Synthetic Methods

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Air-Stable Cationic Gold(I) Catalyst Featuring a Z-Type Ligand: Promoting Enyne Cyclizations**

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Abstract: *An air-stable cationic Au^I complex featuring a Z-type ligand (boron atom) as a σ-acceptor was developed for elucidating the effect of B on catalytic reactions. An enyne cyclization in the presence of either $[Au\rightarrow B]^+$ or $[Au]^+$ showed that $[Au\rightarrow B]^+$ promotes the reactivity, which enabled the effective construction of not only five- and six-membered rings, but also seven-membered rings.*

In 1995, Green described a novel method for classifying covalent bonds in transition metals.[1] Based on this definition, there are three types of ligands, the L, X, and Z types, and they are defined based on the bonding mode of the ligating atom of a ligand (Figure 1). The X ligand provides one electron to the metal to form the covalent bond (M−X) exemplified by a hydride, alkyl, and halogen. The L ligand (e.g., phosphine, carbon monoxide, and olefin) provides two-electrons for occupying an empty orbital on the metal center. A Lewis-acidic atom (borane, aluminum, and silicon) is classified as a Z-type ligand.[2] Although there is quite a wide variety of metal complexes bearing the X- and L-type ligands, metal complexes featuring a Z-type ligand (M→Z interactions) are still limited, and therefore catalytic reactions utilizing the M→Z interaction are scarce.[3,4] In 2011, Britovsek and co-workers[4a] reported the syntheses of novel rhodium(I) complexes, [Rh(DPB)L$_n$X] [DPB = diphosphine-borane: (o-Ph$_2$PC$_6$H$_4$)$_2$BPh], featuring Rh→B interactions for investigating their use in the catalytic carbonylation of methylacetate to acetic anhydride. In this case, no carbonylation activity was observed under the reaction conditions. In the same year, the group of Bourissou[4b] reported the palladium-catalyzed Suzuki–Miyaura cross coupling with MPB [monophosphine-borane: (o-Ph$_2$PC$_6$H$_4$)BMes$_2$, (o-iPr$_2$PC$_6$H$_4$)BMes$_2$] ligands, which improved the reactivity in comparison to the general Pd/PPh$_3$ system. However, a coordination study using relevant Pd^0 species did not show the Pd→B interactions. More recently, Peters et al.[4c] reported the catalytic conversion of nitrogen into ammonia by a [(TPB)Fe] complex[5] [TPB = triphosphine-borane: (o-iPr$_2$PC$_6$H$_4$)$_3$B]. To the best of our knowledge, the work reported herein is the very first example of a catalytic reaction utilizing the M→Z interaction.

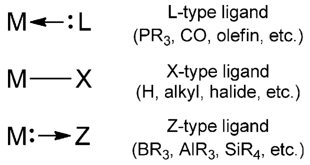
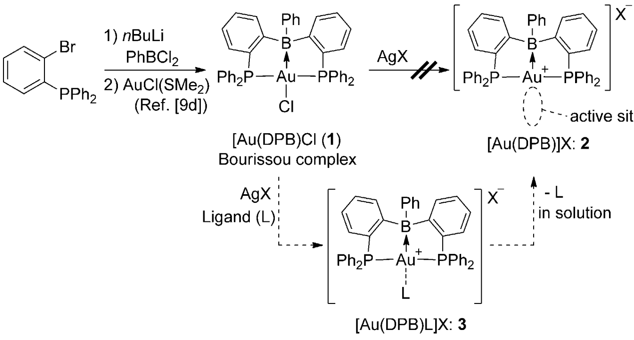


Figure 1. Formal classification of metal ligands.

We expected a novel reactivity for the M→Z type interaction because 1) its electron-withdrawing effect would increase the Lewis acidity on the transition-metal center, 2) the action for decreasing the electron density on its metal atom might promote the reductive elimination step, and 3) the two different types of Lewis acids,[6] metal atom, and its ligand (e.g., borane) might work as multipoint recognition systems. Thus, we initially focused on the synthesis of an air-stable cationic gold(I) catalyst having a Z-type ligand, and its application to the cyclization of enynes.

