2$]ClO$_4$ (**2**). The reactions of Na[B(pz)$_4$] with the cyclometalated gold complexes [AuRCl$_2$] and NaClO$_4$ (1:1:1) produce [Au{κ^2-*N*,*N*′-B(pz)$_4$}(R)]ClO$_4$ [R = κ^2-*C*,*N*-C$_6$H$_4$CH$_2$NMe$_2$-2 (**3**)] or [Au{κ^2-*N*,*N*′-B(pz)$_4$}(R)Cl] [R = C$_6$H$_3$(N=NC$_6$H$_4$Me-4′)-2-Me-5 (**4**)], respectively, although **4** is better obtained in the absence of NaClO$_4$. The crystal structures of **1** and **3**·CHCl$_3$ are reported. Both complexes display the gold center in square planar environments, two coordination sites being occupied by the chelating poly(pyrazolyl)borate ligands.

Introduction

Poly(pyrazolyl)borate ligands are important auxiliary ligands in organometallic, coordination, and bioinorganic chemistry.[1−7] They can be easily prepared,[4,8] their steric and electronic properties may be conveniently tuned by introducing different substituents in the pyrazole rings,[6,7,9−13] and they offer unique opportunities to examine detailed dynamic behavior of their complexes in solution.[14−17] They may act as counterions "κ^0" [17] or display a wide variety of coordination types ranging from κ^1 to κ^4 modes,[9,17] and although they are often mere spectators of the chemical changes in which the metal center or the other ligands are involved, examples are known in which they may have a noninnocent participation by means of hapticity changes.[17] Furthermore, several recent papers have contributed new findings concerning the electronic properties of these ligands and have also shown novel coordination modes and new reaction patterns.[18]

A huge number of poly(pyrazolyl)borate complexes of main-group or transition metals[1,4,5] have been described. The chemistry of copper and silver poly(pyrazolyl)borate complexes has recently attracted much interest, and complexes are known with the ligands BH$_2$(pz*)$_2$, BPh$_2$(pz*)$_2$, BH(pz*)$_3$, and B(pz*)$_4$ [pz* = pyrazolyl (pz) or 3,5-disubstituted pyrazolyl (pzR$_2$)]. Some are homoleptic, as the polymeric [M{BR$_n$(pz*)$_{4-n}$}]$_m$,[19,20] while others contain other ligands

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10.1021/ic011031d CCC: $22.00
Published on Web 03/12/2002

such as CO,[21−25] ^{t}BuNC,[21−25] MeCN, NO,[26] NO_2,[27] ER_3[9,21,22,28] (E = P, As, Sb, R = alkyl, aryl, alcoxy, aryloxy), tetrahydrofuran,[24,29,30] toluene, ethylene, alkynes,[24] etc. This abundance and variety of poly(pyrazolyl)borate complexes of copper and silver contrasts with the scarce number of the corresponding gold complexes described so far, namely, the gold(I) complexes $[Au\{BH(pzMe_2)_3\}L_n]$ [n = 2, L = PPh_3;[31] n = 1, L = ^{t}BuNC, CO[11]] and the gold(III) derivatives $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz^*)_3R\}X_2]$ (X = Me, R = H, pz, pz* = pz;[32] X = Cl, R = pz* = pz; X = Cl, R = H, pz* = pz, $pzMe_2$) and $[Au\{\kappa^2\text{-}N,N'\text{-}BPh_2(pz)_2\}Cl_2]$.[33] After our experience, this scarcity is justified as most attempts to prepare other pyrazolylborate gold(III) complexes were unfruitful.

We report here three new pyrazolylborate gold(III) complexes and an improved synthesis for the previously described complex $[Au\{\kappa^2\text{-}N,N'\text{-}BH(pz)_3\}Cl_2]$, the crystal structure of which has now been determined along with that of the cyclometalated complex $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}(Bz)]ClO_4$ (Bz = κ^2-C,N-$C_6H_4CH_2NMe_2$-2).

Experimental Section

IR and NMR spectroscopy, elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described elsewhere.[34] Chemical shifts are referred to TMS (1H). pz^c and pz^u stand for coordinated and uncoordinated pyrazolyl groups, respectively. Unless otherwise stated, all reactions were carried out at room temperature and without special precautions against moisture. The solvents were distilled over Na/benzophenone (diethyl ether), P_2O_5, and then Na_2CO_3 (dichloromethane) and $KMnO_4$ (acetone). *n*-Pentane was used as received. Bz = κ^2-C,N-$C_6H_4CH_2NMe_2$-2, Az = $C_6H_3(N{=}NC_6H_4Me\text{-}4')$-2-Me-5.

