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Coinage Metal Carbonyls and Isocyanides: Synthesis and Characterization of the Gold(I) Complexes $[HB(3,5-(CF_3)_2Pz)_3]AuCO$ and $[HB(3,5-(CF_3)_2Pz)_3]AuCNBu^t$

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Syntheses and IR spectroscopic and X-ray structural data for the gold(I) carbonyl and *tert*-butyl isocyanide complexes of the fluorinated tris(pyrazolyl)borate ligand $[HB(3,5-(CF_3)_2Pz)_3]^-$ (where $HB(3,5-(CF_3)_2Pz)_3$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate) are reported. The carbonyl complex $[HB(3,5-(CF_3)_2Pz)_3]AuCO$ (**1**) crystallizes in a triclinic unit cell, space group $P\bar{1}$, with $a = 8.3865(6)$ Å, $b = 8.6467(6)$ Å, $c = 19.009(2)$ Å, $\alpha = 98.649(6)°$, $\beta = 93.043(7)°$, $\gamma = 117.446(6)°$, $V = 1197.5(2)$ Å^3, $Z = 2$, and $R = 0.0372$. The gold atom adopts a distorted tetrahedral geometry with an Au−C distance of 1.862(9) Å. The ^{13}C NMR spectrum of **1** displays a signal at δ 172.6 which corresponds to the carbonyl carbon. The ν_{CO} of **1** (2144 cm^{-1}) is similar to that observed for the copper(I) analog. Metal−CO distances and the C−O stretching frequencies of the coinage metal carbonyl adducts of $[HB(3,5-(CF_3)_2Pz)_3]^-$ follow the orders Ag > Au > Cu and Ag > Au ≥ Cu, respectively. Crystals of $[HB(3,5-(CF_3)_2Pz)_3]AuCNBu^t$ (**2**) are monoclinic, space group $P2_1/c$, with $a = 12.082(2)$ Å, $b = 23.551(3)$ Å, $c = 10.780(2)$ Å, $\beta = 106.683(12)°$, $V = 2938.4(7)$ Å^3, $Z = 4$, and $R = 0.0372$. The gold atom coordinates to tris(pyrazolyl)borate in a highly asymmetric fashion with one short Au−N bond and two long Au−N separations. Corresponding Cu(I) and Ag(I) adducts display fairly symmetric structures with pseudo-tetrahedral metal sites. In the isocyanide series, the gold analog exhibits the highest ν_{CN} whereas the Ag adduct has the longest metal−C distance. $[HB(3,5-(CF_3)_2Pz)_3]ML$ (M = Cu, Ag, Au; L = CO, $CNBu^t$) complexes exhibit significantly reduced M-to-L back-bonding.

Among organometallic compounds, metal carbonyls represent one of the most useful, longest known, and widely investigated groups.[1−5] Despite this, the chemistry of carbon monoxide complexes of coinage metals (Cu, Ag, and Au) still remains relatively less developed.[6−8] While there are several well-defined copper(I) carbonyls known,[9−12] the isolable CO complexes of silver(I) and gold(I) are very limited.[8,13−22] They are mostly confined to the salts of weakly coordinating fluoro anions such as $[OTeF_5]^-$, $[B(OTeF_5)_4]^-$, $[Zn(OTeF_5)_4]^{2-}$, $[Ti(OTeF_5)_4]^{2-}$, $[SO_3F]^-$, and $[Sb_2F_{11}]^-$.[8,16] Structurally characterized carbonyl complexes involving heavier group 11 metals are rare, and the only examples in the literature include $[Ag(CO)][B(OTeF_5)_4]$, $[Ag(CO)_2][B(OTeF_5)_4]$, $[HB(3,5-(CF_3)_2Pz)_3]AgCO$ (where $[HB(3,5-(CF_3)_2Pz)_3]$ = hydrotris(3,5-bis(trifluoromethyl)-pyrazolyl)borate), and Au(CO)Cl.[14,15,17,20]

The metal−CO bonding interaction in these species is particularly interesting.[8,13] Carbon monoxide is an excellent π-acid and a poor Lewis base. It readily forms complexes with transition metal ions in low oxidation states or even in formally negative oxidation states, e.g., $Cr(CO)_6$, $[Cr(CO)_5]^{2-}$.[3] The back-donation of electrons from the filled metal d orbitals into the 2π CO orbitals is essential to the stability of these "classical" metal−CO adducts.[3,5] This results in the lowering of the C−O stretching frequency relative to that in free CO (2143 cm^{-1}). Generally, terminal CO ligands of classical metal carbonyls absorb IR radiation in the 2120−1850 cm^{-1} region.[3] In contrast, most of the CO adducts of heavy coinage metals show a ν_{CO} shift in the opposite direction.[8,13] For example, remarkably high ν_{CO} values (relative to free CO) have been observed for $[Au(CO)_2][Sb_2F_{11}]$ (ν_{CO} = 2217 cm^{-1})[22] and $[Ag(CO)][B(OTeF_5)_4]$ (ν_{CO} = 2204 cm^{-1}).[14] This indicates a lack of (or a significant reduction in the) back-donation from the metal to CO ligand in these complexes. Such metal carbonyls where CO acts predominantly as a Lewis base are classified as "nonclassical" metal carbonyls.[8,16,23] In addition to the C−O stretching frequency, ^{13}C NMR chemical shift of the CO ligands

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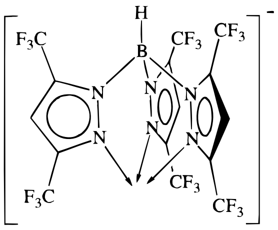
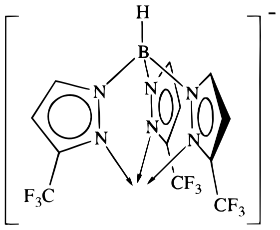
also shows contrasting behavior in classical *versus* nonclassical metal carbonyl systems.[13]

