

**Pt(II)-Chiral Diene-Catalyzed Enantioselective Formal  
[4+2] Cycloaddition Initiated by C-C Bond Cleavage and  
Elucidation of a Pt(II)/(IV) Cycle by DFT Calculations**

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## COMMUNICATION

# Pt(II)-chiral diene-catalyzed enantioselective formal [4+2] cycloaddition initiated by C-C bond cleavage and elucidation of a Pt(II)/(IV) cycle by DFT calculations

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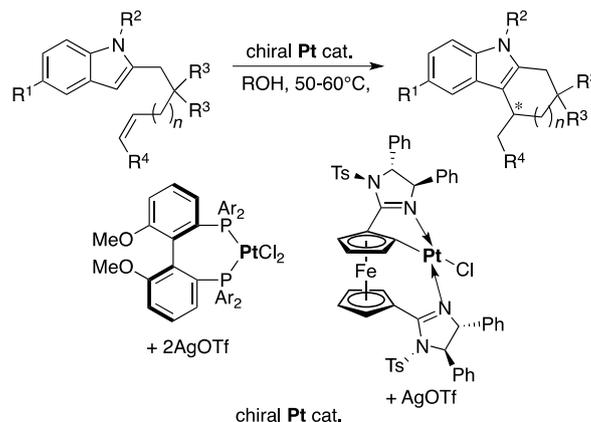
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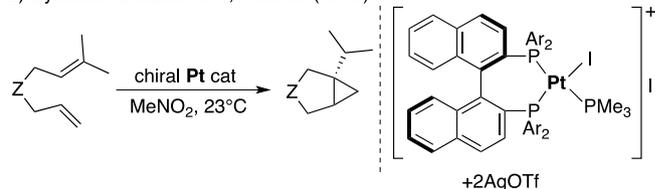
A chiral Pt(II) complex was readily prepared from  $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$  and Hayashi's diene. Its dicationic derivative efficiently catalyzed a formal intramolecular [4+2] cycloaddition of biphenylenes possessing substituted arylalkynes tethered by an *ortho*-phenylene moiety at ambient temperature and axially chiral cycloadducts were obtained in excellent yield and ee. A study of the DFT calculations revealed a Pt(II)/(IV) cycle including oxidative addition of biphenylene along with C-C bond cleavage.

Platinum metal has a long history as a catalyst for hydrogenation. Regarding C-C bond-forming reactions, platinum salts have been used for catalytic cycloisomerization: Blum and Murai independently reported an intramolecular reaction of 1,6-enynes to provide different types of cycloadducts.<sup>1</sup> Since then, various types of cycloisomerizations have been achieved with the use of platinum salts.<sup>2</sup> Enantioselective variants using various types of chiral Pt complexes have been also reported.<sup>3</sup> For example, an intramolecular hydroarylation of an alkene tethered by an indole moiety proceeded by the combination of a cationic Pt species with a chiral diphosphine ligand (Scheme 1a, left).<sup>4</sup> High enantioselectivity was also achieved in the same reaction by a planar-chiral pincer-type dinitrogen ligand (Scheme 1a, right).<sup>5</sup> In enantioselective cycloisomerization of dienes, a chiral diphosphine ligand together with an achiral monophosphine as an ancillary ligand was efficient (Scheme 1b).<sup>6</sup> Other successful examples are the use of an achiral NHC as an ancillary ligand (Scheme 1c):<sup>7</sup> excellent ees were achieved by the combination of a chiral monodentate phosphine<sup>7c</sup> and a phosphoramidite<sup>7d</sup> in the cycloisomerization of nitrogen-tethered 1,6-enynes. Chiral Pt(II) complexes worked well also as Lewis acids in some asymmetric reactions.<sup>8</sup> In all these enantioselective transformations, the valence of Pt(II) is considered to be unchanged.<sup>9</sup> While the reactions involving Pt(II)/(IV) catalytic cycle were reported in a few cross-couplings under heated conditions,<sup>10</sup> enantioselective variants have never been disclosed.