Warning! *Perchlorate salts of organic cations may be explosive. Preparations on a larger scale than that reported herein should be avoided.*

The cyclometalated complexes $[Au(R)Cl_2]$ [R = κ^2-C,N-$C_6H_4CH_2NMe_2$-2,[35] κ^2-C,N-$C_6H_3(N{=}NC_6H_4Me\text{-}4')$-2-Me-5][36] and the salt $Na[B(pz)_4]$[8] were prepared according to literature methods. Other reagents were obtained from commercial sources ($NaClO_4$ and $Na[BH(pz)_3]$ from Fluka, $Na[AuCl_4]\cdot 2H_2O$ from SEMPSA) and used as received.

$[Au\{\kappa^2\text{-}N,N'\text{-}BH(pz)_3\}Cl_2]$ (1). An aqueous solution (5 mL) of $Na[BH(pz)_3]$ (297 mg, 1.26 mmol) was added dropwise to another containing $Na[AuCl_4]\cdot 2H_2O$ (500 mg, 1.26 mmol) in the same solvent (5 mL). A bright yellow suspension immediately formed which was stirred for 5 min and then filtered. The solid was dissolved in acetone (25 mL) and the solution stirred with anhydrous $MgSO_4$ for 5 min and filtered. The yellow solution was concentrated (1 mL), and pentane (20 mL) was added to precipitate **1** as a bright yellow solid which was stirred with pentane (2 × 10 mL), filtered, and air-dried. Yield: 570 mg, 94%. Anal. Calcd for $C_9H_{10}AuBCl_2N_6$: C, 22.48; H, 2.07; N,17.48. Found: C, 22.73; H, 2.24; N, 17.21. Mp: 202 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 12 (in acetone, 5 × 10^{-4} M). IR (cm^{-1}): 3127, 3101 [w, ν(C−H)], 2492 [m, ν(B−H)], 1497 [s, γ(pz ring breathing)], 370 [m, $\nu_{asym}(AuCl_2)$], 333 [m, $\nu_{sym}(AuCl_2)$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 6.39 (s, br, 3 H), 6.74 (s, br, 3 H), 7.99 (s, br, 3 H). ^{1}H NMR (300 MHz, $CDCl_3$, −60 °C, δ): 6.30 [s, 1 H, H4 (pz^u)], 6.51 ["t", 2 H, H4 (pz^c)], 7.67 [d, 1 H, H3 or H5 (pz^u), $^3J_{HH}$ = 1.2 Hz], 7.80 [s, 1 H, H3 or H5 (pz^u)], 7.90 [s, 2 H, H3 or H5 (pz^c)], 8.07 [d, 2 H, H3 or H5 (pz^c), $^3J_{HH}$ = 3.0 Hz]. ^{1}H NMR (200 MHz, d_6-acetone, 25 °C, δ): 6.55 (s, br, 3 H), 7.99 (s, br, 3 H), 8.08 (s, br, 3 H).

$[Au\{\kappa^2\text{-}N,N'\text{-}BH(pz)_3\}_2]ClO_4$ (2). A solution of $Na[AuCl_4]\cdot 2H_2O$ (80 mg, 0.2 mmol) in H_2O (4 mL) was added dropwise to a solution containing $Na[BH(pz)_3]$ (105 mg, 0.45 mmol) and $NaClO_4$ (28 mg, 0.2 mmol) in H_2O (5 mL) over a period of 15 min. A pale yellow suspension formed which was stirred for 20 min and then filtered. The solid was dissolved in acetone (8 mL), stirred with anhydrous $MgSO_4$ for 5 min, and filtered. The yellow solution was concentrated (1 mL), and diethyl ether (20 mL) was added to give a pale yellow solid which was further stirred with diethyl ether (2 × 10 mL), filtered, and air-dried to give **2**. Yield: 71 mg, 49%. Anal. Calcd for $C_{18}H_{20}AuB_2ClN_{12}O_4$: C, 29.92; H, 2.79; N, 23.27. Found: C, 29.88; H, 2.77; N, 23.07. Mp: 165 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 157 (in acetone, 5 × 10^{-4} M). IR (cm^{-1}): 3135 [w, ν(C−H)], 3107 [m, ν(C−H)], 2498 [m, ν(B−H)], 1497 [s, γ(pz ring breathing)], 1114 [s, $\nu(ClO_4)$], 622 [m, $\delta(ClO_4)$]. ^{1}H NMR (300 MHz, d_6-acetone, δ): 6.33 ["t", 2 H, H4 (pz^u)], 6.78 ["t", 4 H, H4 (pz^c)], 7.54 [d, 2 H, H3 or H5 (pz^u)], 7.74 (d, 4 H, H3 or H5 (pz^c), $^3J_{HH}$ = 2.1 Hz), 7.95 [d, 2 H, H3 or H5 (pz^u), $^3J_{HH}$ = 2.1 Hz), 8.48 [d, 4 H, H3 or H5 (pz^c), $^3J_{HH}$ = 1.8 Hz].