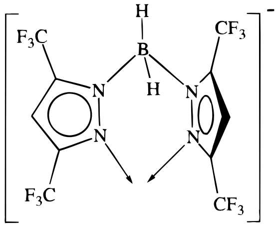
Metal isocyanides have often been compared to metal carbonyls, perhaps due to the isoelectronic relationship between CNH and CO.[1,3] However, isocyanides are much better σ-donors and relatively weaker π-acceptors compared to carbon monoxide.[24] As a result, isocyanides form stable complexes with metals in high oxidation states where π-back-bonding is of little significance.[1,24,25] Furthermore, unlike CO, isocyanides readily form stable complexes with all three coinage metals, and there are a reasonable number of Cu(I), Ag(I), and Au(I) isocyanide adducts with well-defined compositions and complete structural data.[26]



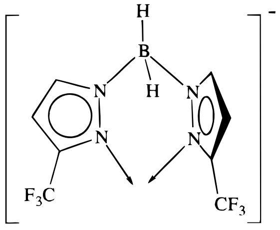
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$



[HB(3-(CF$_3$)Pz)$_3$]$^-$



[H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]$^-$



[H$_2$B(3-(CF$_3$)Pz)$_2$]$^-$

One area of focus in our laboratory is the chemistry of highly fluorinated poly(pyrazolyl)borates. We have reported the synthesis and properties of several such ligand systems (e.g., [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$, [HB(3-(CF$_3$)Pz)$_3$]$^-$, [H$_2$B(3,5-(CF$_3$)$_2$Pz)$_2$]$^-$, and [H$_2$B(3-(CF$_3$)Pz)$_2$]$^-$) and their metal adducts.[12,17,27−32] Metal ions coordinated to these fluoro ligands show increased Lewis acidity compared to their nonfluorinated counterparts. This is apparent from the IR spectroscopic data for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuCO and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuCNBu^t.[12,30] For example, the C−O stretching frequency of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuCO is about 71 cm^{-1} higher than that of the methylated analog, [HB(3,5-(CH$_3$)$_2$Pz)$_3$]CuCO. Among many potential uses, weakly coordinating tris(pyrazolyl)borate ligands such as [HB(3,5-(CF$_3$)$_2$Pz)$_3$]$^-$ would be suitable for the stabilization of metal carbonyls where metal-to-CO π-back-bonding is at a very low level. [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCO and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuCO represent two such examples.[12,17] Between these two, the silver carbonyl has the weaker metal−CO interaction and the higher carbonyl stretching frequency. In order to obtain a complete picture for the coinage metals, we decided to investigate the analogous gold(I) complexes. In this paper, the syntheses and properties of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCNBu^t are described together with their X-ray crystal structures. These results now allow us for the first time to compare structures and properties of an isomorphous group of Cu, Ag, and Au carbonyls and their closely related isocyanides.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of purified nitrogen either with standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources, distilled from conventional drying agents, and degassed twice prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded on a Bruker MSL-300 spectrometer (^{1}H, 300.15 MHz; ^{19}F, 282.36 MHz). IR spectra were recorded on a Bio-Rad 40S spectrometer operating at 2 cm^{-1} spectral resolution. Samples for IR spectroscopy were typically mulls between NaCl plates prepared using solid material and Nujol. Au(CO)Cl (Strem) and *t*-BuNC (Aldrich) were purchased and used as received. [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) and [HB(3,5-(CF$_3$)$_2$Pz)$_3$][NEt$_4$] were prepared according to the literature.[28,31]

Synthesis of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO (1). A methylene chloride (20 mL) solution of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) (401 mg, 0.5 mmol) saturated with CO (∼1 atm) was slowly added to Au(CO)Cl (129 mg, 0.5 mmol) in 10 mL of CH$_2$Cl$_2$ at −70 °C. After the addition, the reaction mixture was slowly brought to 0 °C and kept for 2 h. Then the solution was allowed to warm to room temperature over a 30 min period. The resulting cloudy solution was filtered through Celite to yield a colorless filtrate. The solvent was quickly removed from the filtrate under vacuum. This process resulted in a considerable amount of black/violet decomposition product. The solid residue was extracted into hexane, the extract was filtered, and the filtrate was immediately cooled to −20 °C to obtain **1** as colorless thin plates. ^{1}H NMR (CDCl$_3$): δ 6.97 (s, C*H*). ^{19}F NMR (CDCl$_3$): δ −59.51, −61.95. IR (Nujol mull), cm^{-1}: 2144 (CO), 2609 (BH). IR (cyclohexane), cm^{-1}: 2125 (CO). Compound **1** was also synthesized by using [HB(3,5-(CF$_3$)$_2$Pz)$_3$][NEt$_4$] instead of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) in the above procedure.

Synthesis of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCNBu^t (2). [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) (300 mg, 0.37 mmol) in methylene chloride (15 mL) was added to Au(CO)Cl (98 mg, 0.38 mmol) in methylene chloride (15 mL) at −70 °C. Then *t*-BuNC (2.4 mL of 14.3 mg/mL in toluene, 0.41 mmol) was added and the mixture was slowly brought to 0 °C. After 1 h of stirring, the solution was filtered through Celite, and the filtrate was concentrated under vacuum to give a white solid with some decomposition products. This was recrystallized from hexanes at −25 °C. ^{1}H NMR (CDCl$_3$): δ 1.59 (s, 9H, C*H*$_3$), 6.94 (s, 3H, C*H*). ^{19}F NMR (CDCl$_3$): δ −60.22 (d, ^5J(F,H) = 2.9 Hz), −61.65 (s). IR (Nujol mull), cm^{-1}: 2248 (CN), 2601 (BH).