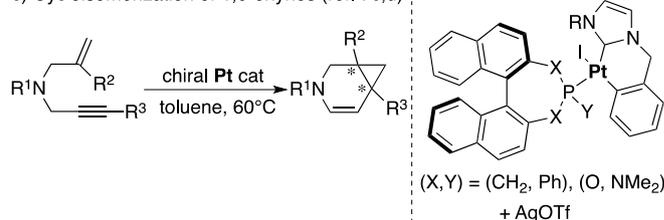
a) Hydroarylation with indoles (ref. 4b, 5)



b) Cycloisomerization of 1,6-dienes (ref. 6)



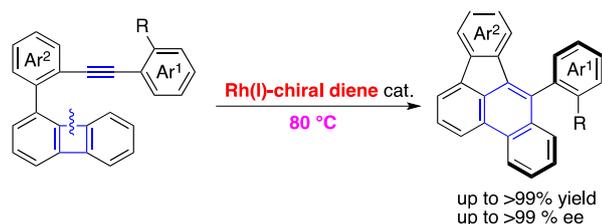
c) Cycloisomerization of 1,6-enynes (ref. 7c,d)



Scheme 1 Selected examples of chiral Pt-catalyzed reactions

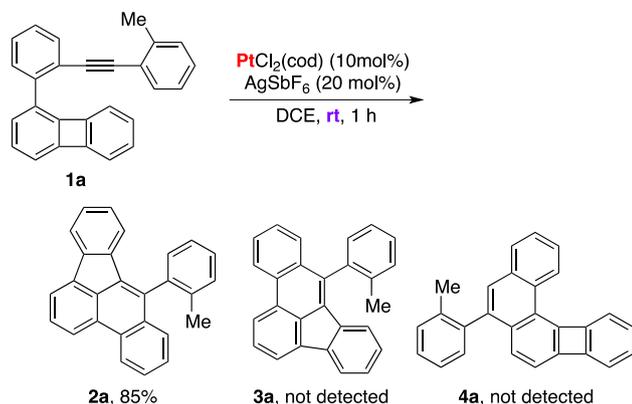
On the other hand, the introduction of chiral dienes opened up a new dimension in the field of asymmetric catalysis. Starting from Hayashi's and Carreira's dienes for the Rh-catalyzed 1,4-addition of aryl boronic acid,<sup>11a,b</sup> various chiral dienes have been generated and used as chiral ligands mainly for Rh-catalyzed enantioselective reactions.<sup>11c-e</sup> Since Ir-chiral diene catalysts were used in the enantioselective reactions including C-H activation,<sup>12</sup> they have been used for several enantioselective reactions.<sup>13</sup> Regarding other metal catalysis, a Pd-chiral diene catalyst realized an enantioselective Suzuki-Miyaura coupling for the generation of axial chirality.<sup>14</sup> The cross coupling of different alkene using a Ru-diene catalyst was also a successful transformation.<sup>15</sup> But there are no example of a Pt-chiral diene catalyst in asymmetric synthesis, as far as we know.

Against this background, we started our investigation of the catalytic activity of a Pt(II)-chiral diene complex and chose the formal intramolecular [4+2] cycloaddition of biphenylenes possessing substituted arylalkynes tethered by an *ortho*-phenylene moiety as a model reaction, because we recently achieved the highly enantioselective reaction using Rh-chiral diene catalyst under heated conditions (Scheme 2).<sup>16</sup>



**Scheme 2** Rh(I)-chiral diene-catalyzed [4+2] cycloaddition under heated conditions

As a preliminary experiment, we conducted the reaction of biphenylene **1a** possessing a (2-methylphenyl)ethynyl moiety in the presence of a dicationic Pt(II) complex prepared from PtCl<sub>2</sub>(cod) and silver salt in 1,2-dichloroethane (DCE) (Scheme 3). Alkyne **1a** was completely consumed at room temperature within an hour and formal [4+2] cycloadduct **2a** was obtained in good yield as the only product. Neither cycloisomerized product **3a** nor **4a** could be detected. Notably, when the combination of [RhCl(cod)]<sub>2</sub> and AgSbF<sub>6</sub> was subjected, no reaction proceeded under room temperature. These results mean that the dicationic Pt(II)-diene complex shows higher catalytic activity than its Rh(I) counterpart.

