

### Article

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# Trans Influence of Ligands on the Oxidation of Gold(I) Complexes

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**ABSTRACT:** Gold(I) complexes are considered active species towards oxidative addition, and current understanding indicates a different mechanism in contrast to other late transition metals, but a rational understanding of the reactivity profile is lacking. Herein, we propose that the accessibility of the gold(I) center to tri- or tetra-coordination is critical in the oxidative process involving a tri- or tetra-coordinate gold(I) with the oxidizing reagent as one of the ligands as an intermediate. A computational study of the geometry of (Phen)R<sub>3</sub>PAu(I)NTf<sub>2</sub> complexes shows that the accessibility of such tri-coordinate species shows a good correlation with the '*trans* influence' of phosphine ligands: the weak  $\sigma$ -donating phosphine ligands promote tri-coordination of gold(I) complexes. The oxidative addition to the asymmetric tri-coordinate (Phen)R<sub>3</sub>PAu(I)NTf<sub>2</sub> complexes with alkynyl hypervalent iodine reagents was built. The kinetic profile of the oxidative addition exhibits a good relationship to the Hammett substituent parameter ( $\rho = 3.75$ , R<sup>2</sup> = 0.934), in which the gold(I) complexes bearing less  $\sigma$ -donating phosphine ligands increase the rate of oxidative addition. The positive  $\rho$  indicates a high sensitivity of the oxidative addition to the *trans* influence. The reactivity profile of oxidative addition to linear bis(pyridine)gold(I) complex further supports that the oxidative addition to gold(I) complexes are promoted by ligands with small *trans* influence.

### INTRODUCTION

Oxidative addition of sp<sup>2</sup>-C-X or sp-C-X bonds to gold(I) complexes is a key step in some gold-catalyzed reactions.<sup>1</sup> A detailed understanding of this process would provide a guideline for the design of new gold catalysis. However, due to the high redox potential of Au(I)/Au(III) (1.41 V) compared to those of Pd(0)/Pd(II) (0.91 V) or Pt(0)/Pt(II) (1.18 V)<sup>2</sup> and the reluctance of gold(I) to form complexes with higher coordination numbers,<sup>3</sup> the oxidative addition to gold(I) is difficult to study. Indeed, only a few investigations on the oxidative addition to gold(I) complexes have been reported in the last years.<sup>4</sup> Recent studies on the oxidative addition of aryl halides to gold(I) complexes showed that electron-rich substrates react faster than electron-poor ones,<sup>4</sup> which is the opposite of the trend for palladium(0) with the same d-electron configuration.<sup>5</sup> We rationalize this contrast by the different coordination behavior of both metals (Figure 1a).<sup>6</sup> The typical linear two-coordinated gold(I) thermodynamically disfavor a coordination of the oxidizing reagents complexes,<sup>7</sup> as different from palladium(0) the tri-coordinated gold(I) complexes are much less stable.

In the last years, the oxidation of gold(I) to gold(III) was enabled by: a) introducing bidentate ligands not allowing a trans-chelation at the gold(I) center (Figure 1b).<sup>4</sup> Such bidentate ligands bend the linear gold(I) complexes,<sup>8</sup> decreasing the oxidative barrier because of the increased energy of the d orbitals,<sup>9</sup> and the pre-organized orbitals facilitate the subsequent coordination to oxidizing agents. b) intramolecularizing the oxidative addition, then a precoordination is not necessary, there is no significant entropic barrier (Figure 1c).<sup>10</sup> Overall, we think that the initial coordination of oxidizing reagents with two-coordinate gold(I) complexes to form tri-coordinate gold(I) intermediates is critical for both of these two strategies.

The rehybridization of two-coordinate linear gold(I) molecular orbitals resembles a three-center four-electron bond,<sup>11</sup> resulting in a coordinate competition of the two ligands, in which electronic density transfers competitively from lone pairs of the ligands to the  $s+d_z 2$  hybrid orbital of the gold(I) complexes, which in general is called *trans*-influence.<sup>12</sup> Analogously, rehybridization of tri-coordinate gold(I) molecular orbitals can resembled four-center six-electron bonds, in which three  $\sigma$ -donor ligands transfer electronic density to gold(I) atom competitively. Accordingly, a strong  $\sigma$ donor ligand on the gold(I) center occupies the s+d hybrid orbitals of gold(I) competitively, undermining the further coordination with other weak  $\sigma$ -donor ligands. Identical  $\sigma$ donor ligands are expected to share the orbitals of gold(I) atom, leading to the formation of tri-coordinate, even tetra-coordinate gold(I) complexes.<sup>12</sup> In fact, precedents to the synthesis of tricoordinate gold(I) complexes indicated that the tri-coordinate geometry is always accessible by using comparable  $\sigma$ -donor ligands.13