$[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}(\kappa^2\text{-}C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)]ClO_4$ (3). Solid $[Au(\kappa^2\text{-}C,N\text{-}C_6H_4CH_2NMe_2\text{-}2)Cl_2]$ (99 mg, 0.25 mmol) was added to a suspension containing $Na[B(pz)_4]$ (75 mg, 0.27 mmol) and $NaClO_4$ (35 mg, 0.25 mmol) in acetone (30 mL). The mixture was stirred for 24 h and the solvent evaporated to dryness. The residue was extracted with CH_2Cl_2 (2 × 20 mL), the combined extracts were filtered through a short pad of Celite, and the solution was concentrated to 2 mL. At this point a white solid appeared, and diethyl ether (20 mL) was added to complete precipitation. The suspension was filtered, and the solid was washed with diethyl ether (2 × 5 mL) and air-dried to give **3**. Yield: 128 mg, 73%. Anal. Calcd for $C_{21}H_{24}AuBClN_9O_4\cdot 0.75CH_2Cl_2$: C, 33.78; H, 3.52; N, 16.30. Found: C, 34.05; H, 3.25; N, 16.13. Mp: 206 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 124 (in acetone, 5 × 10^{-4} M). IR (cm^{-1}): 3113 [w, ν(C−H)], 1506 [m, γ(pz ring breathing)], 1111 [vs, $\nu(ClO_4)$], 621 [s, $\delta(ClO_4)$]. ^{1}H NMR (300 MHz, d_6-acetone, δ): 2.76 (s, 3

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Table 1. Crystal Data

	1	**3**·$CHCl_3$
empirical formula	$C_9H_{10}AuBCl_2N_6$	$C_{22}H_{25}AuBCl_4N_9O_4$
fw	480.91	829.09
space group	*P*2(1)/*n*	*P*2(1)2(1)2(1)
cryst syst	monoclinic	orthorhombic
a (Å)	9.0620(6)	8.5602(9)
b (Å)	13.1237(9)	16.1203(18)
c (Å)	11.9099(7)	21.7920(19)
α (deg)	90	90
β (deg)	100.219(4)	90
γ (deg)	90	90
V (Å^3)	1393.9(2)	3007.1(5)
Z	4	4
d_{calcd} (g cm^{-3})	2.292	1.831
μ (mm^{-1})	10.930	5.293
T (K)	298(2)	298(2)
λ (deg)	0.71073	0.71073
R_w (F^2)[a]	0.099	0.1140
R (*F*)[a]	0.038	0.047
S[b]	1.055	1.020
Δ*ρ* (e Å^{-3})	1.108	1.590

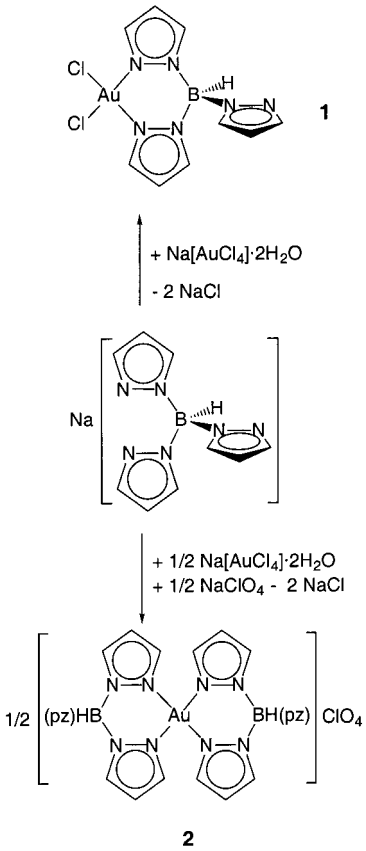
[a] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. $R = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $F > 4\sigma(F_o)$. [b] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where *n* is the number of reflections and *p* is the number of refined parameters.