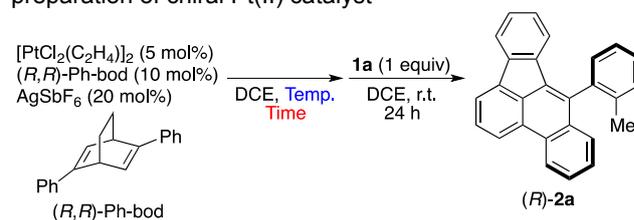


**Scheme 3** Dicationic Pt-catalyzed reaction of substituted biphenylene **1a**

We next examined an enantioselective reaction using chiral Pt catalyst, which was prepared *in situ* from di- $\mu$ -

chlorodichlorobis(ethylene) diplatinum and (1*R*,4*R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene ((*R,R*)-Ph-bod) (Table 1). A DCE solution of the Pt dimer, chiral diene, and Ag salt was stirred at room temperature for 5 min, and then substrate **1a** was added and stirred for 24 h (Entry 1). [4+2] Cycloadduct **2a** was obtained in moderate yield, albeit with low ee, along with the cycloisomerized product **4a**. We considered that ligand exchange with the chiral diene was insufficient and extended the reaction time for catalyst preparation to 24 h (Entry 2). To our delight, the enantioselectivity was drastically improved to 92% ee. To complete the ligand exchange, we conducted ligand exchange at 80 °C, but the ee was decreased (Entry 3). The addition of an excess amount of chiral diene did not affect the selectivity (Entry 4). While we were concerned about the instability of dicationic Pt complex at high temperature, we prepared the neutral Pt-chiral diene complex at 80 °C; the silver salt was then added at room temperature (Entry 5). As a result, compound **1a** was completely consumed within 1 hour and we could obtain the axially chiral compound **2a** with excellent yield and ee, which are comparable to those with Rh-chiral diene catalyst.<sup>16</sup>

**Table 1** Optimization of the reaction conditions for the preparation of chiral Pt(II) catalyst<sup>a</sup>

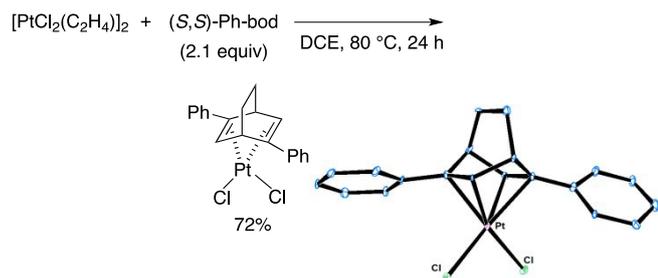


Entry	Temp.	Time	Yield & Ee of <b>2a</b> (%)	Yield of <b>4a</b> (%)
1	rt	5 min	69 / 14	9
2 <sup>b</sup>	rt	24 h	49 / 92	5
3	80 °C	24 h	67 / 83	3
4 <sup>c</sup>	80 °C	24 h	73 / 84	4
5 <sup>d</sup>	80 °C	24 h	91 / 96	6

<sup>a</sup> Reaction conditions: Unless otherwise stated, **1a** (0.05 mmol), Pt dimer (5 mol%), chiral diene (10 mol%), and silver salt (20 mol%) in DCE (0.5 + 0.5 mL). <sup>b</sup> The reaction mixture was stirred for 48 h. <sup>c</sup> The chiral ligand (15 mol%) was added. <sup>d</sup> The silver salt was added at room temperature after stirring the Pt dimer and chiral diene at 80 °C for 24 h. The reaction mixture was stirred for 1 h after the addition of compound **1a**.

The neutral chiral Pt-diene complex can be readily prepared in good yield by mixing the Pt dimer and chiral diene under heating conditions (Figure 1). The structure was determined by X-ray analysis, and this represents is the first synthesis and characterization of chiral Pt-diene complex.

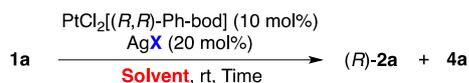
Table 2 shows the effect of the counterion and solvent using prepared chiral Pt complex. While silver salt affected the enantioselectivity slightly, it changed the catalytic activity. In the cases of AgBF<sub>4</sub> and AgPF<sub>6</sub>, the yield was moderate, along with recovery of the substrate even after stirring for 24 h (Entries 2 and 3).