Considering the important role of the initial coordination of oxidizing reagents with gold(I) complexes in the process of oxidative addition, as well as the *trans* influence of ligands on the accessibility of tri- or tetra-coordinate gold(I) complexes, we envisioned the probability of the oxidative addition to the gold(I) complexes enabled by weak  $\sigma$ -donor ligands. We now report our results on a study of reactivity of tri-coordinate and two-coordinate gold(I) complexes towards oxidative addition,

showing a correlation of such reactivity to the *trans* influence of ligands.





b) Bidentate ligands-enabled oxidative addition of sp<sup>2</sup>-C-X or sp-C-X bonds



c) Coordinating environment-enabled oxidative addition of sp<sup>2</sup>-C-X bond



NTf<sub>2</sub> NTf<sub>2</sub> . NTf<sub>2</sub> 2+ OR **₽**R∉ unsynmmetric Àr tri-coordination



Figure 1. a) Assumption for reactive profile of oxidative addition involving a coordinating equilibrium and oxidative barrier. b) Bidentate ligands-enabled oxidative addition to gold(I) complexes. c) Coordinating environment-enabled oxidative addition. d) This work: oxidative addition to tri-coordinate and two-coordinate gold(I) complexes.

### **RESULTS AND DISCUSSION**

Tri-coordination at gold(I). In 1976, Clegg prepared a tricoordinate complex, 2,2'-(bipyridyl)Ph<sub>3</sub>PAuPF<sub>6</sub>, in which the bending of the bidentate bipyridyl ligand is highly asymmetric, and the Au-N bond lengths are 2.406 Å and 2.166 Å respectively.<sup>14</sup> In 2004, Cinellu et al. synthesized another tricoordinate complex, bipyridyl(olefin)AuNTf2,9b which has apparently symmetric geometry (2.092 Å of Au-N bond lengths for both), as a result of much smaller *trans* influence of ethylene than  $Ph_3P$ . The *trans* influence of ligands on the gold(I) complexes was correlated with the Au-Cl distance in linear L-Au-Cl complexes.<sup>15</sup> Now we used (Phen)R<sub>3</sub>PAuNTf<sub>2</sub> complexes to study the trans influence of ligands on the accessibility of tri-coordination in gold(I) complexes, in which the tri-coordinate geometry is thermodynamically stable. A series of (Phen) $R_3PAuNTf_2$  complexes (1) were synthesized by simply mixing of Phen with cationic R<sub>3</sub>PAuNTf<sub>2</sub> complexes in CH<sub>2</sub>Cl<sub>2</sub>. Single crystal structure analyses of gold(I) complexes showed the geometry around the metal center with an extremely unymmetric nitrogen coordination (Figure 2a). Unfortunately, these crystals suffered strong disordering, which originated from the site-exchange of the nitrogen atoms in the unsymmetric tri-coordinate gold(I) complexes (Figure 2b), preventing a detailed quantitative discussion.<sup>16</sup>



Thermal Figure 2. a) ellipsoid representations of (Phen)Ph<sub>3</sub>PAuNTf<sub>2</sub> and (Phen)Cy<sub>3</sub>PAuNTf<sub>2</sub> complexes at the 50% probability level. Hydrogens have been omitted for clarity. b) Energy profile for the site-exchange reaction for (Phen)Ph<sub>3</sub>PAuNTf<sub>2</sub> computed with  $\omega$ B97X-D3 functional and Ahlrichs def2-TZVP basis set.

To gain further insight into ligand effects on the geometry of such tri-coordinate (Phen)R<sub>3</sub>PAuNTf<sub>2</sub>, a computational study of the Au-N bond lengths, one of key parameters for the tricoordination, was carried out using KS-DFT (wB97X-D3 functional with Ahlrichs def2-TZVP basis set). Standard effective core potentials and CPCM solvent model with DCM was used. As we expected, the (Phen)gold(I) complexes coordinated with arylphosphine ligands bearing electron donating group showing weaker Au-N2 bond strength  $((Phen)(p-MeO-C_6H_4)_3PAuNTf_2$  1c, 2.61 Å of Au-N2 distance vs (Phen)Ph<sub>3</sub>PAuNTf<sub>2</sub> 1a, 2.60 Å of Au-N2 distance). On the contrary, the arylphosphine ligands bearing electronwithdrawing groups show a shortened Au-N2 bonds ((Phen)(p-

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CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuNTf<sub>2</sub> **1b**, 2.58 Å of Au-N2 distance). Especially, (Phen)(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>PAuNTf<sub>2</sub> **1d** has a significantly shortened Au-N2 bond (2.33 Å), as a result of small *trans* influence of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P. The molecular structure of **1d** in the solid state also displays a significantly shortened Au-N2 bond. Au-N2 distances of these tri-coordinate gold(I) complexes (1), bearing *para*-substituted phosphine ligands, exhibit a negative proportional relationship to the Hammett substituent parameter, supporting the  $\sigma$ -donor competition among ligands (Figure 3).



