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Fast and Reversible Intramolecular Cleavage of an Au−C Bond in the Spiked-Triangular Metal Complexes $[Fe_3Au(\mu_4,\eta^2\text{-}C\equiv C^tBu)(CO)_9(PR_3)]$ (R = Ph, ^{i}Pr)

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Summary: The C−S bond cleavage in the alkynethiolate ligand of the compound $Li[Fe_3(\mu_3\text{-}SC\equiv C^tBu)(CO)_9]$ *(**1a**) takes place in its reaction with* $[AuClPR_3]$ *(R = Ph,* ^{i}*Pr), affording the complexes* $[Fe_3Au(\mu_4,\eta^2\text{-}C\equiv C^tBu)(CO)_9(PR_3)]$ *(R = Ph (**3a**),* ^{i}*Pr (**3b**)). The gold fragment displays an unexpected bonding mode, and a fast and reversible process of oxidative addition/reductive elimination of the Au−C bond has been observed in solution.*

Transition-metal chemistry with organosulfur ligands is an attractive subject, due to its relevance from a biological, industrial, and environmental point of view.[1] Although thiolate or alkynyl chemistry has been widely explored, only a few complexes containing alkynethiolate ligands have been described.[2] Within the well-known field of mixed gold−transition-metal clusters,[3] we have previously reported some Fe_2Au and Fe_3Au compounds bearing alkane- or arenethiolate ligands.[4] Due to the absence of data on iron−gold alkynyl compounds, we considered it of interest to synthesize clusters bearing $RC\equiv CS^-$ ligands in order to know whether the presence of a C−C triple bond in these sulfur ligands could have an influence on the structure of the new compounds. Unexpectedly, however, we have found that sulfur is easily extruded from the alkynethiolate ligands upon reaction with suitable gold complexes. Moreover, we have discovered a novel dynamic process operating in the resulting Fe_3Au clusters which involves the reversible cleavage of an Au−C(alkyne) bond. To our knowledge, there is no precedent in the literature for this type of metal−carbon bond cleavage.

Reaction of $Fe_3(CO)_{12}$ with $LiSC\equiv C^tBu$ in refluxing THF yields $Li[Fe_3(\mu_3\text{-}SC\equiv C^tBu)(CO)_9]$ (**1a**) as the major product after chromatographic work on silica gel, along with a small amount of $[Fe_2(\mu\text{-}SC\equiv C^tBu)_2(CO)_6]$ (**2**). Complex **2** has been characterized in solution, its ^1H NMR spectrum being indicative of the presence of syn/anti isomers (see the Supporting Information). Compound **1a** and the analogous $(NEt_4)[Fe_3(\mu_3\text{-}SC\equiv C^tBu)(CO)_9]$ (**1b**) exhibit a single resonance for the *tert*-butyl group in the ^1H NMR spectrum, and the pattern of their C−O stretching bands is similar to those reported for the related clusters $Li[Fe_3(\mu_3\text{-}SR)(CO)_9]$ (R = alkyl, aryl).[4a] The FAB$^-$ mass spectrum of **1b** shows peaks corresponding to the molecular ion and those derived from loss of the sulfur atom and up to seven carbonyls in the latter.

Treatment of a THF solution of **1a** with $[AuClPPh_3]$ in the presence of $TlBF_4$ leads[5] to the formation of the new cluster $[Fe_3Au(\mu_4,\eta^2\text{-}C\equiv C^tBu)(CO)_9(PPh_3)]$ (**3a**) and the known complex $[Fe_3Au_2(\mu_3\text{-}S)(CO)_9(PPh_3)_2]$,[6] together with some other unidentified compounds. The main products are obviously derived from a C−S bond cleavage in the alkynethiolate ligand in the starting **1a**. Although the complexes $[M_3Au(\mu_3,\eta^2\text{-}C\equiv CR)(CO)_9(PPh_3)]$ are known for M = Ru,[7] Os,[8] to our knowledge **3a** represents the first example of an Fe_3Au cluster containing an alkynyl group. The molecular structure of **3a** (Figure 1) contains an "out-of-plane" spiked triangular metal core, which interacts with the $C_2{}^tBu$ ligand.[9] Similar $[M_3M'(\mu_4,\eta^2\text{-}C\equiv CR)]$ complexes have been reported.[10]

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(5) $[AuCl(PPh_3)]$ and $TlBF_4$ were added to a THF solution of compound **1a**. After 2 h of stirring at room temperature the solvent was removed under vacuum. Chromatographic workup afforded **3a**.

