New Cationic Bisoxazoline–Au(III) Complex Catalyzed Cycloisomerization of 1-Allenyl-1-ethynyl Acetate

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Abstract: Treatment of 1-allenyl-1-diethynyl acetates in the presence of a Au or Pt catalyst (5 mol%) in toluene at room temperature, followed by methanolysis, gave 4-methylene-2-cyclopentenones. The new cationic bisoxazoline (box)–Au(III) complex {(*S*,*S*)-Phbox- or [(*R*,*R*)-Bnbox $AuCl_2$]SbF_6} accelerated the reaction, providing the products in moderate yield (60–69%).

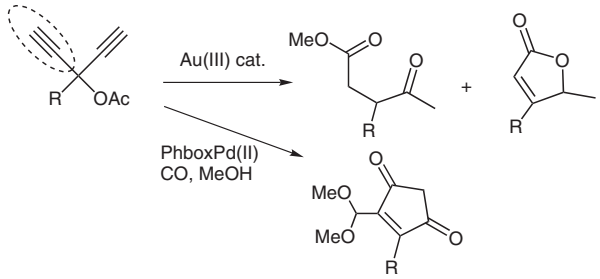
Key words: 1-allenyl-1-diethynyl acetates, 4-alkylidene-2-cyclopentenones, cationic box–Au(III) complex

The transition-metal-catalyzed reaction of unsaturated systems has recently proven to be a powerful method for the construction of a variety of carbo- and heterocycles.[1] A large number of reactions of propargylic esters mediated by gold and platinum catalysts have been recently reported.[2] Rautenstrauch[3a] and Toste et al.[3b] reported on palladium- and gold-catalyzed cycloisomerization of propargylic acetates having a 1,4-enyne structure (Scheme 1). Recently, we have reported on the gold-catalyzed double Wacker-type reaction[4a] of propargylic acetates having a 1,4-diyne structure, and also on a bisoxazoline (Phbox)–palladium complex catalyzed carbonylative cyclization[4b] of the same substrates (Scheme 2).

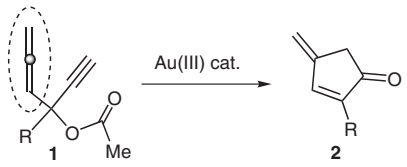
During the course of our study,[4a–d] we became interested in the transition-metal-catalyzed reaction of propargylic acetates having a 1,5-allenyne structure. Herein, we report a cycloisomerization of 1-allenyl-1-ethynyl acetates **1** using new cationic box–Au(III) complexes, [(*S*,*S*)-PhboxAuCl_2]SbF_6 or [(*R*,*R*)-Bnbox $AuCl_2$]SbF_6 (Scheme 3).

1-Allenyl-1-ethynyl acetates **1** were prepared from the corresponding allenyl ketones **3**[5] by a three-step procedure (Scheme 4). Addition of the lithiated acetylene moiety to **3**, followed by desilylation, and subsequent acetylation afforded **1** in moderate to good yields. When the substrate **3f**, containing a benzoyl group, was employed in the reaction, a complex mixture was obtained.

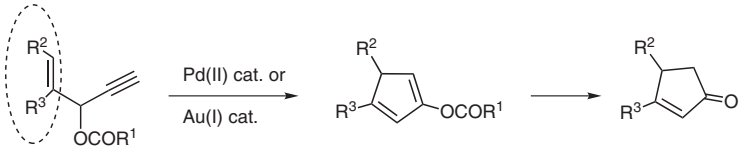
As the starting point in this study, we selected **1a** as a standard substrate to search for potential catalysts and solvents (Scheme 3 and Table 1). Treatment of **1a** in the presence of $HAuCl_4 \cdot 3H_2O$ (5 mol%) in MeCN at room temperature for 96 hours gave the 4-methylene-2-cyclopentenone (**2a**) in 24% yield (entry 1). Among the solvents investigated, toluene produced the desired **2a** with the best yield (entries 2 and 3). Commercially available $AuCl_3$, $PtCl_4$, and $LiAuCl_4$ exhibited similar catalytic activity, while $Ph_3PAuCl/AgSbF_6$[2g] yielded a complex mixture (entries 4–7). Thin-layer chromatography suggested