Hill and co-workers[7a] first reported the interaction between a metal and boron atoms based on the X-ray diffraction study of a ruthenium complex bearing the hydrotris(2-sulfanyl-1-methylimidazolyl)borate ligand. Coordination studies of similar tris(imidazolyl)borate ligands have also been reported.[2,7,8] Alternatively, the group of Bourissou[9] reported that both the L- and Z-type sites of the phosphine-borane ligand, such as MPB, DPB, and TPB, could be coordinated to metal fragments (Cu,[9a] Rh,[9b,c] Pd,[9c] Pt,[9c] and Au[9d] etc.). They reported[9d] the concise preparation of [Au(DPB)Cl] (**1**) as an air-stable powder from commercially available materials (Scheme 1). The electronic effect of the σ-acceptor boron atom would prominently occur on the gold(I)



Scheme 1. Synthesis of gold(I) complex featuring Z-type ligands.

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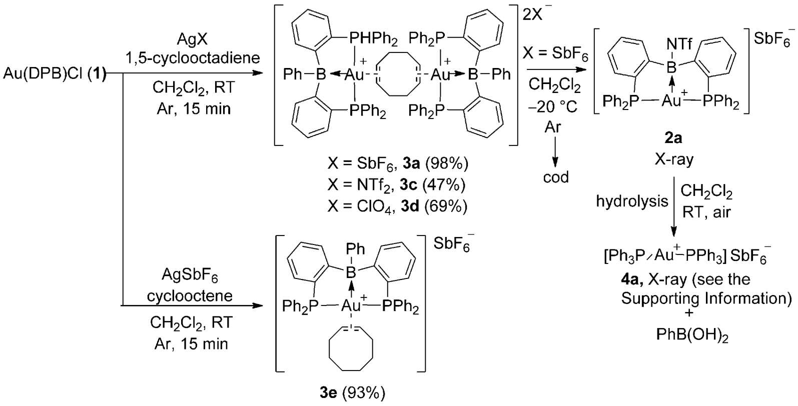
atom at the *trans* position. We first tried to transform **1** into the corresponding cationic gold(I) species by adding silver salts in CH_2Cl_2. However, the expected [Au(DPB)]X (**2a**: X = SbF_6, **2b**: X = BF_4) was not observed, presumably because of its instability. Thus, indirect preparation of the cationic species **2** via the precatalyst **3**, which has a coordinating and releasable ligand,[10] was next investigated.

After several screenings, we found that the simple addition of $AgSbF_6$ to a solution of **1** and 1,5-cyclooctadiene (cod) in CH_2Cl_2 following filtration and crystallization in pentane resulted in the formation of the air-stable [(DPB)Au-(μ_2-cod)Au(DPB)]$(SbF_6)_2$ (**3a**) in 98% yield (Scheme 2). A solution of **3a** in CH_2Cl_2 at −20 °C under an Ar atmosphere stood for several days and afford a crystal, X-ray analysis of which confirmed its structure to be that of [Au(DPB)]SbF_6 (**2a**; CCDC 1009844, see the Supporting Information). This result obviously indicated that the cod ligand of **3a** could easily dissociate from Au in solution (Scheme 2). Further investigation showed that crystallization of **3a** from a CH_2Cl_2 solution at ambient temperature in air produced its hydrolyzed products $[Au(PPh_3)_2]SbF_6$ (**4a**)[11,12] and phenylboronic acid. In contrast, the other counter anion species **3c** (47%) and **3d** (69%) were also obtained by the same procedure. The monomer-type [Au(DPB)(coe)]SbF_6 (**3e**) was formed in 93% yield, when cyclooctene (coe) was employed instead of cod. In contrast to the in situ production of the crystalized **2a** from **3a** in CH_2Cl_2, similar treatment of **3c–e** in solution did not afford the corresponding crystals of [Au(DPB)]X (**2**).



Scheme 2. Syntheses of cationic gold(I) complexes. Tf = trifluoromethanesulfonyl.

Table 1: Experimental data for selected bond lengths and angles of complexes **1** and **2a**.

