Organometallics **2003,** *22,* 4327−4333 4327

New Carbenegold(I) Complexes Synthesized by the “Acac Method”

José Vicente,* María-Teresa Chicote,* María Dolores Abrisqueta, and
Miguel M. Alvarez-Falcón

*Grupo de Química Organometálica, Departamento de Química Inorgánica,
Facultad de Química, Universidad de Murcia, Apartado 4021, E-30071 Murcia, Spain*

M. Carmen Ramírez de Arellano‡

*Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia,
46100 Valencia, Spain*

Peter G. Jones§

*Institut für Anorganische und Analytische Chemie der Technischen Universität,
Hagenring 30, 3300 Braunschweig, Germany*

Received May 19, 2003

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

The reaction of $[AuCl\{C(NEt_2)NH^tBu\}]$ with Tl(acac)] (1:1) gives $[Au(C\text{-acac})\{C(NEt_2)NH^tBu\}]$ (**1**). Complex **1** reacts with 2-pyridinethiol (HSpy-2), $C_6H_4(C{\equiv}CH)_2{-}1,3$ (2:1), $[Ph_3PCH_2CO_2Me]ClO_4$, $[Me_3S(O)]ClO_4$, or $[Me_3NH]ClO_4$ to give, respectively, $[Au(Spy\text{-}2)\{C(NEt_2)NH^tBu\}]$ (**2**), $[\{AuC(NEt_2)NH^tBu\}_2(\mu{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}3)]$ (**3**), $[Au\{C(NEt_2)NH^tBu\}\{CH(PPh_3)CO_2Me\}]ClO_4$ (**4**), $[Au\{C(NEt_2)NH^tBu\}\{CH_2S(O)Me_2\}]ClO_4$ (**5**), or $[Au\{C(NEt_2)NH^tBu\}(NMe_3)]ClO_4$ (**6**). The crystal structures of **1**, **3**, and **5** have been determined.

Introduction

Acetylacetonatogold(I) complexes have been shown to react with a wide variety of substrates containing acidic hydrogen to give gold(I) complexes with ligands such as alkyl,[1,2] alkynyl,[1,3−9] phosphorus[1,10,11] or sulfur[12] ylides, diphenylphosphide,[13] diphenylphosphinomethanide,[1,14] ammonia,[15,16] nitrido, imido,[16] primary, secondary, or tertiary amines,[17] hydrosulfido,[18] thioether,[19] or thiolato.[1,20,21] Recently, it has been reported that the reaction of 2-aminothiazoline with $[Au(acac)(PPh_3)]$ evolves to an unprecedented ring-opening reaction to give the new ligand (2-cyanamide)ethanethiolate.[22] The same reagent has been used in the synthesis of heterodinuclear complexes.[2,23] However, this “acac method”

---

* Corresponding authors. E-mail: jvs@um.es (J.V.); mch@um.es (M.-T.C); www: http://www.um.es/gqo/.

‡ Corresponding author regarding the X-ray diffraction studies of **1** and **5**. E-mail: mcra@uv.es.

§ Corresponding author regarding the X-ray diffraction study of **3**. E-mail: p.jones@tu-bs.de.

(1) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Lagunas, M. C. *J. Chem. Soc., Chem. Commun.* **1992**, 915.

(2) Vicente, J.; Arcas, A.; Bautista, D.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 4544.

(3) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 497.

(4) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

(5) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **2000**, *19*, 2629.

(6) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G.; Humphrey, M. G.; Cifuentes, M. P.; Samoc, M.; Luther-Davies, B. *Organometallics* **2000**, *19*, 2968.

(7) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Abrisqueta, M. D.; Hernández, F. J.; Jones, P. G. *Inorg. Chim. Acta* **2003**, *347*, 67.

(8) Bardaji, M.; Jones, P. G.; Laguna, A. *J. Chem. Soc., Dalton Trans.* **2002**, 3624.

(9) Bardaji, M.; Laguna, A.; Jones, P. G. *Organometallics* **2001**, *20*, 3906.

(10) Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernandez-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163.

(11) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Turpin, J.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1987**, *333*, 129. Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Jones, P. G.; Meyer-Bäse, K.; Erdbrügger, C. F. *Organometallics* **1988**, *7*, 997. Vicente, J.; Chicote, M. T.; Saura-Llamas, I. *J. Chem. Soc., Dalton Trans.* **1990**, 1941. Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2579. Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1730. Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Inorg. Chem.* **1993**, *32*, 3748. Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G.; Ahrens, B. *Inorg. Chem.* **1997**, *36*, 4938. Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Helv. Chim. Acta* **1999**, *82*, 1202. Barranco, E. M.; Gimeno, M. C.; Laguna, A. *Inorg. Chim. Acta* **1999**, *291*, 60.

(12) Vicente, J.; Chicote, M. T.; Guerrero, R.; Jones, P. G. *J. Am. Chem. Soc.* **1996**, *118*, 699.

(13) Vicente, J.; Chicote, M. T.; Jones, P. G. *Inorg. Chem.* **1993**, *32*, 4960. Blanco, M. C.; Fernandez, E. J.; Lopez de Luzuriaga, J. M.; Olmos, M. E.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem. Eur. J.* **2000**, *6*, 4116.

(14) Fernández, E. J.; Gimeno, M. C.; Laguna, A.; Lopez de Luzuriaga, J. M.; Olmos, E. *Polyhedron* **1998**, *17*, 3919. Alvarez, B.; Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Lopez de Luzuriaga, J. M. *Polyhedron* **1998**, *17*, 2029. Gimeno, M. C.; Laguna, A.; Laguna, M.; Sanmartin, F.; Jones, P. G. *Organometallics* **1993**, *12*, 3984. Gimeno, M. C.; Laguna, A.; Laguna, M.; Sanmartin, F.; Jones, P. G. *Organometallics* **1994**, *13*, 1538.

(15) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D.; Guerrero, R.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1203.

(16) Vicente, J.; Chicote, M. T.; Guerrero, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Inorg. Chem.* **1997**, *36*, 4438.

(17) Vicente, J.; Chicote, M. T.; Guerrero, R.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 1251.

(18) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Jones, P. G.; Ahrens, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1852.

(19) Vicente, J.; Chicote, M. T.; Rubio, C. *Chem. Ber.* **1996**, *129*, 327.

(20) Vicente, J.; Chicote, M. T.; Huertas, S.; Ramírez de Arellano, M. C.; Jones, P. G. *Eur. J. Inorg. Chem.* **1998**, 511. Bauer, A.; Schneider, W.; Angermaier, K.; Schier, A.; Schmidbaur, H. *Inorg. Chim. Acta* **1996**, *251*, 249.

(21) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1994**, 3183.

