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Chemistry of Trifluoromethylated Tris(pyrazolyl)borate: Synthesis and Characterization of Carbonyl and Isonitrile Adducts of Silver(I)

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Among the isolable carbon monoxide adducts of coinage metals, the silver carbonyls represent the most recently reported group.[1−4] Structurally characterized silver carbonyl complexes are extremely rare, and the only examples in the literature include $[Ag(CO)][B(OTeF_5)_4]$ and $[Ag(CO)_2][B(OTeF_5)_4]$.[5,6] Interestingly, the Ag−CO interaction in the reported compounds is very weak, and as a result, they lose CO under a vacuum or in the presence of competing ligands.[3] Metal isonitriles have often been compared to metal carbonyls, perhaps due to the isoelectronic relationship between CO and CNH.[7,8] In contrast to CO, isonitriles seem to form much stronger adducts with Ag. Several silver isonitrile complexes have been reported, including a few of their crystal structures.[9−15] However, most of them are limited to isonitriles of silver halides or silver salts of weakly coordinating anions, such as PF_6^-.[16]

Recently, we reported the synthesis and structural characterization of a tris(pyrazolyl)borate ligand, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (where $[HB(3,5\text{-}(CF_3)_2Pz)_3]$ = hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate), containing six highly electron-withdrawing CF_3 substituents.[17] Despite the important and often unique reactivity shown by fluorinated ligands,[18−22] relatively little attention has been paid to such poly(pyrazolyl)borate systems.[23] In the present communication, we report the successful use of this ligand to stabilize a silver(I) carbonyl complex, $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ (**1**). The synthesis and structural data of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCN\text{-}t\text{-}Bu$ (**2**) are also presented. This study represents the first example where closely related silver adducts of CO and CNR have been isolated and structurally characterized.

The treatment of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Na$ with AgOTf in THF, followed by extraction into toluene, leads to a colorless solid in quantitative yield. The NMR and the elemental analysis data indicate the formation of a toluene adduct of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ (**3**).[24] The treatment of **3** with CO (~1 atm) in hexane at room temperature, followed by cooling at −25 °C, led to colorless crystals of **1**.[25] Although compound **1** is stable at room temperature under CO, it very slowly loses CO under reduced pressure. The CO loss is much faster from the solution state. For example, the evolution of gas was evident when **1** was dissolved even in a weakly coordinating solvent such as C_6D_6. Upon exposure to CO, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ readily coordinates CO and reverts back to **1**. This reversible carbon monoxide absorption has been observed in $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ complexes obtained by Strauss *et al.* using pentafluorooxotellurate ($OTeF_5^-$) and related anions such as $B(OTeF_5)_4^-$, $Zn(OTeF_5)_4^{2-}$, $Nb(OTeF_5)_6^-$, and $Ti(OTeF_5)_6^{2-}$.[3] Similar behavior has also been observed in solution species such as $[(C_5H_5)Co\{P(OEt)_2O\}_3]AgCO$.[10] Interestingly, the copper species derived from tris(pyrazolyl)borates or $[(C_5H_5)Co\{P(OEt)_2O\}_3]^-$ from significantly more stable CO adducts.[1,10,26]

The IR spectrum of **1** in hexane shows a strong absorption at 2162 cm^{-1}, corresponding to the carbonyl stretching frequency. The solid state spectrum of *pure crystals* of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ consisted of a band at 2178 cm^{-1} (^{13}CO side band at 2128 cm^{-1}). Surprisingly, a small shoulder was noticed (around 2163 cm^{-1}) on the main peak. Although we cannot provide a definitive reason for the appearance of this unexpected shoulder peak in the IR spectrum of **1**, similar behavior has been reported previously in the solid samples and has been attributed to an intermolecular phenomenon.[27−30] The ν_{CO} of $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCO$ (**1**) can be compared to those of the structurally characterized species $[Ag(CO)][B(OTeF_5)_4]$ (ν_{CO} = 2204 cm^{-1}) and $[Ag(CO)_2][B(OTeF_5)_4]$ (ν_{CO} = 2198 cm^{-1}).[3] Although the carbonyl stretching frequency of **1** is lower than the ν_{CO} values observed for $[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ species, it is significantly higher than that in free CO (2143 cm^{-1}) and much closer to the carbonyl stretching frequency of $BH_3{\cdot}CO$ (ν_{CO} = 2165 cm^{-1}).[31−33] This suggests very little or no $Ag{\rightarrow}CO$ π-back-bonding interaction in **1**. The ν_{CO} in [HB(3,5-

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(24) **3**: mp 95−96 °C, ^1H NMR (C_6D_6, 300 MHz, TMS) δ 2.11 (s, 3 H, CH_3), 6.28 (s, 3 H, Pz), 7.02−7.13 (m, 5 H, Ar−H); IR 2608 (BH) cm^{-1}. Anal. Calcd for $C_{22}H_{12}AgBF_{18}N_6$: C, 32.18; H, 1.47; N, 10.24. Found: C, 32.17; H, 1.03; N, 10.50.