Scheme 2 1,4-Diynes: Kato et al.[4a,b]



Scheme 3 1,5-Allenynes: this work



Scheme 1 1,4-Enynes: Rautenstrauch[3a] and Toste et al.[3b]

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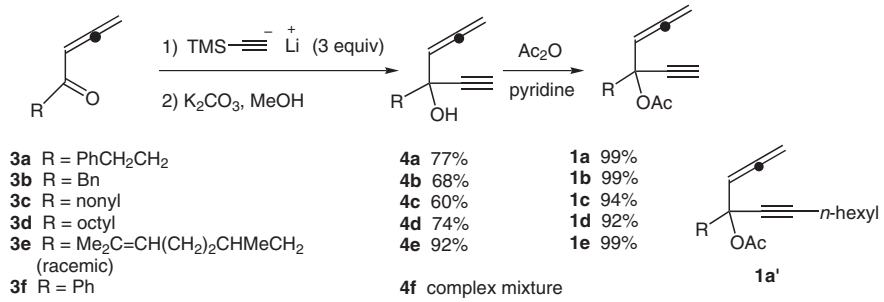


3a R = $PhCH_2CH_2$
3b R = Bn
3c R = nonyl
3d R = octyl
3e R = $Me_2C=CH(CH_2)_2CHMeCH_2$ (racemic)
3f R = Ph

4a 77%
4b 68%
4c 60%
4d 74%
4e 92%
4f complex mixture

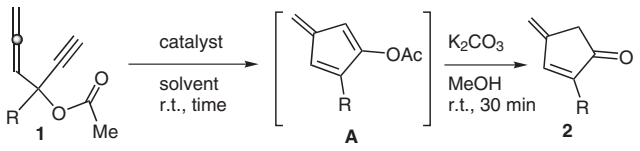
1a 99%
1b 99%
1c 94%
1d 92%
1e 99%

Scheme 4

Table 1 Cycloisomerization of **1a**: One-Step Procedure (Scheme 3)

Entry	Catalyst (5 mol%)	Solvent	Time (h)	Yield (%)
1	$HAuCl_4 \cdot 3H_2O$	MeCN	96	24
2	$HAuCl_4 \cdot 3H_2O$	CH_2Cl_2	0.5	35
3	$HAuCl_4 \cdot 3H_2O$	toluene	0.5	40
4	$AuCl_3$	toluene	48	43
5	$PtCl_4$	toluene	48	49
6	$LiAuCl_4$	toluene	20	36
7	$Ph_3PAuCl/AgSbF_6$	toluene	0.5	complex mixture

that the fulvene derivative **A** is an intermediate in the transformation **1** → **2** (Scheme 5).[3a,b] In ^1H NMR and ^{13}C NMR experiments, the spectra of **A** could barely be observed, and the spectra became increasingly complex after 15 minutes because of the instability of the compound. To increase the efficiency of the cleavage (**A** → **2**), we attempted methanolysis of the intermediates **A** (two-step procedure, Scheme 5, Table 2). A mixture of the substrate **1a** and catalyst in toluene was monitored by TLC until all of the substrate had been consumed (**1** → **A**), then K_2CO_3 and methanol were added, and the mixture was stirred for 30 minutes. The yield of **2a** was slightly improved (Table 2, entry 1).