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(9) Crystal structure analysis (Stoe imaging plate diffraction system): **3a**, monoclinic, $P2_1/n$, $a = 15.087(5)$ Å, $b = 9.997(5)$ Å, $c = 23.272(5)$ Å, $\beta = 98.531(5)°$, $V = 3471(2)$ Å^3, $Z = 4$, 4969 unique reflections, 548 parameters. R1 = 0.0472, wR2 = 0.1162 ($I > 2\sigma(I)$); R1 = 0.0630, wR2 = 0.1238 (all data).

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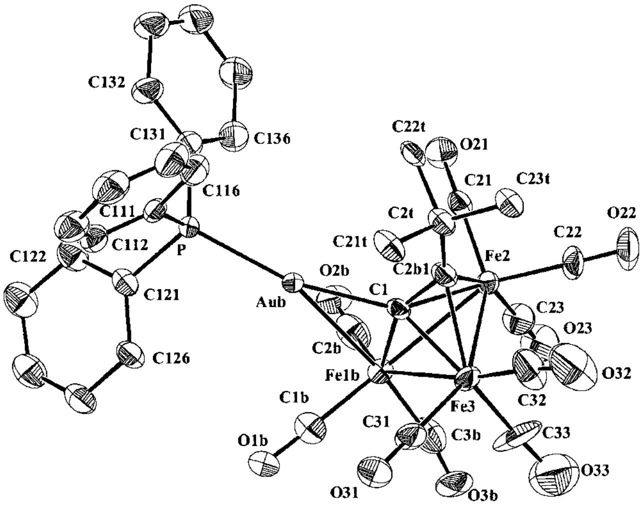
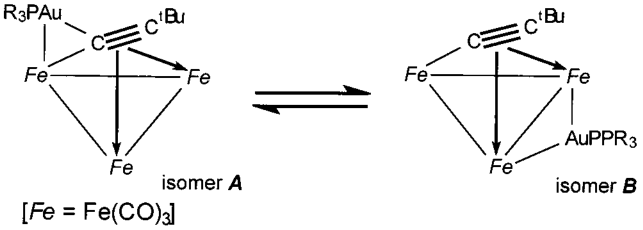


Figure 1. View of compound **3a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1b)−Fe(2), 2.702(8); Fe(1b)−Fe(3), 2.588(7); Fe(2)−Fe(3), 2.476(2); Fe(1b)−Au(b), 2.672(8); Au(b)−C(1), 2.109(10); Fe(1b)−C(1), 1.808(9); Fe(2)−C(1), 2.027(8); Fe(3)−C(1), 2.001(9); Fe(2)−C(2b1), 1.92(4); Fe(3)−C(2b1), 2.054(16); C(1)−C(2b1), 1.348(18); C(1)−C(2b1)−C(2t), 137(2); Fe(1b)−Fe(3)−Fe(2), 64.44(18); Fe(2)−Fe(1b)−Fe(3), 55.78(17); Fe(3)−Fe(2)−Fe(1b), 59.78(14); Fe(3)−Fe(1b)−Au(b), 96.6(2); Fe(2)−Fe(1b)−Au(b), 91.4(2); C(1)−Au(b)−P, 160.9(3); Fe(1b)−Au(b)−P, 156.6(3); Fe(1b)−C(1)−Fe(3), 85.4(4); Fe(2)−C(1)−Fe(3), 75.9(3).

Scheme 1



The coordination position of the gold fragment in **3a** is unexpected, as iron−gold clusters bearing one or more $AuPPh_3$ moieties usually display structures in which the gold unit adopts either edge-bridging or face-capping positions. Compound **3a** appears to be the first example of a mixed M_3Au cluster (M = Fe, Ru, Os) in which the gold fragment displays this unexpected bonding mode. As far as we know, $[Fe_2MAu_2(\mu_4,\eta^2\text{-}C{\equiv}CPh)(CO)_7(PPh_3)_2]$ (M = Ir, Rh)[11] are the only examples where a similar coordination environment for the $Au_2(PPh_3)_2$ unit has been previously observed. Moreover, it should be noted that the structure of compound **3a** contrasts with those of the isoelectronic Ru and Os analogues $[M_3Au(\mu_3,\eta^2\text{-}C{\equiv}C^tBu)(CO)_9(PPh_3)]$,[7,8] the latter having the gold fragment bonded to the metal framework. Thus, in a formal sense, replacement of Fe by Ru or Os favors the oxidative cleavage of the Au−C(acetylide) bond.

