DOI: 10.1002/ejic.201100956

Unexpected Outcomes of the Oxidation of (Pentafluorophenyl)triphenylphosphanegold(I)

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Keywords: Gold / Redox / Oxidation / Ligand transfer / Iodonium salts / Ion pairs

Redox gold(I)/gold(III) catalytic cycles have been proposed as the productive mechanistic manifold in a number of gold mediated C–C and C–X bond forming reactions. These transformations rely on the use of stoichiometric oxidants such as iodonium salts and Selectfluor. We have studied the oxidation of electron deficient [$Au(C_6F_5)(PPh_3)$] (**1**) in the presence of such oxidizing agents. The reaction of **1** with $PhI(OAc)_2$ afforded *cis*-[$Au(C_6F_5)_2Cl(PPh_3)$] (**3**), which seemed to be produced by oxidation of the starting complex followed by a gold(I)/gold(III) transmetalation process or ligand exchange. The reaction of **1** with Selectfluor afforded an unprecedented gold(I)–gold(III) complex [$Au(PPh_3)_2$][$Au(C_6F_5)_4$] (**7**).

Introduction

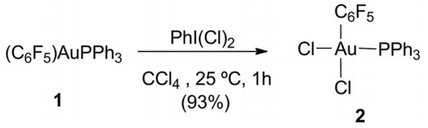
The redox chemistry of gold has recently regained the interest of the organometallic community due to the presumed ability of Au^I/Au^{III} redox catalytic cycles to perform synthetically useful transformations.[1] Following pioneering stoichiometric examples reported by Benett,[2] Lippert,[3] and Hashmi,[4] Wegner et al. have shown that biscoumarins were efficiently formed from arylpropionic esters via cyclization and dimerization in the presence of catalytic amounts of $HAuCl_4$ with *tert*-butyl hydroperoxide as the stoichiometric oxidant.[5] The same catalyst with $PhI(OAc)_2$ as the oxidant has been shown to trigger general oxidative homocoupling of arenes.[6] Zhang et al. have reported the gold-catalyzed dimerization of propargylic acetates with Selectfluor.[7] Beyond dimerization processes, numerous transformations that involve C–C and C–X bond formation have also been devised, which assume the in situ oxidation of gold(I) to gold(III) species in the presence of an external oxidant. Alkynylation reactions,[8] difunctionalization of unactivated alkenes,[9] and cross-coupling with B and Si reagents[10] have been recently added to the toolbox of organic chemists.

Although the synthetic application of gold redox catalytic cycles is an emerging field, the stoichiometric two-electron oxidation of linear gold(I) salts to the corresponding square planar gold(III) complexes is well precedented.[11] Thus, an excess of halogen ($X_2 = Cl_2, Br_2, I_2$) at room temperature or $TlCl_3$ in boiling chloroform have been used to transform YAuL ($Y = C_6Z_5$, Cl; Z = H, Cl, F; $L = PPh_3$, $AsPh_3$) into $YAuX_2L$.[12] In addition, interesting transformations occur when bis(pentafluorophenyl)thallium(III) halides were used as stoichiometric oxidants. Royo and Laguna[13] have reported the oxidation of YAuL with $(C_6F_5)_2TlX$ (X = Cl, Br, I), which occurred with concomitant transfer of the organic perfluorinated ligand to the gold center to give *cis*-$(C_6F_5)_2AuYL$ ($L = PPh_3$, $AsPh_3$; Y = Cl, Br, I) and TlX. Interestingly, [$Au(C_6F_5)PPh_3$] (**1**) did not react under these conditions and also proved to be inert towards oxidation with Cl_2 or Br_2. The lack of reactivity of this electron deficient gold(I) complex fostered our interest in its oxidation chemistry.