	Au-B [Å]	P-Au [Å]	$\Sigma_\alpha B$ [°]	$\Sigma_\alpha Au$ [°]	P-Au-P [°]	B-Au-P [°]
[Au(DPB)]SbF_6 (**2a**)	2.521	2.315, 2.288	355.1	364.1	163.0	82.5, 84.6
[Au(DPB)Cl] (**1**)[a]	2.335	2.307, 2.329	343.8	364.2	157.2	80.5, 83.8

[a] Reported by Bourissou and co-workers.[9]

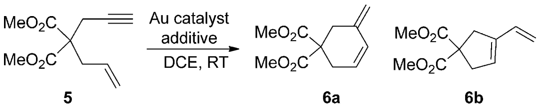
The selected lengths and angles of both the cationic complex **2a** and neutral Bourissou complex **1** (measured by an X-ray crystallographic analysis) are listed in Table 1. From a geometric point of view, the Au–B bond length of **2a** (2.521 Å) is rather long relative to that of the neutral **1** (2.335 Å), whereas no significant change in the lengths of both the Au–P bonds is observed. In addition, increasing the sum of each of the C-B-C angles from **1** ($\Sigma_\alpha B = 343.8°$) to **2a** ($\Sigma_\alpha B = 355.1°$) without change of other angles (Σ_αAu, P-Au-P, and B-Au-P etc.) are recognized. These observations suggest that the decreasing electron density on the gold(I) atom by cationization caused a noticeable weakening of the Au→B interaction.[13]

Does the Z-type ligand (boron atom) activate the metal-catalyzed reaction? A coordination study of **1** and **2a** demonstrated that the strength of its Au→B interaction depends on the electron density of the Au center. This might mean that **2a** acts as a general type of cationic gold(I) catalyst (without a Z-type ligand). It is known that standard cationic gold(I) catalysts possess an alkynophilicity,[14] therefore, **2a** might react with the typical triple bond unit. Increasing the electron density on the gold(I) atom through alkyne coordination would enhance the strong Au→B interaction, which hopefully might end up promoting the subsequent reaction of the coordinated triple bond with suitable nucleophiles. Based on this hypothesis, we examined the gold(I)-catalyzed cycloisomerization of enynes.[15]

Our initial experiment was carried out using the 1,6-enyne **5** in DCE at room temperature in the presence of 2 mol% **1** (Table 2). In contrast to observing no reaction with **1** alone (entry 1), the reaction involving the concomitant addition of **1** and $AgSbF_6$ gave the desired products **6** in 83% yield as a 6:1 mixture of the methylenecyclohexene **6a** and vinylcyclopentene **6b** (entry 2). The group of Shi[16] recently reported that the complexes modified by mixing a silver salt and gold chloride, showed reactivity which was different from that of the genuine $[Au^I]^+X^-$ species. In contrast, the procedure for in situ formation of $[Au^I]^+$ is problematic. Thus, we decided to use the synthesized cationic gold(I) complex **3** to not only avoid these problems, but also observe the effect of the Z-type ligand. After screening (entries 3–6),[17] we found that the reaction using 1 mol% of **3a** proceeded smoothly to produce the desired products in 99% yield (entry 3). The reaction in air also provided the same result (entry 4). In contrast to the result of **3a**, the hydrolyzed catalyst **4a** (lacking the Z-type ligand) gave a low yield (entry 5). $[Au(PPh_3)]SbF_6$ (**4b**; $[P_1Au]^+$) has one donor on the gold atom. Thus, it would be of great interest to see the difference of the reactivity between **3a** and **4b**. As can be seen in entry 6, **4b** provides a similar result to that of entry 2 and an inferior result to that of **3a** (99% versus 84%).

The results in Table 2 encouraged us to implement an investigation[18] into the reactivities of **3a**, **4a**, and **4b**. A decrease in the loading of **3a** from 1 mol% (2 mol% Au) to

Table 2: Gold(I)-catalyzed cycloisomerization of the enyne **5**.



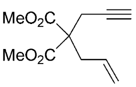
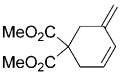
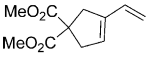
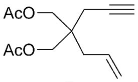
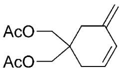
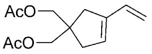
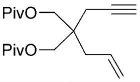
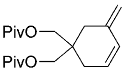
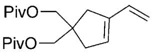
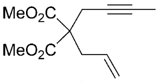
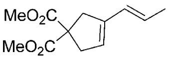
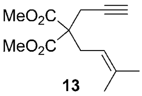
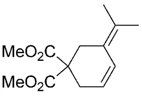
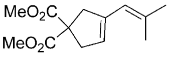
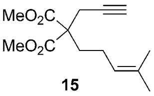
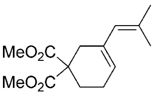
5 **6a** **6b**