H, NMe_2), 3.60 (s, 3 H, NMe_2), 4.34, 5.35 (AB system, 2 H, CH_2, J_{AB} = 14.4 Hz), 5.61 (s, 1.5 H, CH_2Cl_2), 6.35 ("t", 1 H, pz, $^3J_{HH}$ = 2.1 Hz), 6.38 (s, br, 1 H, pz), 6.63 (m, 1 H, Bz), 6.68 ("t", br, 1 H, pz), 6.69 (m, 1 H, Bz), 6.77 ("t", 1 H, pz, $^3J_{HH}$ = 2.3 Hz), 7.14 (m, 1 H, Bz), 7.30−7.40 (m, 2 H, Bz + pz), 7.65 (s, br, 1 H, pz), 7.72 (d, 1 H, pz, $^3J_{HH}$ = 2.1 Hz), 7.79 (s, br, 1 H, pz), 7.86 (d, 2 H, pz, $^3J_{HH}$ = 1.5 Hz), 8.00 (d, 1 H, pz, $^3J_{HH}$ = 1.8 Hz), 8.34 (d, 1 H, pz, $^3J_{HH}$ = 1.8 Hz).

[Au{*κ*^{2}-*N*,*N*′-B(pz)$_4$}{C$_6$H$_3$(N=NC$_6$H$_4$Me-4′)-2-Me-5}Cl] (4). [Au{*κ*^{2}-*C*,*N*′-C_6H_3(N=NC_6H_4Me-4′)-2-Me-5}Cl_2] (80 mg, 0.17 mmol) was added to a suspension of Na[B(pz)$_4$] (56 mg, 0.19 mmol) in acetone (20 mL). The resulting mixture was stirred for 24 h. The solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (2 × 20 mL), and the combined extracts were filtered through Celite. The solution was concentrated (1 mL), and *n*-pentane (20 mL) was added to precipitate a pale orange solid which was filtered and air-dried to give **4**. Yield: 41 mg, 33%. Anal. Calcd for $C_{26}H_{25}AuBClN_{10}$: C, 43.33; H, 3.50; N, 19.43. Found: C, 43.18; H, 3.57; N, 19.25. Mp: 250 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}): 17 (in acetone, 5 × 10^{-4} M). IR (cm^{-1}): 3121 [w, *ν*(C−H)], 1579 [m, *ν*(N=N)], 1497 [m, *γ*(pz ring breathing)], 370 [w, *ν*(Au−Cl)]. ^{1}H NMR (300 MHz, $CDCl_3$, *δ*): 2.32 (s, 3 H, Me), 2.42 (s, 3 H, Me), 6.23 (t, 1 H, pz, $^3J_{HH}$ = 2.4 Hz), 6.34 (s, br, 1 H, pz), 6.50 (s, br, 1 H, pz), 6.58 (m, br, 2 H, pz + Az), 6.89 (d, 1 H, pz, $^3J_{HH}$ = 1.8 Hz), 6.99 (s, br, 1 H, pz), 7.02 (s, br, 1 H, pz), 7.14 (m, 1 H, Az), 7.24−7.27 + 7.69−7.71 (AA′BB′ system, 4 H, Az), 7.36 (d, 1 H, pz, $^3J_{HH}$ = 2.4 Hz), 7.64 (s, br, 1 H, pz), 7.82 (d, 1 H, Az, $^3J_{HH}$ = 8.1 Hz), 7.89 (s, br, 1 H, pz), 7.91 (s, br, 1 H, pz), 8.12 (s, br, 1 H, pz).

X-ray Crystallographic Analysis of 1 and 3·CHCl$_3$. Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a dichloromethane solution of **1** or by slow evaporation of a solution of **3** in chloroform. Crystal data and refinement details are presented in Table 1. Crystals were mounted onto glass fibers on a Siemens P4 diffractometer. Data were registered to $2\theta_{max} = 50°$ in an *ω*-scan mode using Mo Kα radiation (*λ* = 0.71073 Å). Absorption corrections were applied on the basis of Ψ-scans. Structures were solved by the heavy atom method and refined anisotropically on F^2 [programs SHELX-93 (**1**) and SHELX-97 (**3**·CHCl3), G. M. Sheldrick, University of Göttingen]. Hydrogen atoms were included with a riding model. A system of restraints (to local ring symmetry and light atom displacement parameters) was employed to ensure refinement stability.