Results and Discussion

We began our study with oxidants that are commonly used in the gold-catalyzed cross-coupling reactions described above, such as hypervalent iodine reagents[14] and Selectfluor.[15] In this context, the formation of dichlorogold(III) complexes by oxidation of (NHC)AuY (NHC = *N*-heterocyclic carbene; Y = Cl, C_6H_5, C_6F_5) in the presence of $PhI(Cl)_2$ as the oxidant has already been reported,[16] and $PhI(OAc)_2$ has been used to oxidize palladium(II) complexes to stable diacetoxypalladium(IV) species.[17]

The reaction of **1** with $PhI(Cl)_2$ at room temperature in CCl_4 afforded *cis*-dichloro(pentafluorophenyl)triphenylphosphanegold(III) (**2**) in 93% yield (Scheme 1). The *cis*-



Scheme 1. Oxidation of **1** with $PhICl_2$.

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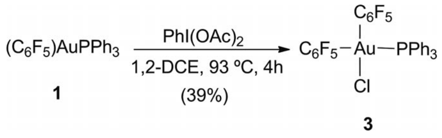
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100956.

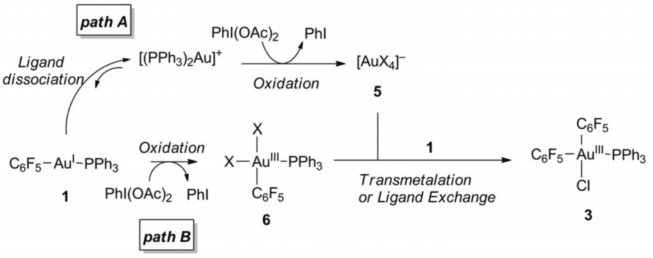
isomer was found exclusively, which was confirmed by single-crystal X-ray structural analysis.[18]

In contrast, the reaction of **1** with PhI(OAc)$_2$ at room temperature returned unreacted starting material. When the reaction was performed in 1,2-dichloroethane at 93 °C, *cis*-chloro(bispentafluorophenyl)triphenylphosphanegold(III) (**3**) was isolated in moderate yield (Scheme 2). The structure of **3** was confirmed by single-crystal X-ray structural analysis.[19]



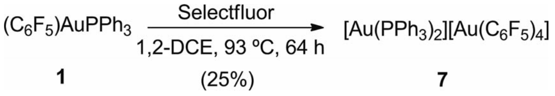
Scheme 2. Oxidation of **1** with PhI(OAc)$_2$.

The formation of **3** from **1** was intriguing, and we decided to monitor the reaction by ^{1}H, ^{31}P, and ^{19}F NMR spectroscopy to understand the mechanism by which **3** is formed.[20] Experiments performed in 1,2-dichloroethane at 93 °C showed an increasing concentration of **3** after 2 h according to ^{31}P NMR spectroscopy. In parallel, a linear decrease of the starting material **1** was observed (Figure S4, Supporting Information). Several intermediates were also identified by ^{31}P NMR spectroscopy. Thus, an increasing concentration of [Au(PPh$_3$)$_2$]$^+$ (46 ppm) was observed,[10c,21] which decreased after three hours. Additionally, Ph$_3$PO and/or [AuCl(Ph$_3$P)$_2$][21b] were responsible for the signal detected at 29 ppm. A third signal with complex multiplicity at 30 ppm was also observed, which could not be assigned to previously described species. A second experiment was designed that used equivalent amounts of **1** and [AuCl(PPh$_3$)] (**4**) as starting materials to evaluate the effect of the anionic ligand on the reaction intermediates and products (Figure S5). The formation of **3** was faster in this case than in the experiment described above, and **3** was detected after only one hour. Compound **1** and the cationic intermediate [Au(PPh$_3$)$_2$]$^+$ were also converted more quickly in this case. Based on these observations, two different mechanisms can be proposed for the formation of **3** (Scheme 3). Pathway A involves the dissociation of **1** to give [Au(PPh$_3$)$_2$]$^+$ followed by oxidation to give [AuX$_4$]$^-$ (**5**, X = OAc or Cl if solvent activation occurs).[22] Alternatively, direct oxidation of **1** by PhI(OAc)$_2$ forms *cis*-[Au(C$_6$F$_5$)(PPh$_3$)X$_2$] (**6**, X = OAc and/or Cl), which could be responsible for the signal observed at 30 ppm. In both cases, **5** or **6** would undergo a gold(III)/gold(I) transmetalation or a ligand exchange process with **1**[7,23] to yield **3** selectively.[24] The dissociation of the anionic ligand in the first step of the reaction and the oxidation of [Au(PPh$_3$)$_2$]$^+$ to **5** have been described previously.[21a,21b] Surprisingly, the redox potential for [Au(PPh$_3$)$_2$]$^+$ is more negative than that of neutral species such as [AuCl(PPh$_3$)]. Additionally, the accelerated formation of **3** in the reaction carried out in the presence of [AuCl(PPh$_3$)] and the fact that no new intermediates were detected in this reaction seems to indicate that dissociated species might be responsible for the formation of the productive gold(III) intermediates in this process. However, at this stage, none of these mechanisms can be ruled out, and the formation of **3** can be explained by the simultaneous interplay of both mechanisms.[25]