Figure 3. Correlation between calculated Au-N2 distance of  $(Phen)R_3PAuNTf_2$  and Hammett substituent parameter.

Reactivity of tri-coordinate (Phen) $R_3PAuNTf_2$  towards oxidative addition. Compared with linear gold(I) complexes, the tri-coordinate geometry of (Phen)R<sub>3</sub>PAuNTf<sub>2</sub> complexes indicates an enhanced reactivity towards oxidation. After screening for some oxidizing agents, an oxidative addition to (Phen)Ph<sub>3</sub>PAuNTf<sub>2</sub> was observed with alkynyl hypervalent iodine reagents in CD2Cl2, surprisingly affording a (Phen)alkynylgold(III) complex 4a (40% yield in 16 h, Scheme 1), along with the side-product of  $(p-F-C_6H_4)Ph_3P^+$  5a (<sup>31</sup>P NMR 6.7 ppm). The NMR spectroscopy of the gold(III) complex is consistent with the one that was synthesized by stoichiometric oxidative addition to (Phen)(ethylene)AuNTf<sub>2</sub>, and characterized with X-ray diffraction in our previous work (Figure S1).<sup>4e</sup> CD<sub>3</sub>CN accelerates the reaction, leading to a yield of 60% in 50 min. In the presence of water (0.6 equiv.) in CD<sub>3</sub>CN, the same yield was observed, along with the decomposition of 5a to Ph<sub>3</sub>PO and the terminal alkyne,<sup>17</sup> as well as 1,4-bisphenylbuta-1,3-diyne being formed by the coupling of the terminal alkyne with the alkynylgold(III) complex (see supporting information 4.3, SI).<sup>18</sup> We have also confirmed that the oxidative addition behaviour is not specific to Phen complex 1a, and the complex (2,2)-bipyridyl)Ph<sub>3</sub>PAu(I)NTf<sub>2</sub> 1e is also competent for the oxidative addition, giving the product in 38% NMR yield after 12 hours.

Scheme 1. Reactivity of 1a towards oxidative addition



The mechanism of this reaction can be rationalized by two pathways, as shown in scheme 2. The first (pathway A) involves a phosphine dissociation from the tri-coordinate gold(I) complex (1a), affording a trigonal gold(I) species, which was reported to be active for an oxidative addition. The second pathway (B) comprises two steps of oxidative addition and one step of reductive elimination. The first oxidative addition to the asymmetric tri-coordinate gold(I) species 1a proceeds with alkynyl hypervalent iodine **3a** through a tetra-coordinate gold(I) transition state I,<sup>19</sup> affording (Phen)(alkynyl)Ph<sub>3</sub>PAu<sup>III</sup> II. The trigonal gold(I) complex III was formed by carbon-phosphorus reductive elimination of gold(III) species II,<sup>20</sup> followed by the second oxidative addition with 3a to afford gold(III) compound 4a. Since the first step of the reaction is rate-determining, we cannot distinguish these two pathways by a detection of intermediates. But, the formation of alkynyl( $Ph_3P$ )<sup>+</sup> **5a**, and the kinetics (see below) support the mechanism **B**. On the other hand, the failed oxidation of Ph<sub>3</sub>P with **3a** as well as the absence of free Ph<sub>3</sub>P (detected by <sup>31</sup>P NMR spectroscopy) in the reactive solution excludes the mechanism A.





The *trans* influence of ligands on oxidative addition is shown in the reactivity profile with (Phen)R<sub>3</sub>PAuNTf<sub>2</sub> (Figure 4). The plot of the initial NMR yields of **4** against the reaction time showed a good linear correlation (Figure 4b), allowing the calculation of the relative initial rate constants k (10<sup>-4</sup> mol. L<sup>-1</sup>.  $h^{-1}$ ) of the oxidative addition to tri-coordinate gold(I) complexes bearing various *para*-substituted Ar<sub>3</sub>P ligands. Weak  $\sigma$ donating phosphine ligands are expected to speed up the oxidative addition by promoting the coordination with Phen ligand and oxidizing agent. Accordingly, we found that triaryl phosphine ligands bearing electron-withdrawing substituents are highly effective (**L8, L9**). Especially, in the case of the

