Inorganic Chemistry

Communication

Gold(I) Ethylene and Copper(I) Ethylene Complexes Supported by a Polyhalogenated Triazapentadienyl Ligand

Jaime A. Flores and H. V. Rasika Dias*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019

A rare gold(I) ethylene complex and the closely related copper(I) ethylene adduct have been isolated using $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]^-$ as the supporting ligand. $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Au(C_2H_4)$ (**1**) is an air-stable solid. It features a U-shaped triazapentadienyl ligand backbone and a three-coordinate, trigonal-planar gold center. The copper(I) adduct $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Cu(C_2H_4)$ (**2**) also has a similar structure. The ^{13}C NMR signal corresponding to the ethylene carbons of **1** appears at about 64 ppm upfield from the free ethylene, while the ethylene carbons of **2** show a relatively smaller (39 ppm) upfield shift. $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]M(C_2H_4)$ (M = Cu, Au) mediate carbene-transfer reactions from ethyl diazoacetate to saturated and unsaturated hydrocarbons.

Although 1,3,5-triazapentadienyl systems are closely related to the popular and widely used 1,5-diazapentadienyl (β-diketiminate) ligands,[1] they have not received the same attention as metal ion chelators.[2–10] Recently, we reported the isolation of several thermally stable copper(I) and silver(I) complexes (including some featuring Cu−CO and Cu−ethylene bonds) using 1,3,5-triazapentadienyl anions as auxiliary ligands.[2,6,7] The resulting adducts also display quite interesting and diverse coordination modes. For example, $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ (Dipp = 2,6-$(Pr^i)_2C_6H_3$) and

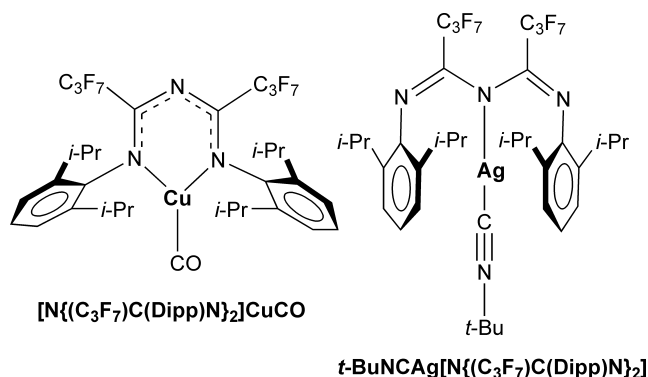**Figure 1.** 1,3,5-Triazapentadienyl complexes of copper and silver showing two different coordination modes.

$[N\{(C_3F_7)C(Dipp)N\}_2]AgPPh_3$ have κ^2-bonded U-shaped ligand backbones,[6,7] while t-BuNCAg$[N\{(C_3F_7)C(Dipp)N\}_2]$ features a κ^1-bonded ligand with a W-shaped backbone (Figure 1).[7]

In this paper, we report the utility of a 1,3,5-triazapentadienyl ligand in gold(I) ethylene chemistry and some catalytic properties of the resulting adduct. The related copper chemistry is also presented. A gold phosphine complex, $[N\{(C_3F_7)C(Ph)N\}_2]AuPPh_3$, supported by a 1,3,5-triazapentadienyl ligand has been reported, but X-ray structural data are not available.[5,11] The ^{19}F NMR spectroscopic data of this molecule indicate the presence of a κ^1-bonded triazapentadienyl ligand. It is also noteworthy that isolable gold ethylene complexes are very rare[12] and structurally

* To whom correspondence should be addressed. E-mail: dias@uta.edu.

(1) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031–3066.

(2) Dias, H. V. R.; Singh, S.; Flores, J. A. *Inorg. Chem.* **2006**, *45*, 8859–8861.

(3) Dias, H. V. R.; Singh, S. *Dalton Trans.* **2006**, 1995–2000.

(4) Dias, H. V. R.; Singh, S.; Cundari, T. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 4907–4910.

(5) Siedle, A. R.; Webb, R. J.; Brostrom, M.; Newmark, R. A.; Behr, F. E.; Young, V. G., Jr. *Organometallics* **2004**, *23*, 2281–2286.

(6) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 5786–5788.

(7) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 7396–7402.

(8) Siedle, A. R.; Webb, R. J.; Behr, F. E.; Newmark, R. A.; Weil, D. A.; Erickson, K.; Naujok, R.; Brostrom, M.; Mueller, M.; Chou, S.-H.; Young, V. G., Jr. *Inorg. Chem.* **2003**, *42*, 932–934.

