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Oxidative Rearrangement in Gold Organometallics

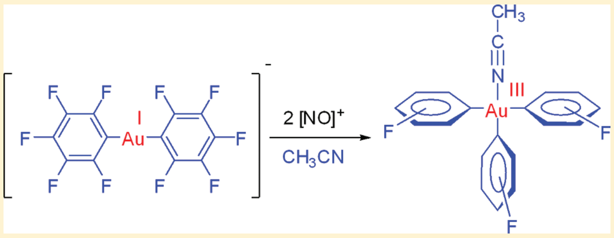
Atiya T. Overton,[†] José M. López-de-Luzuriaga,[‡] M. Elena Olmos,[‡] and Ahmed A. Mohamed*,[†]

[†]Department of Chemistry, Delaware State University, 1200 N DuPont Highway, Dover, Delaware 19901, United States

[‡]Departamento de Química, Universidad de la Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC Complejo Científico Tecnológico, E-26001 Logroño, Spain

Supporting Information

ABSTRACT: The one-electron oxidizing agent $[NO]PF_6$ was reacted with $Bu_4N[Au(C_6X_5)_2]$ (X = F, Cl) complexes in CH_3CN. The gold(III) complexes $[Au(C_6F_5)_3(CH_3CN)]$ and *cis*-$[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$ were synthesized by the oxidation of gold(I) to gold(III) with the concomitant ligand rearrangement "oxidative rearrangement". The supramolecular crystal packing in the perfluorinated aryl gold(III) complex is dictated by the notably short $C(sp^2)-F\cdots H(CH_3CN)$ bond distance. The $[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$ complex exhibits antisymbiosis, displaying equal ligands in the cis position. The electrochemical oxidation of $Bu_4N[Au(C_6X_5)_2]$ (X = F, Cl) complexes in CH_3CN showed two irreversible peaks at 0.71 and 1.21 V (X = F) and at 0.65 and 0.91 V (X = Cl) vs Ag/AgCl.



Perhalogenated arylgold complexes and in particular the perfluorinated derivatives have been widely utilized as volatile organic compound (VOC) sensors,[1] liquid crystal materials,[2] and strongly luminescent materials with tunable emissions.[3] Arylgold(III) complexes are good catalysts for the addition of nucleophiles to alkynes.[4] Gold(III) complexes with nitrogen and carbon donor ligands are widely utilized in catalytic cycle design and occupy a leading place in the cycloaurated derivatives for $C(sp^3)-H$ bond activation.[5] Knowledge gained from gold(III) oxidative chemistry should significantly aid in the advance of catalytic gold(III) systems for the selective functionalization of sp^3-hybridized C−H bonds.

Although the terminology "oxidative rearrangement" is not used uniformly in the organic literature, it refers in this study to the alteration in one or more gold−carbon connectivities, in which the complex undergoes a net oxidation.[6] Generally these rearrangements occur simultaneously and are driven by the metal oxidation. The oxidative rearrangement reactions are predicted to occur in gold organometallics in a mannaer comparable to that for organic compounds, as gold and carbon possess similar Pauling electronegativities (gold 2.54, carbon 2.55).[7] The rearrangement in organic reactions has been catalyzed by some metals, including gold. Toste reported the gold(I)-catalyzed oxidative rearrangement reactions of alkynes using sulfoxides as stoichiometric oxidants.[8a] Zhang developed a convenient and reliable method to access reactive α-oxo gold carbenes via gold-catalyzed pyridine *N*-oxide intermolecular oxidation of terminal alkynes.[8b]

Oxidative addition, the use of the oxidizing and arylating agent $[Tl(C_6F_5)_2X]_2$ (X = Cl, Br), is a common reaction used in the oxidation and modification of the gold−carbon bonding in perhalogenated arylgold organometallics.[9] $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophene) was prepared by the oxidative addition of $[Tl(C_6F_5)_2Cl]_2$ to $[Au(C_6F_5)(tht)]$ with the transfer of two C_6F_5 groups via an inner-sphere mechanism.[9] Also, nonoxidative routes have been used to modify the gold−carbon bonding such as the synthesis of $[Au(C_6F_5)_3(tht)]$ by the addition of the arylating agents $Ag(C_6F_5)$ and LiC_6F_5 to *trans*-$[AuCl_2(C_6F_5)(tht)]$.[9]