X-ray Structure Determination of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream.[33] Data were collected on a Siemens P4 diffractometer at −90 °C using Mo Kα X-radiation (λ = 0.710 73 Å, graphite monochromator). Cell parameters were determined using 45 reflections. Three standard reflections were measured at every 97th data point to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by the Patterson method followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using

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Table 1. Crystal Data and Summary of Data Collection and Refinement

	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCNBu^t
empirical formula	$C_{16}H_4AuBF_{18}N_6O$	$C_{20}H_{13}AuBF_{18}N_7$
fw	846.03	901.15
space group	$P\bar{1}$	$P2_1/c$
a, Å	8.3865(6)	12.082(2)
b, Å	8.6467(6)	23.551(3)
c, Å	19.009(2)	10.780(2)
α, deg	98.649(6)	90
β, deg	93.043(7)	106.683(12)
γ, deg	117.446(6)	90
V, Å^3	1197.5(2)	2938.4(7)
Z	2	4
ρ_{calc}, g/cm^3	2.346	2.037
μ, mm^{-1}	6.308	5.147
λ, Å	0.710 73	0.710 73
T, °C	−90(2)	−90(2)
R1, wR2 ($I > 2\sigma(I)$)^a	0.0372, 0.1008	0.0372, 0.0879
R1, wR2 (all data)^a	0.0435, 0.1126	0.0557, 0.0968

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	M		
	Au	Ag	Cu
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]MCO			
M−C	1.862(9)	2.037(5)	1.808(4)
C−O	1.113(11)	1.116(7)	1.110(5)
M−N12	2.312(5)	2.297(4)	2.035(3)
M−N22	2.317(5)	2.320(4)	2.061(2)
M−N32	2.384(6)	2.366(4)	2.061(2)
B−N11	1.559(8)	1.558(7)	1.565(4)
B−N21	1.566(8)	1.568(6)	1.569(3)
B−N31	1.548(9)	1.554(6)	1.569(3)
N11−N12	1.363(7)	1.362(5)	1.357(4)
N21−N22	1.349(8)	1.368(5)	1.354(3)
N31−N32	1.361(8)	1.353(5)	1.354(3)
B···M	3.442	3.365	3.075
M−C−O	179.0(10)	175.6(6)	179.8(4)
C−M−N12	133.7(3)	127.0(2)	124.4(2)
C−M−N22	135.7(3)	135.4(2)	125.7(1)
C−M−N32	128.1(3)	130.4(2)	125.7(1)
N11−B−N21	108.3(5)	109.4(4)	108.1(2)
N11−B−N31	110.1(5)	111.3(4)	108.1(2)
N21−B−N31	109.1(5)	109.1(4)	108.7(3)
B···M−C	175.3	174.8	179.2
[HB(3,5-(CF$_3$)$_2$Pz)$_3$]MCNBu^t			
M−C1	1.939(8)	2.059(4)	1.827(6)
C1−N	1.131(10)	1.139(5)	1.151(8)
M−N12	2.077(6)	2.349(3)	2.072(5)
M−N22	{2.734}	2.390(3)	2.093(4)
M−N32	{2.787}	2.387(3)	2.093(4)
B−N11	1.585(10)	1.552(5)	1.562(9)
B−N21	1.532(9)	1.564(5)	1.554(5)
B−N31	1.548(10)	1.561(4)	1.554(5)
N11−N12	1.360(8)	1.358(3)	1.363(6)
N21−N22	1.352(8)	1.354(3)	1.368(4)
N31−N32	1.352(8)	1.347(3)	1.368(4)
B···M	3.523	3.401	3.101
M−C1−N	178.8(8)	173.7(4)	178.1(7)
C1−N−C2	175.7(11)	176.2(4)	177.2(9)
C1−M−N12	165.7(3)	134.8(1)	123.1(3)
C1−M−N22	{109.4}	133.7(1)	127.2(1)
C1−M−N32	{110.7}	126.9(1)	127.2(1)
N11−B−N21	110.0(6)	109.0(2)	108.7(3)
N11−B−N31	108.8(5)	110.3(3)	108.7(3)
N21−B−N31	110.4(6)	108.7(3)	109.7(5)
B···M−C1	147.1	174.9	177.3

the Siemens SHELXTL (PC version 5) software package.[34,35] All nonhydrogen atoms were refined anisotropically. The hydrogen atom on B was located from the difference map, and the positions and the isotropic thermal parameters were refined. The pyrazole ring hydrogens (C−H, 0.93 Å; U(H) = 1.2U_{iso}(C)) were included in calculated positions. Crystal data and data collection and refinement parameters are summarized in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

X-ray Structure Determination of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCNBu^t. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream.[33] Data were collected on a Siemens P4 diffractometer at −90 °C using Mo Kα X-radiation (λ = 0.710 73 Å, graphite monochromator). Cell parameters were determined using 18 reflections. Three standard reflections were measured at every 97th data point to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by the Patterson method followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the Siemens SHELXTL (PC version 5) software package.[34,35] A rotational disorder was observed for the CF$_3$ group on the C23 carbon. These fluorines were disordered over two sites, each in a 0.86:0.14 ratio. All non-hydrogen atoms, except the minor-occupancy fluorines on C26, were refined anisotropically. The hydrogen atom on B was located from the difference map, and the positions and the isotropic thermal parameters were refined. The pyrazole ring hydrogens (C−H, 0.93 Å; U(H) = 1.2U_{iso}(C)) and methyl hydrogens (C−H, 0.96 Å; U(H) = 1.5U_{iso}(C)) were included in calculated positions. Crystal data and data collection and refinement parameters are summarized in Table 1. Selected bond lengths and angles for **2** are listed in Table 2.

Results and Discussion

The gold carbonyl complex [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO (**1**) was prepared by the reaction of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) with Au(CO)Cl in methylene chloride (Scheme 1). Compound **1** is a thermally sensitive, colorless solid which slowly decomposes at room temperature with the deposition of a metallic gold film on the walls of the container. It is soluble in *n*-hexane. Slightly improved solution stability was noted in cyclohexane whereas in toluene faster decomposition was observed. The treatment of Au(CO)Cl with [HB(3,5-(CF$_3$)$_2$Pz)$_3$][NEt$_4$] also leads to **1**. The isocyanide adduct [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCNBu^t (**2**) was prepared by treating a mixture of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) and CNBu^t with Au(CO)Cl (Scheme 1). It also slowly decomposes at room temperature, and the stability is not very different from that of the carbonyl adduct [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO.