(9) (a) Aris, D. R.; Barker, J.; Phillips, P. R.; Alcock, N. W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1997**, 909–910. (b) Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1994**, 3615–3620. (c) Robinson, V.; Taylor, G. E.; Woodward, P.; Bruce, M. I.; Wallis, R. C. *J. Chem. Soc., Dalton Trans.* **1981**, 1169–1173. (d) Bottrill, M.; Goddard, R.; Green, M.; Hughes, R. P.; Lloyd, M. K.; Taylor, S. H.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 1150–1155. (e) Brown, H. C.; Schuman, P. D. *J. Org. Chem.* **1963**, *28*, 1122–1127.

(10) (a) Zhang, J.-P.; Lin, Y.-Y.; Huang, X.-C.; Chen, X.-M. *J. Am. Chem. Soc.* **2005**, *127*, 5495–5506. (b) Kopylovich, M. N.; Tronova, E. A.; Haukka, M.; Kirillov, A. M.; Kukushkin, V. Y.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2007**, 4621–4627. (c) Kopylovich, M. N.; Haukka, M.; Kirillov, A. M.; Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem.−Eur. J.* **2007**, *13*, 786–791. (d) Walther, M.; Wermann, C.; Lutsche, M.; Guenther, W.; Goerls, H.; Anders, E. *J. Org. Chem.* **2006**, *71*, 1399–1406. (e) Guzei, I. A.; Crozier, K. R.; Nelson, K. J.; Pinkert, J. C.; Schoenfeldt, N. J.; Shepardson, K. E.; McGaff, R. W. *Inorg. Chim. Acta* **2006**, *359*, 1169–1176. (f) Guo, J.-P.; Wong, W.-K.; Wong, W.-Y. *Eur. J. Inorg. Chem.* **2006**, 3634–3640. (g) Hesse, R.; Froehlich, R.; Humelnicu, I.; Wuerthwein, E.-U. *Eur. J. Inorg. Chem.* **2005**, 2189–2197. (h) Kajiwara, T.; Ito, T. *Eur. J. Inorg. Chem.* **2004**, 3084–3088. (i) Guo, J.; Wong, W.-K.; Wong, W.-Y. *Eur. J. Inorg. Chem.* **2004**, 267–275. (j) Turnbull, M. M.; Wei, M. Y.; Willett, R. D. *J. Coord. Chem.* **1995**, *35*, 11–17.

(11) 1,5-Diazapendadienyl complexes of gold are also rare. Dias, H. V. R.; Flores, J. A. *Inorg. Chem.* **2007**, *46*, 5841–5843.

(12) Dias, H. V. R.; Wu, J. *Eur. J. Inorg. Chem.* **2008**, 509–522, and **2008**, 2113, and the references cited therein.

Scheme 1. Synthesis of Ethylene Adducts of Gold and Copper Using [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]H
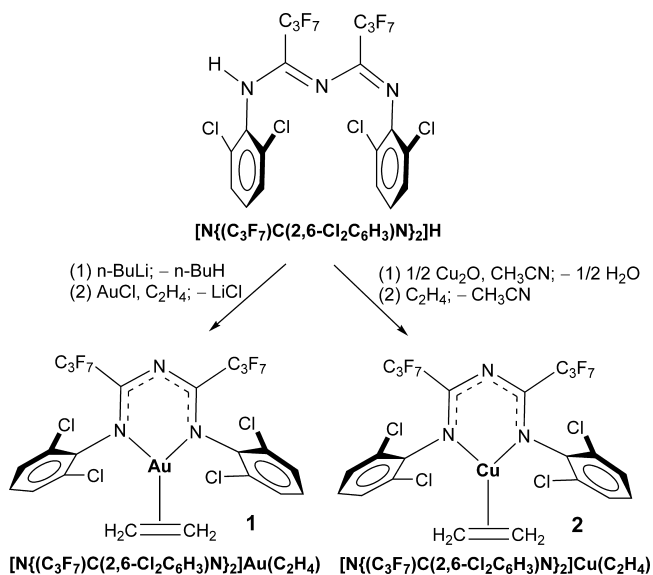
characterized examples are limited to [HB(3-(CF₃),5-(R)Pz)₃]Au(C₂H₄) (R = CF₃, Ph)[13] and [Au(C₂H₄)₃][SbF₆].[14]

The 1,3,5-triazapentadiene used in this study, [N{(C₃F₇)-C(2,6-Cl₂C₆H₃)N}₂]H, was synthesized using a procedure similar to that reported earlier for highly fluorinated 1,3,5-triazapentadienes.[2] It is a colorless crystalline solid with good solubility in solvents such as toluene, THF, CH₂Cl₂, and Et₂O but sparingly soluble in *n*-hexane. The X-ray crystal structure of [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]H shows that its NCNCN backbone adopts a somewhat twisted, W-shaped configuration with a long−short−long−short N−C bond distance pattern, while the acidic proton is bonded to one of the terminal nitrogen atoms.

