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Gold(I) ethylene complexes supported by electron-rich scorpionates

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Ethylene complexes of gold(I) have been stabilized by electron-rich, κ^2-bound tris(pyrazolyl)borate ligands. Large up-field shifts of olefinic carbon NMR resonances and relatively long C=C distances of gold bound ethylene are indicative of significant Au(I)→ethylene π-backbonding relative to the analog supported by a weakly donating ligand, consistent with the computational data.

Gold plays an important role in the transformations of olefins[1] including ethylene,[2] to more complex molecules. These include hydrogenation, oxidation, hydroamination, diarylation, heteroarylation, cyclopropanation, and aziridination of olefins leading to a variety of substances with new C-C, C-O, C-N and other C-hetero atom bonds. The gold-olefin π-complexes are the commonly invoked intermediates in many of these processes,[3] which result in the activation of the C=C bond by the soft Lewis acid gold towards various nucleophiles and transformations.[4] Gold olefin bonding (especially comprising ethylene) has also attracted the attention by computational chemists for many years.[5]

Despite the interest, reliable structural or spectroscopic information on gold-ethylene complexes is quite limited.[6] Furthermore, structurally authenticated ethylene complexes of gold in the literature involve either cationic gold centers[7] or fluorinated and weakly coordinating ligand supports (e.g., [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**1**), Figure 1),[8] and feature molecules with enhanced Lewis acidity at the metal (Table S1). Considering the current interest and dearth on information of gold-ethylene complexes containing relatively electron-rich gold sites, we embark on a project to uncover molecules with such features. The tris(pyrazolyl)borates (commonly referred to as scorpionates)[9] were chosen as the supporting ligands for this

purpose because, their steric-electronic properties can be altered readily spanning a wide spectrum by varying the substituents on the pyrazolyl moieties,[9] and also [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**1**)[8a] featuring a very weakly coordinating ligand representing an electron-poor extreme is available for comparisons. The CO stretching frequencies of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Cu(CO),[10] [HB(3,5-(Ph)$_2$Pz)$_3$]Cu(CO),[11] and [HB(3-(i-Pr),5-(t-Bu)Pz)$_3$]Cu(CO)[12] of 2137, 2086 and 2057 cm^{-1}, illustrate the broad electronic tuning one can achieve at a metal in a related series of neutral, copper(I) carbonyl complexes using scorpionates. Furthermore, gold complexes supported by scorpionates are also useful in catalysis.[13]

In this paper, we describe the use of relatively electron-rich tris(pyrazolyl)borates [HB(3,5-(Ph)$_2$Pz)$_3$]$^-$ and [HB(3,5-(t-Bu)$_2$Pz)$_3$]$^-$ to stabilize ethylene on gold(I), and probe the supporting ligand effects on the structures and bonding of the resulting complexes [HB(3,5-(Ph$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**2**).
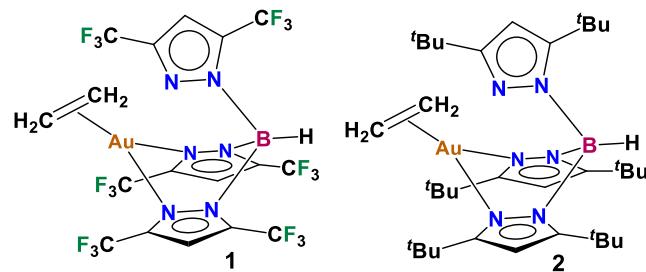
Figure 1. Gold(I) ethylene complexes of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**1**) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**2**).

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The [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) has been synthesized by treating [HB(3,5-(Ph)$_2$Pz)$_3$]K with gold(I) chloride in CH$_2$Cl$_2$ saturated with ethylene at -20 °C (ESI). The related [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) was prepared in hexane using a similar process. Both these ethylene complexes are not very stable in solution, particularly in halogenated solvents, at room