Compound **1** was characterized by NMR and IR spectroscopy and by X-ray crystallography. The room-temperature ^{1}H NMR spectrum of **1** exhibited a peak at δ 6.97, which corresponds to the pyrazole ring hydrogens. ^{19}F NMR resonances due to CF$_3$ groups appear in the expected region.[36] The corresponding ^{1}H and ^{19}F NMR signals of the related complexes [HB(3,5-(CF$_3$)$_2$Pz)$_3$]CuCO (in CDCl$_3$: ^{1}H, δ 6.95; ^{19}F, −59.74, −62.25) and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgCO (in CD$_2$Cl$_2$: ^{1}H, δ 6.96; ^{19}F, −59.07, −62.15) appear at almost identical positions.[12,17]

The ^{13}C{^{1}H} NMR spectrum of **1** in CDCl$_3$ displayed a resonance at δ 172.6 which could be assigned to the CO carbon. Consistent with several other reports, the coupling between ^{13}C and ^{197}Au (I = $^3/_2$) was not observed.[22,37,38] The ^{13}C chemical shift of CO in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AuCO may be compared to

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(34) *Siemens SHELXTL (PC version 5.0)*; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

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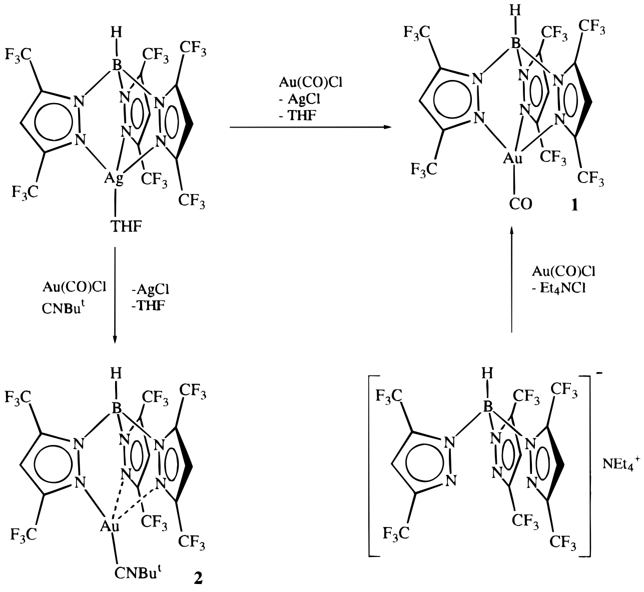
Scheme 1



the corresponding chemical shift values reported for coinage metal carbon monoxide adducts. As evident from the Table 3, only minor variations are apparent between the $^{13}C(CO)$ chemical shifts of **1** and compounds such as Au(CO)Cl (δ 172 in CD_2Cl_2), $[Au(CO)_2]^+$ (δ 174 in HSO_3F), and $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]AgCO$ (δ 175.4 in CD_2Cl_2). The ^{13}C NMR signal of CO in $[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ could not be observed under analogous conditions. The corresponding signal of free carbon monoxide appears at 184 ppm.[13,16]

In general, ^{13}C NMR resonances for the terminal CO ligands in classical metal carbonyls appear in the range 184−223 ppm.[13] For example, the ^{13}CO signals of $Cr(CO)_6$ and $Fe(CO)_5$ are observed at 212.3 and 211.9 ppm, respectively.[39,40] On the other hand, terminal CO ligands in nonclassical metal carbonyls show relatively lower chemical shift values (Table 3). For instance, the ^{13}CO resonances for noble metal carbonyl cations generally appear in the range 189−140 ppm.[13] Therefore, on the basis of the ^{13}C NMR data, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ may be classified with the members in the latter group.

The IR spectrum of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$ displayed a strong absorption band around 2144 cm^{-1} which is very close to ν_{CO} for free CO (2143 cm^{-1}).[42] The C−O stretching frequency of **1** is much lower than those reported for cationic Au(I) compounds such as $Au(CO)SO_3F$ (ν_{CO} = 2196 cm^{-1}), $[Au(CO)_2][Sb_2F_{11}]$ (ν_{CO} = 2217 cm^{-1}), and Au(CO)Cl (ν_{CO} = 2170 cm^{-1}).[21,22] This indicates a relatively weak C−O (compared to the above gold carbonyls) and a strong Au−C bonding interaction in **1**. The C−O stretching frequency places **1** in an interesting category. The ν_{CO} of 2144 cm^{-1} for **1** rules out a strong σ-only Au−CO bond since it would lead to a considerably higher ν_{CO} value relative to that for free CO (2143 cm^{-1}).[8] Alternatively, a weak σ-donor and a strong π-acceptor Au−CO interaction is also unlikely because it should lower the ν_{CO} significantly below 2143 cm^{-1} as in classical metal carbonyls. Typically, terminal CO ligands of classical metal carbonyls show IR absorptions in the region 2120−1850 cm^{-1}.[3] Since the effect of π-bonding on the C−O stretching frequency is much higher than the effect of σ-bonding, the metal CO interaction in **1** may be described as a combination of a strong σ-bond and a weak π-back-bond.

It is possible to examine trends within the coinage metal family. The C−O stretching frequencies of $[HB(3,5\text{-}(CF_3)_2\text{-}Pz)_3]CuCO$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ were observed at 2137 and 2178 cm^{-1}, respectively.[12,17] The solution C−O stretching frequencies are relatively lower for all three carbonyl adducts (Cu, 2124 cm^{-1} in hexane; Ag, 2162 cm^{-1} in hexane; Au, 2125 cm^{-1} in cyclohexane). The C−O bond strength in **1** is therefore similar to that in the copper system. The silver analog exhibits the highest ν_{CO}. Unfortunately, there are no other reports of chemically similar carbonyl adducts involving all three coinage metals. However, this Ag (ν_{CO}) > Au (ν_{CO}) ≥ Cu (ν_{CO}) order can be partially substantiated from earlier results (Table 3). For example, a comparison between $[Ag(CO)][OTeF_5]$ (ν_{CO} = 2189 cm^{-1}) and $[Au(CO)][OTeF_5]$ (ν_{CO} = 2179 cm^{-1}) shows higher ν_{CO} for Ag.[16] Similar C−O stretching frequencies have been observed for $[Au(CO)][OTeF_5]$ and $[Cu(CO)][AsF_6]$,[14,47] but the anions which significantly influence the ν_{CO} of metal adducts are different in the two systems. In the chloro adducts, Au(CO)Cl and Cu(CO)Cl, the gold system shows the higher ν_{CO} value.[37,51,52] However, the two structures are different in the solid state (Au(CO)Cl is linear whereas Cu(CO)Cl is polymeric with pseudotetrahedral copper sites).[20,46] The solution species $[(C_5H_5)Co\{P(O)(OEt)_2\}_3]AgCO$ (ν_{CO} in hexane, 2125 cm^{-1}) and $[(C_5H_5)Co\{P(O)(OEt)_2\}_3]CuCO$ (ν_{CO} in hexane, 2072 cm^{-1}) illustrates the difference between Ag and Cu.[44,48] More data are needed before arriving at a general trend (if any is present) for the ν_{CO} values of the coinage metals.