The treatment of [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]Li (prepared in situ by reacting [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]H with *n*-BuLi) with AuCl in the presence of ethylene led to [N{(C₃F₇)C(2,6-Cl₂C₆H₃)N}₂]Au(C₂H₄) (**1**) in 55% yield (Scheme 1). It is a yellow solid that does not lose ethylene under reduced pressure and is air- and light-stable for more than 1 month at room temperature. A solution of the **1** in CDCl₃ shows no decomposition, as is evident from the ¹H NMR analysis after 1 week at room temperature in the absence of light. It is fairly soluble in solvents such as CH₂Cl₂ and C₆H₆ but less soluble in *n*-hexane.

The ¹H NMR signal corresponding to the ethylene protons of **1** in CDCl₃ appears as a singlet at $\delta = 2.71$ ppm, which is a quite significant upfield shift from the free ethylene ¹H NMR signal ($\delta = 5.40$ ppm).[12] The ¹³C NMR signal of the coordinated ethylene in **1** appears at 59.1 ppm ($^1J_{CH} = 162$ Hz), which is again considerably upfield-shifted relative to the corresponding peak of the free ethylene ($\delta = 123.3$ ppm ($^1J_{CH} = 156$ Hz).[12] The NMR data of [HB(3-(CF₃)-5-(Ph)Pz)₃]Au(C₂H₄) have been reported, and its ethylene proton and carbon resonances appear at $\delta = 3.69$ and 59.3

ppm, respectively.[13] Similar ethylene ¹³C NMR chemical shifts of **1** and [HB(3-(CF₃)-5-(Ph)Pz)₃]Au(C₂H₄) but a significantly different and upfield-shifted proton signal in **1** points to an additional contribution to the ¹H NMR shift of the 1,3,5-triazapentadienyl adduct, which is most likely the shielding caused by the ligand aryl group ring currents flanking the ethylene moiety.

We also prepared the analogous copper(I) adduct [N{(C₃-F₇)C(2,6-Cl₂C₆H₃)N}₂]Cu(C₂H₄) (**2**) for a direct comparison. It was obtained in high yield starting with the free ligand and Cu₂O (Scheme 1). The ¹H and ¹³C NMR (in CDCl₃) signals corresponding to the coordinated ethylene in this molecule appear at $\delta = 3.53$ and 84.2 ppm ($^1J_{CH} = 161$ Hz), respectively. These are relatively smaller upfield shifts from the free ethylene signals compared to those observed for the analogous gold adduct. The upfield shift of the ethylene protons and, more importantly, the ethylene carbons of metal−ethylene adducts has been attributed to the increased shielding caused by the metal-to-ethylene π back-donation.[12,15] Therefore, these NMR data point to significantly higher π back-bonding in the gold system.

In contrast to gold(I), a number of well-authenticated copper(I) ethylene adducts are known.[12] [HC{(Me)C(2,6-Me₂C₆H₃)N}₂]Cu(C₂H₄)[16] and [*t*-Bu₂P(Me₃SiN)₂]Cu(C₂H₄)[17] represent two examples of three-coordinate copper ethylene adducts with relatively electron-rich (compared to that in **2**) auxiliary ligands. The ethylene ¹³C NMR signal in these adducts were observed at $\delta = 74.7$ and 73.0 ppm, respectively.

Treatment of **1** in CDCl₃ with excess ethylene yielded two sharp signals in the ¹H NMR spectrum at $\delta = 2.71$ and 5.39 ppm for the coordinated and free ethylene, respectively. The same experiment with **2**, however, led to the coalescence of the bound ethylene signal, indicating fast ethylene exchange on the NMR time scale and the presence of a relatively more labile M−ethylene bond in the copper system.