temperature for prolonged periods. For example, the more reactive [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) decomposes vigorously in halogenated solvents like CHCl$_3$. The [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) shows about 30% decomposition after 12h in CH$_2$Cl$_2$. ^{1}H NMR signal of the ethylene protons of [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) in CD$_2$Cl$_2$ and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) in toluene-d$_8$ exhibited resonances at δ 2.61 and 3.00 ppm, respectively. Interestingly, this signal in the latter species appears as an AA'BB' multiplet (Figure S2), indicating that the ethylene moiety is in an environment with hindered free rotation, likely constrained by the bulky t-butyl groups that surround the coordination pocket. These peaks are significantly upfield shifted relative to the free ethylene (δ 5.40 ppm in CD$_2$Cl$_2$ and 5.25 ppm in toluene-d$_8$)[14] or [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) (δ 3.81 ppm). A large upfield shift of ethylene protons of [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) is impressive considering that it is not affected by ring-currents from flanking aryl moieties as in [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) that could contribute to the shielding. The ^{13}C NMR signal of the ethylene carbons of [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) was detected at δ 55.3 and 56.9 ppm, respectively, and represent a very large metal coordination induced upfield shifts relative to free ethylene (i.e., Δδ of 67.9 and 66.0 ppm for these two complexes; Δδ = δ of free ethylene – δ of coordinated ethylene). They are also notably shielded than the corresponding values of Au(I)-C$_2$H$_4$ complexes supported by electron-withdrawing scorpionate ligands (e.g., [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) (δ 63.7 ppm), Table 1 and Table S1). These NMR chemical shifts suggest that gold(I) exerts notable shielding effects on coordinated ethylene through Au→ethylene π-back bonding.[6b, 6c, 15] The effects are however comparatively smaller when contrasted with d^{10}-molecules involving zero-valent group 10 metal sites. For example, [{MeC(2,6-(i-Pr)$_2$Ph)N}$_2$]Ni(C$_2$H$_4$), [i-Pr$_2$Im]$_2$Ni(C$_2$H$_4$) and (Ph$_3$P)$_2$Pt(C$_2$H$_4$) display their ethylene carbon resonances at δ 31.8, 24.85, and 39 ppm, respectively.[16]

Table 1. Selected bond distances (Å), angles (°), and NMR spectroscopic data (ppm). The non-bonded Au•••N separation in italics.

Parameter	[HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$)	[HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$)	[HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$)
C=C	1.410(5)	1.413(7)	1.380(10)
Au-C	2.092(3)	2.082(4)	2.096(6)
	2.112(3)	2.100(5)	2.108(6)
Au-N	2.180(3)	2.177(4)	2.221(5)
	2.230(3)	2.211(3)	2.224(5)
	(2.876(3))	*(2.858(4))*	*(2.710(4))*
C-Au-C	39.20(14)	39.49(18)	38.3(3)
N-Au-N	85.59(10)	86.12(13)	86.05(16)
^{1}H H_2C=	3.00	2.61	3.81
^{13}C H$_2$$C$=	56.9	55.3	63.7
Ref	This work	This work	[8a]

Both these gold(I) complexes afford crystalline material suitable for X-ray crystallographic analysis. X-ray structures of [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**2**)

are illustrated in Figure 2 (see also ESI). The ethylene coordinates to gold in a typical η^2-fashion. The gold centers adopt a trigonal planar geometry while tris(pyrazolyl)borates coordinate to gold in $κ^2$-fashion, which is not the common mode of chelation (in contrast to $κ^3$) for this ligand family.[9] These gold-ethylene complexes, regardless of the electron-rich or poor nature of the pyrazolyl donor sites, prefer 3-coordinate geometry (as evident from the sum of angles at Au of ~360°) over the tetrahedral option. Computational data also support this observation (see below). Selected bond distances and angles are listed in Table 1.
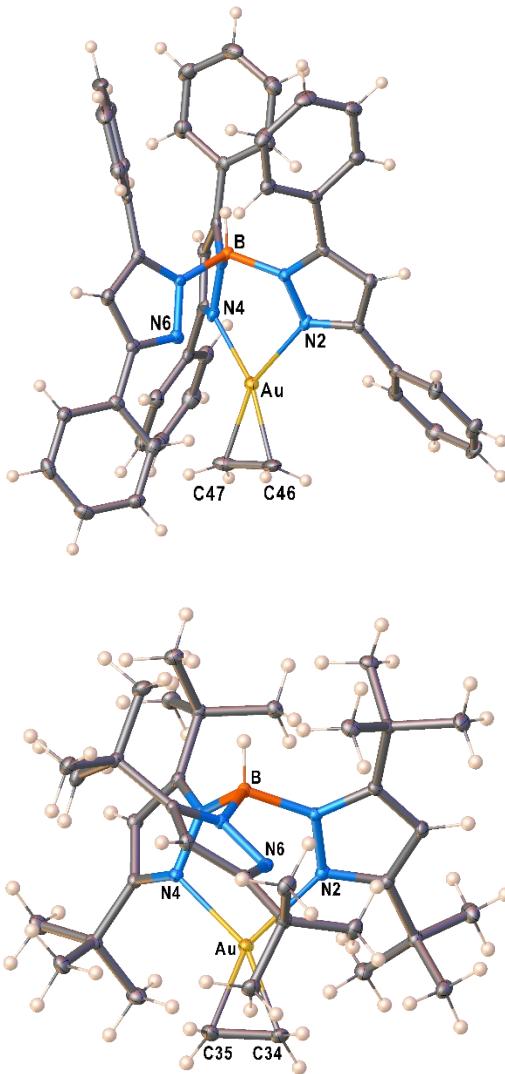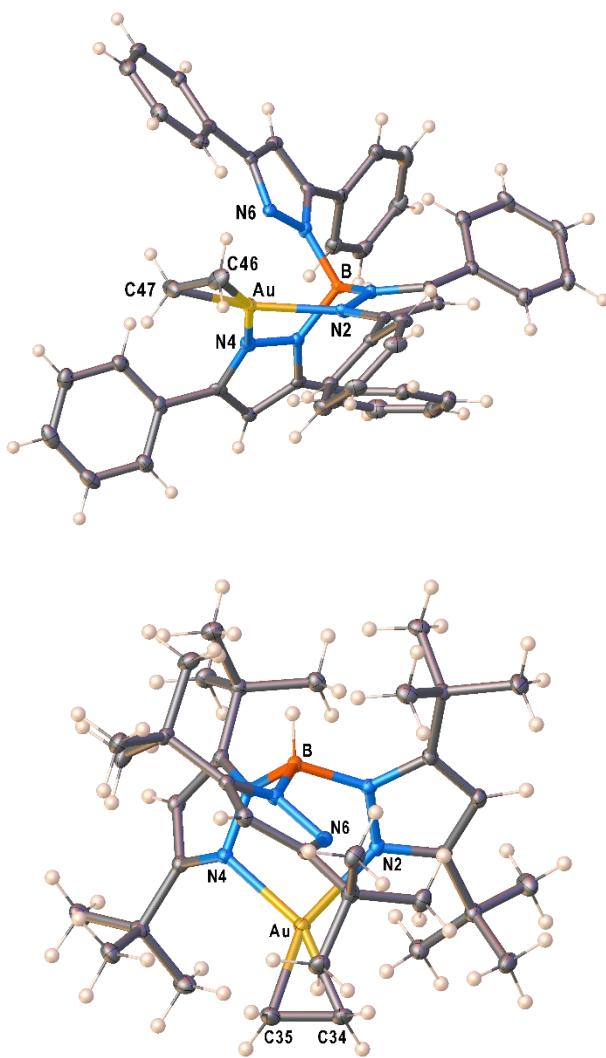
Figure 2. X-ray crystal structures of [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) (top) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) (**2,** bottom).