**Figure 1** Synthesis and ORTEP diagram of Pt(II)-chiral diene complex.<sup>17</sup>

In contrast, the substrate was completely consumed within 1 h when  $\text{SbF}_6^-$  or BARF was used as a counterion, and  $\text{AgSbF}_6$  realized the highest yield and ee (Entries 1 and 5).<sup>18</sup> The solvent effect was significant: compared with monocationic Rh catalyst, which can work well even in etherate solvent such as cyclopentyl methyl ether (CPME),<sup>16</sup> halogenated solvent was critical for dicationic Pt catalyst (Entries 1 and 6-9). Notably, the present reaction proceeded at 0 °C by extended reaction time, but the yield was decreased because of substrate recovery even under more concentrated conditions (entry 10). The limit of catalyst loading was 5 mol% and the significant decrease of ee was observed in the use of 2 mol% catalyst (Entries 11 and 12). We determined that entry 1 represented the optimal conditions for the chiral Pt-catalyzed reaction.

**Table 2** Effect of counterion and solvent<sup>a</sup>



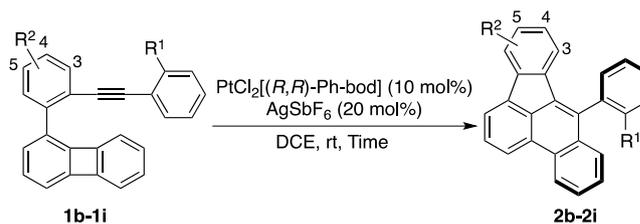
Entry	X	Solvent	Time (h)	Yield & Ee of 2a (%)
1	$\text{SbF}_6^-$	DCE	1	91 / 97
2 <sup>b</sup>	$\text{BF}_4^-$	DCE	24	69 / 97
3	$\text{PF}_6^-$	DCE	24	53 / 93
4	OTf	DCE	2	77 / 95
5	BARF <sup>c</sup>	DCE	1	88 / 94
6	$\text{SbF}_6^-$	DCM	1	91 / 94
7	$\text{SbF}_6^-$	PhCl	24	66 / 89
8 <sup>b</sup>	$\text{SbF}_6^-$	CPME	24	33 / 77
9 <sup>b</sup>	$\text{SbF}_6^-$	Toluene	24	16 / 74
10 <sup>d</sup>	$\text{SbF}_6^-$	DCE	24	70 / 97
11 <sup>e</sup>	$\text{SbF}_6^-$	DCE	2	79 / 96
12 <sup>f</sup>	$\text{SbF}_6^-$	DCE	3	71 / 68

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<sup>a</sup> Reaction conditions: Unless otherwise stated, **1a** (0.05 mmol), chiral Pt complex (10 mol%), and silver salt (20 mol%) in the solvent (1.0 mL). <sup>b</sup> The formation of by-product **4a** could not be detected. In other entries, ca. 5% of **4a** was formed. <sup>c</sup> Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) was used. <sup>d</sup> The reaction was conducted at 0 °C in the solvent (0.5 mL). <sup>e</sup> The chiral Pt complex (5 mol%), and silver salt (10 mol%) were used. <sup>f</sup> The chiral Pt complex (2 mol%) and silver salt (4 mol%) were used.

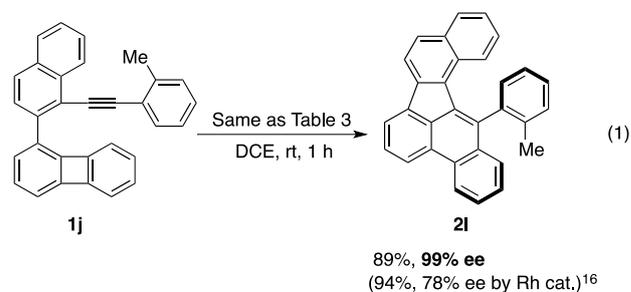
The reactions of various substrates were conducted under the optimal reaction conditions (Table 3). Regarding the substituent ( $\text{R}^1$ ) on the aryl group of the alkyne termini, electron-withdrawing substituents were available by extension of the reaction time and comparable ee and yield as with Rh-catalysis were achieved. (Entries 1-3). In contrast, the electron-donating group deteriorated the enantioselectivity (Entries 4 and 5). In particular, the ee was significantly decreased by the introduction of alkoxy group probably due to the strong coordination to the metal center, which induces dissociation of part of the chiral diene ligand from the metal center. We could introduce both electron-withdrawing and -donating substituents at the 3-, 4-, and 5-positions of the *ortho*-phenylene tether: the reaction was completed within 1 h and higher ee was achieved except with compound **2g** than the Rh-chiral diene catalyst (Entries 6-10). Notably, a significant increase in ee was observed in the reaction of naphthylene-tethered compound **11** (Eq. (1)).