(25) **1**: mp >74 °C dec, ^1H NMR (CD_2Cl_2, TMS) δ 6.96 (s, 3 H, Pz); IR (hexane) 2162 (CO), 2612 (BH) cm^{-1}; IR (Nujol mull) 2178, 2163 sh (CO), 2616 (BH) cm^{-1}. Anal. Calcd for $C_{16}H_4AgBF_{18}N_6O$: C, 25.39; H, 0.53; N, 11.10. Found: C, 25.29; H, 0.29; N, 11.24.

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(30) Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed.; John Wiley & Sons: New York, 1990; p 341. See also ref 31, p 174. Better mixing (longer time) in Nujol mull resulted in the increased intensity of the shoulder band to give two partially resolved (separation was evident only at the apex) peaks at 2172 and 2167 cm^{-1}. Similar splitting was noticeable on the band corresponding to the ^{13}CO signal (2124, 2118 cm^{-1}). Powdered material showed the same behavior. Although we cannot conclusively rule out all the other possibilities for the appearance of split bands (e.g., Fermi coupling), the lack of splitting in the solution (only a single sharp band at 2162 cm^{-1} in hexane and at 2164 cm^{-1} in CH_2Cl_2) and the splitting in both the ^{12}CO and ^{13}CO bands suggest correlation field effect as the likely cause. See supporting information for the relevant FT-IR spectra.

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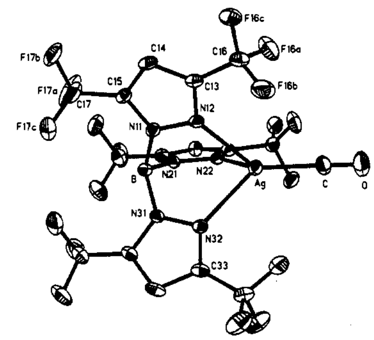

Figure 1. Molecular structure of **1** (ellipsoids are shown at the 30% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag–C 2.037(5), C–O 1.116(7), Ag–N12 2.297(4), Ag–N22 2.320(4), Ag–N32 2.366(4), B–N11 1.558(7), B–N21 1.568(6), B–N31 1.554(6); Ag–C–O 175.6(6), N12–Ag–N22 80.6(1), N12–Ag–N32 83.0(1), N22–Ag–N32 81.2(1), C–Ag–N12 127.0(2), C–Ag–N22 135.4(2), C–Ag–N32 130.4(2).

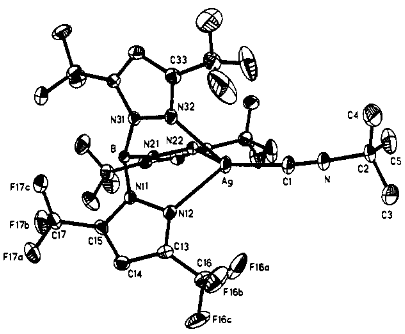

Figure 2. Molecular structure of **2** (ellipsoids are shown at the 30% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag–C1 2.059(4), C1–N 1.139(5), N–C2 1.472(5), Ag–N12 2.349(3), Ag–N22 2.390(3), Ag–N32 2.387(3), B–N11 1.552(5), B–N21 1.564(5), B–N31 1.561(4); Ag–C1–N 173.7(4), C1–N–C(2) 176.2(4), N12–Ag–N22 81.4(1), N12–Ag–N32 81.8(1), N22–Ag–N32 77.1(1), C1–Ag–N12 134.8(1), C1–Ag–N22 133.7(1), C1–Ag–N32 126.9(1).

$(CF_3)_2Pz)_3]AgCO$ (ν_{CO} = 2162 cm^{-1} in hexane) is also much higher than that of $[(C_5H_5)Co\{P(OEt)_2O\}_3]AgCO$ (ν_{CO} = 2125 cm^{-1} in hexane).[10]

The isonitrile adduct $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgCN\text{-}t\text{-}Bu$ (**2**) was prepared by treating **3** with 1 equiv of *t*-BuNC in toluene. It was isolated as a colorless solid in quantitative yield.[34] Compound **2** melts around 170–172 °C and is stable both in solution and as a pure solid at room temperature. This indicates the presence of much stronger Ag–C interaction in **2**. Compound **2** exhibits ν_{CN} at 2214 cm^{-1}. It is significantly higher than the ν_{CN} value observed for free *t*-BuNC (ν_{CN} = 2138 cm^{-1}).[35,36] The ν_{CN} for **2** can be compared to $[B(Pz)_4]AgCN\text{-}t\text{-}Bu$ (ν_{CN} = 2185 cm^{-1})[11] or $[(C_5H_5)Co\{P(OEt)_2O\}_3]AgCN\text{-}t\text{-}Bu$ (ν_{CO} = 2187 cm^{-1}).[10] The relatively higher ν_{CN} for **2** may be a result of increased Lewis acidity of Ag due to the presence of the highly electron-deficient tris(pyrazolyl)borate ligand.

