

Tris-(pentafluorophenyl)phosphine Gold(I) Complexes as New Highly Efficient Catalysts for the Oxycarbonylation of Homopropargyl Carbonates

Seunghoon Shin

Department of Chemistry, Hanyang University, Seoul 133-791, Korea. E-mail: sshin@hanyang.ac.kr

Received November 7, 2005

Key Words : Oxycarbonylation, Tris-(pentafluorophenyl)phosphine, Gold catalysis, Ligand tuning

Catalysis mediated by Au(I) and Au(III) complexes has recently received great attention as an emerging tool for the various useful organic transformations.¹ Typically employed catalytic systems are AuCl₃ or the combined use of a phosphine Au(I) chloride and a silver salt. We projected that appropriate choice of phosphine ligand could have a direct impact on the reactivity, especially in case where the reactivity is not sufficient. However, there have been limited studies on enhancing catalytic activity of Au complexes by changing steric and/or electron-demand of ligand systems, although it is highly desirable considering the high cost of gold complexes.² In quest for the more reactive species, we describe herein a tris-(pentafluorophenyl)phosphine gold(I) chloride in the presence of silver salts, as new efficient catalytic system and report our preliminary results of oxycarbonylation of carbonates derived from homopropargyl alcohol.

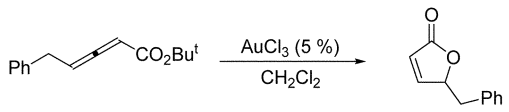
In our previous work on gold(III) catalyzed cyclization of *tert*-butyl allenates, we have noted that the activity of Au(III) complex is greatly affected by the choice of ligand (Table 1): electron-density on phosphorus directly affects the conversion.³ For example, when triphenylphosphine was used along with AuCl₃, no reaction occurred after a prolonged heating. Use of electron-deficient tris-(pentafluorophenyl)phosphine ligand increased the yield up to 85% (isolated yield) in 2 h, almost fully restoring the original

reactivity of AuCl₃. Encouraged by the result, we were intrigued by the possibility of tuning the reactivity in a more general context of gold catalysis.

The synthesis of phosphine gold(I) complexes is shown in Scheme 1. By analogy with the report by Gagosz for the preparation of triphenylphosphine gold(I) *bis*-(trifluoromethanesulfonyl)imidate,⁴ we have treated chlorodimethylsulfide gold(I) with tris-(pentafluorophenyl)phosphine (1 equiv.) at rt in CH₂Cl₂ (Scheme 1). After concentration and precipitation with excess *n*-hexane, the desired Au{P(C₆F₅)₃}Cl complex **1a** was obtained in 86% yield as air-stable and non-hygroscopic powder. ³¹P NMR (121 MHz, CDCl₃) indicates peak centered at -32.3 ppm. Further treatment of this complex with AgNTf₂ in CH₂Cl₂ led to the corresponding NTf₂ complex **2a** (³¹P NMR: δ -39.6) in 85% yield, after filtration of the insolubles and evaporation to dryness.⁵

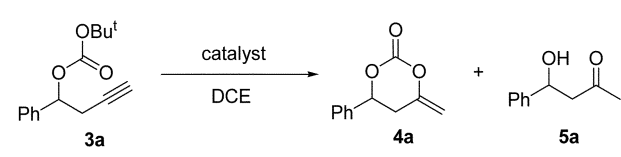
Based on the high “alkynophilicity” of gold(I) complexes, we set out to examine the oxycarbonylation of *tert*-butyl carbonate **3a** derived from homopropargyl alcohol under the various conditions (Table 2).⁶ The resulting product has protected aldol synthon, thus the current reaction constitutes an important surrogate aldol reaction.⁷ A related reaction using stoichiometric amount of IBr has been known for some time, but the corresponding catalytic version is unprecedented as far as we are aware.⁸

Table 1. Effect of Phosphine Ligand on the Lactonization of *tert*-Butyl Allenate

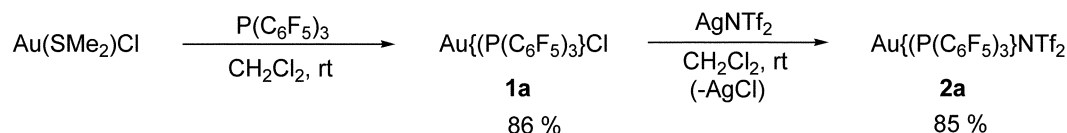


ligand	conditions	yield (borsm)
no ligand	80 °C, 2 h	88
PPh ₃	80 °C, 24 h	no reaction
P(OEt) ₃	80 °C, 1 h	55(73)
P(C ₆ F ₅) ₃	80 °C, 2 h	85(99)

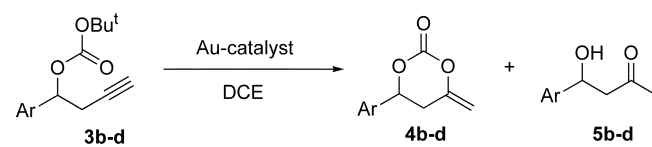
Table 2. Oxycarbonylation of **3a** using Au(PAr₃)Cl (5%) / AgSbF₆ (5%)



ligand	conditions	yield (borsm)
1a (5%) / AgSbF ₆ (5%)	5 h/RT	99% (4/5=3.2/1)
2a (5%)	12 h/RT	61% (4/5=3.5/1)
1b (5%) / AgSbF ₆ (5%)	8 h/RT	57% (4/5=3.4/1)
2a (5%)	12 h/RT	60% (4/5=3.6/1)



Scheme 1. Preparation of Au{P(C₆F₅)₃}Cl (**1a**) and Au{P(C₆F₅)₃}NTf₂ (**2a**).