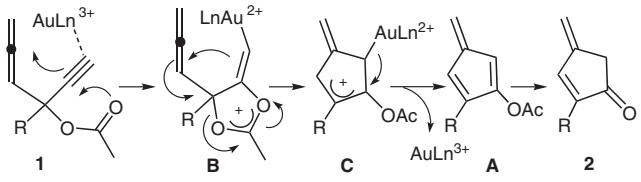


Scheme 5

Next, we screened catalysts with a two-step procedure (entries 2–4). Among the catalysts investigated, $PtCl_4$ gave the best yield (entry 4). Recently, we reported the first examples of asymmetric cyclization–carbonylation of *meso*-2-alkyl-2-propargylcyclohexane-1,3-diol and 2-methyl-2-propargylcyclohexane-1,3-dione catalyzed by several kinds of box–palladium complexes.[6] To the best of our knowledge, box–Au(III) complex has not been reported to date.[7] This prompted us to prepare new cationic box–Au(III) complexes. The complexes were prepared from a commercially available box ligand [(*S*,*S*)-Phbox or (*R*,*R*)-Bnbox], $KAuCl_4$, and $AgSbF_6$. The use of [(*S*,*S*)-Phbox $AuCl_2$]SbF_6 or [(*R*,*R*)-Bnbox $AuCl_2$]SbF_6 gave the best results overall, providing **2a** in 60% yield (entries 5 and 6). Next, substrates **1b–e** were tested for the reaction using 5 mol% of [(*R*,*R*)-Bnbox $AuCl_2$]SbF_6 as catalyst; the corresponding products **2b–e** were afforded in 60–69% yield (entries 7–10). The use of internal acetylene **1a′** resulted in no reaction.

Table 2 Cycloisomerization of **1**: Two-Step Procedure (Scheme 5)

Entry	Catalyst (5 mol%)	R	Time (**1** → **A**)	Yield of **2** (%)
1	$AuCl_3$	$Ph(CH_2)_2$	1 h	49
2	AuCl	$Ph(CH_2)_2$	48 h	36
3	$KAuCl_4$	$Ph(CH_2)_2$	1 h	52
4	$PtCl_4$	$Ph(CH_2)_2$	9 h	56
5	[(*S*,*S*)-Phbox $AuCl_2$]SbF_6	$Ph(CH_2)_2$	10 min	60
6	[(*R*,*R*)-Bnbox $AuCl_2$]SbF_6	$Ph(CH_2)_2$	10 min	60
7	[(*R*,*R*)-Bnbox $AuCl_2$]SbF_6	$PhCH_2$	10 min	69
8	[(*R*,*R*)-Bnbox $AuCl_2$]SbF_6	Nonyl	30 min	66
9	[(*R*,*R*)-Bnbox $AuCl_2$]SbF_6	Octyl	10 min	63
10	[(*R*,*R*)-Bnbox $AuCl_2$]SbF_6	$Me_2C=CH(CH_2)_2$ $CHMeCH_2$	10 min	60



Scheme 6

A plausible mechanism of the present reaction is proposed as shown in Scheme 6.[3b] 5-*exo-dig* Cyclization of 1-allenyl-1-ethynyl acetates **1** via nucleophilic attack of the alkyne by a carbonyl oxygen in accordance with Markovnikov's rule generates vinyl gold species **B**. Cyclization of vinyl gold species **B** produces cationic intermediate **C**, which upon elimination of cationic gold(III), affords fulvene derivative **A**. Methanolysis of **A** gives the product **2**.

In conclusion, we have reported the cycloisomerization of 1-allenyl-1-ethynyl acetates **1** using new cationic box–Au(III) complexes, [(*S*,*S*)-PhboxAuCl$_2$]SbF$_6$ or [(*R*,*R*)-Bnbox AuCl$_2$]SbF$_6$ afforded 4-methylene-2-cyclopentenones **2** in 60–69% yield. An application of the complexes to an asymmetric reaction is now in progress.