10.1021/om030372r CCC: $25.00 © 2003 American Chemical Society
Publication on Web 09/09/2003

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

is rather limited in view of the scarcity of acetylacetonatogold(I) precursors available. In fact, apart from complexes [Au(acac)ER$_3$] (E = P, R = Me, Ph, C$_6$H$_4$OMe-4, C$_6$H$_{11}$; E = As, R = Ph)[1,24] and [Au(acac)$_2$]$^-$,[1,25] only three other acetylacetonatogold(I) derivatives have been described so far, namely, [Au^{I}(acac){vddpAu^{III}(C$_6$F$_5$)$_3$}][26] [vddp = vinylidenebis(diphenylphosphine)], the tetranuclear complex [Au$_2$(acac){CH(PPh$_2$)$_2$}]$_2$,[27] [Au(acac)Cl],[28] and the recently reported [Au(acac){C(PPh$_3$)$_2$}].[29] The reactivity of these four complexes has not been studied as thoroughly as that of [Au(acac)PPh$_3$] or [Au(acac)$_2$]$^-$.[30]

We have now prepared the first acetylacetonato(carbene)gold derivative [Au(*C*-acac){C(NEt$_2$)NH^{t}Bu}] and studied its reactivity toward terminal alkynes (C$_6$H$_4$(C≡CH)$_2$-1,3), 2-pyridinethiol (pySH-2), and ammonium ([Me$_3$NH]ClO$_4$), phosphonium ([Ph$_3$PCH$_2$CO$_2$Me]ClO$_4$), or sulfoxonium ([Me$_3$S(O)]ClO$_4$) salts, with the intention of widening the scope of the “acac method”.

The tendency of gold(I) centers to aggregate giving structures with short Au···Au contacts has been termed aurophilicity. It has been attributed to correlation and relativistic effects; its strength is comparable to hydrogen bonding (ca. 7−11 kcal/mol)[31] and seems to be responsible for the luminescence behavior displayed by some gold(I) complexes.[32,33] In this context, some bis(carbene)gold(I) complexes have been recently shown to display unusual luminescent behavior.[34]

Carbene-gold complexes have been prepared via six methods:[4,6,35] (1) nucleophilic addition of alcohols or amines to gold-coordinated isocyanides;[36] this is the main method and was employed to prepare the complex [AuCl{C(NEt$_2$)NH^{t}Bu}],[4] in turn used as starting material for the synthesis of [Au(*C*-acac){C(NEt$_2$)NH^{t}Bu}]; (2) use of electron-rich olefins as nucleophilic carbene transfer reagents;[37] (3) carbene transfer from Fischer-type carbene complexes of Cr, Mo, and W;[38] (4) protonation or alkylation of gold azolyl compounds;[39] (5) transmetalation reactions using lithium[40] or silver carbene complexes;[41] (6) reaction of 1,3-R$_2$-benzimidazolonium salts with Ag$_2$O and [AuCl(Me$_2$S)].[42] The resulting gold(I) complexes are of the following three families: [AuX(carbene)] (X being mainly Cl or C$_6$F$_5$. but there are a few examples with X = Br, I, C$_6$Cl$_5$, C$_6$Br$_5$, CN, PhC≡C, PhS), [Au(carbene)$_2$]$^+$, and [Au(carbene)L]$^+$ (L = PPh$_3$). We have recently reported complexes [Au(C≡CR){C(NEt$_2$)NH^{t}Bu}] (R = H, ^{t}Bu, Me$_3$Si, C$_6$H$_4$R′-4, R = NO$_2$, C$_6$H$_4$NO$_2$-4, CH=CHC$_6$H$_4$NO$_2$-4) and [{Au{C(NEt$_2$)NH^{t}Bu}}$_2$(μ-C≡C(CH$_2$)$_5$C≡C)] by reacting [AuCl(CN^{t}Bu)] with the corresponding alkyne in the presence of Et$_2$NH.[4,6] Therefore, although there are many carbene gold(I) complexes, they differ mainly in the nature of the carbene ligand. The other ligand tends to be Cl, C$_6$F$_5$, alkyne, or PPh$_3$. The compound [Au(*C*-acac){C(NEt$_2$)NH^{t}Bu}], which we report in this paper, not only represents a new type of complex of the family [AuX(carbene)] (the first with X = alkyl) but is also the starting material for the synthesis of new types of carbene complexes with X = 2-pyS, or [Au(carbene)L]$^+$, L being a phosphorus or a sulfur ylide, such as Ph$_3$P=CHCO$_2$Me or H$_2$C=S(O)Me$_2$, or a nitrogen donor ligand such as Me$_3$N. We also report the crystal structures of [Au(*C*-acac){C(NEt$_2$)NH^{t}Bu}], [{Au{C(NEt$_2$)NH^{t}Bu}}$_2$(μ−C≡CC$_6$H$_4$C≡C-3)], and [{Au{C(NEt$_2$)NH^{t}Bu}{CH$_2$S(O)Me$_2$}].

Experimental Section

The IR spectra, elemental analyses, and melting point determinations were carried out as described earlier.[43] Unless otherwise stated, the reactions were carried out at room temperature without special precautions against moisture. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded with Varian Unity 300 or Bruker AC-200 spectrometers using CDCl$_3$ as solvent unless otherwise stated. Chemical shifts, given in ppm, are referred to TMS (^{1}H) or H$_3$PO$_4$ [^{31}P{^{1}H}]. The molar conductivities were measured in acetone solution (ca. 5×10^{-4} mol L^{-1}). The neutral complexes **1**−**3** show very low molar conductivities (in the range 0−4 Ω^{-1} cm^2 mol^{-1}).

Technical grade solvents were purified by standard procedures. 2-Pyridinethiol (pySH-2) (Fluka) and AgClO$_4$ and CS$_2$ (Aldrich) were obtained from commercial sources. The syntheses of [Me$_3$NH]ClO$_4$,[17] Tl(acac),[25] [AuCl(tht)],[44] 1,3-diethynylbenzene,[45] and [AuCl{C(NH^{t}Bu)NEt$_2$}][4] were previ-

---

(22) Bardaji, M.; Laguna, A.; Perez, M. R.; Jones, P. G. *Organometallics* **2002**, *21*, 1877.

(23) Paredes, P.; Miguel, D.; Villafañe, F. *Eur. J. Inorg. Chem.* **2003**, 995.

(24) Gibson, D.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 367. Gregory, J.; Ingold, C. K. *J. Chem. Soc. B* **1969**, 276. Bailey, J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1921. Nesmeyanov, A. N.; Perevalova, E. G.; Smyslova, E. I.; Dyadchenko, V. P.; Grandberg, K. I. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1977**, 2417. Nesmeyanov, A. N.; Grandberg, K. I.; Dyadchenko, V. P.; Lemenovskii, D. A.; Perevalova, E. G. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1974**, 1139. Dyadchenko, V. P. *Moscow Univ. Chem. Bull.* **1976**, *31*, 72.

(25) Vicente, J.; Chicote, M. T. *Inorg. Synth.* **1998**, *32*, 172.

(26) Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Lopez de Luzuriaga, J. M.; Olmos, E. *Chem. Ber.* **1997**, *130*, 1513.

(27) Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Lopez de Luzuriaga, J. M.; Rodriguez, M. A. *Chem. Ber.* **1995**, *128*, 121.

(28) Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Lopez de Luzuriaga, J. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3365.

(29) Vicente, J.; Singhal, A. R.; Jones, P. G. *Organometallics* **2002**, *21*, 5887.

(30) Vicente, J.; Chicote, M. T. *Coord. Chem. Rev.* **1999**, *193*−*195*, 1143.

(31) Schmidbaur, H. *Nature* **2001**, *413*, 31.

(32) Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323.

(33) Leung, K. H.; Phillips, D. L.; Tse, M. C.; Che, C. M.; Miskowski, V. M. *J. Am. Chem. Soc.* **1999**, *121*, 4799.

(34) White-Morris, R. L.; Olmstead, M. M.; Jiang, F.; Tinti, D. S.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 2327.