In solution, **3a** exists as an equilibrium mixture of two isomers[12] (labeled ***A*** and ***B*** in Scheme 1). Interconversion between isomers is fast at room temperature on the NMR time scale, so that averaged ^1H, ^{13}C, and ^{31}P spectra are observed at this temperature. When the temperature is lowered, all resonances broaden, and each of them eventually splits into two resonances with ca. 2:1 relative intensities, except for the carbonyl resonances, which exhibit a more complex behavior. The relative intensities of the resonances assigned to each of the two isomers change moderately with temperature, so that the major isomer ***A*** is more abundant as the temperature is lowered (ratio ***A***:***B*** = 2.0 at 203 K, 2.2 at 188 K). From this we conclude that the minor isomer ***B*** must be more abundant at room temperature, in agreement with the averaged chemical shifts observed at 291 K. In fact, from the averaged value of *J*(PC) of the ipso carbon of PPh_3, we can estimate a ratio ***A***:***B*** of 2:3 at 291 K.

Examination of the carbonyl resonances for **3a** reveals severe geometric differences between isomers. Isomer ***B*** seems to have the symmetry of the hydrido complex $[Fe_3(\mu\text{-}H)(\mu_3,\eta^2C{\equiv}C^tBu)(CO)_9]$ (**4**) (see below), having an $AuPPh_3$ fragment bridging an Fe−Fe edge, as found for $[M_3Au(\mu_3,\eta^2\text{-}C{\equiv}C^tBu)(CO)_9(PPh_3)]$ (M = Ru, Os).[7,8] The major isomer gives rise at 188 K to just two resonances (2:1 intensity) and is consistent with the more symmetrical structure found for this compound in the crystal, after allowing for rapid rotation of the $Fe(CO)_3$ moieties of the cluster. The above proposal is consistent with the spectroscopic properties of the alkyne resonances. In fact, although chemical shifts for C_α or C_β are found in similar regions (around 185 or 140 ppm, respectively), only the C_α resonance of the major isomer (181.3 ppm) exhibits P−C coupling (J_{PC} = 58 Hz). Moreover, the large value of this coupling is fully consistent with a carbon atom directly bonded to the $AuPPh_3$ fragment. Finally, the above assignment is also consistent with the temperature dependence of the equilibrium between isomers, as the isomer more abundant at low temperature corresponds to that found in the crystal.

In all, the interconversion between isomers ***A*** and ***B*** represents a reversible process of oxidative addition/reductive elimination of an Au−C bond across a metal−metal bond (Scheme 1). To our knowledge, this is the first time that a process like that has been detected.[3a,13] To gain further insight into the factors governing the equilibrium between isomers for **3a**, we have prepared the related cluster $[Fe_3Au(\mu_4,\eta^2\text{-}C{\equiv}C^tBu)(CO)_9(P^iPr_3)]$ (**3b**), which also exists in solution as a equilibrium

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(10) Deabate, S.; Giordano, R.; Sappa, E. *J. Cluster Sci.* **1997**, *8*, 407.

(11) Bruce, M. I.; Koutsantonis, G. A.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *408*, 77.

