Gold Ethylene Complexes

DOI: 10.1002/ange.200703328

Thermally Stable Gold(I) Ethylene Adducts: [(HB{3,5-$(CF_3)_2Pz$}$_3$)-Au(CH_2=CH_2)] and [(HB{3-(CF_3),5-(Ph)Pz}$_3$)Au(CH_2=CH_2)]**

H. V. Rasika Dias and Jiang Wu*

In memory of Dmitry M. Rudkevich

Despite the significant interest, isolable gold(I) ethylene complexes are exceedingly rare.[1–6] Literature available on coinage metal (Cu^I, Ag^I, Au^I) ethylene complexes also gets increasingly sparse moving down the group towards gold. For example, Thompson et al. in 1983[7] and our group in 1997[8] reported the first crystal-structural data on the ethylene adducts of copper(I) and silver(I), respectively. Since then, several copper(I) ethylene complexes[9–18] and a few well authenticated silver(I) ethylene adducts[19–23] have been described. However with gold(I), even complexes of substituted olefins are quite limited, and structurally characterized ethylene adducts are unknown.[3,4,24–36]

Herein, we report the synthesis and X-ray crystal structures of two remarkably stable gold(I) ethylene complexes (Figure 1) that are easily obtained by using tris(pyrazolyl)borates $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]^-$ (where $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate) and $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$ as supporting ligands.[37–39] The treatment of $[HB\{3,5\text{-}(CF_3)_2Pz\}_3]Na$ with gold(I) chloride under an ethylene atmosphere led to the gold(I) ethylene complex $[(HB\{3,5\text{-}(CF_3)_2Pz\}_3)Au(C_2H_4)]$ (**1**) in good yield. It is a colorless solid which does not lose ethylene under reduced pressure. Crystals of this compound can be handled in open air for short periods without any apparent signs of decomposition.

The ^{1}H NMR spectrum of **1** in C_6D_{12} or $CDCl_3$ exhibited a resonance at $\delta = 3.81$ ppm, which could be assigned to the protons of the ethylene moiety. The ^{1}H NMR spectrum taken in C_6D_6 (a π-donor solvent) also displays this peak at $\delta =$ 3.59 ppm. More importantly, no free ethylene signal (expected at $\delta = 5.24$ ppm in C_6D_6 under similar conditions)[10] was detected in such solutions. A $CDCl_3$ solution of **1** treated with excess ethylene exhibited two sharp signals at $\delta = 3.81$ and 5.39 ppm for coordinated and free ethylene,

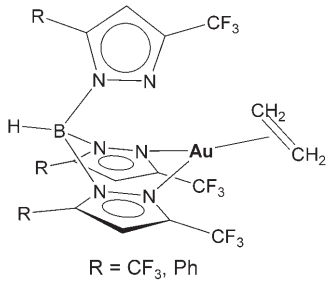

Figure 1. Gold(I) ethylene complexes $[(HB\{3,5\text{-}(CF_3)_2Pz\}_3)Au(C_2H_4)]$ (**1**) and $[(HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3)Au(C_2H_4)]$ (**2**).

signifying no associative alkene exchange on the NMR time scale. These NMR data also indicate that the ^{1}H NMR resonance arising from the ethylene protons shift quite significantly ($\Delta\delta(H) = \delta(H)_{complex} - \delta(H)_{ethylene} = -1.6$ ppm) upfield upon coordination to gold(I). The ^{13}C NMR signal of the ethylene of **1** in $CDCl_3$ was detected at $\delta = 63.7$ ppm ($^1J_{C-H} = 165$ Hz), which is shifted significantly upfield relative to that of the free ethylene ($\delta = 123.5$ ppm).[10]