(35) Raubenheimer, H. G.; Cronje, S. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Eds.; John Wiley & Sons: Chichester, England, 1999; p 608. Usón, R.; Laguna, A.; Vicente, J.; García, J.; Bergareche, B.; Brun, P. *Inorg. Chim. Acta* **1978**, *28*, 237. Usón, R.; Laguna, A.; Vicente, J.; García, J.; Bergareche, B. *J. Organomet. Chem.* **1979**, *173*, 349.

(36) Minghetti, G.; Bonati, F.; Banditelli, G. *Inorg. Chem.* **1976**, *15*, 1718. Bandini, A. L.; Banditelli, G.; Minghetti, G.; Peli, B.; Traldi, B. *Organometallics* **1989**, *8*, 590.

(37) Cetinkaya, B.; Dixneuf, P. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1827.

(38) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1981**, *114*, 1853. Minghetti, G.; Bonati, F. *J. Organomet. Chem.* **1974**, *73*, C43.

(39) Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B. *J. Organomet. Chem.* **1991**, *408*, 271. Bovio, B.; Burini, A.; Pietroni, B. R. *J. Organomet. Chem.* **1993**, *452*, 287. Desmet, M.; Raubenheimer, H. G.; Kruger, G. J. *Organometallics* **1997**, *16*, 3324. Vaughan, L. G. *J. Am. Chem. Soc.* **1970**, *92*, 730. Jutzi, P.; Hensler, H. *J. Organomet. Chem.* **1976**, *8*, 829.

(40) Frankel, R.; Kniczek, J.; Ponikwar, W.; Noth, H.; Polborn, K.; Fehlhammer, W. P. *Inorg. Chim. Acta* **2001**, *312*, 23. Raubenheimer, H. G.; Lindeque, L.; Cronje, S. *J. Organomet. Chem.* **1996**, *511*, 177.

(41) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

(42) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216.

(43) Vicente, J.; Chicote, M. T.; Guerrero, R.; Saura-Llamas, I. M.; Jones, P. G.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **2001**, *7*, 638.

(44) Usón, R.; Laguna, J.; Vicente, J. *J. Organomet. Chem.* **1977**, *131*, 471.

(45) Neenan, X. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

Table 1. Crystal Data for Compounds 1, 3·0.722 Me_2CO·0.139Et_2O, and 5

	1	**3**·0.722Me_2CO·0.139Et_2O	**5**
formula	$C_{14}H_{27}AuN_2O_2$	$C_{30.73}H_{49.72}Au_2N_4O_{0.86}$	$C_{12}H_{28}AuClN_2O_5S$
fw	452.34	882.86	544.84
space group	$P2_1/c$	$C2/c$	$P2_12_12_1$
unit cell params			
a (Å)	11.948(3)	24.661(2)	8.9449(6)
b (Å)	9.259(2)	11.2933(10)	9.3065(10)
c (Å)	15.876(4)	17.4464(16)	23.292(3)
α (deg)	90	90	90
β (deg)	110.84(2)	130.518(3)	90
γ (deg)	90	90	90
V (Å^3)	1689.4(7)	3693(6)	1939.0(3)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.778	1.588	1.866
μ (mm^{-1})	8.709	7.958	7.853
T (K)	172(2)	143(2)	293(2)
$R(F)^a$	0.0235	0.0258	0.0384
$R_w(F^2)^b$	0.0507	0.0635	0.0859
$\Delta\rho$ (e Å^{-3})	1.321	0.779	0.679

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $F > 2\sigma(F)$. [b] $R_w(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

ously described. [$Me_3S(O)$]ClO_4 was prepared from $AgClO_4$ and [$Me_3S(O)$]I (1:1 in acetone, 15 min). [$Me_3S(O)$]I precipitated upon refluxing a mixture of Me_2SO (12 mL) and MeI (8 mL) for 2 days. Diethyl ether was added to help precipitation.

X-ray Structure Determinations. Crystals of **1**, **3**, and **5** were measured (see Table 1). Structures were solved by the heavy-atom method, and all non hydrogen atoms refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). The hydrogen of the NH group was refined freely but with a restrained N−H distance. Other hydrogen atoms were included using a riding model or as rigid methyl groups. To increase stability of refinement, a system of restraints to local ring geometry and light atom U values was employed in complex **3**. In this complex, an ill-defined region of residual electron density in the region around the 2-fold axis at 0.5, 0.81, 0.75 was tentatively interpreted as a superposition of acetone and diethyl ether; the quoted composition corresponds to 0.722 acetone and 0.139 ether per molecule of the gold complex. However, the refinement was far from satisfactory. For this reason the program SQUEEZE was used to cancel out the effects of the disordered solvent. SQUEEZE is part of the PLATON program system (A. L. Spek, University of Utrecht, Netherlands, 2003) and attempts to remove mathematically the effects of disordered solvent. Physically, of course, the solvent is still present. In compound **5**, the absolute structure was determined (0.03(1) Flack parameter).[46] The programs use neutral atom scattering factors, $\Delta f'$ and $\Delta f''$, and absorption coefficients from International Tables for Crystallography.[47]

Synthesis of [Au(*C*-acac){C(NEt_2)NH^tBu}] (1). [Tl(acac)] (acac = acetylacetonate, 660 mg, 2.18 mmol) was added to a solution of [AuCl{C(NH^tBu)NEt_2}] (766 mg, 1.97 mmol) in dichloromethane (20 mL). After 40 min of stirring in a nitrogen atmosphere, the resulting suspension was filtered through a short column of Celite. The solution was concentrated (1 mL), and diethyl ether (20 mL) was added to precipitate a solid that was filtered and dried in a nitrogen stream to give **1** as a white crystalline solid, which was stored at −10 °C. Yield: 645 mg, 73%. Mp: 85 °C dec. Anal. Calcd for $C_{14}H_{27}AuN_2O_2$: C, 37.17; H, 6.02; N, 6.19. Found: C, 37.26; H, 5.97; N, 6.09. ^1H NMR (200 MHz): δ 1.17 (t, 3 H, CH_2Me, $^3J_{HH}$ = 7 Hz), 1.27 (t, 3 H, CH_2Me, $^3J_{HH}$ = 7 Hz), 1.58 (s, 9 H, ^{t}Bu), 2.31 (s, 6 H, C(O)*Me*), 3.24 (q, 2 H, CH_2), 3.85 (q, 2 H, CH_2), 4.47 (s, 1 H, CH), 5.82 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR (50.3 MHz): δ 11.68 (CH_2Me), 14.603 (CH_2Me), 30.26 [C(O)*Me*], 31.55 (C*Me*$_3$), 40.20 (CH_2), 53.49 (*C*Me$_3$), 54.35 (CH_2), 71.21 (CH), 199.57 (*C*N$_2$), 202.93 (CO). IR (cm^{-1}): ν(NH), 3308; ν(CO), 1652, 1636; ν(CN_2), 1552. Crystals of **1** suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a solution of **1** in dichloromethane.

