6632 *Organometallics* **2010,** *29,* 6632–6635
DOI: 10.1021/om1009704

ORGANOMETALLICS
Communication

A Unique Functional Group Transformation of Planar Chiral Diolefinic Organonitrogen Cycles Utilizing $PtCl_2$(2,4,6-trimethylpyridine) Complexes

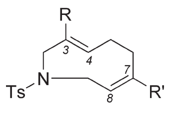
Katsuhiko Tomooka,*,[†] Maki Shimada,[‡] Kazuhiro Uehara,[†] and Masato Ito[†]

[†]*Institute of Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan, and* [‡]*Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152-8552, Japan*

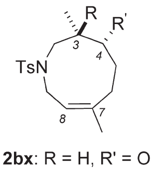
Received October 7, 2010

Summary: The planar chiral diolefinic organonitrogen cycles ***1*** *underwent stereospecific and group-selective olefin exchange with* ***3*** *to give* ***4****, whose molecular structure was characterized on the basis of NMR and X-ray diffraction. The bonded (E)-olefin moieties in* ***4*** *were robust enough to allow untouched (Z)-olefin to undergo epoxidation and hydrogenation to give the corresponding $PtCl_2(\eta^2$-olefin) complexes, whose treatment with PPh_3 smoothly liberated their olefinic parts, which would be otherwise difficult to synthesize.*

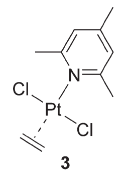
Recently, we have found a novel class of planar chiral nine-membered organonitrogen compounds **1a**−**d**, in which two distinct (*E*)- and (*Z*)-olefins are suitably embedded in the C3−C4 and C7−C8 positions, respectively.[1] Their stereogenic planes are easily constructed by the cyclization of readily available acyclic precursors, in which sugar-derived chiral lithium alkoxides determine whether the mode of cyclization is sinistral or dextral.[1d] Also noteworthy is their adequate reactivity to allow further synthetic elaborations, in which multiple stereogenic centers are developed with perfect stereospecificity.[1a−c] The molecular structures of **1a**−**d** are characterized by their restricted orientation of olefinic parts, whose π orbitals should be effectively bisected to be located either inside or outside of the loop. More specifically, the (*E*)-olefins in **1a**−**d** may bear a distorted structure while the (*Z*)-olefins may not, as exemplified by the solid-state structure of **1b** with the dihedral angles of C(2)−C(3)−C(4)−C(5) (29.5°) and C(6)−C(7)−C(8)−C(9) (2.8°).[1a] These two unique structural features should be the underlying basis of the high selectivity observed in their transformation.



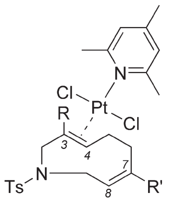
1a: R = R' = H
1b: R = R' = CH_3
1c: R = H, ,R' = CH_3
1d: R = CH_3, R' = H



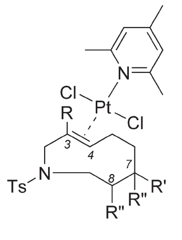
2bx: R = H, R' = OH
2by: R = R' = O



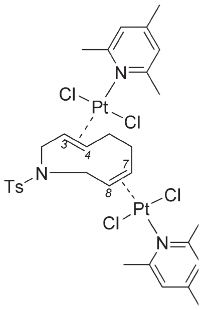
3



4a: R = R' = H
4b: R = R' = CH_3



4ax: R = R' = H, R" = O
4ay: R = R' = H, R" = H
4bx: R = R' = CH_3, R" = O



5a

For example, the reaction of (*S*)-(+)-**1b** with 9-BBN followed by oxidative workup provided (3*S*,4*R*)-**2bx** exclusively,[1a] and a similar reaction with *m*-CPBA predominantly afforded (3*R*,4*R*)-**2by**.[1e] These selectivities can be interpreted as a result of the preferential electrophilic attack of reagents on the outer π orbital at the (*E*)-olefin. This result has led us to anticipate that a stereoselective coordination of an appropriate transition-metal fragment[2] would provide a new complex with a unique π-bonding property, whose effect on the molecular chirality of the original skeleton would also be of great interest. In fact, we have found that *trans*-$PtCl_2$-(2,4,6-trimethylpyridine)(η^2-ethylene) (**3**)[3] undergoes an olefin exchange[4,5] with (±)-**1a** or (±)-**1b** at their (*E*)-olefin to give the corresponding platinum(II) complexes (±)-**4a** and (±)-**4b**, whose structures have been unequivocally determined by X-ray diffraction studies. Notably, the *trans*-$PtCl_2$-(2,4,6-trimethylpyridine) fragment has proved to serve as a protecting group to enable selective functionalization at the

---

*ktomooka@cm.kyushu-u.ac.jp.