(12) Data for **3a** are as follows. ^1H NMR: at 291 K in $CDCl_3$ δ 7.61−7.47 (m, 15H, C_6H_5), 1.57 (s, 9H, $C(CH_3)_3$); in CD_2Cl_2 at 223 K δ 7.70−7.35 (m, 30H, C_6H_5), 1.54, 1.49 (2 × s, br, 2 × 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 291 K: δ 214.2 (br, 6CO), 213.3 (br, 3CO), 134.3 (d, J_{PC} = 14 Hz, C_6H_5), 132.4 (s, $^4C(C_6H_5)$), 129.8 (d, J_{PC} = 12 Hz, C_6H_5), 129.7 (d, J_{PC} = 55 Hz, $^1C(C_6H_5)$), 39.9 (s, $\mathit{C}(CH_3)_3$), 35.4 (s, CH_3), alkynyl signals are too broad to be observed. $^{31}P\{^1H\}$ NMR in CD_2Cl_2: at 291 K δ 50.6 (PPh_3); at 223 K δ 52.2, 46.6 (PPh_3). Data for isomer ***A*** are as follows. $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 188 K: δ 214.9 (s, 6CO), 211.7 (s, 3CO), 181.3 (d, J_{PC} = 58 Hz, $C_\alpha(C{\equiv}C^tBu)$), 144.9 (s, $C_\beta(C{\equiv}C^tBu)$), 134.4 (d, J_{PC} = 14 Hz, C_6H_5), 132.8 (s, $^4C(C_6H_5)$), 129.9 (d, J_{PC} = 11 Hz, C_6H_5), 128.2 (d, J_{PC} = 59 Hz, $^1C(C_6H_5)$), 41.1 (s, $\mathit{C}(CH_3)_3$), 35.9 (s, CH_3). Data for isomer ***B*** are as follows. $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 188 K: δ 219.5 (s, 2CO), 216.7 (br, 2CO), 215.5 (s, CO), 211.7 (s, 2CO), 210.3 (s, 2CO), 193.4 (s, $C_\alpha(C{\equiv}C^tBu)$), 134.3 (d, J_{PC} = 15 Hz, C_6H_5), 132.0 (s, $^4C(C_6H_5)$), 130.9 (s, $C_\beta(C{\equiv}C^tBu)$), 130.2 (d, J_{PC} = 52 Hz (obtained from the spectrum recorded at 223 K), $^1C(C_6H_5)$), 129.6 (d, J_{PC} = 11 Hz, C_6H_5), 38.5 (s, $\mathit{C}(CH_3)_3$), 33.5 (s, CH_3).

(13) (a) Farrugia, L. J.; Orpen, A. G. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol. 2, Chapter 3.4. (b) Dyson, P. J.In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol. 2, Chapter 3.5.

mixture[14] of isomers ***A*** and ***B***. The ratio ***A***:***B*** is now much higher (ca. 8:1 at 203 K) and also increases slightly at lower temperatures. The equilibrium between isomers seems to be also somewhat slower for the ^{i}Pr derivative, as judged from the fact that at room temperature the ^{31}P resonance for **3b** is much broader than that for **3a**, while the relevant chemical shift difference is similar (ca. 900 Hz). Apart from this, spectroscopic data for both isomers in **3b** are similar to those for **3a** and need no further comment. Fehlner and co-workers[15] have studied the related tautomeric equilibrium E−H−M ↔ M−H−M observed in some main-group−transition-metal atom clusters.

In view of the $H^+/AuPPh_3^+$ isolobal relationship, the exchange process between isomers ***A*** and ***B*** found for compounds **3** can be related to an alkyne/hydrido alkynyl isomerization process. In fact, replacement of $AuPPh_3^+$ by H^+ makes the structure of type ***B*** the preferred one even for iron. This transformation can be accomplished through treatment of **3a** with hydrochloric acid, thus giving the hydrido cluster $[Fe_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}C{\equiv}C^tBu)(CO)_9]$ (**4**) in good yield.[16] Compound **4** is also obtained from **1** and $HBF_4{\cdot}OEt_2$, thus completing the $H^+/AuPPh_3^+$ analogy. The ν(CO) pattern and chemical shift of the hydrido ligand are similar to those found for the compound $[Fe_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}C{\equiv}CSiMe_3)(CO)_9]$.[17] As deduced from NMR data,[18] compound **4** exhibits dynamic behavior in solution, which is similar to that well established for the related ruthenium cluster $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}C{\equiv}C^tBu)(CO)_9]$.[19]

The preliminary results reported in this paper show that the Au−C bond cleavage equilibrium operating in clusters **3** has a low kinetic barrier and results from a subtle balance of factors. Further studies are now in progress in order to evaluate the influence that the nature of phosphine, alkyne, or group 11 metal has on this novel Au−C cleavage process.