Scheme 1



Results and Discussion

Synthesis of Tris(pyrazolyl)borate Gold(III) Complexes. Tris(pyrazolyl)borate complexes of gold(III) [Au{*κ*^{2}-*N*,*N*′-$BH(pz)_3$}Cl_2] (**1**) and [Au{*κ*^{2}-*N*,*N*′-$BH(pz)_3$}$_2$]ClO_4 (**2**) were prepared from Na[$AuCl_4$]·$2H_2O$ and Na[$BH(pz)_3$]. Thus, Na[$BH(pz)_3$] reacts in water with Na[$AuCl_4$]·$2H_2O$ (1:1), producing almost quantitative precipitation of **1** (See Scheme 1). This complex had been obtained previously by reacting in water H[$AuCl_4$]·$3H_2O$ and K[$BH(pz)_3$] in 60% yield.[33] The differences between the reported melting point (153−155 °C) and ^{1}H NMR spectrum [(d_6-acetone, 100 or 60 MHz, *δ*): 6.48 (s, 3H), 8.00 (s, 6H)] and our data [mp: 202 °C. ^{1}H NMR (d_6-acetone, 200 MHz, *δ*): 6.55 (s, br, 3H), 7.99 (s, br, 3H), 8.08 (s, br, 3H)] could be attributed to some impurity and to the higher resolution of our NMR spectrometer, respectively. The solvent used in the synthesis is important. In fact, if acetone is used instead of water, a mixture results from which we could not isolate pure **1**. When the same reagents are treated with 1 equiv of PPh_3 (1:1:1, in acetone) or **1** is reacted with PPh_3 and $NaClO_4$ (1:1:1, in acetone), reduction to gold(I) occurs and [$AuCl(PPh_3)$] is obtained. Similar results were reported previously.[33]

The slow addition of an aqueous solution of Na[$AuCl_4$]·$2H_2O$ to another containing Na[$BH(pz)_3$] and $NaClO_4$ in the same solvent (1:2:1) produced precipitation of the homoleptic

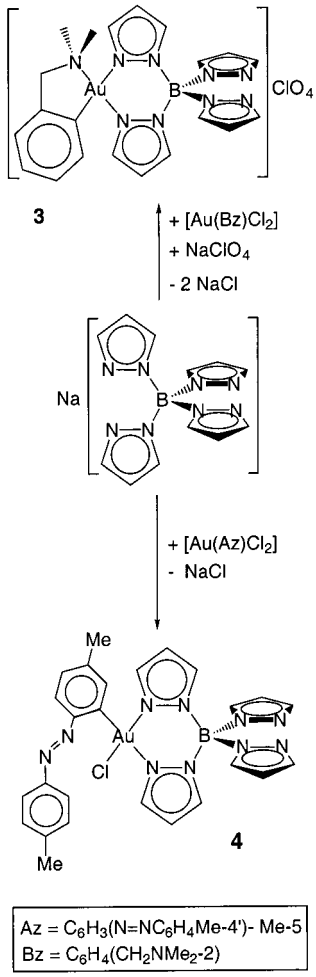
complex **2** in moderate yield (see Scheme 1). It seemed reasonable that **2** could also be obtained from the reaction of **1** with an additional 1 equiv of $Na[BH(pz)_3]$ in the presence of $NaClO_4$. However, this reaction (1:1:1, in acetone) proved not to be a convenient way to **2** since it produces a mixture of species in which **2** is present but could not be isolated pure. The attempted synthesis of **2** from **1**, $AgClO_4$, and $[Ag\{\kappa^2\text{-}N,N'\text{-}BH(pz)_3\}(THF)]$ (1:1:1) also failed, and an insoluble material was obtained that we could not identify. Although these results are surprising, they were not unexpected since some attempts to replace chloro ligands in complexes $[AuCl_2L]$ [L = $BH(pz)_3$, $BH(pzMe_2)_3$, $B(pz)_4$, $BPh_2(pz)_2$] were reported to be unsuccessful.[33] Thus, the original complexes were recovered after treatment with NH_4PF_6 or NH_4BF_4, and the reaction of $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}Cl_2]$ with $Na[BPh_2(pz)_2]$, probably designed to prepare a mixed cationic complex related to **2**, was reported to give $[Au\{\kappa^2\text{-}N,N'\text{-}BPh_2(pz)_2\}Cl_2]$. Different attempts to replace the chloro ligands in **1** by other mono- or dianionic ligands [Br^-, N_3^-, $C_2O_4^{2-}$, $(MeOC)_2C{=}CS_2^{2-}$] (by reacting it with the corresponding sodium or potassium salts) or by 1,1′-bipyridine (bpy) (**1** + bpy + TlOTf, 1:1:2) were also fruitless since the unreacted materials ($C_2O_4^{2-}$) or complex mixtures were obtained from which we could not isolate any pure complex.