The easy removal of the gaseous byproduct nitric oxide from the nitrosonium cation $[NO]^+$ oxidation reactions provides an advantage over other oxidizing and oxidative addition reagents utilized in gold chemistry. The oxidation potential of $[NO]^+$ is comparable with that of gold (approximately 0.87 V vs Fc/Fc^+ in CH_3CN).[10] The one-electron-oxidizing agent $[NO]PF_6$ was reacted with $Bu_4N[Au(C_6X_5)_2]$ (X = F, Cl) complexes in CH_3CN (2/1) followed by crystallization from CH_3CN/ether (Scheme 1). Unlike the abundant oxidative addition reactions, the oxidative rearrangement reaction is described for the first time.[11,12]

The gold(III) complex $[Au(C_6F_5)_3(CH_3CN)]$ was synthesized in a 64% yield by the addition of 2 equiv of $[NO]PF_6$ in CH_3CN with respect to the $Bu_4N[Au(C_6F_5)_2]$ complex (Supporting Information). An unidentifiable product in a small yield was formed according to the reaction equation, but no attempts have been made to characterize it. The oxidation reaction of $Bu_4N[Au(C_6Cl_5)_2]$ with 2 equiv of $[NO]PF_6$ in CH_3CN formed colorless crystals of the cationic complex $[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$ in a 68% yield (Supporting Information). The off-white powder turns gray, provided the acetonitrile is removed in vacuo. The two gold(III) complexes displayed ^{13}C NMR peaks in $CDCl_3$ at δ 2.25 and 118.7 ppm. The $\nu(C{\equiv}N)$ stretching vibrational modes appeared at 2346 and 2311 cm^{-1} for $[Au(C_6F_5)_3(CH_3CN)]$ and at 2360 and 2337 cm^{-1} for $[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$.

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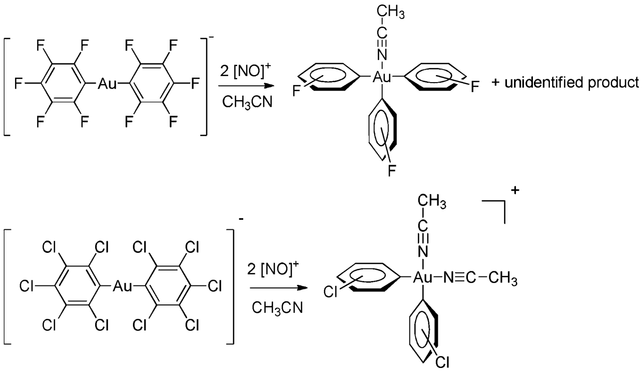
Scheme 1. Synthesis of $[Au(C_6F_5)_3(CH_3CN)]$ and $[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$ Complexes



Colorless crystals of $[Au(C_6F_5)_3(CH_3CN)]$ were obtained as one polymorph, unlike the two polymorphs of $[Au(C_6F_5)_3(tht)]$ due to the orientation of the bound tht ligand (Figure 1). The gold−carbon distance trans to CH_3CN, 1.987(2) Å, is slightly shorter than the other two identical Au−C distances, 2.063(2) Å. The fluorine-directed crystal packing is believed to be the reason for the complex stability. The notable $C(sp^2)-F\cdots H(CH_3CN)$ bond distance of 2.33 Å leads to dimer formation. Additional weaker F···H bonding of 2.85 Å added more interactions and leads to a supramolecular arrangement.