General Procedure for the Preparation of 4

To a solution of trimethylsilyl acetylene (3.81g, 38.8 mmol) in THF (30 mL) under Ar was added *n*-BuLi (12.8 mL of 2.6 M in hexane, 33.3 mmol) at –78 °C and the mixture was stirred for 0.5 h at 0 °C. After the solution was cooled to –78 °C, the corresponding allenylketone **3** (11.1 mmol) in THF (3 × 8 mL) was added slowly dropwise. The mixture was stirred at –15 °C for 12 h and quenched with H_2O (80 mL) and EtOAc (80 mL). The layers were separated, the aqueous layer was extracted with EtOAc (50 mL), and combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel. The fraction eluted with hexane–EtOAc (100:1 to 50:1) afforded **4**.

Compound **4**[a]: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07–2.12 (2 H, m), 2.39 (1 H, br s), 2.60 (1 H, s), 2.85–2.90 (2 H, m), 5.03 (2 H, d, *J* = 6.9 Hz), 5.43 (1 H, t, *J* = 6.9 Hz), 7.17–7.30 (5 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.8, 44.1, 68.8, 73.2, 80.0, 85.0, 97.4, 125.9, 128.4 (2 C), 128.4 (2 C), 141.6, 206.1. IR (neat): 3390, 2114, 1956, 852 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1039.

Compound **4b**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (1 H, s), 2.56 (1 H, s), 3.06 (1 H, d, *J* = 13.6 Hz), 3.10 (1 H, d, *J* = 13.6 Hz), 4.98 (2 H, d, *J* = 6.7 Hz), 5.43 (1 H, t, *J* = 6.7 Hz), 7.25–7.35 (5 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.4, 68.8, 74.0, 79.9, 84.8, 97.0, 127.1, 128.0 (2 C), 131.0 (2 C), 135.3, 206.1. IR (neat): 3403, 1958, 699 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{13}H_{12}O$: 184.0888; found: 184.0882.

Compound **4c**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 7.2 Hz), 1.24–1.33 (12 H, m), 1.46–1.56 (2 H, m), 1.75–1.80 (2 H, m), 2.25 (1 H, br s), 2.53 (1 H, s), 5.01 (2 H, d, *J* = 6.4 Hz), 5.37 (1 H, t, *J* = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.3, 29.3, 29.5, 29.5, 29.5, 31.9, 42.5, 69.1, 72.7, 79.7, 85.4, 97.5, 206.1. IR (neat): 3387, 3309, 2923, 2116, 1958 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{15}H_{24}O$: 220.1827; found: 220.1831.

Compound **4d**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.8 Hz), 1.25–1.35 (10 H, m), 1.47–1.57 (2 H, m), 1.71–1.83 (2 H, m), 2.32 (1 H, br s), 2.53 (1 H, s), 5.00 (2 H, d, *J* = 6.6 Hz), 5.37 (1 H, t, *J* = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.3, 29.3, 29.5, 29.6, 31.9, 42.5, 69.1, 72.7, 79.7, 85.4, 97.5, 206.1. IR (neat): 3399, 3309, 1958, 1738, 988 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{14}H_{22}O$: 206.1671; found: 206.1671.

Compound **4e**: colorless oil (diastereomeric mixture, dr = 6:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 and 1.04 (total 3 H, each as d, *J* = 6.5 Hz), 1.18–1.28 (1 H, m), 1.39–1.53 (1 H, m), 1.60 (3 H, s), 1.63–1.66 (1 H, m), 1.68 (3 H, s), 1.78–1.86 (2 H, m), 1.91–2.03 (2 H, m), 2.27 (1 H, br s), 2.55 (1 H, s), 5.01 (2 H, d, *J* = 6.4 Hz), 5.11 (1 H, t, *J* = 6.8 Hz), 5.38 (1 H, t, *J* = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major diastereomer) = 17.7, 21.1, 25.4, 25.7, 29.2, 38.2, 49.0, 68.9, 73.0, 79.8, 85.8, 98.3, 124.8, 131.2, 205.9. IR (neat): 3419, 3306, 1957, 847 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{15}H_{22}O$: 218.1671; found: 218.1669.