Compounds **1** and **2** have been characterized by X-ray crystallography.[37] The molecular structures of **1** and **2**, with some important structural parameters, are presented in Figures 1 and 2, respectively. Silver centers adopt a distorted tetrahedral coordination. The Ag–C–O and Ag–C–N angles are almost linear at 175.6(6)° and 173.7(4)°, respectively.

The Ag–C bond distance for **1** (2.037(5) Å) can be compared to the Ag–C separations of 2.10(1) Å for $[Ag(CO)][B(OTeF_5)_4]$ and 2.06(5)–2.20(4) Å for $[Ag(CO)_2][B(OTeF_5)_4]$.[3] The C–O distance in **1** (1.116(7) Å) is slightly longer compared to those in $[Ag(CO)][B(OTeF_5)_4]$ (1.077(16) Å) and $[Ag(CO)_2][B(OTeF_5)_4]$ (1.07–1.09 Å). These trends are consistent with the results from infrared studies.

Except for the key differences due to the Ag–CN–*t*-Bu moiety, other structural features of **2** are very similar to those of **1**. The Ag–C and C–N distances in **2** are 2.059(4) and 1.139(5) Å, respectively. To our knowledge, there are no examples of structurally characterized silver(I) isonitriles involving tris(pyrazolyl)borate ligands.[16] However, the Ag–CN bond distance in **2** can be compared with those of compound such as $Ag_2(dmb)_2X_2$ (2.10(2)–2.19(2) Å, where X = Cl, Br, I; dmb = 1,8-diisocyano-*p*-menthane),[12] $Ag_3(dmb)_2I_3$ (2.01(3)–2.16(3) Å),[15] $[Ag_2L'_2](ClO_4)_2$ (average 2.14 Å, where L′ = 2,5-dimethyl-2,5-diisocyanohexane),[14] and $Ag(2,4,6\text{-}t\text{-}Bu_3C_6H_2\text{-}NC)_2PF_6$ (2.075(14) Å).[13] The C–N distance in **2** is closer to the average distance (1.149 Å) found in metal isocyanides.[38] The Ag–C separation in **2** is slightly longer than the corresponding value in the silver carbonyl adduct **1**.

In conclusion, the carbon monoxide and *tert*-butyl isocyanide complexes of silver involving the highly fluorinated tris(pyrazolyl)borate ligand, $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, have been isolated in crystalline form and characterized using X-ray crystallography. These complexes show much higher ν_{CO} and ν_{CN} values compared to their free ligand ($\Delta\nu$ = 35 and 76 cm^{-1}, respectively) and seem to have predominantly σ-type Ag–ligand interaction.[39] We are currently pursuing the synthesis of other metal complexes of trifluoromethylated poly(pyrazolyl)borates and studying the effects of fluoro substituents on their physical properties and chemical reactivity.

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Supporting Information Available: Solution and solid state IR spectra for **1**, tables of crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for **1** and **2** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(34) **2**: mp 170–172 °C, ^1H NMR (C_6D_6, TMS) δ 0.83 (s, 9 H, *t*-Bu), 6.30 (s, 3 H, Pz); IR (Nujol mull) 2214 (CN), 2604 (BH) cm^{-1}. Anal. Calcd for $C_{16}H_4BCuF_{18}N_6O$: C, 29.58; H, 1.61; N, 12.07. Found: C, 29.83; H, 1.45; N, 11.76.

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(37) Crystal data for **1**: orthorhombic, $P2_12_12_1$ with a = 8.1794(5) Å, b = 15.230(1) Å, c = 19.311(1) Å, V = 2405.69(25) Å^3, Z = 4, D_{calc} = 2.090 g cm^{-3}. Data were collected on a Siemens P4 diffractometer at T = 183 K with Mo Kα (λ = 0.710 73 Å) radiation using ω scan technique up to $2\theta_{max}$ = 52°. Of the 3480 reflections measured, 3238 (R_i = 2.53%) were unique. R = 3.15%, R_w = 4.09% for 2969 reflections with $F > 4\sigma(F)$ and 395 parameters. Crystal data for **2**: monoclinic, $P2_1/c$ with a = 11.911(2) Å, b = 23.758(4) Å, c = 10.752(2) Å, β = 104.118(14)°, V = 2950.7(8) Å^3, Z = 4, D_{calc} = 1.828 g cm^{-3}. Data were collected on a Siemens P4 diffractometer at T = 193 K with Mo Kα (λ = 0.710 73 Å) radiation using ω scan technique up to $2\theta_{max}$ = 50°. Of the 6389 reflections measured, 5190 (R_i = 2.45%) were unique. R = 4.06%, R_w = 5.96% for 4392 reflections with $F > 4\sigma(F)$ and 453 parameters.

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