X-ray crystal structures of **1** and **2** are shown in Figure 2. The gold atom in **1** displays a rare, trigonal-planar coordination.[18] The triazapentadienyl ligand binds to the metal center in a κ² fashion with Au−N distances of 2.1467(16) and 2.1549(17) Å. The C=C bond length of the bonded ethylene [1.405(4) Å] is significantly longer than that of the free ethylene [1.313(1) Å (X-ray)[19] and 1.338 Å (calcd)].[14]

Crystals of **2** show some twinning, but it was resolved satisfactorily. The copper adduct crystallizes in the P1̄ space group with two chemically similar molecules in the asymmetric unit. The basic structure is similar to that of the gold adduct **1**. The Cu−C(ethylene) and Cu−N bond distances are shorter than the corresponding Au−C and Au−N distances. This follows the trend expected based on the smaller covalent

(13) Dias, H. V. R.; Wu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 7814–7816.
(14) Dias, H. V. R.; Fianchini, M.; Cundari, T. R.; Campana, C. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 556–559.
(15) (a) Cinellu, M. A.; Minghetti, G.; Cocco, F.; Stoccoro, S.; Zucca, A.; Manassero, M.; Arca, M. *Dalton Trans.* **2006**, 5703–5716. (b) Hahn, C. *Chem.—Eur. J.* **2004**, *10*, 5888–5899.
(16) Dai, X.; Warren, T. H. *Chem. Commun.* **2001**, 1998–1999.
(17) (a) Straub, B. F.; Eisentrager, F.; Hofmann, P. *Chem. Commun.* **1999**, 2507–2508. (b) Straub, B. F.; Gruber, I.; Rominger, F.; Hofmann, P. *J. Organomet. Chem.* **2003**, *684*, 124–143.
(18) Carvajal, M. A.; Novoa, J. J.; Alvarez, S. *J. Am. Chem. Soc.* **2004**, *126*, 1465–1477.
(19) Van Nes, G. J. H.; Vos, A. *Acta Crystallogr., Sect. B* **1979**, *35*, 2593–2601.
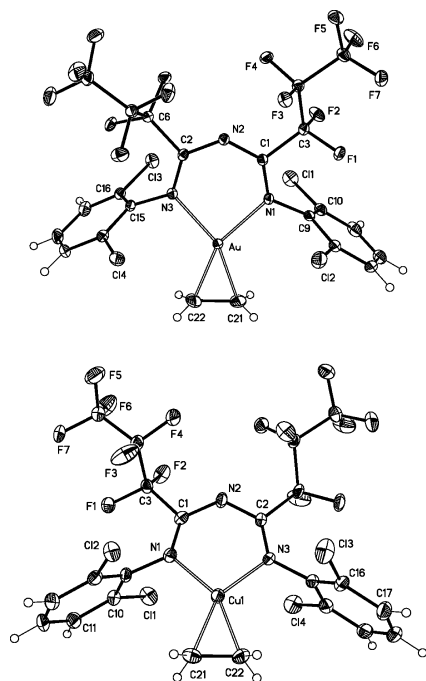
Figure 2. Molecular structures of **1** (top) and **2** (bottom). Selected bond lengths (Å) and angles (deg): **1**: Au−C21 2.089(2), Au−C22 2.098(2), Au−N1 2.1467(16), Au−N3 2.1549(17), C21−C22 1.405(4); C21−Au−C22 39.22(11), N1−Au−N3 86.38(6). **2**, molecule 1: Cu1−N3 1.946(5), Cu1−N1 1.958(5), Cu1−C21 2.004(6), Cu1−C22 2.004(6), C21−C22 1.364(9); N3−Cu1−N1 96.4(2), C21−Cu1−C22 39.8(3). **2**, molecule 2 (not shown): Cu2−N4 1.933(5), Cu2−N6 1.950(5), Cu2−C44 1.998(7), Cu2−C43 2.020(7), C43−C44 1.377(10); N4−Cu2−N6 95.2(2), C44−Cu2−C43 40.1(3).

radius of copper(I) compared to that of gold(I). The C═C distances 1.364(9) and 1.377(10) Å of coordinated ethylene in **2** are slightly shorter than those of the gold complex **1** (which is consistent with the NMR data and the low M→ethylene back-bonding in copper), but the difference is within the 3σ value of estimated standard deviations.