Many other attempts to prepare tris(pyrazolyl)borate gold complexes also failed. Thus, the reactions of $Na[BH(pz)_3]$ with gold(I) complexes of the types $PPN[AuCl_2]$, [AuXL] [X = Cl, L = tetrahydrothiophene (tht), PPh_3; X = acetylacetonato (acac), L = PPh_3], and $[Au(L)(L')]ClO_4$ [L = L′ = NH_3; L = PPh_3, L′ = NH_3, NH=CMe_2] or with the gold(III) derivatives $[AuCl_3(tht)]$, $PPN[Au\{S_2C{=}C(C(O)Me)_2\}Cl_2]$, and $[AuRCl_2]$ (R = Bz, Az), the latter with or without added $NaClO_4$, resulted in very unstable products that we could not identify.

Synthesis of Tetrakis(pyrazolyl)borate Gold(III) Complexes. The reactions in acetone between $Na[B(pz)_4]$ and complexes $[Au(R)Cl_2]$ [R = κ^2-*C*,*N*-$C_6H_4CH_2NMe_2$-2,[35] κ^2-*C*,*N*′-C_6H_3(N=NC_6H_4Me-4′)-2-Me-5[36]] in the presence of $NaClO_4$ (1:1:1) produced the cationic complex $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}(R)]ClO_4$ [R = κ^2-*C*,*N*-$C_6H_4CH_2NMe_2$-2 = Bz (**3**)] or the neutral derivative $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}(R)Cl]$ [R = C_6H_3(N=NC_6H_4Me-4′)-2-Me-5 = Az (**4**)] although the latter is best obtained in the absence of $NaClO_4$ (see Scheme 2). In both cases, coordination of one $[B(pz)_4]^-$ ligand occurs, producing the displacement of both chloro ligands when R = Bz or only one in the case of R = Az. The byproduct is in both cases NaCl, which can be removed by extracting the reaction mixture with dichloromethane.

Spectroscopic data, conductivity measurements, and the crystal structure of **3** prove that the $[B(pz)_4]^-$ ligand is κ^2-coordinated in complexes **3** and **4**. Therefore, the two other coordination sites are occupied by the chelating Bz in the case of **3** and by chloro and monocoordinate Az ligands in **4**. These results are supported by our previous observations on the greater tendency of 2-(arylazo)arylgold(III) complexes to split the Au−N bond,[36−38] compared to 2-{(dimethylamino)-

Scheme 2



methyl}phenylgold(III) derivatives,[35,38,39] although a few examples of the latter are known.[40−42]

The complex $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}_2]ClO_4$ could not be prepared using the same reaction conditions used to prepare its analogous **2**, as the reaction in water between $Na[B(pz)_4]$, $Na[AuCl_4]$, and $NaClO_4$ (2:1:1) led to an unresolved mixture of complexes in which $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}Cl_2]$[33] was detected.

We have also failed, after many attempts, to prepare gold complexes with bis(pyrazolyl)borate ligands, which is likely due to its greater reduction ability. The reactions of $Na[BH_2(pz)_2]$ with $Na[AuX_4]$ (X = Cl, Br), with $PPN[AuCl_2]$, or even with $[Au(Bz)Cl_2]$ produced abundant decomposition to metallic gold in all cases despite the increased stability toward reduction of gold(III) complexes bearing N,C-cyclometalated ligands.[43−45]