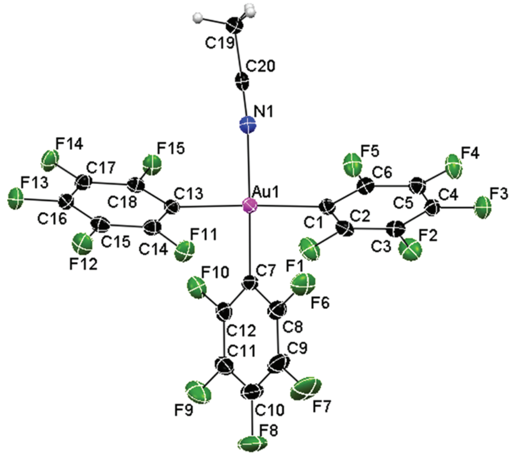


Figure 1. Structure of $[Au(C_6F_5)_3(CH_3CN)]$ complex with ellipsoids given at the 50% probability level. Bond distances (Å): Au(1)−N(1) = 2.062(2), Au(1)−C(7) = 1.987(2), Au(1)−C(13) = 2.063(2), Au(1)−C(1) = 2.063(2). Bond angles (deg): C(7)−Au(1)−N(1) = 178.51(9), C(1)−Au(1)−C(13) = 177.58(9).

The crystal structure of $[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$ shows the ligands bonded to the gold center in a cis disposition (Figure 2). The repulsive Cl···Cl interactions and the larger size of the chlorine compared with the fluorine substituents are believed to contribute to the structural differences in the perhalogenated aryls. The modification in the aryls about the gold(III) center to cis positions cannot rule out the ligand scrambling. Kochi reported the *trans*-$CH_3CH_2(CH_3)_2AuPPh_3$ to *cis*-$CH_3CH_2(CH_3)_2AuPPh_3$ isomerization which is hypothesized to occur via an intermolecular rearrangement involving a tetrahedral intermediate.[13]

Square-planar gold(III) complexes of the general formula $[AuR_2L_2]$ exhibit antisymbiosis, displaying equal ligands in the cis positions. This is in agreement with the Pearson π-competition theory, which states that in four-coordinate complexes, two soft ligands in mutually trans positions will have a destabilizing effect on each other.[14] There are a few examples of perfluorinated aryl gold(III) complexes in which the cis arrangement has been isolated. For example, the reaction of *cis*-$Bu_4N[Au(C_6F_5)_2Cl_2]$ with $AgClO_4$ in ether formed the *cis*-$[Au(C_6F_5)_2(Et_2O)_2]ClO_4$ complex.[9]

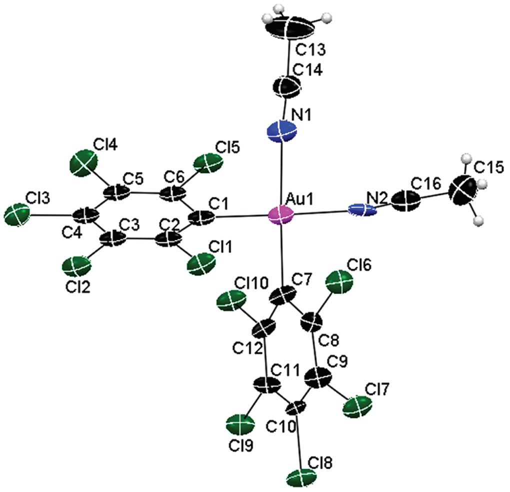


Figure 2. Structure of $[Au(C_6Cl_5)_2(CH_3CN)_2]^+$ with ellipsoids given at the 50% probability level. Bond distances (Å): Au(1)−N(1) = 2.080(15), Au(1)−N(2) = 2.045(17), Au(1)−C(1) = 1.980(17), Au(1)−C(7) = 1.995(15). Bond angles (deg): C(1)−Au(1)−N(2) = 173.6(6), C(7)−Au(1)−N(1) = 175.8(6).

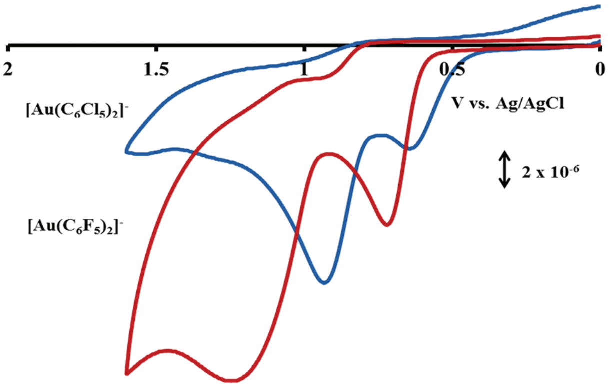


Figure 3. Cyclic voltammograms of the oxidation of 0.1 mM $[Au(C_6X_5)_2]^-$ (X = F, Cl) complexes in CH_3CN/0.1 M $[Bu_4N]PF_6$ at a 100 mV/s scan rate vs Ag/AgCl.