Table 3. Oxycarbonylation of **3** using Au(PAR₃)Cl (5%) / AgSbF₆ (5%)


entry	substrate (3)	condition	yield (4/5)
3b	<i>m</i> -MeO-C ₆ H ₄	rt, 3.5 h	70% (1.2/1)
3c	<i>p</i> -Cl-C ₆ H ₄	3 °C, 7 h	65% ^b (2.5/1)
3d	<i>p</i> -NC-C ₆ H ₄	rt, 10 h	68% (1.2/1)

^aThe reaction was carried out using Au(PAR₃)Cl (5%) and AgSbF₆ (5%) in DCE (0.2 M). ^b75% borsm (PAR₃=P(C₆F₅)₃).

To our delight, when we treated **3a** with complex **1a** and an equimolar amount of AgSbF₆ in 1,2-dichloroethane (DCE), we obtained desired products **4a** and **5a** in a combined 99% isolated yield (3.2/1 = **4a/5a**) in an exceptionally clean reaction after 5 h at room temperature (Table 2).⁹ Compared to **1a**/AgSbF₆ system, the corresponding triphenylphosphine complex **1b** (AuPPh₃Cl) and AgSbF₆ led to only 57% yield (3.4/1 = **4a/5a**) after 8 h at rt, clearly indicating the enhanced reactivity of our new catalytic system.

Brief scope of the current method was examined as in Table 3 using substrates **3b-d** having varying electronic demands. Substrates having electron-poor as well as electron-rich aromatic ring underwent cyclization smoothly without event.

In summary, we have synthesized new phosphine Au(I) complexes based on the use of P(C₆F₅)₃. Examples of pronounced effect of electron-density on the overall efficiency were demonstrated in the oxycarbonylation of **3**. The fact that *O*-transfer of a carbonate occurs better with **1a** (vs. **1b**) suggest that P(C₆F₅)₃ is the ligand of choice when the reactivity is not sufficient. Studies on the full scope of the current methodology is currently undergoing in our laboratory.

Acknowledment. This work was supported by a research fund from Korea Sanhak Foundation in 2005. SS gratefully

thank Profs. Cho, Chun-Gyu and Oh, Chang-Ho for generously providing chemicals.

References

- For an excellent review on homogeneous gold catalysis, see (a) Hashmi, A. S. K. *Gold Bulletin* **2004**, *37*, 51. (b) Hoffmann-Roeder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387. For recent reports on the novel reactivity of Au(I) and Au(III) catalysts, see: (c) Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 15978. (d) Nieto-Oberhuber, C.; Munoz, M. P.; Bunuel, E.; Nevado, C.; Cardenas, D. J.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 2402. (e) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 11806. (f) Shi, Z.; He, C. *J. Am. Chem. Soc.* **2004**, *126*, 5964. (g) Asao, N.; Sato, K.; Menggenbater, Y.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 3682. (h) Shin, S.; Gupta, A. K.; Rhim, C. Y.; Oh, C. H. *Chem. Commun.* **2005**, *35*, 4429. (i) Kim, N.; Kim, Y.; Sung, D.; Gupta, A. K.; Oh, C. H. *Org. Lett.* **2005**, *7*, 5289. (j) Yao, T.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 11164. (k) Hashmi, A. S. K.; Schwarz, L.; Chio, J.-H.; Frost, T. M. *Angew. Chem. Int. Ed.* **2000**, *39*, 2285. (l) Mizushima, E.; Hayashi, T.; Tanaka, M. *Org. Lett.* **2003**, *5*, 3349.
- (a) Hashmi, A. S. K.; Weyrauch, J. P.; Rudolph, M.; Kurpejovic, E. *Angew. Chem. Int. Ed.* **2004**, *43*, 6545. (b) Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.
- Kang, J. E.; Lee, E. S.; Park, S. I.; Shin, S. *Tetrahedron Lett.* **2005**, *46*, 7431.
- (a) Mezailles, N.; Richard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133. (b) Gagosz, F. *Org. Lett.* **2005**, *7*, 4129.
- We have noted that Au(PPh₃)NTf₂ complex is light-sensitive and turns to darker purple upon continued storage under room light, although the reactivity remains essentially the same. However, **1b** does not change color when kept under room-light for months.
- For an excellent review on related topics, see Alfonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3097.
- (a) Trost, B. M.; Ball, Z. T.; Joege, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 3415. (b) Davies, H. M. L.; Beckwith, R. E.; Antoulinakis, E. G.; Jin, Q. *J. Org. Chem.* **2003**, *68*, 6126. (c) Bode, J. W.; Carreira, E. K. *J. Org. Chem.* **2001**, *66*, 6410. (d) Nelson, S. G.; Wan, Z. *Org. Lett.* **2000**, *2*, 1883. (e) Nelson, S. G.; Zhu, C.; Shen, X. *J. Am. Chem. Soc.* **2003**, *126*, 14.
- Marshall, J. A.; Yanik, M. W. *J. Org. Chem.* **1999**, *64*, 3798.
- (**4a**) ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.30 (m, 5H), 5.44 (dd, *J* = 3.3, 10.2 Hz, H), 4.87 (t, *J* = 2.2 Hz, H), 4.43 (t, *J* = 1.8 Hz, H), 2.94 (dd, *J* = 3.3, 15.4 Hz, H), 2.80 (tdd, *J* = 1.5, 10.2, 15.6 Hz, H). ¹³C (100 MHz, CDCl₃): δ 151.1, 137.1, 130.0, 129.6, 129.2, 126.4, 95.5, 79.5, 33.9.