The X-ray structure of **1** shows a gold ion with trigonal-planar coordination geometry bonded to an ethylene in a typical η^2-fashion with Au–C bond lengths of 2.096(6) and 2.108(6) Å (Figure 2). The C=C bond of the coordinated ethylene (1.380(10) Å; corrected value for libration 1.381 Å) is slightly longer than that for the free molecule (1.313 Å, corrected for libration).[20,40] These Au–C and C=C distances are in good agreement with the calculated values for the $[Au(bipy)(C_2H_4)]^+$ ion (bipy = 2,2′-bipyridine) and the experimental data of the related styrene adducts.[4] The tris(pyrazolyl)borate ligand coordinates to gold in κ^2-fashion with Au–N distances of 2.221(5) and 2.224(5) Å, while the nitrogen atom (N6) of the free pyrazolyl moiety is 2.710 Å away, which is within the sum of van der Waals radii of Au and N. However, this does not distort the trigonal-planar geometry at gold as evident from the sum of angles at Au (359.5°).

In solution **1** shows fluxional behavior. For example, we could not observe different signals for coordinated and free pyrazolyl moieties in the ^{1}H and ^{19}F NMR spectra taken in CD_2Cl_2 even at −80 °C. The signal corresponding to the ethylene protons appears as a sharp singlet at temperatures ranging from room temperature to −80 °C (with a minor ca. 0.1 ppm upfield shift). These data suggest that the exchange between free and coordinated nitrogen atoms is fast on the NMR time scale even at −80 °C, which is not surprising in view of the orientation and the close proximity of the free pyrazolyl arm (see N6 in Figure 2).

[*] Prof. Dr. H. V. R. Dias, J. Wu
Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019 (USA)
Fax: (+1) 817-272-3808
E-mail: dias@uta.edu
Homepage: http://www.uta.edu/chemistry/html/dias.html

[**] H.V.R.D. thanks the Robert A. Welch Foundation (grant Y-1289) for financial support of this research. This paper is dedicated to the memory of Prof. Dr. Dmitry M. Rudkevich, a true friend, wonderful colleague, and an outstanding chemist. [HB-{3,5-$(CF_3)_2Pz\}_3$] = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