**Table 3** Substrate scope of chiral Pt-catalyzed reaction<sup>a</sup>



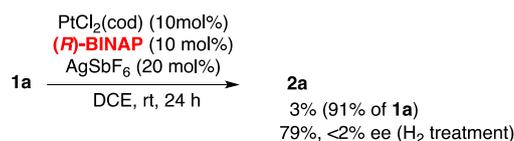
Entry	$\text{R}^1$	$\text{R}^2$	Time (h)	Yield & Ee of 2 (%) <sup>b</sup>
1	Cl	H	<b>1b</b>	24 94 / 91 (91 / 94)
2	Br	H	<b>1c</b>	24 91 / 96 (96 / 92)
3	$\text{CF}_3$	H	<b>1d</b>	4 90 / 98 (89 / 98)
4	$n\text{-C}_8\text{H}_{17}$	H	<b>1e</b>	1 74 / 92 (93 / 97)
5	$n\text{-OC}_8\text{H}_{17}$	H	<b>1f</b>	1 63 / 31 (>99 / 68)
6	Me	3-OMe	<b>1g</b>	1 91 / 99 (82 / 93)
7	Me	3-F	<b>1h</b>	1 86 / 98 (>99 / 94)
8	Me	4-OMe	<b>1i</b>	1 94 / 83 (61 / 97)
9	Me	4-Cl	<b>1j</b>	1 93 / 94 (92 / 91)
10	Me	5-F	<b>1k</b>	1 93 / 96 (79 / 93)

<sup>a</sup> Reaction conditions: **1a** (0.05 mmol), chiral Pt complex (10 mol%), and  $\text{AgSbF}_6$  (20 mol%) in DCE (1.0 mL). <sup>b</sup> In all entries, the formation of cycloisomerized products **4** was ascertained (3-10%). Yield and ee by chiral Rh-diene catalyzed reaction at 80-100 °C are shown in the parentheses as a reference.<sup>16</sup>

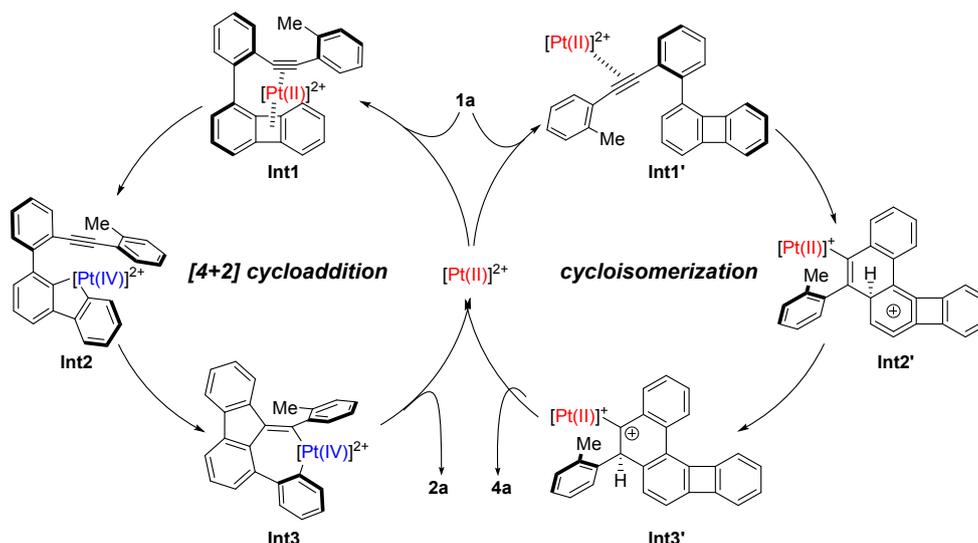


We conducted a control experiment using a chiral diphosphine ligand (Scheme 4). When  $\text{PtCl}_2(\text{cod})$ , (*R*)-BINAP, and  $\text{AgSbF}_6$  were

1 mixed at room temperature, almost no reaction proceeded and most of  
 2 substrate **1a** was recovered. Treatment with H<sub>2</sub> to exclude the COD  
 3 ligand generated the active catalyst and **2a** was obtained in high yield,  
 4 but almost no enantioinduction was observed. These results mean that  
 5 the combination of dicationic platinum and chiral diene ligand is  
 6 critical for the present enantioselective transformation.<sup>19</sup>