Synthesis of [Au(Spy-2){C(NEt_2)NH^tBu}] (2). To a suspension of **1** (124 mg, 0.27 mmol) in diethyl ether (10 mL) was added a solution of 2-pyridinethiol (pySH-2) (31 mg, 0.27 mmol) in acetone (5 mL). The resulting solution was stirred for 14 h, the solvents were removed under vacuum, and the residue was stirred with diethyl ether (20 mL, 10 min). The precipitate was recrystallized from acetone and diethyl ether to give **2** as a white solid. Yield: 106 mg, 83%. Mp: 108 °C. Anal. Calcd for $C_{14}H_{24}AuN_3S$: C, 36.29; H, 5.22; N, 9.07; S, 6.92. Found: C, 36.41; H, 5.32; N, 9.16; S, 7.14. ^1H NMR (300 MHz): δ 1.18 (t, 3 H, CH_2Me, $^3J_{HH}$ = 7 Hz), 1.31 (t, 3 H, CH_2Me, $^3J_{HH}$ = 7 Hz), 1.64 (s, 9 H, ^{t}Bu), 3.27 (q, 2 H, CH_2), 4.07 (q, 2 H, CH_2), 5.82 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR (50.3 MHz): δ 11.79 (CH_2Me), 14.72 (CH_2Me), 31.62 (C*Me*$_3$), 40.21 (CH_2), 54.09 (CH_2), 54.42 (*C*Me$_3$), 117.51, 126.82, 134.80, 148.42 (CH, py), 167.43 (CS), 199.54 (*C*N$_2$). IR(cm^{-1}): ν(NH), 3260; ν(CN_2), 1548.

Synthesis of [{AuC(NEt_2)NH^tBu}$_2$(μ-C≡CC_6H_4C≡C−3)] (3). To a solution of **1** (318 mg, 0.7 mmol) in dichloromethane (20 mL) was added 1,3-diethynylbenzene (44 mg, 0.35 mmol), the reaction mixture was stirred in a nitrogen atmosphere for 8 h and then filtered through a short column of Celite. The solution was concentrated under vacuum (to ca. 1 mL), and *n*-pentane (20 mL) was added to precipitate an oily solid that was stirred with *n*-pentane (3 × 10 mL) until it became a solid that was filtered, washed with *n*-pentane (2 × 5 mL), and air-dried to give **3** as a pale yellow solid. Yield: 220 mg, 76%. Mp: 165 °C dec. Anal. Calcd for $C_{28}H_{44}Au_2N_4$: C, 40.49; H, 5.34; N, 6.75. Found: C, 40.33; H, 5.24; N, 6.34. ^1H NMR (200 MHz): δ 1.05 (t, 6 H, CH_2Me, $^3J_{HH}$ = 7 Hz), 1.17 (t, 6 H, CH_2Me, $^3J_{HH}$ = 7 Hz), 1.53 (s, 18 H, ^{t}Bu), 3.13 (q, 4 H, CH_2), 3.91 (q, 4 H, CH_2), 5.75 (s, 2 H, NH), 6.93 [t, 1 H, H5 (C_6H_4), $^3J_{HH}$ = 8 Hz], 7.16 [dd, 2 H, H4 + H6 (C_6H_4), $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz], 7.47 [t, 1 H, H2 (C_6H_4), $^4J_{HH}$ = 1.5 Hz]. $^{13}C\{^1H\}$ NMR (50.3 MHz): δ 11.86 (Me), 14.92 (Me), 31.96(C*Me*$_3$), 39.98 (CH_2), 53.91 (*C*Me$_3$), 54.11 (CH_2), 105.31 (*C*≡CAu), 125.45 [C1 + C3 (C_6H_4)], 126.03 (C≡*C*Au), 127.08 [C2 (C_6H_4)], 130.23 [C4 + C6 (C_6H_4)], 135.81 [C5 (C_6H_4)], 205.44 (CN_2). IR (cm^{-1}): ν(NH), 3305; ν(C≡C), 2104; ν(CN_2), 1531. Crystals of **3** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using acetone and diethyl ether.

Synthesis of [Au{C(NEt_2)NH^tBu}{CH(PPh_3)CO_2Me}]-ClO_4 (4). To a solution of **1** (150 mg, 0.33 mmol) in dichloro-

---

[46] Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

[47] Wilson, A. J. C. In *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199).

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

methane (10 mL) was added $(Ph_3PCH_2CO_2Me)ClO_4$ (144.2 mg, 0.33 mmol). The reaction mixture was stirred for 6 h and filtered through a short column of Celite. The solution was concentrated to dryness, and the residue was stirred with diethyl ether (2 × 20 mL). It was then dissolved in dichloromethane (2 mL) and the solution added dropwise over *n*-pentane (20 mL) vigorously stirred to precipitate **4** as a white solid. Yield: 190 mg, 73%. Mp: 68 °C. Anal. Calcd for $C_{30}H_{39}AuClN_2O_6P$: C, 45.78; H, 5.00; N, 3.56. Found: C, 46.15; H, 4.92; N, 3.44. Λ_M (Ω^{-1} cm^2 mol^{-1}): 116. ^{1}H NMR (200 MHz): δ 0.93 (t, 3 H, CH_2Me, $^3J_{HH} = 7$ Hz), 1.14 (t, 3 H, CH_2Me, $^3J_{HH} = 7$ Hz), 1.45 (s, 9 H, ^{t}Bu), 3.34 ("q", 2 H, CH_2), 3.46 (m, 2 H, CH_2), 3.62 (s, 3 H, CO_2Me), 3.90 (d, 1 H, CH, $^2J_{PH} = 4$ Hz), 6.19 (s, 1 H, NH), 7.60−7.78 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR (75.43 MHz): δ 11.70 (CH_2Me), 14.77 (CH_2Me), 30.95 (d, CH, $J_{CP} = 54$ Hz), 31.49 (CMe_3), 40.84 (CH_2), 52.04 (CO*Me*), 53.74 (CH_2), 54.08 (CMe_3), 123.38 (d, C_{ipso}, $J_{CP} = 89$ Hz), 129.86 (d, C_{ortho}, $^2J_{CP} = 13$ Hz), 133.32 (d, C_{meta}, $^3J_{CP} = 10$ Hz), 134.13 (d, C_{para}, $^4J_{CP} = 3$ Hz), 172.31 (CO), 197.26 (CN_2). $^{31}P\{^1H\}$ NMR (81 MHz): δ 27.42 (s). IR (cm^{-1}): ν(NH), 3323; ν(CO), 1692; $\nu(CN_2)$, 1546; ν(ClO), 1084; δ(OClO), 622.