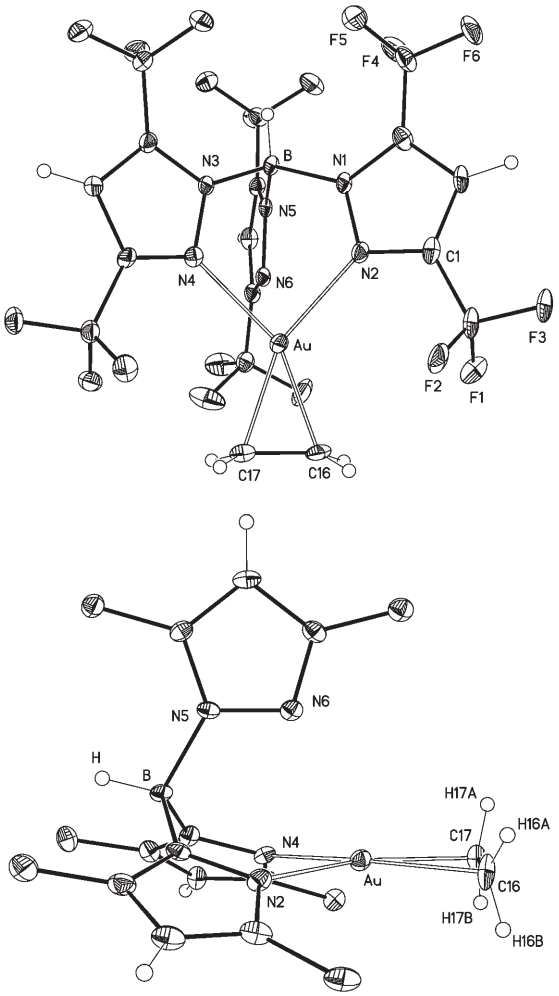

Figure 2. Top: ORTEP diagram of **1** (thermal ellipsoids set at 35% probability). Bottom: a view showing trigonal-planar coordination environment of the gold atom (fluorine atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au–C17 2.096(6), Au–C16 2.108(6), Au–N4 2.221(5), Au–N2 2.224(5), N1–B 1.564(7), N3–B 1.568(10), N5–B 1.565(9), C16–C17 1.380(10); C17-Au-C16 38.3(3), C17-Au-N4 116.8(2), C16-Au-N4 154.6(2), C17-Au-N2 156.4(2), C16-Au-N2 118.3(2), N4-Au-N2 86.05(16).

Considering the relatively high stability of **1**, we decided to explore the chemistry of gold ethylene complexes of various other tris(pyrazolyl)borates. Accordingly, we prepared $[(HB\{3\text{-}(CF_3),5\text{-}(Ph)Pz\}_3)Au(C_2H_4)]$ (**2**) using the corresponding sodium salt, AuCl, and ethylene. Complex **2** is a thermally stable colorless solid. It did not show signs of decomposition even after exposure to air and indoor light for several days. Like **1**, complex **2** is soluble (albeit to a lesser degree) and fairly stable in nonpolar hydrocarbons, such as pentane and hexane. These adducts are also soluble in solvents such as benzene and chloroform, but solutions darken after several hours at room temperature. In its ^1H and ^{13}C NMR spectra, **2** displays the resonances of the ethylene protons and carbon atoms at $\delta = 3.69$ ppm ($\Delta\delta(H) = -1.7$ ppm) and 59.3 ppm, respectively. We have also treated $CDCl_3$ solutions of **2** with excess ethylene. The ^1H NMR spectrum of this mixture at room temperature shows two sharp signals, one at the coordinated ethylene chemical shift value of the gold adduct ($\delta = 3.69$ ppm) and the second peak at $\delta = 5.39$ ppm corresponding to the free ethylene.

X-ray analysis revealed that **2** has a three-coordinate, trigonal planar gold site (Figure 3). The donor nitrogen atom in the free pyrazolyl arm (N6) of the κ^2-bonded tris(pyrazolyl)-borate lies at a distance of 2.750 Å. The Au–C (2.093(5), 2.096(5) Å) and C=C (1.387(9); corrected value for libration = 1.388 Å) distances of **2** are very similar to those observed for **1**, but the Au–N bond lengths are marginally shorter.

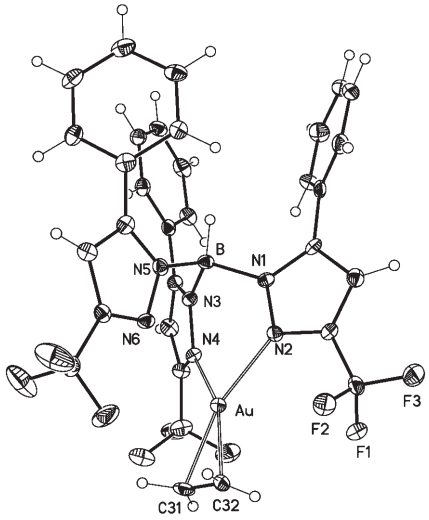

Figure 3. ORTEP diagram of **2** (thermal ellipsoids set at 35% probability). Selected bond lengths [Å] and angles [°] Au–C31 2.093(5), Au–C32 2.096(5), Au–N2 2.175(4), Au–N4 2.205(4), N1–B 1.558(7), N3–B 1.558(6), N5–B 1.544(7), C31–C32 1.387(9); C31-Au-C32 38.7(2), C31-Au-N2 156.3(2), C32-Au-N2 117.8(2), C31-Au-N4 116.12(19), C32-Au-N4 154.7(2), N2-Au-N4 87.13(14).