Scheme 3. Possible mechanism for the formation of **3**.

The reaction of **1** with Selectfluor in 1,2-dichloroethane also delivered an unexpected result: a gold(I)–gold(III) complex, [Au(PPh$_3$)$_2$][Au(C$_6$F$_5$)$_4$] (**7**), was isolated in 25% yield and its structure was confirmed by single-crystal X-ray structural analysis (Scheme 4). This compound, which, to the best of our knowledge, has not been previously reported,[26] might stem from an oxidation reaction of **1** followed by a ligand exchange process, which highlights the instability of the potential fluorinated gold(III) species in the absence of electron-donor ligands.[27]



Scheme 4. Oxidation of **1** with Selectfluor.

Conclusions

A study of the oxidation of the electron deficient gold(I) complex [Au(C$_6$F$_5$)(PPh$_3$)] in the presence of strong oxidants commonly used in redox gold(I)/gold(III) catalytic cycles has been carried out. The reaction in the presence of PhI(OAc)$_2$ afforded *cis*-[Au(C$_6$F$_5$)$_2$Cl(PPh$_3$)], which is likely to be a result of ligand dissociation followed by oxidation and ligand exchange or transmetalation with the starting gold(I) complex. In analogy, the reaction in the presence of Selectfluor delivers a new gold(I)–gold(III) ion pair: [Au(PPh$_3$)$_2$][Au(C$_6$F$_5$)$_4$].

Experimental Section

General: NMR spectra were recorded with AV2 400 or AV2 500 MHz Bruker spectrometers. High-resolution electrospray ionization MS was performed with a Finnigan MAT900 (Thermo Finnigan) doublefocusing magnetic sector mass spectrometer. Unless otherwise stated, all reagents were used as received except for iodobenzene diacetate, which was recrystallized from an aqueous solution of acetic acid (5 M) and dried overnight under vacuum. Solvents were purchased of HPLC quality, degassed by purging thoroughly with nitrogen, and dried with activated molecular sieves. All reactions were performed in anhydrous conditions under nitrogen in sealed Schlenk flasks.