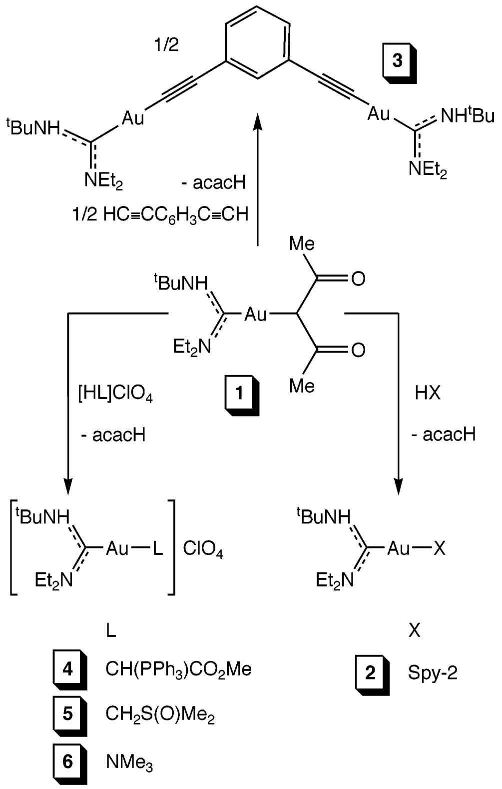
Synthesis of $[Au\{C(NEt_2)NH^tBu\}\{CH_2S(O)Me_2\}]ClO_4$ (5). $[Me_3S(O)]ClO_4$ (58 mg, 0.30 mmol) was added to a solution of **1** (135 mg, 0.3 mmol) in acetone (10 mL). The reaction mixture was stirred for 6 h and filtered through a short column of Celite. The solution was concentrated (2 mL), and diethyl ether (20 mL) was added to precipitate a solid. The solvent was decanted off, and the solid was stirred with diethyl ether (10 mL, 10 min), filtered, and suction dried to give **5** as a white solid. Yield: 133 mg, 82%. Mp: 114 °C. Anal. Calcd for $C_{12}H_{28}AuClN_2O_5S$: C, 26.45; H, 5.18; N, 5.14. Found: C, 26.72; H, 5.09; N, 5.22. Λ_M (Ω^{-1} cm^2 mol^{-1}): 97. ^{1}H NMR (300 MHz): δ 1.20 (t, 3 H, CH_2Me, $^3J_{HH} = 7$ Hz), 1.31 (t, 3 H, CH_2Me, $^3J_{HH} = 7$ Hz), 1.60 (s, 9 H, ^{t}Bu), 3.20 (s, 2 H, CH_2S), 3.29 (q, 2 H, CH_2Me, $^3J_{HH} = 7$ Hz), 3.59 (s, 6 H, MeS), 3.92 (q, 2 H, CH_2Me, $^3J_{HH} = 7$ Hz), 5.94 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR (50.3 MHz): δ 11.70 (Me), 14.86 (Me), 32.02 (CMe_3), 39.91 (CH_2), 44.11 (SMe), 52.43 (SCH_2), 53.84 (CMe_3), 54.20 (CH_2), 201.14 (CN_2). IR (cm^{-1}): ν(NH), 3330; $\nu(CN_2)$, 1545; ν(ClO), 1091; δ(OClO), 620. Crystals of **5** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using dichloromethane and diethyl ether.

Synthesis of $[Au\{C(NEt_2)NH^tBu\}(NMe_3)]ClO_4$ (6). $(Me_3NH)ClO_4$ (38.5 mg, 0.24 mmol) was added to a solution of **1** (109 mg, 0.24 mmol) in acetone (15 mL). The resulting solution was stirred for 4 h and filtered through anhydrous $MgSO_4$ to remove traces of colloidal gold. The filtrate was concentrated (1 mL), and diethyl ether (20 mL) was added to precipitate a solid, which was recrystallized from acetone and diethyl ether to give **6** as a white solid. Yield: 106 mg, 86%. Mp: 72 °C. Anal. Calcd for $C_{12}H_{28}AuClN_3O_4$: C, 28.16; H, 5.71; N, 8.21. Found: C, 28.57; H, 5.89; N, 7.89. Λ_M (Ω^{-1} cm^2 mol^{-1}): 114. ^{1}H NMR (300 MHz): δ 1.21 (t, 3 H, CH_2Me, $^3J_{HH} = 8$ Hz), 1.33 (t, 3 H, CH_2Me, $^3J_{HH} = 8$ Hz), 1.64 (s, 9 H, ^{t}Bu), 2.91 (s, 9 H, NMe_3), 3.46 (m, 2 H, CH_2), 3.89 (m, 2 H, CH_2), 6.16 (s, br, 1 H, NH). $^{13}C\{^1H\}$ NMR (50.3 MHz, APT): δ 11.69 (CH_2Me), 14.79 (CH_2Me), 31.78 (CMe_3), 41.13 (CH_2), 52.79 (NMe_3), 53.98 (CMe_3), 55.55 (CH_2), 182.01 (CN_2). IR (cm^{-1}): ν(NH), 3334; $\nu(CN_2)$, 1556; ν(ClO), 1084; δ(OClO), 622.

Results and Discussion

Synthesis. The synthesis of **1** was achieved by reacting [Tl(acac)] with $[AuCl\{C(NEt_2)NH^tBu\}]$ in dichloromethane. To prevent contamination of **1** with the starting gold complex, a small excess of [Tl(acac)] was used, which was removed along with the byproduct TlCl by filtration of the resulting suspension through Celite. The reactions of **1** with 2-pyridinethiol (HSpy-2), $C_6H_4(C{\equiv}CH)_2$-1,3 (2:1), $[Ph_3PCH_2CO_2Me]ClO_4$, $[Me_3S(O)]ClO_4$, or $[Me_3NH]ClO_4$ are acid−base processes that produce the desired complexes $[Au(Spy\text{-}2)\{C(NEt_2)NH^tBu\}]$ (**2**), $[\{AuC(NEt_2)NH^tBu\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}3)]$ (**3**), $[Au\{C(NEt_2)NH^tBu\}\{CH(PPh_3)CO_2Me\}]ClO_4$ (**4**), $[Au\{C(NEt_2)NH^tBu\}\{CH_2S(O)Me_2\}]ClO_4$ (**5**), or $[Au\{C(NEt_2)NH^tBu\}(NMe_3)]ClO_4$ (**6**) together with acetylacetone (Scheme 1). The reactions were carried out in acetone (**5**, **6**), dichloromethane (**3**, **4**), or diethyl ether/acetone (**2**) using a 1:1 molar ratio of the reagents with the exception of that giving **3**, which required a **1**:dialkyne ratio of 2:1. The presence of the byproduct acetylacetone caused the complexes to precipitate as oily materials, and in some cases, stirring with *n*-pentane or diethyl ether was necessary in order to convert them into solid products.

Scheme 1



Only a few 2-pyridinethiolate gold(I) complexes are known. The majority contain a phosphine co-ligand[48,49] and are of the type $[Au(Spy\text{-}2)(PR_3)]$. Complex **2**, the polymer $[Au(Spy\text{-}2)_n]$,[48,50] and the anionic $[Au(Spy\text{-}2)_2]^-$ [21] are the only exceptions.

Arenediethynylgold(I) complexes, such as **3**, are currently attracting considerable attention because some show interesting photophysical properties.[51,52] The reported complexes are polymeric derivatives $[AuC{\equiv}C(Ar)C{\equiv}CAu]_n$[7,53,54] or complexes containing a phos-

---

(48) Usón, R.; Laguna, A.; Laguna, M.; Jimenez, J.; Gómez, M. P.; Sainz, A.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3457.

(49) Hao, L. J.; Mansour, M. A.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 5520. Canales, F.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Sarroca, C. *Inorg. Chem.* **1997**, *36*, 5206. Cookson, P. D.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1993**, 259. Bardaji, M.; Connelly, N. G.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2245.

(50) Jia, G. C.; Puddephatt, R. J.; Vittal, J. J. *Polyhedron* **1992**, *11*, 2009.