Complex **1** completes the isoleptic, coinage-metal–ethylene adducts the $[(HB\{3,5\text{-}(CF_3)_2Pz\}_3)M(C_2H_4)]$[8,10] (M = Cu, Ag, Au) series. Therefore, it is now possible for the first time to examine group trends using these well characterized molecules. The M–C and M–N distances of the $[(HB\{3,5\text{-}(CF_3)_2Pz\}_3)M(C_2H_4)]$ complexes follow the same trend (e.g., Cu–C < Au–C < Ag–C) as the covalent radii of M^I.[41,42] The ^1H NMR spectra of $CDCl_3$ solutions of the copper and silver analogues show the ethylene signal at $\delta = 4.96$ and 5.56 ppm, respectively (which correspond to $\Delta\delta(H)$ of −0.4 and 0.2 ppm). Thus the gold ethylene adduct shows the largest upfield shift of the ethylene protons. The upfield shift of the ^{13}C NMR resonance is also high compared to other coinage-metal family members (i.e., $\Delta\delta(C)$ ($\delta(C)_{complex} - \delta(C)_{ethylene}$) for Cu, Ag, and Au are −34.4, −18.6, −59.8 ppm, respectively). The upfield shift of the ^{13}C and ^1H NMR resonance of ethylene signal has been attributed to the increased metal-to-ethylene π-back-donation contribution.[4,12] Thus, these NMR data point to a significantly higher π-back-donation component in the gold(I)–ethylene bond than in the lighter members, and are in good agreement with the latest computational work and NMR spectroscopic studies of gold(I) ethylene adducts.[4]

In conclusion, we describe the isolation and structural characterization of the first thermally stable, neutral gold(I)

ethylene adducts. These adducts feature κ^2-bonded tris(pyrazolyl)borate ligands.[43] The proton and carbon NMR signals of the ethylene unit show notable upfield shifts upon coordination to Au^I. We are currently examining the ligand exchange chemistry and catalytic properties[44,45] of gold(I) tris(pyrazolyl)borates.

Experimental Section

1: X-ray quality crystals were obtained from hexane solution saturated with ethylene at −20 °C. M.p.: the Crystal darkens at 65 °C and melts completely at 105 °C with decomposition. ^{1}H NMR (300.53 MHz; $CDCl_3$, 298 K): $\delta = 3.81$ (s, 4H, CH_2=CH_2), 6.97 ppm (s, 3H, 4-C*H*); ^{1}H NMR (300.53 MHz; C_6D_6, 298 K): $\delta = 3.59$ (s, 4H, CH_2=CH_2), 6.25 ppm (s, 3H, 4-C*H*); ^{1}H NMR (300.53 MHz; C_6D_{12}, 298 K): $\delta = 3.81$ (s, 4H, CH_2=CH_2), 6.86 ppm (s, 3H, 4-C*H*). ^{13}C NMR (75.57 MHz; C_6D_{12}, 298 K) selected: $\delta = 63.4$ ppm (t, $^1J_{CH} = 163$ Hz, *C*H_2=*C*H_2). ^{13}C NMR (75.57 MHz; $CDCl_3$, 298 K) selected: $\delta =$ 63.7 ppm (t, $^1J_{CH} = 165$ Hz, *C*H_2=*C*H_2). X-ray data; $C_{17}H_8AuBF_{18}N_6$, monoclinic, $P2_1/n$; 100 K; $a = 8.7827(3)$, $b = 20.0745(8)$, $c =$ 14.0504(5) Å, $\beta = 90.060(1)°$, $V = 2477.20(16)$ Å^3, $Z = 4$; $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0312, $wR2 = 0.0819$.