The C=C bond of the coordinated ethylene in both [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) is significantly longer than that for the free ethylene (1.3305 Å). Furthermore, they are at the longest end among gold-ethylene complexes, except for that reported by Daugulis and co-workers for a cationic, diimine-gold ethylene complex with a C=C of 1.455(13) Å (but it has a ^{13}C shift of δ 65.4 ppm, indicating comparatively poor Au→ethylene π-backdonation).[7c]

Unfortunately, deeper analysis of experimentally observed C=C bond distance variations is not very useful here because, subtle C=C bond distance differences due to metal-ethylene σ/π-bonding among different metal complexes are overshadowed by standard uncertainties (esds) associated with that measurement. For example, the ethylene C=C distance of 1.420(4) Å for [i-Pr$_2$Im]$_2$Ni(C$_2$H$_4$), which displays one of the most upfield-shifted olefinic ^{13}C resonances (δ 24.85 ppm),[16b] is not significantly different statistically from those observed for [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$).

The gold(I)-ethylene bonding was evaluated via DFT calculations including relativistic corrections, which renders a bond energy of -60.6, -64.8, and -64.3 kcal.mol^{-1} for [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$), [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$), and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$), respectively (Tables S8-S9). In addition, the corresponding energies computed for [HB(Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(CH$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) are -66.0 and -66.1 kcal.mol^{-1}, respectively. Somewhat low value for [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$) could be a result of steric effects. Further evaluation via the energy decomposition analysis (EDA) reveals that electrostatic interactions contribute to ~61% while covalent bonding character (based on Au←π-C$_2$H$_4$ σ-donation and Au→π*-C$_2$H$_4$ backdonation bonding schemes) represents ~36% of the overall stabilization energy (Figure S9, Table S8). Furthermore, backdonation is the major component that contributes to ~ 49-52% of the total covalent bonding interaction while Au←C$_2$H$_4$ σ-donation is the smaller contributor with ~ 38-31% of the interaction, showing that the π*-backbonding is significant in these gold-ethylene complexes.

A comparison of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(CH$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) bearing weakly and strongly donating scorpionates (focusing on these two because they are less affected by steric effects of substituents at pyrazolyl ring 3,5-positions that could interfere with Au-ethylene bonding) shows a clear difference in donation and backdonation constituents as evident from the corresponding percentage contributions to the total ΔE_{orb} of 37.8% and 48.8% for the former molecule and 30.9% and 57.9% for the latter (featuring relatively electron-rich gold site). These findings are reflected in the population of π_1 and $\pi*_2$ ethylene orbitals affected by Au←π-C$_2$H$_4$ σ-donation and Au→π*-C$_2$H$_4$ backdonation, respectively, with values 1.47/0.31 ē and 1.54/0.47 ē for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) and [HB(3,5-(CH$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$). The calculated $v_{C=C}$ (1480 and 1492 cm^{-1}) and ^{13}C NMR shift of the ethylene carbon (δ 50.5 and 66.6 ppm) are also consistent with the results of the bonding analysis (Table S8).