(51) Wong, W. Y.; Choi, K. H.; Lu, G. L.; Shi, J. X.; Lai, P. Y.; Chan, S. M.; Lin, Z. Y. *Organometallics* **2001**, *20*, 5446.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

phine or isocyanide as the co-ligand.[7,51−55] The first anionic arenediethynylgold(I) complexes have been recently reported.[56] Complex **3** is the first arenediethynylgold(I) complex containing a carbene. We are only aware of one gold(I) complex containing an alkyne and a carbene as ligands, obtained by reacting [Au(carbene)-Cl] with PhC≡CH and K_2CO_3.[42]

Phosphorus-ylide gold(I) complexes form one of the most numerous families of organogold(I) complexes.[57] However, complex **4** is the first containing a carbene ligand. By contrast, the only sulfur-ylide gold(I) complexes are $[AuCl\{CH_2S(O)Me_2\}_2]$,[58] two containing the anionic ylide μ-$(CH_2)_2S(O)NMe_2$ and phosphine ligands,[59] $[(AuPPh_3)_n\{CH_mS(O)Me_2\}_2]^{q+}$ [(*n*, *m*, *q*) = (1, 2, 1), (3, 0, 1), (4, 0, 2)],[12] and a family of complexes containing the mixed P-, S-ylide ligand $Ph_3PCHS(O)_2C_6H_4Me$-4, recently reported.[29] Therefore, complex **5** is the first carbenegold(I) complex containing a sulfur-ylide ligand. Complex **6** is also the first with an additional amine ligand.

We failed to prepare complexes $[Au\{C(NEt_2)NH^tBu\}(NH_3)]ClO_4$ or $[\{Au\{C(NEt_2)NH^tBu\}\}_4(\mu^4\text{-}N)]ClO_4$ from **1** and NH_4ClO_4 1:1 or 4:1, respectively. The homologous complexes with triarylphosphines PR_3 (R = Ph, C_6H_4-OMe-4) instead of the carbene were easily obtained from NH_4ClO_4 and the appropriate $[Au(acac)PR_3]$ complexes. In the reactions of **1** and NH_4ClO_4 oily materials formed that we could not convert into solid products even after stirring them with different solvents or after prolonged vacuum. Their NMR spectra show the presence of the carbene ligand and solvents that cannot be removed probably due to some strong hydrogen bond interactions.

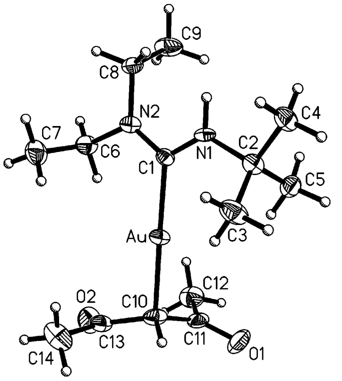


Figure 1. 50% probability thermal ellipsoid plot of **1** with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(1) 2.049(5), Au−C(10) 2.122(5), N(1)−C(1) 1.329(6), N(2)−C(1) 1.332(6), C(1)−Au−C(10) 177.78(18), C(1)−N(1)−C(2) 127.5(4), C(1)−N(2)−C(8) 124.6(4), C(1)−N(2)−C(6) 121.7(4), C(8)−N(2)−C(6) 113.7(4), N(1)−C(1)−N(2) 117.8(4), N(1)−C(1)−Au 123.3(4), N(2)−C(1)−Au 118.8(3).

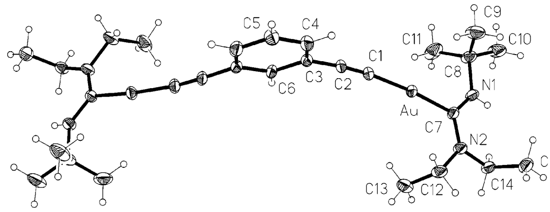


Figure 2. 50% probability thermal ellipsoid plot of **3** with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(1) 1.992(4), Au−C(7) 2.043(4), N(1)−C(7) 1.328(5), N(1)−C(8) 1.508(5), N(2)−C(7) 1.359(5), N(2)−C(14) 1.459(5), N(2)−C(12) 1.472(5), C(1)−C(2) 1.207(5), C(2)−C(3) 1.429(5), C(1)−Au−C(7) 174.94(14), C(7)−N(1)−C(8) 126.5(3), C(7)−N(2)−C(14) 124.9(3), C(7)−N(2)−C(12) 119.8(3), C(14)−N(2)−C(12) 115.4(3), C(2)−C(1)−Au 173.1(3), C(1)−C(2)−C(3) 176.8(4).

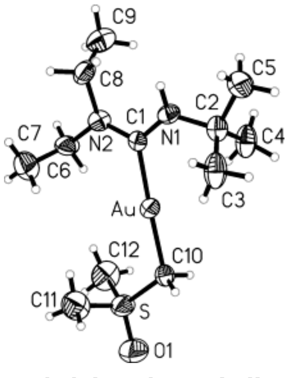


Figure 3. 50% probability thermal ellipsoid representation of the cation of **5** with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(4) 2.026(9), Au−C(1) 2.072(10), S−O(1) 1.445(9), S−C(1) 1.701(9), S−C(2) 1.750(14), S−C(3) 1.760(12), N(1)−C(4) 1.306(12), N(2)−C(4) 1.352(10), C(4)−Au−C(1) 176.6(4), S−C(1)−Au 117.0(5), N(1)−C(4)−N(2) 116.1(9), N(1)−C(4)−Au 122.1(6), N(2)−C(4)−Au 121.7(7).

X-ray Crystal Structures of 1, 3, and 5. Figures 1−3 show the structures of complexes **1**, **3**, and **5**, respectively, which display many common features. Thus, all of them show the gold atom in an essentially linear environment [C−Au−C bond angles: 177.8(2)° (**1**); 174.94(14)° (**3**); 176.6(4)° (**5**)]. The carbene ligand shows a planar disposition for the C(2)−H(1)−N(1)−C(1)−N(2)−C(6)−C(8) (**1** and **5**) and C(8)−H(1)−N(1)−C(7)−N(2)−C(12)−C(14) (**3**) fragments [mean deviation (Å): 0.022 (**1**), 0.006 (**3**), and 0.026 (**5**)] with the gold atom slightly out of the plane (Å): 0.16(2) (**1**), 0.02(2) (**3**), and 0.26(4) Å (**5**). Both, C−NH^tBu and C−NEt_2 bond distances are similar and intermediate between those corresponding to single and double $C(sp^2)$−$N(sp^2)$ bonds [**1**: C(1)−N(1), 1.331(6); C(1)−N(2), 1.333(6); **3**: C(7)−N(1), 1.328(5); C(7)−N(2), 1.359(5); **5**: C(1)−N(1), 1.306(12); C(1)−N(2), 1.352(10) Å].[60] Both the planar

---

(52) Chao, H. Y.; Lu, W.; Li, Y. Q.; Chan, M. C. W.; Che, C. M.; Cheung, K. K.; Zhu, N. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14696. Hurst, S. K.; Cifuentes, M. P.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Asselberghs, I.; Persoons, A. *J. Organomet. Chem.* **2002**, *642*, 259. Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541.

(53) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *216*, 313. Macdonald, M. A.; Puddephatt, R. J.; Yap, G. P. A. *Organometallics* **2000**, *19*, 2194. Puddephatt, R. J. *Chem. Commun.* **1998**, 1055. Irwin, M. J.; Jia, G. C.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51.

(54) Jia, G. C.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565.

(55) Irwin, M. J.; Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Chem. Commun.* **1996**, 1281.

(56) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Abrisqueta, M. D.; Hernández, F. J.; Jones, P. G. *J. Organomet. Chem.* **2002**, *663*, 40.

(57) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Eds.; John Wiley & Sons: Chichester, England, 1999; p 681.

(58) Yamamoto, A.; Ozawa, F.; Osakada, K.; Huang, L.; Son, T. I.; Kawasaski, N.; Doh, M. K. *Pure Appl. Chem.* **1991**, *63*, 687. Konno, H.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2561.