2: X-ray quality crystals were obtained from a hexane solution saturated with ethylene at −20 °C. M.p. white powder darkens at 75 °C and melts completely at 98 °C with decomposition. ^{1}H NMR (300.53 MHz, $CDCl_3$, 298 K): $\delta = 3.69$ (s, 4H, CH_2=CH_2), 6.56 (s, 3H, 4-C*H*), 6.88 (d, $^3J = 8.3$ Hz, *Ph*), 6.95 (t, $^3J = 8.3$ Hz, *Ph*), 7.23 ppm (m, *Ph*). ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): selected $\delta =$ 59.3 ppm (t, $^1J_{CH} = 165$ Hz, *C*H_2=*C*H_2). ^{19}F NMR (470.62 MHz, $CDCl_3$, 298 K): $\delta = -61.4$ ppm (s). X-ray data; $C_{32}H_{23}AuBF_9N_6$, orthorhombic, $Pna2_1$; 100 K; $a = 23.1405(9)$, $b = 9.7956(4)$, $c =$ 13.8399(6) Å, $V = 3137.2(2)$ Å^3, $Z = 4$; $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0247, $wR2 = 0.0571$.

Further details of the synthesis, characterization, and additional figures and X-ray crystallographic data tables are given in the supporting materials. The CCDC-648451 (**1**) and CCDC-648452 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: July 24, 2007
Published online: September 4, 2007