The overall electron density reorganization is depicted in Figure 3, obtained from the difference in electron density of each constituent fragment before and after ethylene coordination. It leads to a charge depletion at the Au center and π_1 orbital of C$_2$H$_4$, and a charge accumulation at the ethylene backbone. In addition, a charge accumulation is observed at sides of the Au-C=C plane due to the Au→π*-C$_2$H$_4$ backbonding component of the interaction.

A comparison between the relaxed κ^2- and κ^3- coordination modes of the tris(pyrazolyl)borate ligand on gold indicates the latter to be dis-favoured owing primarily to the decrease in the Au-ethylene bond energies (Table S9). The relative energy difference between κ^2- and κ^3- structures for [HB(3,5-(t-Bu)$_2$Pz)$_3$]Au(C$_2$H$_4$), [HB(3,5-(Ph)$_2$Pz)$_3$]Au(C$_2$H$_4$), and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Au(C$_2$H$_4$) amounts to 11.0, 9.1 and 6.2 kcal.mol^{-1}, respectively.

[HB(3,5-(t-Bu)₂Pz)₃]Au(C₂H₄)

[HB(3,5-(CH₃)₂Pz)₃]Au(C₂H₄)

[HB(3,5-(CF₃)₂Pz)₃]Au(C₂H₄)
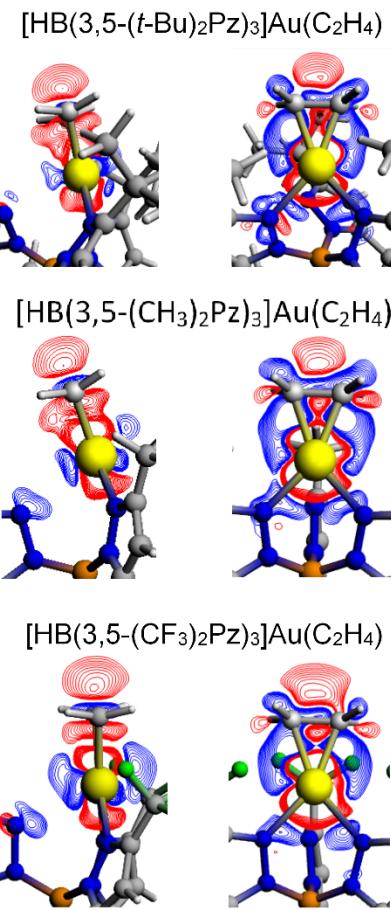
Figure 3. Two views of the electron density re-organization upon gold-ethylene bond formation. Mainly the gold-ethylene moiety is highlighted for clarity. Plane bisecting the C=C bond (Left), and lying on the Au-C=C plane (Right). **Red**: Charge depletion. **Blue**: Charge accumulation. Specific details such as the population of π and π^* orbitals affected by Au$\leftarrow\pi$-C_2H_4 σ-donation and Au$\rightarrow\pi^*$-C_2H_4 backdonation are given in ESI.

In summary, ethylene complexes of gold(I) have been stabilized for the first time by electron-rich, tris(pyrazolyl)borate ligands [HB(3,5-(Ph)₂Pz)₃]⁻ and [HB(3,5-(t-Bu)₂Pz)₃]⁻ and characterized by NMR spectroscopy and X-ray crystallography. The carbon NMR resonance of the gold bound ethylene display large upfield shifts relative to the corresponding peak of the free ethylene, and appears upfield from the signal of [HB(3,5-(CF₃)₂Pz)₃]Au(C₂H₄), indicating relatively high Au$\rightarrow$ethylene backbonding. X-ray crystal structures reveal that the gold atom these complexes bind to scorpionate in κ²-fashion, and ethylene in η²-fashion resulting in significant lengthening of ethylene C=C bond distances. Analysis of the bonding scheme from relativistic DFT calculations indicates that the Au$\rightarrow\pi^*$-C_2H_4 backbonding is the larger contributor in comparison to the Au$\leftarrow\pi$-C_2H_4 σ-donation. The σ/π bonding interaction between the Au(I) and ethylene can be further fine-tuned by the strongly and weakly donating supporting ligands, as demonstrated with tris(pyrazolyl)borates in this work. We are currently exploring the chemistry of gold-alkene complexes involving even more electron-rich gold sites using different supporting ligands and their chemistry.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Details of synthesis, characterization, and computational work, crystallographic data and CIF (CCDC 2045804-2045805) are provided in ESI.

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