(59) Feng, D. F.; Tang, S. S.; Liu, C. W.; Lin, I. J. B. *Organometallics* **1997**, *16*, 901. Lin, I. J. B.; Liu, C. W.; Liu, L. K.; Wen, Y. S. *Organometallics* **1992**, *11*, 1447.

(60) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, S1.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

geometry and the C−N bond distances suggest that extensive electron delocalization occurs within the CN_2 moiety, as previously described.[6] Although the partial double bond character of the C−NH^{t}Bu bond in the carbene ligand allows it to exist in two possible conformations (*E* or *Z*), only the *Z* form is present in complexes **1**, **3**, and **5** in the solid state. This is also the case in other "Au-{C(NH^{t}Bu)NEt$_2$}" complexes structurally characterized by us[6] and seems to be due to steric reasons. In fact, the most bulky ^{t}Bu group is *cis* to the gold fragment to avoid contact with the more congested NEt_2 group. The Au−$C_{carbene}$ bond distances are similar for the three compounds described [2.047(5) (**1**); 2.043(4) (**3**); 2.026(9) Å (**5**)].

In **1** both carbonyl groups of the acac ligand are in *anti* disposition, the torsion angles defined by the C−H and each of the C═O bonds being −140° and −10.6°. This is also the case for the only three other acetylacetonatogold complexes structurally characterized so far [Au(acac)PPh$_3$][61] and [Au$_2$(acac){CH(PPh$_2$)$_2$}]$_2$[27] and the gold(III) complex [Au(Azot)(acac)Cl],[62] in which the analogous torsion angles are 6.2° and −116.9°, −140° and −10.6°, or 13.8° and 145.4°, respectively. The Au−C_{acac} bond distance in **1** [2.121(5) Å] is similar to that found in [Au$_2$(acac){CH(PPh$_2$)$_2$}]$_2$[27] [2.120 Å] but longer than the analogous bond in [Au(acac)PPh$_3$][61] and [Au(Azot)(acac)Cl][62] [2.092 and 2.084 Å, respectively]. The differences could be accounted for in terms of the charge of the metal center and the nature of the ligand in *trans* position. As expected, the shortest Au−C_{acac} bond distance is found in the gold(III) complex with a nitrogen donor ligand in *trans* position, whereas the longer distances correspond to gold(I) complexes with carbon donor ligands in *trans* position, that of the gold(I) phosphine complex being intermediate.

In **3**, which displays crystallographic 2-fold symmetry, the Au−$C_{alkynyl}$ and C≡C bond distances [1.992(4) and 1.207(6) Å, respectively] are similar to those found in other alkynylgold(I) complexes, in the ranges 1.998(5)−2.046(4) and 1.204(4)−1.215(4) Å, respectively.[4,6,54,63]

In **5**, the S−C_{ylide} and S═O bond distances [1.701(9) and 1,445(9) Å, respectively] are similar to the analogous ones in [{Ph$_3$PAu}$_4${μ^4-CS(O)Me$_2$](ClO$_4$)$_2$ [1.699(9) and 1.466(7) Å, respectively], the only other complex with the same sulfur ylide ligand characterized by X-ray diffraction studies.[12] However, the Au−C_{ylide} bond distance in **5** [2.072 (10) Å] is shorter than those found in the tetranuclear complex [2.131(8), 2.162(10), 2.167(10), and 2.198(8) Å], which must be due to the electronically deficient nature of the Au−C bonds (4 bonds/3 pairs of electrons) in the tetranuclear complex.

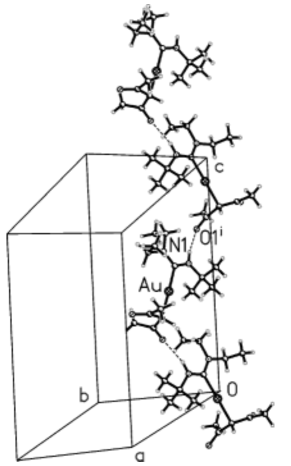


Figure 4. Linear chain parallel to the *c* axis formed through NH···O^i hydrogen bonds in complex **1** [i: *x*, $-y - 3/2$, $z + 1/2$, N(1)···O(1)^i 3.114(6), H(1)···O(1)^i 2.21(2) Å, and N(1)−H(1)···O(1)^i 165(4)°].

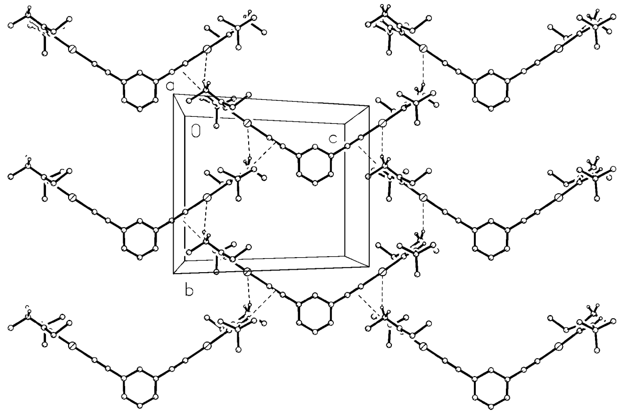


Figure 5. Layer of molecules of complex **3**, showing hydrogen bonds [H(14A)···Au 3.06 Å (C−H normalized to 1.08 Å), C(14)−H(14A)···Au 162° ($0.5 - x$, $-0.5 + y$, $0.5 - z$); N(1)−H(1) 0.91 Å, H(1)···Cent(C1−C2) 2.94 Å, N(1)−H(1)···Cent(C1−C2) 158° ($0.5 - x$, $-0.5 + y$, $0.5 - z$)]. H atoms not involved in H bonds are omitted.

In the three complexes the NH hydrogen atom is involved in hydrogen bonding. In **1** the interaction is with one of the carbonyl oxygen atoms of the acetylacetonato ligand of an adjacent molecule (Figure 4). In **3**, the hydrogen atom is directed to the center of a triple bond (C_{cent}) of a neighboring molecule [N−H, 0.91 Å; H···C_{cent}, 2.94 Å; N−H···C_{cent}, 158°]. In addition, a C−H···Au contact also exists [C(14)−H(14A)···Au, normalized to C−H 1.08, H···Au distance 3.06 Å, C−H···Au angle, 162°], reinforcing each other. The net effect is to form layers of molecules parallel to the planes $(40\bar{2})$ (Figure 5). C−H···Au contacts [H···Au distance range: 2.73−3.07 Å; C−H···Au angle range: 143−172°] have been recently reported in the literature.[8,29,51,64] In **5** a molecular layer is formed through hydrogen bonds with oxygen atoms of two different perchlorate anions (see Figure 6a). Weak C−H···OClO$_3$ hydrogen bonds connect the molecular layers (see Figure 6b).

NMR Spectra. The position of each of the ^{1}H and ^{13}C NMR resonances of the carbene ligand in complexes **1**−**6** varies within a very narrow range from one to

---

(61) Grandberg, K. I.; Kuz'mina, L. G.; Smyslova, E. I.; Zinin, A. I.; Krut'ko, D. P.; Dyadchenko, V. P. *Zh. Neorg. Khim.* **1996**, *41*, 231. Kuz'mina, L. G. *Koord. Khim.* **1994**, *20*, 540.

(62) Vicente, J.; Bermudez, M. D.; Escribano, J.; Carrillo, M. P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3083.