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Supporting Information Available: Text describing the synthesis and the characterization of the new compounds **1**−**4** and tables giving X-ray structural information for compound **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Data for **3b** are as follows. ^{1}H NMR in CD_2Cl_2 at 291 K: δ 2.38 (m, 3H, C*H*$(CH_3)_2$), 1.62 (s, 9H, $C(CH_3)_3$), 1.29 (d, J_{PH} = 7 Hz, 9H, CH(C*H*$_3$)$_2$), 1.27 (d, J_{PH} = 7 Hz, 9H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 291 K: δ 214.4 (br, 6CO), 213.2 (br, 3CO), 40.2 (s, *C*$(CH_3)_3$), 35.5 (s, *C*H$(CH_3)_2$), 24.9 (s, CH(*C*H$_3$)$_2$), 24.6 (s, CH(*C*H$_3$)$_2$), 20.0 (s, C(*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR in CD_2Cl_2 at 291 K: δ 78.7 (vbr, P^iPr_3). Data for isomer ***A*** are as follows. ^{1}H NMR in CD_2Cl_2 at 203 K: δ 2.40 (m, 3H, C*H*$(CH_3)_2$), 1.67 (s, 9H, $C(CH_3)_3$), 1.27 (d, J_{HH} = 7 Hz, 9H, CH(C*H*$_3$)$_2$), 1.23 (d, J_{HH} = 7 Hz, 9H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 188 K: δ 216.8 (s, CO), 215.1 (s, 6CO), 212.2 (s, 2CO), 181.9 (d, J_{PC} = 54 Hz, C_α ($C{\equiv}C^tBu$)), 145.4 (s, C_β ($C{\equiv}C^tBu$)), 41.4 (s, *C*$(CH_3)_3$), 36.1 (s, *C*H$(CH_3)_2$), 24.1 (s, CH(*C*H$_3$)$_2$), 23.8 (s, CH(*C*H$_3$)$_2$), 20.3 (s, C(*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR in CD_2Cl_2 at 203 K: 76.2 (P^iPr_3). Data for isomer ***B*** are as follows. ^{1}H NMR in CD_2Cl_2 at 203 K: δ 2.30 (m, 3H, C*H*$(CH_3)_2$), 1.41 (s, 9H, $C(CH_3)_3$), 1.21 (d, J_{HH} = 7 Hz, 9H, CH(C*H*$_3$)$_2$), 1.18 (d, J_{HH} = 7 Hz, 9H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 188 K: δ 220.0, 215.6, 212.5, 212.1, 210.5 (CO), 193.7 (s, C_α ($C{\equiv}C^tBu$)), 129.5 (s, C_β ($C{\equiv}C^tBu$)), 38.3 (s, *C*$(CH_3)_3$), 33.7 (*C*H$(CH_3)_2$), 20.0 (s, C(*C*H$_3$)$_3$), other resonances obscured by those from the major isomer. $^{31}P\{^1H\}$ NMR in CD_2Cl_2 at 203 K: δ 82.4 (P^iPr_3).

[15] Fehlner, T. P. *Polyhedron* **1990**, *9*, 1955 and therein.

[16] A solution of **3a** in THF was treated with a few drops of hydrochloric acid and stirred at room temperature for 30 min. The solvent was removed under vacuum and the residue extracted with *n*-hexane. The solution cooled at −20 °C gave compound **4**.

[17] Schneider, J. J.; Nolte, M.; Krüger, C. *J. Organomet. Chem.* **1991**, *403*, C4.

[18] Data for **4** are as follows. ^{1}H NMR: in $CDCl_3$ at 291 K δ −26.73 (s, H, FeH), 1.24 (s, 9H, $C(CH_3)_3$); in CD_2Cl_2 at 223 K δ −26.78 (s, H, FeH), 1.24 (s, 9H, $C(CH_3)_3$), 1.51 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR in CD_2Cl_2 at 223 K: δ 214.0 (s, 2CO), 213.0 (s, CO), 211.0 (s, 2CO), 206.9 (s, 2CO), 205.2 (s, 2CO), 185.0 (s, C_α ($C{\equiv}C^tBu$)), 123.2 (s, C_β ($C{\equiv}C^tBu$)), 33.7 (s, CH_3), *C*CH_3 resonance obscured by those from the solvent.

[19] Farrugia, L. J.; Rae, S. E. *Organometallics* **1992**, *11*, 196.