Efficient carbene-transfer chemistry mediated by polyhalogenated molecules like [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag(THF) and [HB(3,4,5-Br$_3$Pz)$_3$]Cu(NCMe) suggests that [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)N}$_2$]M(C$_2$H$_4$) (M = Au, Cu) may also show interesting catalytic properties.[20,21] Accordingly, we investigated their ability to facilitate the carbene unit transfer from ethyl diazoacetate (EDA, a widely used carbene source) to saturated and unsaturated hydrocarbons like cyclopentane, styrene, and benzene (Scheme 2). The reaction of cyclopentane with EDA employing [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)-N}$_2$]Au(C$_2$H$_4$) (5 mol %) afforded C−H activation product

Scheme 2. [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)N}$_2$]M(C$_2$H$_4$) (M = Au, Cu) Catalyzed Carbene-Transfer Reactions from EDA
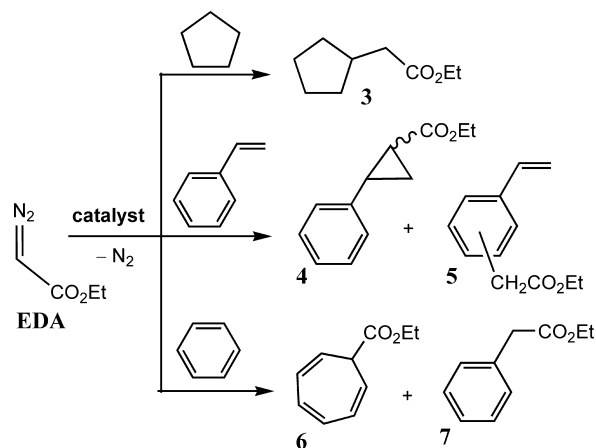
3 in 42% yield. The related copper catalyst gave **3** in much higher yield (74%). The copper adduct also gave a much higher styrene cyclopropanation product **4** (93%) with no detectable sp^2 C−H bond insertion product (**5**). The gold adduct gave **4** in good yield (69%), while a small amount of **5** was also detected (2%). [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)-N}$_2$]M(C$_2$H$_4$) (M = Au, Cu) also catalyzes the Büchner chemistry[22] with benzene, producing **6** in comparable yields: 68% (Au) and 67% (Cu). The gold adduct also leads to sp^2 C−H bond activation product **7** in about 8% yield. Overall, these preliminary data are promising and show, for the first time, that triazapentadienyl complexes of coinage metals are indeed useful catalysts for a variety of transformations. Carbene-transfer chemistry mediated by isolable gold adducts of any type is also rare,[23] and the reports in the literature mainly concern the cationic gold catalysts supported by N-heterocyclic carbenes.[24] As for the copper, tris(pyrazolyl)borate complexes are the most widely used in carbene-transfer chemistry.[21]

Overall, we describe the isolation and structural characterization of three-coordinate gold(I) and copper(I) ethylene adducts using a polyhalogenated 1,3,5-triazapentadienyl ligand. The NMR and structural data suggest strong metal-to-ethylene π back-bonding in the gold adduct **1** (despite the presence of a weakly donating auxiliary ligand). [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)-N}$_2$]M(C$_2$H$_4$) (M = Au, Cu) also mediate carbene-transfer reactions from EDA to saturated and unsaturated hydrocarbons. Further studies are underway to explore the coordination chemistry of triazapentadienyl ligands and catalytic properties of triazapentadienyl metal adducts.

Note Added after ASAP Publication. There was an error in the NMR shift of compound [HB(3-(CF$_3$)-5-(Ph)Pz)$_3$]-Au(C$_2$H$_4$) in the version published ASAP April 23, 2008; the corrected version published ASAP May 2, 2008.

Supporting Information Available: X-ray crystallographic data for [N{(C$_3$F$_7$)C(2,6-Cl$_2$C$_6$H$_3$)N}$_2$]H complexes **1** and **2** (CIF) and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800373U

(20) (a) Krishnamoorthy, P.; Browning, R. G.; Singh, S.; Sivappa, R.; Lovely, C. J.; Dias, H. V. R. *Chem. Commun.* **2007**, 731–733. (b) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9270–9271. (c) Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. *Organometallics* **2004**, *23*, 1200–1202. (d) Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. *Organometallics* **2005**, *24*, 5784. (e) Lovely, C. J.; Browning, R. G.; Badarinarayana, V.; Dias, H. V. R. *Tetrahedron Lett.* **2005**, *46*, 2453–2455.

(21) Diaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Perez, P. J. *Dalton Trans.* **2006**, 5559–5566.

(22) Doyle, M. P.; McKervey, M. A.; Tao, Y. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998; Chapter 6, p 289.

(23) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211.

(24) Fructos, M. R.; De Fremont, P.; Nolan, S. P.; Mar Dauiiaz-Requejo, M.; Perez, P. J. *Organometallics* **2006**, *25*, 2237–2241.