Scheme 4. Control experiment using BINAP



Scheme 5. Reaction mechanism of formal [4+2] cycloaddition and cycloisomerization

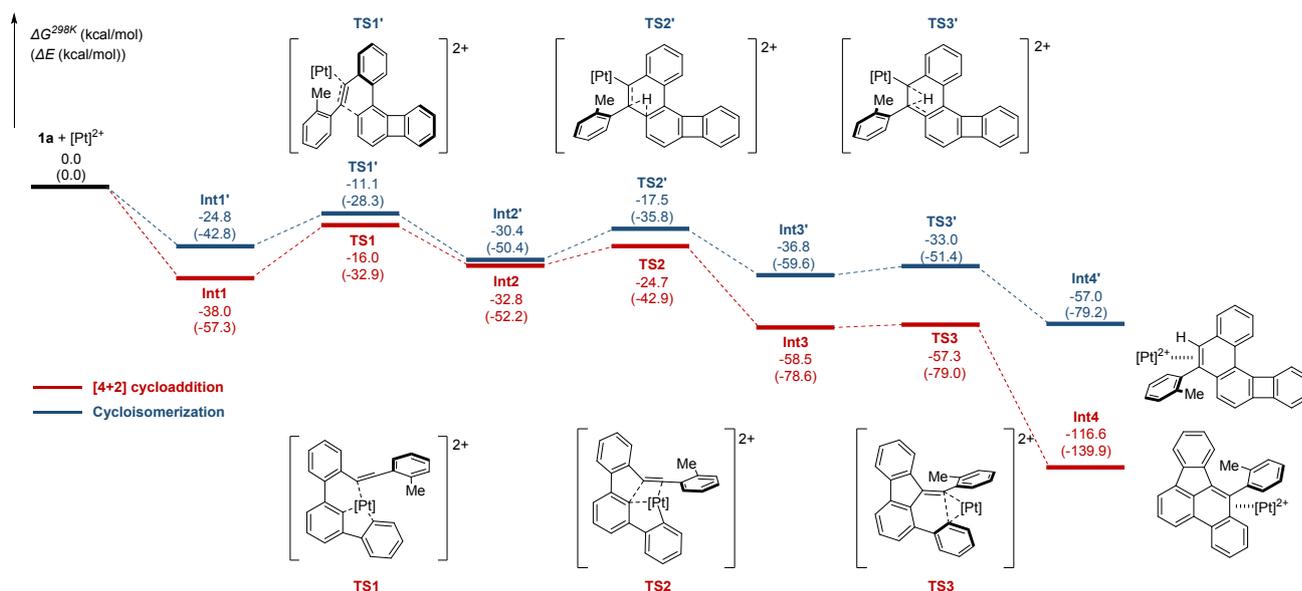


Figure 2. Free energy diagram of formal [4+2] cycloaddition and cycloisomerization ([Pt] = Pt[(R,R)-Ph-bod])

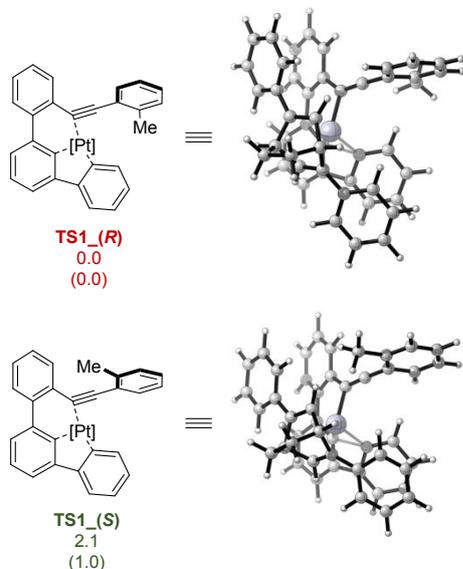
7 Regarding the previously reported Rh-catalyzed formal [4+2]  
 8 cycloaddition of biphenylene **1a** under heating conditions, the  
 9 reaction mechanism is considered to involve a Rh(I)/Rh(III) cycle  
 10 initiated by oxidative addition via C-C bond cleavage.<sup>16</sup> On the other  
 11 hand, in most Pt(II)-catalyzed reactions, the valence of Pt metal is  
 12 unchanged and a Pt(II)/Pt(IV) cycle has rarely been explained.<sup>10</sup> To  
 13 elucidate the mechanism of the present dicationic Pt-chiral diene  
 14 complex-catalyzed reaction under ambient temperature, we performed  
 15 DFT calculations using SC-AFIR<sup>20</sup> of GRRM program<sup>21</sup> as an  
 16 automated reaction path search method. In SC-AFIR, various  
 17 possible transition-states and intermediate structures, including  
 18 conformational isomers, in the reaction paths of byproducts can be