***cis*-$[Au(C_6F_5)(PPh_3)Cl_2]$ (2):** To a mixture of $[Au(C_6F_5)(PPh_3)]$ (**1**, 37.6 mg, 0.06 mmol) and iodobenzene dichloride (18.1 mg, 0.066 mmol) was added CCl_4 (3.8 mL). The mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure to ca. 0.2 mL, and the product was precipitated by the addition of hexane. The product was separated to give **2** as a white solid. Yield: 93% (39.0 mg, 0.056 mmol). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.72–7.36 (m, 15 H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 143.7 (dm, *J* = 235.0 Hz), 140.4 (dm, *J* = 244.0 Hz), 138.0 (dm, *J* = 240.0 Hz), 134.9 (d, *J* = 10.7 Hz), 134.2 (d, *J* = 3.0 Hz), 129.8 (d, *J* = 12.5 Hz), 123.7 (d, *J* = 69.8 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 35.64 (s) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –123.48 to –124.35 (m), –156.90 (t, *J* = 19.8 Hz), –159.92 to –160.91 (m) ppm. MS (EI): *m*/*z* = 626.0 $[M - Cl_2]^+$.

***cis*-$[Au(C_6F_5)_2Cl(PPh_3)]$ (3):** To a mixture of **1** (12.5 mg, 0.02 mmol) and iodobenzene diacetate (7.0 mg, 0.022 mmol) was added 1,2-dichloroethane (2.5 mL). The mixture was heated at 93 °C for 3–4.5 h. The reaction was monitored by TLC using hexane/CH_2Cl_2 (1:1) as the mobile phase. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (hexane/CH_2Cl_2, 1:4) to give **3** as a white solid. Yield: 38% (2.8 mg, 0.0034 mmol). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.63–7.40 (m, 15 H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 145.0 (dm, *J* = 235.0 Hz), 143.5 (dm, *J* = 236.0 Hz), 139.8 (dm, *J* = 250.0 Hz), 137.6 (dm, *J* = 252.0 Hz), 134.3 (d, *J* = 10.5 Hz), 132.7 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 12.0 Hz), 124.3 (d, *J* = 59.8 Hz), 117.5 (dt, *J* = 150.0, 43.0 Hz), 109.9 (t, *J* = 39.0 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 28.30 (t, *J* = 12.3 Hz) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –122.07 to –122.46 (m), –122.99 to –123.59 (m), –157.31 (t, *J* = 19.8 Hz), –157.58 (t, *J* = 19.8 Hz), –160.70 to –161.02 (m), –161.71 to –162.08 (m) ppm. MS (EI): *m*/*z* = 625.9 $[M - C_6F_5Cl]^+$.

$[Au(PPh_3)_2][Au(C_6F_5)_4]$ (7): To a mixture of **1** (50.1 mg, 0.08 mmol) and Selectfluor® (62.3 mg, 0.18 mmol) was added 1,2-dichloroethane (5.0 mL). The mixture was heated at 93 °C for 64 h. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (hexane/CH_2Cl_2, 1:4) to give **7** as a white solid. Yield: 25% (8.1 mg, 0.005 mmol). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.66–7.42 (m, 30 H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 145.8 (ddm, *J* = 235.0, 18.0 Hz), 138.3 (dtm, *J* = 245.0, 14.0 Hz), 137.0 (dm, *J* = 250.0 Hz), 134.1 (t, *J* = 7.5 Hz), 132.8 (s), 129.9 (t, *J* = 5.8 Hz), 127.1 (t, *J* = 30.0 Hz), 116.0 (t, *J* = 48.0 Hz) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 46.01 (s) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –121.66 (d, *J* = 19.1 Hz), –161.57 (t, *J* = 19.8 Hz), –164.05 to –164.57 (m) ppm. MS (ESI$^+$, $CHCl_3$/MeOH, 4:6): *m*/*z* = 721.4 $[M]^+$. MS (ESI$^-$, $CHCl_3$/MeOH, 4:6): *m*/*z* = 865.1 $[M]^-$.

CCDC-843007 (for **2**), -842899 (for **3**), and -851182 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Characterization of **2**, **3**, and **7** and data for the oxidation of **1**.

Acknowledgments

The Organic Chemistry Institute of the University of Zürich is acknowledged for its continuous support of our research. We thank Dr. A. Linden for the X-ray crystal structure determination of **2**, **3**, and **7**.

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Received: September 8, 2011