Keywords: ethylene · gold · N ligands · structure elucidation

[1] C. Elschenbroich, *Organometallics* 3rd ed., VCH, Weinheim, **2006**.
[2] H. Schmidbaur, A. Schier, *Comprehensive Organometallic Chemistry III*, *Vol. 2*, Elsevier, Amsterdam, **2007**, pp. 251–307; M. C. Gimeno, A. Laguna, *Comprehensive Coordination Chemistry II*, *Vol. 6*, Elsevier, Amsterdam, **2004**, pp. 911–1145.
[3] M. A. Cinellu, G. Minghetti, S. Stoccoro, A. Zucca, M. Manassero, *Chem. Commun.* **2004**, 1618–1619.
[4] M. A. Cinellu, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, M. Arca, *Dalton Trans.* **2006**, 5703–5716, and references therein.
[5] R. H. Hertwig, W. Koch, D. Schroeder, H. Schwarz, J. Hrusak, P. Schwerdtfeger, *J. Phys. Chem.* **1996**, *100*, 12253–12260.
[6] C. K. Kim, K. A. Lee, C. K. Kim, B.-S. Lee, H. W. Lee, *Chem. Phys. Lett.* **2004**, *391*, 321–324.
[7] J. S. Thompson, R. L. Harlow, J. F. Whitney, *J. Am. Chem. Soc.* **1983**, *105*, 3522–3527.
[8] H. V. R. Dias, Z. Wang, W. Jin, *Inorg. Chem.* **1997**, *36*, 6205–6215.
[9] J. Dai, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, M. Munakata, *Inorg. Chem.* **1997**, *36*, 2688–2690.
[10] H. V. R. Dias, H.-L. Lu, H.-J. Kim, S. A. Polach, T. K. H. H. Goh, R. G. Browning, C. J. Lovely, *Organometallics* **2002**, *21*, 1466–1473, and references therein.
[11] H. Masuda, N. Yamamoto, T. Taga, K. Machida, S. Kitagawa, M. Munakata, *J. Organomet. Chem.* **1987**, *322*, 121–129.
[12] M. Munakata, S. Kitagawa, S. Kosome, A. Asahara, *Inorg. Chem.* **1986**, *25*, 2622–2627.
[13] B. F. Straub, F. Eisentrager, P. Hofmann, *Chem. Commun.* **1999**, 2507–2508.
[14] Y. Suenaga, L. P. Wu, T. Kuroda-sowa, M. Munakata, M. Maekawa, *Polyhedron* **1997**, *16*, 67–70.
[15] H. V. R. Dias, S. Singh, J. A. Flores, *Inorg. Chem.* **2006**, *45*, 8859–8861.
[16] H. V. R. Dias, X. Wang, H. V. K. Diyabalanage, *Inorg. Chem.* **2005**, *44*, 7322–7324.
[17] R. M. Sullivan, H. Liu, D. S. Smith, J. C. Hanson, D. Osterhout, M. Ciraolo, C. P. Grey, J. D. Martin, *J. Am. Chem. Soc.* **2003**, *125*, 11065–11079.
[18] X. Dai, T. H. Warren, *Chem. Commun.* **2001**, 1998–1999.
[19] H. V. R. Dias, X. Wang, *Dalton Trans.* **2005**, 2985–2987.
[20] I. Krossing, A. Reisinger, *Angew. Chem.* **2003**, *115*, 5903–5906; *Angew. Chem. Int. Ed.* **2003**, *42*, 5725–5728.
[21] H. A. Chiong, O. Daugulis, *Organometallics* **2006**, *25*, 4054–4057.
[22] H. V. R. Dias, J. Wu, X. Wang, K. Rangan, *Inorg. Chem.* **2007**, *46*, 1960–1962.
[23] H. V. R. Dias, M. Fianchini, *Angew. Chem.* **2007**, *119*, 2238–2241; *Angew. Chem. Int. Ed.* **2007**, *46*, 2188–2191.
[24] A. J. Chalk, *J. Am. Chem. Soc.* **1964**, *86*, 4733–4734.
[25] P. Tauchner, R. Hüttel, *Chem. Ber.* **1974**, *107*, 3761–3770.
[26] R. Hüttel, H. Reinheimer, *Chem. Ber.* **1966**, *99*, 2778–2781.
[27] R. Hüttel, H. Reinheimer, H. Dietl, *Chem. Ber.* **1966**, *99*, 462–468.
[28] R. Hüttel, H. Dietl, *Angew. Chem.* **1965**, *77*, 456; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 438.
[29] H. Coutelle, R. Hüttel, *J. Organomet. Chem.* **1978**, *153*, 359–368.
[30] R. Hüttel, P. Tauchner, H. Forkl, *Chem. Ber.* **1972**, *105*, 1–7.
[31] R. Hüttel, H. Reinheimer, K. Howak, *Chem. Ber.* **1968**, *101*, 3761–3776.
[32] A. Johnson, R. J. Puddephatt, *J. Chem. Soc. Dalton Trans.* **1977**, 1384–1388.
[33] S. Komiya, J. K. Kochi, *J. Organomet. Chem.* **1977**, *135*, 65–72.
[34] D. Belli Dell'Amico, F. Calderazzo, R. Dantona, J. Straehle, H. Weiss, *Organometallics* **1987**, *6*, 1207–1210.
[35] R. M. Davila, R. J. Staples, J. P. Fackler, Jr., *Organometallics* **1994**, *13*, 418–420.
[36] M. Håkansson, H. Eriksson, S. Jagner, *J. Organomet. Chem.* **2000**, *602*, 133–136.
[37] O. Renn, L. M. Venanzi, A. Marteletti, V. Gramlich, *Helv. Chim. Acta* **1995**, *78*, 993–1000.
[38] H. V. R. Dias, T. K. H. H. Goh, *Polyhedron* **2004**, *23*, 273–282.
[39] H. V. R. Dias, W. Jin, H.-J. Kim, H.-L. Lu, *Inorg. Chem.* **1996**, *35*, 2317–2328.
[40] G. J. H. Van Nes, A. Vos, *Acta Crystallogr. Sect. B* **1979**, *35*, 2593–2601.
[41] M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage, H. V. R. Dias, *Inorg. Chem.* **2005**, *44*, 8200–8210.
[42] A. Bayler, A. Schier, G. A. Bowmaker, H. Schmidbaur, *J. Am. Chem. Soc.* **1996**, *118*, 7006–7007.
[43] C. Pettinari, C. Santini, *Comprehensive Coordination Chemistry II*, *Vol. 1*, Elsevier, Amsterdam, **2004**, pp. 159–210.
[44] D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403.
[45] A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211.