The crystals of **1** grown from pure hexane were extremely thin and often formed clusters. However, we were able to grow X-ray quality crystals from a hexane solution of **1** containing a few drops of benzene (or toluene). The structure was determined by X-ray crystallography. The ORTEP drawing of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AuCO$ is depicted in Figure 1.[53] A view down the C−Au axis is presented in Figure 2 (only selected atoms are included). The overall structure is very similar to those seen for copper and silver analogs (e.g., Figure 3).[12,17] Structural parameters of the three coinage metal carbonyl complexes of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ are listed in Table 2. The gold center in **1** adopts a pseudotetrahedral geometry and the Au−C−O angle (179.0(10)°) is linear within the experimental error. The more important Au−C and C−O distances are 1.862(9) and 1.113(11) Å, respectively. These bonds may have been affected by libration. The libration analysis of rigid-body motion gave slightly longer bond distances (Au−C = 1.869(6),

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Table 3. Comparison of Vibrational (ν_{CO}, cm^{-1}), Structural (Bond Distances, Å), and NMR Spectroscopic Data (Chemical Shifts, ppm) for Copper(I), Silver(I), and Gold(I) Carbonyls

compound	ν_{CO}	M−C	C−O	^{13}CO	ref
CO	2143		1.12822(7)	184 (CD_2Cl_2)	8, 41, 42
$[HB(3,5-(CF_3)_2Pz)_3]CuCO$	2137	1.808(4)	1.110(5)		12
$[HB(Pz)_3]CuCO$	2083	1.765(14)	1.120(6)		11, 43
$[(C_5H_5)Co\{P(O)(OMe)_2\}_3]CuCO$	2073	1.765(4)	1.107(5)		44
Cu(CO)Cl	2157	1.856(16)	1.112(18)		22, 45, 46
$[Cu(CO)][AsF_6]$	2180			169 (HSO_3F/H_2SO_4)	40, 47
$[HB(3,5-(CF_3)_2Pz)_3]AgCO$	2178	2.037(5)	1.116(7)	175 (CD_2Cl_2)	17
$[(C_5H_5)Co\{P(O)(OEt)_2\}_3]AgCO$	2125[a]				48
$[Ag(CO)][OTeF_5]$	2189			173 (solid)	16
$[Ag(CO)][B(OTeF_5)_4]$	2204	2.10(1)	1.077(16)	174 (CD_2Cl_2)	16
$[Ag(CO)_2][B(OTeF_5)_4]$	2198	2.14(5)[b]	1.08(6)[b]		16
$[HB(3,5-(CF_3)_2Pz)_3]AuCO$	2144	1.862(9)	1.113(11)	173 ($CDCl_3$)	this work
Au(CO)Cl	2170	1.93(2)	1.11(3)	172 (CD_2Cl_2)	19, 20, 49
Au(CO)Br	2153[c]			174 (CD_2Cl_2)	19
$Au_2(CO)Cl_4$	2180[d]			171 (CD_2Cl_2)	19, 38
$Au(CO)SO_3F$	2196			162 (HSO_3F)	21, 22
$[Au(CO)][OTeF_5]$	2179				16
$[Au(CO)_2][Sb_2F_{11}]$	2217			174 (HSO_3F)	22
$[Au(CO)_2][UF_6]$	2200				50

[a] In hexane. [b] Average values. [c] In *sym*-dibromoethane. [d] In SO_2Cl_2.

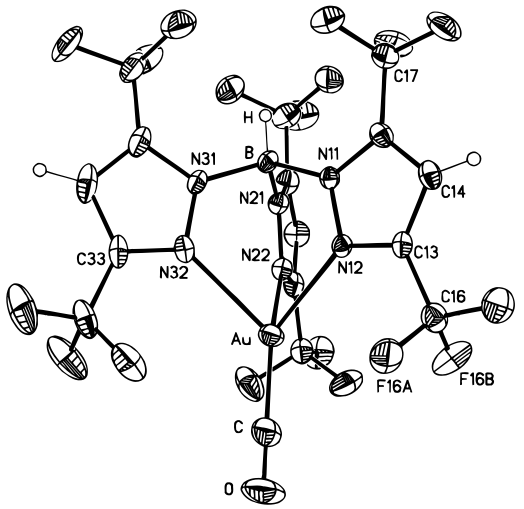

Figure 1. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]AuCO$ (**1**).

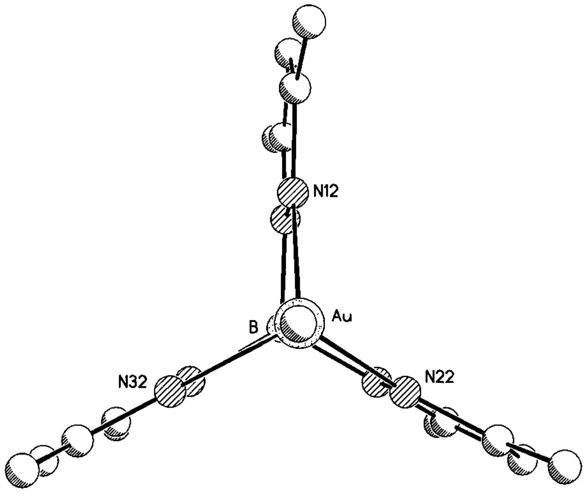

Figure 2. View of $[HB(3,5-(CF_3)_2Pz)_3]AuCO$ down the C−Au axis (only selected atoms included).