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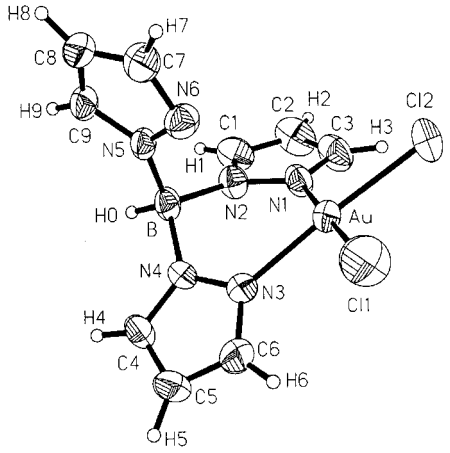

Figure 1. Ellipsoid plot of compound **1** with labeling scheme (50% probability levels). H atoms are ommited for clarity. Selected bond lengths (Å) and angles (deg): Au−N(1) 2.008(8), Au−N(3) 2.019(7), Au−Cl(1) 2.259(3), Au−Cl(2) 2.265(3), N(1)−Au−N(3) 91.6(3), N(3)−Au−Cl(1) 89.3(2), N(1)−Au−Cl(2) 90.7(2), Cl(1)−Au−Cl(2) 88.45(12).

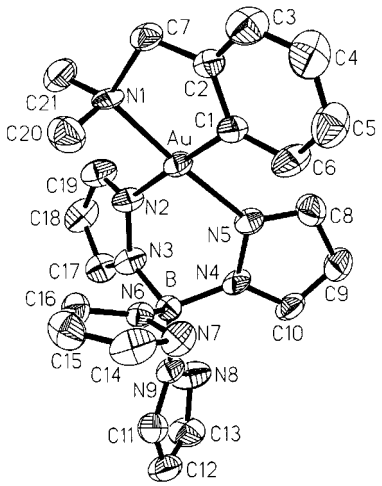

Figure 2. Ellipsoid plot of compound **3**·$CHCl_3$ with labeling scheme (50% probability levels). H atoms are ommited for clarity. Selected bond lengths (Å) and angles (deg): Au−C(1) 2.020(12), Au−N(1) 2.069(9), Au−N(2) 2.128(10), Au−N(5) 2.011(10), C(1)−Au−N(5) 93.5(4), C(1)−Au−N(1) 80.6(5), N(5)−Au−N(2) 85.1(4), N(1)−Au−N(2) 100.9(4).

Crystal Structures of 1 and 3·$CHCl_3$. The crystal structure of **1** (see Figure 1) shows the gold atom in a nearly perfect square planar environment coordinated to two *cis*-chloro ligands and two nitrogen atoms from the tris(pyrazolyl)borate ligand. The Au−Cl bond distances [2.259(3) and 2.265(3) Å] are normal,[46] while the Au−N bond distances are shorter [2.008(8) and 2.019(7) Å] than those found in the homologous [Au{κ^2-*N*,*N*′-$BH(pz)_3$}Me_2] [2.12(2) and 2.13(1) Å],[47] in agreement with the greater *trans* influence of Me with respect to chloro ligands. The N−Au−N and Cl−Au−Cl angles in **1** [91.6(3)° and 88.45(12)°, respectively] are both wider than the homologous N−Au−N and C−Au−C in [Au{κ^2-*N*,*N*′-$BH(pz)_3$}Me_2] [88.2(6)° and 86.5(10)°, respectively]. The same differences are observed when the homologous pair of complexes [AuX_2{$(py\text{-}2)_2C(OH)_2$}] (X = Y = Cl;[48] X = Me, Y = NO_3[49]) are compared: [X = Cl, N−Au−N = 86.4(6)°, Cl−Au−Cl = 89.6(6)°; X = Me, N−Au−N = 84.7(3)°, C−Au−C = 86.569(5)°]. The most surprising feature arising from the comparison of these four complexes is the wider Cl−Au−Cl angles with respect to the C−Au−C angles despite the greater van der Waals covalent radius of Me with respect to Cl.[50] Other main features of the Au−N−N−B−N−N heterocycle found in the structure of [Au{κ^2-*N*,*N*′-$BH(pz)_3$}Me_2] are preserved in that of **1**. In both cases it adopts a boat conformation, the uncoordinated pyrazolyl group being close to the vacant axial site and the pyrazole rings being planar with a maximum deviation of 0.0094 Å from the mean plane.