The irreversible electrochemical oxidation of $[Au(C_6F_5)_2]^-$ in CH_3CN/0.1 M $[Bu_4N]PF_6$ displayed two peaks at 0.71 and 1.21 V vs Ag/AgCl at a platinum working electrode (Figure 3). Similarly, the complex $[Au(C_6Cl_5)_2]^-$ showed irreversible oxidation potentials at lower values of 0.65 and 0.91 V. It is predictable that the strongly electronegative fluorine will show higher oxidation potential compared with the chlorine substituents. The electron-withdrawing effect of the C_6F_5 group is comparable with that of the haloborons BF_3 and BCl_3.[15] The $[NO]^+$ chemical oxidation complex $[Au(C_6Cl_5)_2(CH_3CN)_2]PF_6$ is sparingly soluble in most organic solvents, and it is likely that the electrochemical oxidation complex blocks the electrode surface from further oxidation at the second potential. This observation is in support of the smaller current passed in the second oxidation peak. The electrochemical oxidation of [Au(C_6F_5)$_3$(CH_3CN)] and [Au(C_6Cl_5)$_2$(CH_3CN)$_2$]PF_6 complexes under the same conditions showed the absence of the two peaks. The Bruces reported the chemical oxidation of the gold(I) thiolate complexes to disulfide, using the ferrocenium cation, with the concomitant formation of multinuclear gold(I) thiolate clusters. However, the electrochemical oxidation of the gold(I) thiolate complexes indicated the irreversible behavior of the thiolate and gold oxidations at approximately 0.9 and 1.2 V vs Ag/AgCl.[16]

The oxidative rearrangement reactions are unique in comparison with the oxidative coupling. Gold rarely undergoes the oxidation state changes necessary in the catalytic reactions under homogeneous conditions. The most common approach to access Au(I)/Au(III) in the catalytic cycles is to use a sacrificial external oxidant. However, on reaction in the presence of strong external oxidants with "F+" donors such as Selectfluor, Au(I)/Au(III) redox cycles become accessible but lead to C−C homo- and cross-coupling reactions.[17]

We have reported the chemical and electrochemical oxidation of gold organometallics which showed "oxidative rearrangement" for the first time. The formation of gold(III)−CH_3CN organometallic complexes is significant, as they are valuable precursors in various synthetic pathways and also can be utilized for designing catalytic cycles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and text giving details of the synthesis and characterization data for the complexes [Au(C_6F_5)$_3$(CH_3CN)] and [Au(C_6Cl_5)$_2$(CH_3CN)$_2$]PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: amohamed@desu.edu. Tel: 302-857-6531.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Puelles, R. C.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *Inorg. Chem.* **2008**, *47*, 8069−8076. (b) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022−2023.

(2) (a) Bardají, M. In *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications*; Laguna, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 403−428. (b) Coco, S.; Espinet, P. In *Gold Chemistry: Highlights and Future Directions*; Mohr, F., Ed.; Wiley-VCH: Weinheim, Germany, 2009; pp 357−396.

(3) Lasanta, T.; Olmos, M. E.; Laguna, A.; López-de-Luzuriaga, J. M.; Naumov, P. *J. Am. Chem. Soc.* **2011**, *133*, 16358−16361.

(4) (a) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925−11935. (b) Sanz, S.; Jones, L. A.; Mohr, F.; Laguna, M. *Organometallics* **2007**, *26*, 952−957.