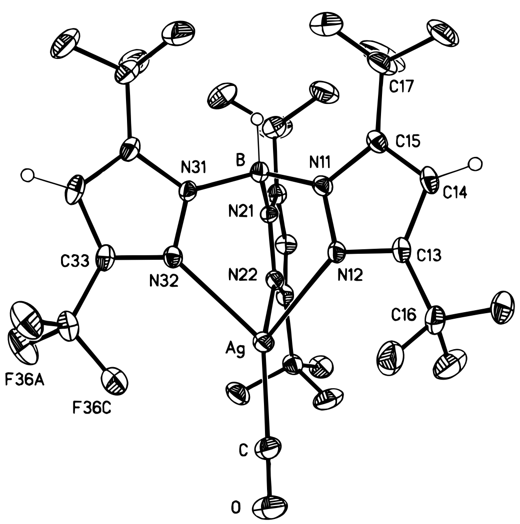

Figure 3. Molecular structure of $[HB(3,5-(CF_3)_2Pz)_3]AgCO$. Reproduced with permission from ref 17. Copyright 1995 American Chemical Society.

Au−N = 2.318(6), 2.325(8), 2.392(8), C−O = 1.116(4) Å) with $R_G = 0.287$ for the agreement between observed and calculated U_{ij}.[34,54,55]

During the structure analysis, it is important to keep in mind the inaccuracies commonly associated with the light-atom positions in gold-containing structures.[20,56−61] Nevertheless, the relatively short Au−CO distance of **1** is consistent with the results from the IR study. The Au−C separation is shorter than the corresponding distance reported for the linear molecule Au(CO)Cl (1.93(2) Å), but the difference is statistically not significantly at the 3σ level.[20] It can also be compared to metal−CO distances observed in 5d metal carbonyl complexes. A survey of available structural data shows that the Pt−CO bond lengths range from 1.821 to 1.878 Å with a mean distance of 1.853 Å (for 29 Pt−C values) whereas Ir−CO bond distances vary from 1.839 to 1.898 Å with a mean distance of 1.870 Å (for 148 Ir−C values).[62] The C−O separation of 1.113(11) Å

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observed for **1** is in good agreement with the C−O distances reported for other coinage metal structures (Table 3).

As evident from the values in Table 2, metal−carbon separations in [HB(3,5-$(CF_3)_2Pz)_3$]MCO systems follow the order Cu < Au < Ag. The observed group trend is consistent with the results from the IR spectroscopic study. This trend is also in good agreement with the previous experimental and theoretical results.[8,16,20,63−66] For example, metal−CO distances for Cu(CO)Cl (with a tetrahedral Cu center), Au(CO)Cl (linear geometry at Au), and [Ag(CO)][B$(OTeF_5)_4$] (three-coordinate Ag atom) are 1.82(2), 1.93(2), and 2.10(1) Å, respectively.[16,20,46] Interestingly, the difference in metal−C distances (0.17 Å) in the two molecules [Ag(CO)][B$(OTeF_5)_4$] and Au(CO)Cl is very similar to that seen with the pseudotetrahedral species [HB(3,5-$(CF_3)_2Pz)_3$]AgCO and [HB(3,5-$(CF_3)_2Pz)_3$]AuCO. The Ag(I) ionic radius (0.68 Å) is only slightly longer than that of Au(I) (0.62 Å).[64,66] Therefore, a greater reduction in metal−C separation in **1** suggests a stronger metal−C bond in the gold(I) analog compared to [HB(3,5-$(CF_3)_2Pz)_3$]AgCO. Very high relativistic effects, higher polar contributions, and more covalent bonding interactions with gold are some of the reasons commonly attributed to the stronger Au−C bonds.[18,22,64] Unlike the cases of Ag and Au, the difference in bond strength between Cu(I)−CO and Au(I)−CO may be relatively minor. It is also possible to consider the results from two high-level ab initio calculations performed by two separate groups which report the metal−CO bond dissociation energies for $[CuCO]^+$ and $[AgCO]^+$ as 33 and 19 kcal mol^{-1} and for $[AuCO]^+$ and $[AgCO]^+$ as 45 and 21 kcal mol^{-1}, respectively.[64,67] Furthermore, a recent theoretical study involving MCH_3 and MC_6H_5 (M = Cu, Ag, Au) predicts a metal−carbon bond strength order of Au > Cu > Ag.[65] However, unlike the situation for gold(I) or silver(I), we note that there are many reports of stable copper(I) carbonyl adducts.[7,9−12,68−71]

Compound **1** represents the first structurally characterized gold(I) poly(pyrazolyl)borate.[72−74] However, related Au(III) adducts are known. This allows a comparison of Au−N bond lengths of **1** with square planar complexes such as [η^2-HB$(Pz)_3$]-$AuMe_2$ (2.13(1), 2.12(2) Å) and [η^2-B$(Pz)_4$]$AuMe_2$ (2.098(6), 2.113(7) Å).[75,76] Copper−nitrogen bond distances in [HB(3,5-$(CF_3)_2Pz)_3$]CuCO are significantly shorter than Ag−N and Au−N bond lengths observed for [HB(3,5-$(CF_3)_2Pz)_3$]AgCO and [HB(3,5-$(CF_3)_2Pz)_3$]AuCO (Table 2). Metal−nitrogen distances between **1** and [HB(3,5-$(CF_3)_2Pz)_3$]AgCO are not very different. The boron center adopts a tetrahedral geometry, and the B−N distances range from 1.548(9) to 1.566(8) Å. The nonbonded Au···B separation is 3.442 Å, which is the highest among those of the three coinage metal carbonyl adducts of the [HB(3,5-$(CF_3)_2Pz)_3$]$^-$ ligand.