 $(Phen)(C_6F_5)_3PAuNTf_2$  L10, the addition of alkynyl hypervalent iodine reagent 3a led to an immediate colour change, and NMR spectroscopy showed the complete conversion of gold(I) complex 4a in 5 min, which indicates an extremely fast oxidative addition to (Phen)(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>PAuNTf<sub>2</sub>. Conversely, phosphine ligands bearing alkyl groups (L1, L2) and phosphite ligands (L3, L4) are completely ineffective as a result of increased *trans*-influence,<sup>21</sup> and the oxidative addition proceeds much slower with electron-rich arvl phosphines than that with Ph<sub>3</sub>P (L5, L6). Additionally, the sterically more demanding  $(o-Me-C_6H_4)_3P$  L11 and  $(Mesityl)_3P$  (k=0) strongly inhibit the oxidative addition, which is apparently attributed to the crowded gold transition state. This result excludes the mechanism A (Scheme 2), in which the steric hindrance of phosphine ligands would be expected to promote the phosphine dissociation, accelerating the oxidative addition. The reaction does not proceed with pyridineAuPPh<sub>3</sub>.

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The effects of bidentate ligands on this oxidative reactivity were also investigated (Figure 4a). The 2,2'-bipyridine ligand shows a ligand effect identical to Phen. Introducing electronwithdrawing chloride to the 4,4'-position of Phen L14 strongly decreases the oxidative reactivity. The Cl-substituted Phen ligand weakens its coordination with gold(I) atom, thus increasing the oxidative barrier of the oxidative addition. Phen ligand bearing electron-donating MeO- groups L13 is also less effective than Phen, since the raised  $\sigma$ -donation of Phen ligand prevents the coordination of oxidizing agent with gold(I) atom in the oxidative process. These two negative effects are illustrative of an increased reactivity of gold(I) complex bearing Ph-substituted (Hammett substituent parameter  $\sigma = 0.009$ ) Phen L15 with neutral  $\sigma$ -donation.

Analysis of the relative reaction rates of oxidative addition to **1a** showed that electron-rich alkynyl hypervalent iodine reagent react faster than electron-poor systems (initial rate order for 4-R substituted **3**:  $R = CH_3 > H > NO_2$ , k = 6.8, 6.28, 2.4 respectively; Figure 4c). This order of reactivity is expected based on the former analysis on the oxidative addition that involves a critical coordination. The increased reactivity of electron-rich alkynyl hypervalent iodine reagent towards oxidative addition to **1a** could be derived from the enhanced coordination of **3** with **1a**.



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Figure 4. Ligand effects on the oxidative addition.

The kinetic profile of the oxidative addition exhibits a good relationship to the Hammett substituent parameter (Figure 5,  $\rho = 3.75$ ,  $R^2 = 0.9344$ ). The positive  $\rho$  value (> 1) indicates a high sensitivity of the oxidative addition to the *trans* influence of phosphine ligands. Recently, Amgoune, Bourissou, and coworkers published a catalytic Au(I)/Au(III) arylation with hemilabile MeDalphos ligand.<sup>3g</sup> The moderate Hammett correlations ( $\rho = -1.09$ ,  $R^2 = 0.93$ ) for the oxidative addition of different *para*-substituted iodoarenes indicated a coordination of iodoarenes with gold(I) catalyst in the process of the oxidative addition, which also supports the  $\sigma$ -donor competition among ligands (including bidentate ligand and iodoarenes) at the gold(I) center.



Figure 5. Hammett plot of  $\ln(k/k0)$  vs  $\sigma$  for oxidative addition.

Reactivity of linear bis(pyridine)gold(I) towards oxidative addition. Based on the correlation of the trans influence of ligands with the tri-coordinate accessibility of gold(I) complex, as well as oxidative reactivity, we assumed that a linear twocoordinate gold(I) complex bearing weak  $\sigma$ -donor ligands might also be competent for the oxidative addition. We synthesized a bis(p-Me-pyridine)Au(I) complex 6a by simply mixing DMSAuCl (1 eq.), p-Me-pyridine (2 eq.) and AgNTf<sub>2</sub> (1 eq.) in CH<sub>2</sub>Cl<sub>2</sub>, followed by filtration and crystallization.<sup>22</sup> Treatment of bis(p-Me-pyridine)Au(I)NTf2 with 1.0 equivalent of alkynyl hypervalent iodine reagent **3a** generated smoothly a new species in only one hour (76% NMR yield, Scheme 3). The compound was assigned to be gold(III) complex 7a, formed by the oxidative addition with 3a, which is consistent with the <sup>1</sup>H NMR spectrum. The gold(III) complex 7a is not stable enough for <sup>13</sup>C NMR spectroscopy and X-ray analysis. In ESI-MS analysis, an ion was observed at m/z 871.0337, which is in agreement with the calculated m/z value for the cationic species 7a (871.0325). This is the first experimental proof of such an intermolecular oxidative addition to a linear gold(I) complex coordinated to two mono-dentate ligands.