(5) (a) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896−7936. (b) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351−3378. (c) Rudolph, M.; Hashmi, A. S. K. *Chem. Commun.* **2011**, *47*, 6536−6544. (d) Hashmi, A. S. K.; Schäfer, S.; Wölfle, M.; Diez, G. C.; Fischer, P.; Laguna, A.; Blanco, M. C.; Gimeno, M. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6184−6187. (e) Hashmi, A. S. K.; Salathe, R.; Frost, T. M.; Schwarz, L.; Choi, J. H. *Appl. Catal., A* **2005**, *291*, 238−246. (f) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439−2463. (g) Bergman, R. G. *Nature* **2007**, *446*, 391−393.

(6) McKillop, A.; Taylor, E. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 7.

(7) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1931.

(8) (a) Witham, C. A.; Mauleon, P.; Shapiro, N. D.; Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 5838−5839. (b) Ye, L.; Cui, L.; Zhang, G.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 3258−3259.

(9) (a) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85−91. (b) Usón, R.; Laguna, A.; Laguna, M.; Fernández, E.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1971−1976. (c) Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Durana, M. E. *Inorg. Chim. Acta* **1990**, *168*, 89−92. (d) Usón, R.; Laguna, A.; Vicente, J. *J. Chem. Soc., Chem. Commun.* **1976**, 353−354. (e) Usón, R.; Laguna, A.; Vicente, J. *J. Organomet. Chem.* **1977**, *131*, 471−475. (f) Vaughan, L. G.; Sheppard, W. A. *J. Organomet. Chem.* **1970**, *22*, 739−742. (g) Nyholm, R. S.; Royo, P. *J. Chem. Soc. D: Chem. Commun.* **1969**, 421. (h) Usón, R.; Royo, P.; Laguna, A. *J. Organomet. Chem.* **1974**, *69*, 361−365. (i) Coetzee, J.; Gabrielli, W. F.; Coetzee, K.; Schuster, O.; Nogai, S. D.; Cronje, S.; Raubenheimer, H. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2497−2500.

(10) Connelly, N. G.; Geiger, W. *Chem. Rev.* **1996**, *96*, 877−910.

(11) (a) Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 1−17. (b) Schneider, D.; Schuster, O.; Schmidbaur, H. *Organometallics* **2005**, *24*, 3547−3551. (c) Bachman, R. E.; Bodolosky-Bettis, S. A.; Pyle, C. J.; Gray, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 14303−14310. (d) Pažický, M.; Loos, A.; Ferreira, M. J.; Serra, D.; Vinokurov, N.; Rominger, F.; Jäkel, C.; Hashmi, A. S. K.; Limbach, M. *Organometallics* **2010**, *29*, 4448−4458.

(12) Mohamed, A. A. *Coord. Chem. Rev.* **2010**, *254*, 1918−1947.

(13) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140−6148.

(14) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967.

(15) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1−77.

(16) (a) Mohamed, A. A.; Bruce, A. E.; Bruce, M. R. M. Electrochemistry of Gold and Silver Complexes. In *Organic Derivatives of Gold and Silver*; Patai, S., Ed.; Wiley: New York, 1999; pp 313−352. (b) Mohamed, A. A.; Chen, J.; Hill, D.; Bauer, J. A. K.; Bruce, A. E.; Bruce, M. R. M. *Inorg. Chem.* **2003**, *42*, 2203−2205. (c) Mohamed, A. A.; Abdou, H. E.; Chen, J.; Bruce, A. E.; Bruce, M. R. M. *Comments Inorg. Chem.* **2002**, *23*, 321−334. (d) Mohamed, A. A.; Bruce, M. R. M.; Bruce, A. E. *Met.-Based Drugs* **1999**, *6*, 233−238.

(17) (a) Brenzovich, W. E., Jr.; Brazeau, J. F.; Toste, F. D. *Org. Lett.* **2010**, *12*, 4728−4731. (b) Hashmi, A. S. K.; Ramamurthi, T. D.; Rominger, F. *J. Organomet. Chem.* **2009**, *694*, 592−597. (c) Hashmi, A. S. K.; Ramamurthi, T. D.; Todd, M. H.; Tsang, A. S. K.; Graf, K. *Aust. J. Chem.* **2010**, *63*, 1619−1626. (d) Hopkinson, M. N.; Gee, A. D.; Gouverneur, V. *Chem. Eur. J.* **2011**, *17*, 8248−8262.