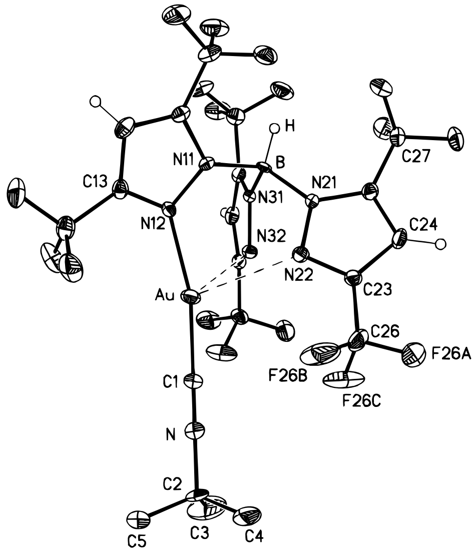

Figure 4. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]AuCNBu^t (**2**). Hydrogens on the methyl groups have been omitted.

The gold isocyanide complex **2** was also characterized by NMR and IR spectroscopy and by X-ray crystallography. The room-temperature ^{1}H NMR spectrum of [HB(3,5-$(CF_3)_2Pz)_3$]-AuCNBu^t (**2**) exhibits a peak at δ 6.94, which corresponds to the pyrazole ring hydrogens. Compound **2** also shows a sharp singlet at δ 1.59 for the hydrogens of the *tert*-butyl group. The ^{19}F NMR spectrum exhibits two resonances for the CF_3 groups on the pyrazole ring 3- and 5-positions. The IR spectrum displays a strong absorption band at 2248 cm^{-1}. This is the highest ν_{CN} value observed for the [HB(3,5-$(CF_3)_2Pz)_3$]MCNBu^t series (M = Ag, 2214 cm^{-1}; M = Cu, 2196 cm^{-1}).[17,30] Interestingly, the carbonyl adducts exhibit a different trend (Ag > Au ≥ Cu). The ν_{CN} of **2** can be compared to the corresponding values for ClAuCNBu^t (2250 cm^{-1}), Au_2(dmb)-$(CN)_2$ (2290 cm^{-1}; dmb = 1,8-diisocyano-*p*-menthane), and $Au_2(tmb)Cl_2$ (2239 cm^{-1}; tmb = 2,5-dimethyl-2,5-diisocyanohexane).[77−79]

Compound **2** crystallizes as well-separated monomers. The ORTEP drawing of [HB(3,5-$(CF_3)_2Pz)_3$]AuCNBu^t is illustrated in Figure 4.[53] A view down the C1−Au axis is presented in Figure 5 (only selected atoms are included). Interestingly, compound **2** shows a structure very different from that of the Cu(I) or Ag(I) (see Figure 6) analog or from those of the related carbonyl adducts. The coordination geometry of Au can be best described as bent rather than pseudotetrahedral. The Au−N distances show notable differences in length with one short bond length of 2.077(6) Å and two long separations of 2.734 and 2.787 Å. The C1−Au−N12 angle (165.7(3)°) is significantly distorted from the typical 180° angle observed in linear molecules. Gold has a very high tendency to form linear complexes.[18,80] In fact, similar behavior has been noted for many other gold(I) complexes involving multidentate ligand systems.[80] Although, these examples do not involve poly-

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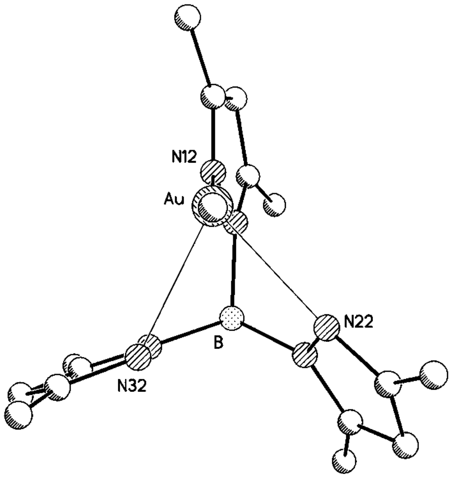

Figure 5. View of [HB(3,5-$(CF_3)_2Pz)_3$]AuCNBu^t down the C1−Au axis (only selected atoms included).

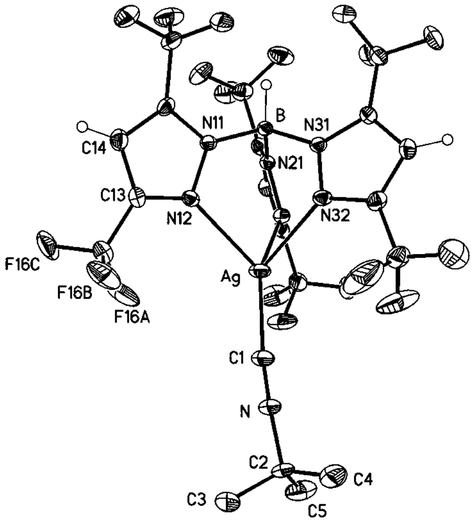

Figure 6. Molecular structure of [HB(3,5-$(CF_3)_2Pz)_3$]AgCNBu^t, with hydrogens on the methyl groups omitted. Reproduced with permission from ref 17. Copyright 1995 American Chemical Society.

(pyrazolyl)borates of gold(I), there is one such example involving a silver(I) bis(pyrazolyl)borate, [$Ph_2B(Pz)_2$]AgP(C_6H_4Me-*p*)$_3$ (Ag−N, 2.194(4), 2.411(4) Å; P−Ag−N, 160°).[81]

The Au−C1−N angle (178.8(8)°) in **2** is linear within the experimental error. The Au−C1 distance is 1.939(8) Å.[82] Similar Au−CNR (R = alkyl group) distances have been observed previously, e.g., in NCAuCNBu^t (1.93(3) Å) and ClAuCNBu^t (1.92(1) Å).[83,84] The Au−N12 distance is relatively short, but much shorter Au−N distances are known in the literature.[22] The boron center is tetrahedral and the B−N distances range from 1.532(9) to 1.585(10) Å.