Entry	Catalyst (mol%)	Form	Atm.	*t*	Yield [%] (**6a**/**6b**)[a]
1	Au(DPB)Cl (**1**) (2)	$XP_2Au \rightarrow Z$	Ar	24 h	n.r.
2	Au(DPB)Cl (**1**) (2) + $AgSbF_6$ (2)	$[P_2Au \rightarrow Z]^+$ (in situ)	Ar	<5 min	83 (6:1)
3	$[Au(DPB)SbF_6]_2(cod)$ (**3a**) (1) (2 mol% Au)	$[P_2Au \rightarrow Z]^+$	Ar	<5 min	99 (6:1)
4	$[Au(DPB)NTf_2]_2(cod)$ (**3c**) (1) (2 mol% Au)	$[P_2Au \rightarrow Z]^+$	Ar	24 h	75 (6:1)
5	$[Au(DPB)ClO_4]_2(cod)$ (**3d**) (1) (2 mol% Au)	$[P_2Au \rightarrow Z]^+$	Ar	24 h	n.r.
6	$[Au(DPB)(coe)]SbF_6$ (**3e**) (2)	$[P_2Au \rightarrow Z]^+$	Ar	24 h	n.r.
7	$[Au(DPB)SbF_6]_2(cod)$ (**3a**) (1) (2 mol% Au)	$[P_2Au \rightarrow Z]^+$	air	<5 min	99 (6:1)
8	$[Au(PPh_3)_2]SbF_6$ (**4a**) (2)[b]	$[P_2Au]^+$ (without B)	air	24 h	9 (8:1)[c]
9	$[Au(PPh_3)]SbF_6$ (**4b**) (2)[b]	$[P_1Au]^+$ (without B)	air	10 min	84 (6:1)

[a] Isolated yield. Ratio was determined by ^{1}H NMR spectroscopy. [b] Catalyst was prepared under Ar atmosphere by mixing, filtering, and adding as a stock solution. [c] The starting material **5** was recovered in 90% yield. DCE = 1,2-dichloroethane, n.r. = no reaction.

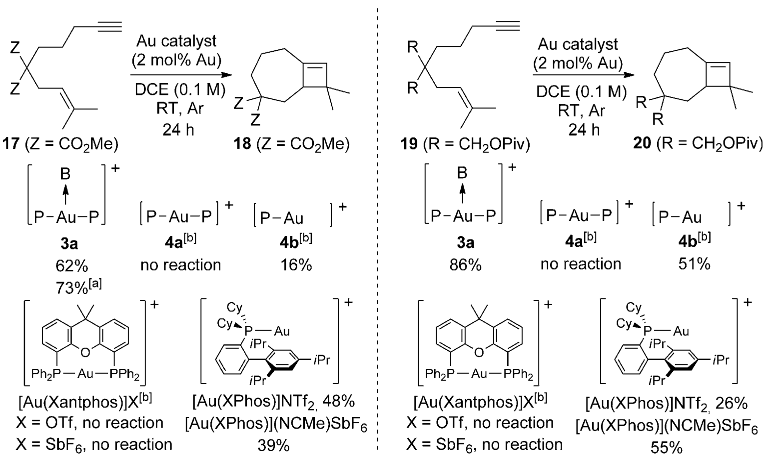
0.2 mol% (0.4 mol% Au) maintained a high yield (98%; **6a**/**6b** = 6:1). No reaction or low yield was observed when treated with 0.4 mol% $[P_nAu]^+$ (see **4a,b**; Table 3, entry 1). The complex **3a** retained its catalytic activity after three months of storage (entry 2). The bis(acetoxymethyl) derivative **7** and bis(pivaloyloxymethyl) derivative **9** showed similar behaviors to that of **5** in the presence of $[P_2Au \rightarrow B]^+$ (see **3a**) to furnish **8** and **10**, respectively, in good to high yields (entries 3 and 4). $[P_2Au]^+$ (see **4a**) provided a very low yield in both cases. Although the reactions with $[P_1Au]^+$ (see **4b**) were faster than those with **3a**, chemical yields were rather low. Treatment of the terminal methyl-enyne **11** with $[P_2Au \rightarrow B]^+$ (see **3a**) afforded the cyclized products **12** in high yield (entry 5). $[P_nAu]^+$ (see **4a,b**) showed either no reaction or a low yield. In the case of the trisubstituted alkene substrates **13** and **15**, no difference in the chemical yields between $[P_2Au \rightarrow B]^+$ (see **3a**) and $[P_1Au]^+$ (see **4b**) was observed (entries 6 and 8). $[P_2Au]^+$ (see **4a**) was inactive in both cases. Given these results, **3a** seems to be superior to **4a,b** (in situ preparation) with respect to generality and chemical yield. Thus, it is concluded that the hydrolyzed and/or partially dissociated catalysts $[P_nAu]^+$ (see **4a,b**) are not active species in the cycloisomerization of enynes using $[P_2Au \rightarrow B]^+$ (see **3a**).