General Procedure for the Preparation of Substrates 1

To a solution of **4** (5 mmol) in pyridine (2 mL) and Ac_2O (1.5 mL) was added 4-dimethylaminopyridine (20 mg) and the mixture was stirred for 1.5–3 h at r.t. The mixture was diluted with H_2O (50 mL) and EtOAc (50 mL). The layers were separated, the aqueous layer was extracted with EtOAc (50 mL), and the combined organic layers were washed with 10% HCl aq, sat. $NaHCO_3$ aq, and H_2O. The organic layers were dried with $MgSO_4$ and concentrated in vacuo. The product was pure enough to use for further reaction.

Compound **1a**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (3 H, s), 2.16–2.23 (1 H, m), 2.31–2.38 (1 H, m), 2.70 (1 H, s), 2.82–2.90 (2 H, m), 5.00–5.06 (2 H, m), 5.68 (1 H, t, *J* = 6.8 Hz), 7.17–7.31 (5 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 30.6, 42.1, 74.6, 74.9, 79.6, 81.6, 94.1, 126.0, 128.4 (2 C), 128.5 (2 C), 141.3, 169.0, 207.5. IR (neat): 1954, 1747, 1231 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{16}H_{16}O_2$: 240.1150; found: 240.1147.

Compound **1b**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (3 H, s), 2.64 (1 H, s), 3.21 (1 H, d, *J* = 13.6 Hz), 3.33 (1 H, d, *J* = 13.6 Hz), 4.92–5.02 (2 H, m), 5.57 (1 H, t, *J* = 6.8 Hz), 7.25–7.31 (5 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 46.4, 74.8, 75.8, 79.6, 81.4, 94.1, 127.1, 127.8 (2 C), 131.1 (2 C), 135.0, 168.9, 207.4. IR (neat): 3284, 2120, 1957, 1743, 1216 cm^{-1}. HRMS (EI): *m/z* [M$^+$] $C_{15}H_{14}O_2$: 226.0994; found: 226.0992.

Compound **1c**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.8 Hz), 1.25–1.32 (12 H, m), 1.46–1.55 (2 H, m), 1.85–1.93 (1 H, m), 1.97–2.03 (1 H, m), 2.04 (3 H, s), 2.62 (1 H, s), 4.94–5.03 (2 H, m), 5.60 (1 H, t, *J* = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.7, 22.7, 24.1, 29.3, 29.4, 29.5, 29.6, 31.9, 40.4, 74.4, 75.1, 79.3, 81.9, 94.3, 169.0, 207.5. IR (neat): 2925, 2120, 1957, 1746, 1226 cm^{-1}. HRMS (EI): *m/z* [M$^+$] $C_{17}H_{26}O_2$: 262.1933; found: 262.1933.

Compound **1d**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 6.8 Hz), 1.25–1.34 (10 H, m), 1.45–1.55 (2 H, m), 1.85–1.93 (1 H, m), 1.97–2.03 (1 H, m), 2.04 (3 H, s), 2.62 (1 H, s), 4.94–5.03 (2 H, m), 5.60 (1 H, t, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.8, 22.7, 24.1, 29.2, 29.4, 29.5, 31.9, 40.4, 74.4, 75.1, 79.2, 82.0, 94.3, 169.0, 207.5. IR (neat): 2954, 2120, 1957, 1746, 1227 cm^{-1}. HRMS (EI): *m/z* [M$^+$] $C_{16}H_{24}O_2$: 248.1776; found: 248.1775.