(63) Li, D.; Hong, X.; Che, C. M.; Lo, W. C.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929. Payne, N. C.; Ramachandran, R.; Puddephatt, R. J. *Can. J. Chem.* **1995**, *73*, 6. Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A.; Hockless, D. C. R. *Organometallics* **1996**, *15*, 5738. Muller, T. E.; Choi, S. W. K.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Yam, V. W. W. *J. Organomet. Chem.* **1994**, *484*, 209. Shieh, S. J.; Hong, X.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3067. Carriedo, G. A.; Riera, V.; Solans, X.; Solans, J. *Acta Crystallogr. C* **1988**, *44*, 978. Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163. Bruce, M. I.; Duffy, D. N. *Aust. J. Chem.* **1986**, *39*, 1697. Bruce, M. I.; Grundy, K. R.; Liddell, M. J.; Snow, M. R.; Tieknik, E. R. T. *J. Organomet. Chem.* **1988**, *344*, C49.

(64) Barranco, E. N.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G.; Ahrens, B. *Inorg. Chem.* **2000**, *39*, 680.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on September 9, 2003 on http://pubs.acs.org | doi: 10.1021/om030372r

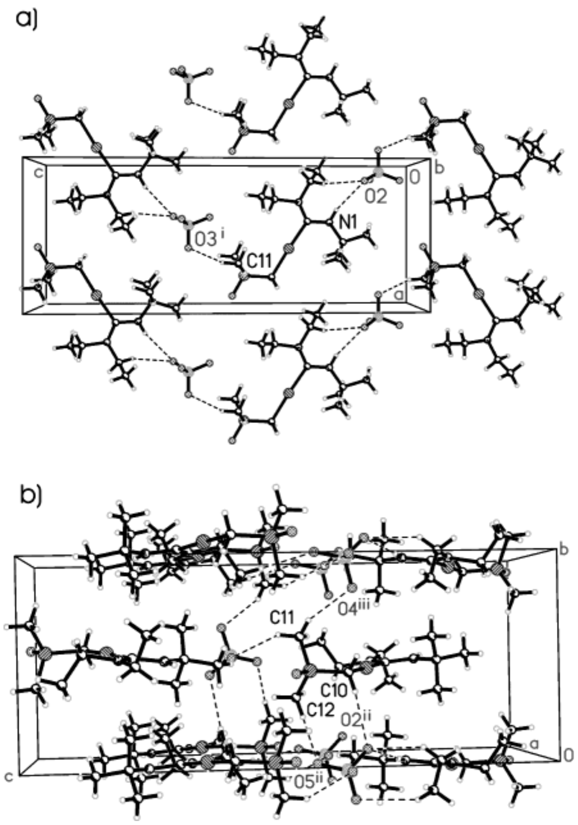


Figure 6. (a) Molecular layer perpendicular to the *b* axis formed through NH$\cdots$OClO$_3$ [N(1)$\cdots$O(2) 3.372(12), H(1)$\cdots$O(2) 2.54(3) Å, N(1)−H(1)$\cdots$O(2) 168(9)°] and CH$\cdots$OClO3 [C(11)$\cdots$O(3)^{i} (i: $-x + 5/2$, $-y + 1$, $z + 1/2$) 3.301(16), H(11A)$\cdots$O(3)^{i} 2.40 Å, C(11)−H(11A)$\cdots$O(3)^{i} 156.3°] hydrogen bonds. (b) Packing view showing the layer connection through CH$\cdots$OClO$_3$ hydrogen bonds [C(10)−H(10A)$\cdots$O(2)^{ii} (ii: $-x + 2$, $y + 1/2$, $-z + 3/2$): C(10)$\cdots$O(2)^{ii} 3.532(19), H(10A)$\cdots$O(2)^{ii} 2.60 Å, C(10)−H(10A)$\cdots$O(2)^{ii} 161.0°; C(12)−H(12B)$\cdots$O(5)^{ii}: C(12)$\cdots$O(5)^{ii} 3.570(19), H(12B)$\cdots$O(5)^{ii} 2.67 Å, C(12)−H(12B)$\cdots$O(5)^{ii} 156.4°; C(11)−H(11C)$\cdots$O(4)^{iii} (iii: $-x + 2$, $y - 1/2$, $-z + 3/2$): C(11)$\cdots$O(4)^{iii} 3.501(18), H(11C)$\cdots$O(4)^{iii} 2.69 Å, C(11)−H(11C)$\cdots$O(4)^{iii} 142.6°]

another complex. The partial multiple bond character of the C−N bond in the CNH^{t}Bu moiety can give rise to two possible isomers of each complex, *E* and *Z*, depending on the *trans or cis* disposition of the ^{t}Bu group with respect to the gold fragment. As only one resonance is observed in both the ^{1}H and ^{13}C{^{1}H} NMR spectra of these complexes for each of the nuclei in the NH^{t}Bu fragment, we can assume that only one of the possible isomers is present in solution or the C−NH^{t}Bu bond is weak enough to allow a free rotation of the NH^{t}Bu group. In the solid state, and probably in solution if only one isomer existed, the geometry could be *Z* because it is sterically more favored and is observed in the crystal structures of complexes **1**, **3**, and **5** and all the “{C(NH^{t}Bu)NEt$_2$}gold(I)” complexes structurally characterized by us.[6] The duplication of each of the resonances due to the NEt$_2$ nuclei observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of these complexes is indicative of the inequivalence of both ethyl groups and must be attributed to the restricted rotation of the NEt$_2$ group around the C−N bond. The same NMR pattern has been found in other {C(NH^{t}Bu)NEt$_2$} complexes.[4,65]

The resonances due to the other ligands are at δ values similar to those observed in other acetylacetonato,[25−27] ethynyl,[3,4] 1,3-diethynylbenzene,[56] trimethylamine,[17] acetylmethylenetriphenylphosphorane,[10] dimethylsulfoxylide,[12] or 2-pyridylthiolate[1] gold(I) complexes.

IR Spectra. The IR spectra of all these carbene ligands show a medium absorption in the range 3205−3334 cm^{-1} due to the ν(NH) mode. The great differences observed in the position of this band may be attributed to the participation of the NH group in hydrogen bonding as observed in the crystal structures of **1**, **3**, and **5**. They show also one intense band in the 1531−1562 cm^{-1} region that has been assigned to the CN$_2$ moiety in other carbenegold(I) complexes.[65,66] The alkynyl complex **3** shows the ν(C≡C) absorption at 2104 cm^{-1}. Complexes **1** and **4** show one intense absorption in the 1652−1692 cm^{-1} region due to the carbonyl groups they contain. The cationic complexes **5** and **6** show characteristic bands of the perchlorato anion at 1084−1091 [ν(ClO)] and 620−622 [δ(OClO)] cm^{-1}.

Acknowledgment. We thank the Ministerio de Ciencia y Tecnología, FEDER (BQU2001-0133), and the Fonds der Chemischen Industrie for financial support. M.M.A.-F. thanks Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain) for a grant.

Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and CIF files for **1**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030372R

---

(65) Banditelli, G.; Bonati, F.; Calogero, S.; Valle, G. *J. Organomet. Chem.* **1984**, *275*, 153.

(66) Zhang, S. W.; Ishii, R.; Takahashi, S. *Organometallics* **1997**, *16*, 20. Usón, R.; Laguna, A.; Villacampa, M. D.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 2035. McCleverty, J. A.; Da Mota, M. M. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2571.