Table 3: Gold(I)-catalyzed cycloisomerization of the enynes **5**, **7**, **9**, **11**, **13** and **15**.

Entry	Substrate	Products		Au (mol%)	$\left[\overset{B}{\overset{\uparrow}{P{-}Au{-}P}}\right]^+$ **3a**	$[P{-}Au{-}P]^+$ **4a**[a]	$[P{-}Au]^+$ **4b**[a]
1	 **5**	 **6a**	 **6b**	0.4	98% (6:1) 15 min	no reaction 24 h	40% (2:1) 10 min
2				0.4 (stored for 3 months at RT under air)	97% (6:1) 15 min		
3	 **7**	 **8a**	 **8b**	0.4	71% (6:1) 4 h	9% (5:1)[b] 10 d	61% (5:1) 10 min
4	 **9**	 **10a**	 **10b**	1	90% (5:1) 2 h	9% (3:1)[c] 10 d	76% (4:1) 20 min
5	 **11**		 **12b**	1	99% <5 min	no reaction 7 d	45% 6 h
6	 **13**	 **14a**	 **14b**	0.1	99% (1:7) <5 min	no reaction 24 h	99% (1:5) 5 min
7				0.05	96% (1:7) 1 h		
8	 **15**		 **16b**	1	99% <5 min	no reaction 24 h	99% 3 h
9				0.2	99% 1 h		

Reaction was performed using catalytic amount of Au^{I+} in DCE (0.1 M) at room temperature under air. Product ratios shown within parentheses. Isolated yield. Ratio was determined by ^{1}H NMR spectroscopy. [a] Catalyst was prepared under Ar atmosphere by mixing, filtering, and adding as a stock solution. [b] The starting material **7** was recovered in 76% yield. [c] The starting material **9** was recovered in 79% yield.

At the final stage of this study, we examined the catalytic reactivity of **3a**, **4a**, and **4b** for the [2+2] cycloaddition[19–21] of 1,8-enynes. When the 1,8-enyne **17** was exposed to 1 mol% of $[P_2Au \rightarrow B]^+$ (see **3a**; 2 mol% Au) in DCE (0.1 M) at room temperature under an Ar atmosphere, the desired bicyclic product **18** was formed in 62% yield (Scheme 3). The diluted solution (0.01 M in DCE) provided **18** in a better yield (73%). $[P_2Au \rightarrow B]^+$ (see **3a**) as also effective for a differ-



Scheme 3. Gold(I)-catalyzed [2+2] cycloaddition of the 1,8-enynes **17** and **19**. [a] 0.01 M in DCE. [b] Catalyst was prepared under Ar atmosphere by mixing, filtering, and adding as a stock solution. Piv = pivaloyl.

ent substrate (**19**). Indeed, the cyclized **20** was obtained in high yield (86%). In both cases, $[P_2Au]^+$ (see **4a**) was inactive. The reaction with $[P_1Au]^+$ (see **4b**) produced the desired cycloadducts in rather low yield. These observations are in good accordance with those in Table 2. For additional comparison of the reactivity between the Z-type ligand and others, XPhos and Xantphos ligands were examined for this cycloaddition. The reaction with [Au(XPhos)]NTf$_2$ and [Au(XPhos)](NCMe)SbF$_6$ gave the desired products **18** and **20**, respectively, in low to good yields. [Au(Xantphos)]X[22] (X = OTf, SbF$_6$), however, did not afford the desired products (**18** and **20**).

In conclusion, we have succeeded in the preparation of the air-stable cationic Au^I complex [(DPB)Au(μ_2-cod)Au(DPB)](SbF$_6$)$_2$ (**3a**) which features a Z-type ligand as a σ-acceptor. The complex **3a** has an exceptionally efficient catalytic ability for the construction of not only five- and six-membered rings, but also seven-membered rings. Further studies of the effect of Z-type ligands on this reaction and other reactions are currently in progress.

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