19 generated in addition to the desired one. After searching the reaction  
 20 path by SC-AFIR using GRRM interfaced with Orca program<sup>22</sup>, we  
 21 conducted structural optimization calculations for the selected  
 22 transition states or intermediate structures using ωB97X-D/Def2-  
 23 SVPP and the CPCM model for the solvent effect, and performed  
 24 single-point energy calculations using ωB97X-D/Def2-TZVP and the  
 25 SMD model for the solvent effect of DCE. We finally concluded that  
 26 the reaction proceeded via a Pt(II)/Pt(IV) cycle including oxidative  
 27 addition, alkyne insertion, and reductive elimination (Scheme 5).  
 28 Figure 2 shows the free energy diagram of the formal [4+2]

cycloaddition (in red) and cycloisomerization (in blue) for the preparation of **2a** and **4a**, respectively.<sup>23</sup>

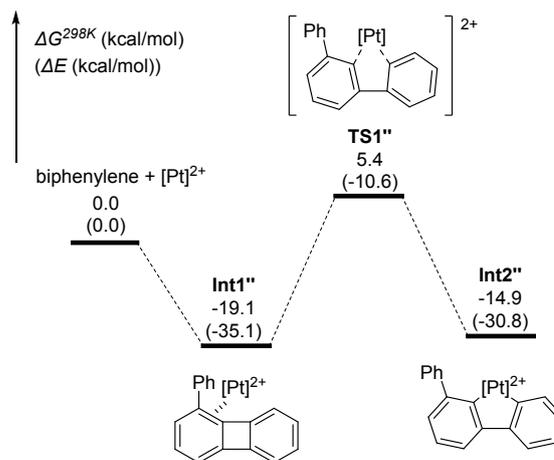
Isomerization between Int1 and Int1' can proceed (see SI), thus the activation energy should be estimated from Int1 according to Curtin-Hammett principle. The rate-determining step for the formal [4+2] cycloaddition was oxidative addition, where the activation energy was 22.0 kcal/mol ( $\Delta\Delta G_{\text{TS1-Int1}}$ ) and the reaction proceeds reasonably at room temperature. On the other hands, the activation energy for the cycloisomerization was 26.9 kcal/mol ( $\Delta\Delta G_{\text{TS1'-Int1}}$ ), which is higher than 22.0 kcal/mol. Therefore, the formal [4+2] cycloaddition is preferable to cycloisomerization.

To elucidate the origin of enantioselectivity, the structure of TS1<sub>(R)</sub> and TS1<sub>(S)</sub> for generating corresponding enantiomers were calculated. Based on experimental results, *R* isomer was obtained as a major isomer when (*R,R*)-Ph-bod was used. The computational results displayed that the relative energy of TS1<sub>(R)</sub> for major isomer was 2.1 kcal/mol lower than that of TS1<sub>(S)</sub> for minor isomer (Figure 3). It is likely caused that methyl group on the alkyne termini is directed to a platinum side which is more crowded region in the reaction intermediate. This energy difference corresponded to 94.8% ee, and these computational results would support the experimental result.



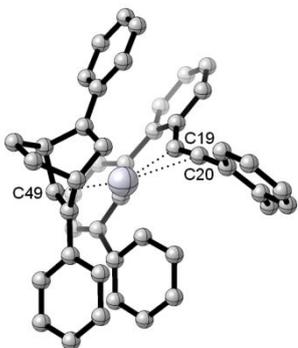
**Figure 3** Calculated structures and relative Gibbs energies of TS1<sub>(R)</sub> and TS1<sub>(S)</sub> (relative electron energies were shown in parentheses)<sup>24</sup>

To ascertain whether coordination of the alkyne moiety to metal facilitates oxidative addition, we conducted DFT calculations for C-C bond cleavage of 1-phenylbiphenylene using a Pt-diene complex (Figure 4). As a result, the activation energy was 24.5 kcal/mol, which is larger than 22.0 kcal/mol from Int1 to TS1. It means that an alkyne moiety act as a directing group to facilitate oxidative addition of C-C bond of biphenylene.