The crystal structure of **3·$CHCl_3$** (see Figure 2) also displays the gold atom in a perfectly square planar environment surrounded by three nitrogen atoms and one carbon atom. Among the three Au−N bond distances in **3** [Au−N(1), 2.069(9) Å; Au−N(2), 2.128(10) Å; Au−N(5), 2.011(10) Å] that *trans* to carbon is significantly longer with respect to those *trans* to nitrogen, in agreement with the greater *trans* influence of aryl with respect to nitrogen donor ligands. As in **1**, the Au−N−N−B−N−N ring adopts a boat configuration and the pyrazolyl rings are planar within 0.087 Å of the mean plane.

NMR Spectra. The room temperature ^1H NMR spectrum of **1** in $CDCl_3$ or d_6-acetone shows only three (1:1:1) broad resonances for the pyrazolyl protons, suggesting that, in solution, a fluxional process takes place interchanging coordinated and uncoordinated pyrazolyl groups.[32] At −60 °C, the interchange is slow on the NMR time scale and a six-line pattern (2:2:1:1:2:1) develops in both solvents as expected for a structure like that shown by the crystal structure. A VT-NMR study of **1** in d_6-acetone was previously reported[51] in which coincidence of the H3 and H5 resonances must occur to account for the only two (2:1) broad resonances observed in the room temperature spectrum. From the low-temperature spectra of **1** it is apparent that the resonances of the uncoordinated pyrazolyl group are at high field with respect to those of the coordinated ones and that the protons in the 4-position are also at high field with respect to those in the 3- and 5-positions, which cannot be distinguished.

Complex **2** is not fluxional in d_6-acetone solution at room temperature since its ^1H NMR spectrum shows one resonance for each of the six different types of protons, the pattern being similar to that described for **1** at low temperature.

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The pyrazolyl protons of complexes **3** and **4** are shown in the ^{1}H NMR spectra as 11 (one of double intensity) or, respectively, 12 resonances of the same intensity corresponding to four different pyrazolyl groups in agreement with their structures and the absence of fluxional processes. The boat conformation of the $[B(pz)_4]^-$ ligand and the absence of fluxionality above-mentioned makes different both the methylene protons and the methyl groups of the Bz ligand in **3**. The former are shown in the ^{1}H NMR spectrum as an AB system and the latter as two singlets, while the aryl protons appear as multiplets in the same region as the pyrazolyl protons. The aromatic protons of the metalated aryl group are seen as three multiplets, while those of the pendant aryl group give an AA′BB′ system.

IR Spectra. All complexes show in their IR spectra one absorption assigned to a ring breathing mode of the pyrazolylborate ligand in the 1497−1506 cm^{-1} range. Additionally, the spectra of **1** and **2** show a BH stretching absorption toward 2500 cm^{-1}. In the spectra of the cationic complexes **2** and **3** two bands at around 1100 and 620 cm^{-1} are assigned to the perchlorate counterion. The chlorogold complexes show two (**1**) or one (**4**) ν(AuCl) band in the 330−370 cm^{-1} region according to the *trans* ligands being nitrogen donors. Coordination of the chloro ligand is proved by the ν(AuCl) band at 370 cm^{-1} and by the low value of its molar conductivity.

Conclusions

The synthesis of pyrazolylborate complexes of gold is difficult due not only to the reducing character of these ligands but also to other causes. Thus, sometimes the nature of the solvent is essential, as occurs in the synthesis of **1**. Some common substitution reactions do not take place. For example, attempts to substitute one chloro ligand in **1** for PPh_3 led instead to $[AuCl(PPh_3)]$. Many attempts to replace the chloro ligands in **1** by other mono- or dianionic or neutral ligands were also unsuccessful. Complex **2** can easily be obtained in one step from $Na[AuCl_4]\cdot 2H_2O$ but not from **1**. Sometimes, the reaction conditions that worked for one pyrazolylborate did not work for another one. Thus, $[Au\{\kappa^2\text{-}N,N'\text{-}B(pz)_4\}_2]ClO_4$ could not be prepared under the same reaction conditions used to prepare its analogous **2**. Many attempts to prepare tris- or bis(pyrazolyl)-borate gold complexes starting from neutral, anionic, or cationic gold(I) or gold(III) complexes resulted in very unstable products that we could not identify or reduction to metallic gold, respectively. Therefore, the synthesis of new pyrazolylborate complexes of gold remains a challenge for synthetic chemists.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (Grant PB97-1047) for financial support. R.G. thanks Caja Murcia (Spain) for a grant.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of complexes **1** and **3**·$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011031D