Under these conditions for the efficient oxidative addition of **7a** to bis(pyridine)gold(I) **6a**, we explored the scope of the reaction with respect to the alkynyl hypervalent iodine and bipyridylgold(I) components. Within 1 hour at room temperature, full conversion to the corresponding Au(III) complex was observed with a range of alkynyl hypervalent iodine regents, as determined by <sup>1</sup>H NMR spectroscopy. Oxidative addition products **7a**-**h** were characterized by ESI-MS, <sup>1</sup>H NMR and <sup>19</sup>F NMR spectroscopy, among these

products, 7c and 7d were stable enough for the time of the  ${}^{13}C$ NMR spectroscopy. An analysis of the relative reaction rates of oxidative addition to 6b showed that electron-donating substituents on the alkynyl hypervalent iodine regents accelerate the reaction. On the other hand, the electron-poor system (such as NO<sub>2</sub>-subsituted alkynyl hypervalent iodine regent) slow down the reaction significantly, resulting in the failure of the characterization of these gold(III) products. Additionally, the relative reaction rates of oxidative addition to bis(pyridine)gold(I) complexes bearing different substituents were also analyzed. As expected, the electron poor bis(pyridine)gold(I) complex react significantly faster than electron-rich systems. Especially, in the case of 7h, the addition of alkynyl hypervalent iodine reagent led to an immediate colour change, and <sup>1</sup>H NMR spectroscopy showed the complete conversion of gold(I) complex in 4 min, which indicates an extremely fast oxidative addition. On the other hand, the oxidative addition to (4-dimethylaminopyridyl)<sub>2</sub>Au<sup>I</sup>NTf<sub>2</sub> failed, as a result of high *trans* influence of 4-dimethylaminopyridyl ligand.





#### CONCLUSION

In summary, we propose that the accessibility of the gold(I) atom to tri- or tetra-coordination is critical in the oxidative

process that involves a tri- or tetra-coordinate gold(I) intermediate with oxidizing agent. Computational studies for the bond lengths and bond angles of tri-coordinate (Phen) $R_3PAuNTf_2$  shows that the tri-coordinate accessibility increases as trans influence of phosphine ligands decreases. The oxidative addition to the asymmetric tri-coordinate (Phen)R<sub>3</sub>PAu(I)NTf<sub>2</sub> complexes with alkynyl hypervalent iodine reagents was built. The reactivity profile of these gold(I) complexes exhibits a good relationship to the Hammett substituent parameter ( $\rho = 3.75$ ,  $R^2 = 0.934$ ), in which the gold(I) complexes bearing less  $\sigma$ -donating phosphine ligands increase the rate of oxidative addition. The positive  $\rho$  indicated a strong ligand effects for the oxidative addition. Different from the common understanding that ligands with strong  $\sigma$ -donation could increase the oxidative reactivity of gold(I) complexes by increase the electron density on the gold center, this study suggests that the weakened  $\sigma$ -donor ligands increase the oxidative reactivity by promoting tri- or tetra-coordinate accessibility of gold(I) complexes. It was also supported by a facile oxidative addition of alkynyl hypervalent iodine reagent to linear bis(pyridine)lgold(I) complex, in which the less  $\sigma$ donating pyridyl ligands increase the tri-coordinate accessibility of gold(I) intermediate with the oxidizing agent.<sup>23</sup> From a strategic standpoint, we anticipate that this process, which employs weakened  $\sigma$ -donor ligands to enable the oxidative addition to gold(I), would find widespread and practical use in various disciplines of chemical science.

# ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures and compound characterization (PDF)

X-ray diffraction data of 1a, 1d, 1e (CIF)

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### Notes

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(23) While the bis(trifluoromethyl)-substituted hypervalent iodine reagent **3a** allowed an isolation of the gold(III) compounds, with the corresponding carbonyl hypervalent iodine reagent a reaction was observed, but the product could not be isolated. With alkynyl iodides, the (bispyridine)gold(I) complex is consumed, but the desired product was not detected in the <sup>1</sup>H NMR spectra. We think the product is not stable enough for characterization. With aryl iodides the oxidative addition does not occur.

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gold(I)