Compound **1e**: colorless oil (diastereomeric mixture, dr = 6:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 and 1.03 (total 3 H, each as d, *J* = 6.8 Hz), 1.20–1.31 (1 H, m), 1.41–1.52 (1 H, m), 1.61 (3 H, s), 1.68 (3 H, s), 1.77–1.90 (3 H, m), 1.95–2.07 (2 H, m), 2.04 (3 H, s), 2.64 (1 H, s), 4.94–5.03 (2 H, m), 5.10 (1 H, t, *J* = 6.8 Hz), 5.58–5.62 (1 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major diastereomer) = 17.7, 21.1, 21.8, 25.3, 25.7, 29.1, 38.0, 47.1, 74.7, 75.1, 79.4, 82.1, 94.9, 124.7, 131.2, 168.9, 207.3. IR (neat): 2918, 1957, 1746, 1225 cm^{-1}. HRMS (EI): *m/z* [M$^+$] $C_{17}H_{24}O_2$: 260.1776; found: 260.1770.

General procedure for the cycloisomerization reaction of 1

To a solution of **1** (50 mg) in toluene (5 mL) was added the catalyst (5 mol%) and the mixture was stirred at r.t. The mixture was monitored by TLC until all the substrate had been consumed (**1** → **A**), then K_2CO_3 (86 mg, 0.62 mmol) and MeOH (3 mL) were added. After stirring for 30 min, the mixture was diluted with EtOAc (20 mL), and washed with 3% $NaHCO_3$ aq (20 mL). The layers were separated, the aqueous layer was extracted with EtOAc (20 mL),

and the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel. The fraction eluted with hexane–EtOAc (100:1 to 50:1) afforded **2**.

Compound **2a**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (2 H, t, *J* = 7.6 Hz), 2.84 (2 H, t, *J* = 7.6 Hz), 2.99 (2 H, s), 5.15 (1 H, s), 5.25 (1 H, s), 7.17–7.30 (5 H, m), 7.34 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 33.7, 39.8, 111.0, 126.1, 128.4 (2 C), 128.4 (2 C), 141.1, 142.9, 148.2, 154.2, 205.9. IR (CCl_4): 3027, 1698, 1638 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1043.

Compound **2b**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 (2 H, t, *J* = 1.2 Hz), 3.59 (2 H, s), 5.15 (1 H, s), 5.22 (1 H, s), 7.20–7.33 (6 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.3, 39.9, 111.5, 126.5, 128.6 (2 C), 129.0 (2 C), 138.3, 142.8, 148.6, 154.6, 205.29. IR (CCl_4): 3028, 1699, 1639 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{13}H_{12}O$: 184.0888; found: 184.0889.

Compound **2c**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 7.1 Hz), 1.23–1.32 (12 H, m), 1.47–1.55 (2 H, m), 2.26 (2 H, t, *J* = 7.1 Hz), 2.98 (2 H, t, *J* = 1.2 Hz), 5.14 (1 H, s), 5.26 (1 H, s), 7.41 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.8, 27.7, 29.3, 29.4, 29.4, 29.5, 31.9, 39.9, 110.5, 143.1, 149.6, 153.5, 206.2. IR (neat): 2923, 1704, 1639 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{15}H_{24}O$: 220.1827; found: 220.1824.

Compound **2d**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.8 Hz), 1.25–1.34 (10 H, m), 1.47–1.55 (2 H, m), 2.26 (2 H, t, *J* = 7.4 Hz), 2.99 (2 H, t, *J* = 1.2 Hz), 5.15 (1 H, s), 5.27 (1 H, s), 7.41 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 24.8, 27.7, 29.2, 29.4, 29.4, 31.9, 39.9, 110.5, 143.1, 149.6, 153.5, 206.2. IR (neat): 2924, 1704, 1639 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{14}H_{22}O$: 206.1671; found: 206.1671.

Compound **2e**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (3 H, d, *J* = 6.8 Hz), 1.12–1.21 (1 H, m), 1.31–1.40 (1 H, m), 1.60 (3 H, s), 1.68 (3 H, s), 1.68–1.78 (1 H, m), 1.91–2.05 (2 H, m), 2.10 (1 H, dd, *J* = 7.2, 14.8 Hz), 2.23 (1 H, dd, *J* = 7.2, 14.8 Hz), 2.99 (2 H, t, *J* = 1.2 Hz), 5.06–5.11 (1 H, m), 5.16 (1 H, s), 5.27 (1 H, s), 7.40 (1 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 19.5, 25.5, 25.7, 31.6, 32.2, 36.9, 39.8, 110.5, 124.6, 131.4, 143.1, 148.2, 154.6, 206.2. IR (neat): 2914, 1704, 1638 cm^{-1}. HRMS (EI): *m/z* [M$^+$] calcd for $C_{15}H_{22}O$: 218.1671; found: 218.1673.