Metal−CNBu^t distances follow a trend similar to that of the metal−CO distances, with the Cu distance being the shortest followed by the Au and Ag distances. The metal−CNBu^t bond length is longer than the corresponding metal−CO disatnce (e.g., 1.939(8) Å in **2**, 1.862(9) in **1**). The most notable difference in the structures of [HB(3,5-$(CF_3)_2Pz)_3$]MCO and [HB(3,5-$(CF_3)_2Pz)_3$]MCNBu^t (where M = Cu, Ag, or Au) is in the coordination geometry of the gold atom in **2**. That the Au center in **2** adopts a bent geometry while **1** prefers a tetrahedral arrangement may be an indication of reduced electrophilicity of the metal center due to the presence of the relatively better σ-donor and weaker π-acceptor CNBu^t ligand.[1,24]

The stability of [HB(3,5-$(CF_3)_2Pz)_3$]Au complexes also deserves a comment. Compound **1** shows the lowest stability relative to the closely related complexes [HB(3,5-$(CF_3)_2Pz)_3$]CuCO and [HB(3,5-$(CF_3)_2Pz)_3$]AgCO. For example, the copper(I) analog is stable both as a pure solid and in solution. In contrast, solid samples or hexane solutions of **1** kept even in a −20 °C freezer show some decomposition over a period of several hours. The silver analog shows no signs of decomposition under similar conditions. [HB(3,5-$(CF_3)_2Pz)_3$]CuCNBu^t and [HB(3,5-$(CF_3)_2Pz)_3$]AgCNBu^t are also stable complexes whereas the Au analog shows fairly low stability.[17,30] Our attempts to prepare [HB(3,5-$(CF_3)_2Pz)_3$]AuPPh$_3$ from **1** and PPh$_3$ did not result in an isolable product. One possible reason for the instability of [HB(3,5-$(CF_3)_2Pz)_3$]AuL (L = CO, CNBu^t, PPh$_3$) systems regardless of the nature of L may be associated with the tris(pyrazolyl)borate ligand itself. Stable gold complexes of isocyanides, phosphines, etc. are well-known.[80] Even gold carbonyls such as Au(CO)SO_3F (stable to 190 °C) and [Au$(CO)_2$][Sb_2F_{11}] (stable to 130 °C) show fairly high thermal stability.[8] However, to our knowledge, there are no stable tris(pyrazolyl)borate complexes of Au(I) in the literature.[72] In contrast, Ag(I) and in particular Cu(I) poly(pyrazolyl)borates are well-known.[28,68,72−74,85−87] Often, the attempted synthesis of Au(I) complexes of poly(pyrazolyl)borates has resulted in decomposition products.[74] Therefore, lower thermal stability of **1** and **2** may at least be partly attributed to a decomposition pathway associated with the hydrotris(pyrazolyl)borate ligand framework. More importantly, the instability may not be due to a weakness in the Au−C interaction.

Our observations concerning the reactivity of the [HB(3,5-$(CF_3)_2Pz)_3$]MCO complexes provide some insights into the strength of the M−CO interactions. The [HB(3,5-$(CF_3)_2Pz)_3$]CuCO adduct is stable in aromatic solvents. However, [HB(3,5-$(CF_3)_2Pz)_3$]AgCO loses CO in aromatic solvents such as toluene, resulting in the formation of [HB(3,5-$(CF_3)_2Pz)_3$]Ag(η^2-C_7H_8). This process is reversible. Upon exposure to CO, [HB(3,5-$(CF_3)_2Pz)_3$]Ag(η^2-C_7H_8) easily reverts back to the CO adduct.[17] Reversible CO absorption has been observed in silver(I) carbonyl systems such as [(C_5H_5)Co{P(O)$(OEt)_2$}$_3$]AgCO and [AgCO][B$(OTeF_5)_4$].[14,48] Although, the lower stability of **1** did not permit us to explore its reactivity in detail, the fact that we were able to crystallize **1** from a solution containing small amounts of benzene or toluene without displacing CO indicates a relatively strong Au−CO interaction. These preliminary results are in harmony with the data from the X-ray structural and IR spectroscopic study.

Summary

We have reported the synthesis, isolation, and X-ray crystal structural characterization of the first (tris(pyrazolyl)borato)-

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(82) Thermal motion correction using a rigid-body model (SHELXTL 5.0 which uses the method of: Shomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, *B24*, 63) gave Au−C1 1.943(5) Å, Au−N12 2.082(5) Å, and C1−N 1.134 (3) Å with R_G = 0.396; a riding model (SHELXTL 5.0 which uses the method of: Johnson. *Crystallogr. Comput.* **1970**, 220) gave Au−C1 1.944 Å with a lower limit of 1.939 Å and an upper limit of 2.036 Å.

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gold(I) complexes as their carbonyl and isocyanide adducts. This study also permited the analysis of group trends among an isoleptic series of coinage metal carbonyls. In general, silver shows the weakest metal−CO interaction and the longest metal−CO bond distance. The ^{13}C NMR and the IR spectroscopic data for coinage metal carbonyls of $[HB(3,5-(CF_3)_2Pz)_3]^-$ show significantly reduced metal-to-CO π-donation. The solid state structure of the gold isocyanide adduct **2** is very different from those of the coinage metal carbonyl or silver and copper isocyanide complexes of $[HB(3,5-(CF_3)_2Pz)_3]^-$. However, the room-temperature NMR spectroscopic data are very similar among copper, silver, and gold isocyanide analogs.

One particularly attractive feature associated with the use of tris(pyrazolyl)borates is the possibility of investigating the ligand substituent effects. The properties of the metal adducts could be altered through variations of the steric and electronic properties of the substituents on the tris(pyrazolyl)borate ligand framework.[72] In fact, a series of closely related Cu(I)−CO adducts have been prepared using tris(pyrazolyl)borate ligands.[11,12,71,88,89] The carbonyl stretching frequency closely follows the relative basicity of the tris(pyrazolyl)borate ligand (and the electron-donor properties of the substituent). The Cu(I)−CO and Cu(I)−CNBu^t adducts derived from $[HB(3,5-(CF_3)_2Pz)_3]^-$ show relatively high ν_{CO} and ν_{CN} frequencies.[12,30] However, the copper carbonyl complexes derived from the electron-rich, nonfluorinated tris(pyrazolyl)borates show ν_{CO} values in the typical classical carbonyl region.[12] Whether a similar group of compounds can be synthesized using silver(I) and gold(I) ions still remains to be seen.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for **1** and **2** (11 pages). Ordering information is given on any current masthead page.

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