**Figure 4** Free energy diagram of oxidative addition of 1-phenylbiphenylene to cationic Pt(II)

To get more direct proof for the interaction of the metal center and alkyne moiety, we performed a natural bond orbital (NBO) analysis for **Int1**, **TS1**, and **Int2** (Table 4).<sup>25</sup> In **Int1**, donation bonding ( $\Delta E^{2ij} = 73.78$  kcal/mol) from a bonding orbital of alkyne (C19-C20) to a vacant orbital of platinum and back-donation bonding ( $\Delta E^{2ij} = 30.48$  kcal/mol) from the lone-pair of platinum to an anti-bonding orbital of alkyne were ascertained. The distance between the alkyne moiety and platinum of ca. 2.2 Å also supports the existence of this interaction. Notably, in **TS1**, very strong donation bonding ( $\Delta E^{2ij} = 337.63$  kcal/mol) from a bonding orbital of alkyne to a vacant orbital of platinum was observed, which means that the metal center becomes electron-rich and oxidative addition readily proceeds at ambient temperature. In **Int2**, donation and back-donation bonding between the alkyne and metal center were around 10 kcal/mol. In addition, there was interaction ( $\Delta E^{2ij} = 47.28$  kcal/mol) between the bonding orbital of the alkyne and the anti-bonding orbital of the diene ligand (C49) and the metal center, which is located in the *trans* position to the alkyne moiety. This result implies that the alkyne still coordinates to the metal center after oxidative addition. According to the NBO analysis, while the metal center is Pt(II) possessing a  $d^8$  electron configuration in Int1, it is Pt(IV) possessing a  $d^6$  electron configuration in Int2. In the aspect of natural population orbital, an alkyne moiety became more electron deficient, and the Pt center became more electron rich in TS1 compared with Int1. Moreover, in Int2, NPA value of the Pt center increased, which indicated that an electron density of the Pt center decreased. As results of NBO analysis and NPA, the present catalytic cycle apparently involves a Pt(II)/Pt(IV) redox pathway (Table 5) (see supporting information in details).<sup>25</sup>

**Table 4** Structure of TS1 and selected second-order interaction energies ( $\Delta E^{2ij}$  kcal/mol) by NBO analysis

Donor NBO	Acceptor NBO	Int1	TS1	Int2
BD(3) C19-C20	LP*(5) Pt	<b>73.78</b>		
BD(3) C19-C20	LP*(6) Pt	11.22		
BD(3) C19-C20	BD*(1) C48-Pt	27.00		
LP(4) Pt	BD*(3) C19-C20	<b>30.48</b>		
BD(3) C19-C20	LP*(5) Pt		<b>337.63</b>	
BD(3) C19-C20	LP*(6) Pt		<b>78.42</b>	
BD(1) C19-C20	LP*(4) Pt			11.62
BD(3) C19-C20	LP*(4) Pt			13.79
BD(3) C19-C20	BD*(1) C49-Pt			<b>47.28</b>
LP(3) Pt	BD*(3) C19-C20			12.84

**Table 5** Results of NPA analysis

Atoms	Int1	TS1	Int2
C19	0.002	-	-
C20	0.066	0.3363	0.1331
Sum of alkyne (C19 and C20)	0.068	<b>0.1340</b>	0.0842
Pt	<b>0.615</b>	<b>0.5820</b>	0.8733

In conclusion, we have described a possibility for Pt catalysis in enantioselective synthesis. This is the first example of the Pt(II)-chiral diene complex as an asymmetric catalyst and its high catalytic activity was demonstrated in enantioselective formal [4+2] cycloaddition along with C-C bond cleavage of biphenylene at room temperature. DFT calculations elucidated the reaction mechanism of alkyne-coordination-assisted C-C bond cleavage, alkyne insertion, and reductive elimination. Moreover, the origin of enantioselectivity derived from chiral diene ligand was elucidated by the computational studies. The NBO analysis further supported a Pt(II)/Pt(IV) cycle. The development of a new enantioselective reaction using the Pt(II)-chiral diene catalysts is under investigation in our laboratory.

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## Notes and references

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