Fulvene intermediate **A** [R = Ph(CH$_2$)$_2$]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (3 H, s), 2.60 (2 H, t, *J* = 7.8 Hz), 2.89 (2 H, t, *J* = 7.8 Hz), 5.68 (1 H, s), 5.73 (1 H, s), 5.93 (1 H, s), 6.14 (1 H, s), 7.18–7.31 (5 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 28.7, 34.4, 106.9, 119.3, 121.5, 126.0, 128.4 (2 C), 128.4 (2 C), 141.8, 143.2, 147.8, 154.3, 167.8.

[(*R*,*R*)-Bnbox $AuCl_2$]SbF_6: yellow needles. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.61 (6 H, s), 2.99 (2 H, dd, *J* = 10.0, 13.6 Hz), 3.56 (2 H, dd, *J* = 2.8, 13.6 Hz), 4.76 (2 H, t, *J* = 9.4 Hz), 4.81 (2 H, dd, *J* = 3.6, 9.4 Hz), 5.21–5.27 (2 H, m), 7.29–7.38 (10 H, m). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 25.1 (2 C), 39.7 (2 C), 42.2, 67.2 (2 C), 76.3 (2 C), 128.2 (2 C), 129.6 (4 C), 130.0 (4 C), 134.5 (2 C), 175.9 (2 C). X-ray crystallographic analysis (Figure 1): X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite crystal and incident beam monochromator using MoKa radiation (λ = 0.71073 Å) at 173 K. The structure was solved by direct method[8] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Crystallographic parameters: $C_{23}H_{26}Au1Cl_2F_6N_2O_2Sb_1$, M_W = 866.07, orthorhombic, space group $P2_12_12_1$, with unit cell *a* = 8.9774(6) Å, *b* = 14.5518(10) Å, *c* = 21.3864(15) Å and *V* = 2793.9(3) Å^3. *Z* = 4, D_{calcd} = 2.059 g cm^{-3}, *R*1 [*I* > 2σ(*I*)] = 0.0747, *wR*2 = 0.1669, *R*1 (all data) = 0.0875, *wR*2 = 0.1729, 6915 independent reflections [*R* (int) = 0.1409], 337 parameters refined on F^2. The flack parameter was 0.03(2). Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 645186.

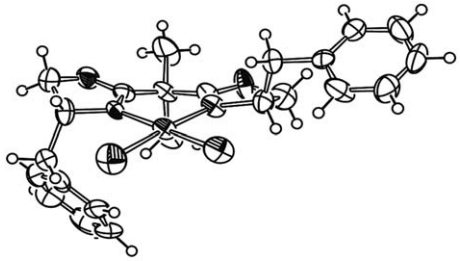


Figure 1 X-ray crystal structure of [(*R*,*R*)-Bnbox $AuCl_2$]SbF_6

[(*S*,*S*)-Phbox $AuCl_2$]SbF_6: yellow needles. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.10 (6 H, s), 4.75 (2 H, dd, *J* = 5.0, 9.6 Hz), 5.27 (2 H, t, *J* = 9.6 Hz), 6.02 (2 H, dd, *J* = 5.0, 9.6 Hz), 7.24–7.27 (4 H, m), 7.41–7.50 (6 H, m). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 26.0 (2 C), 42.8, 69.7 (2 C), 80.3 (2 C), 126.5 (4 C), 130.0 (2 C), 130.1 (4 C), 137.7 (2 C), 176.4 (2 C).

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