(1) (a) Tomooka, K.; Suzuki, M.; Shimada, M.; Yanagitsuru, S.; Uehara, K. *Org. Lett.* **2006**, *8*, 963–965. (b) Tomooka, K.; Suzuki, M.; Uehara, K.; Shimada, M.; Akiyama, T. *Synlett* **2008**, 2518–2522. (c) Tomooka, K.; Akiyama, T.; Man, P.; Suzuki, M. *Tetrahedron Lett.* **2008**, *49*, 6327–6329. (d) Tomooka, K.; Uehara, K.; Nishikawa, R.; Suzuki, M.; Igawa, K. *J. Am. Chem. Soc.* **2010**, *132*, 9232–9233. (e) Details will be reported separately.

(2) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994; Chapter 5. (b) Gladysz, J. A.; Boone, B. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 550–583.

(3) (a) Orchin, M.; Schmidt, P. J. *Inorg. Chim. Acta Rev.* **1968**, 123–135. (b) Chottard, J. C.; Mansuy, D.; Bartoli, J. F. *J. Organomet. Chem.* **1974**, *65*, C19–C22. (c) Mansuy, D.; Bartoli, J. F.; Chottard, J. C. *J. Organomet. Chem.* **1974**, *73*, C39–C42. (d) Caruso, F.; Spagna, R.; Zambonelli, L. *J. Cryst. Mol. Struct.* **1978**, *8*, 47–57. (e) Natile, G.; Maresca, L.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1977**, 651–655. (f) Canovese, L.; Tobe, M. L.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1985**, 27–30.

(4) (a) Joy, J. R.; Orchin, M. *J. Am. Chem. Soc.* **1959**, *81*, 305–309. (b) Joy, J. R.; Orchin, M. *J. Am. Chem. Soc.* **1959**, *81*, 310–311. (c) Cramer, R. *Inorg. Chem.* **1965**, *4*, 445–447. (d) Olsson, A.; Kofod, P. *Inorg. Chem.* **1992**, *31*, 183–186. (e) Plutino, M. R.; Otto, S.; Roodt, A.; Elding, L. I. *Inorg. Chem.* **1999**, *38*, 1233–1238.

(5) (a) Meester, M. A. M.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1977**, *21*, 251–258. (b) Kurosawa, H.; Urabe, A.; Emoto, M. *J. Chem. Soc., Dalton Trans.* **1986**, 891–893.

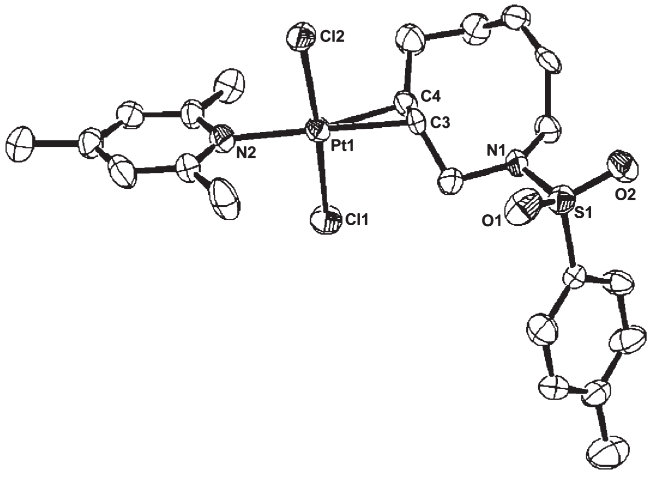


Figure 1. Molecular structure of (±)-**4a**. Thermal ellipsoids are drawn at the 40% probability level. The H atoms are omitted for clarity.

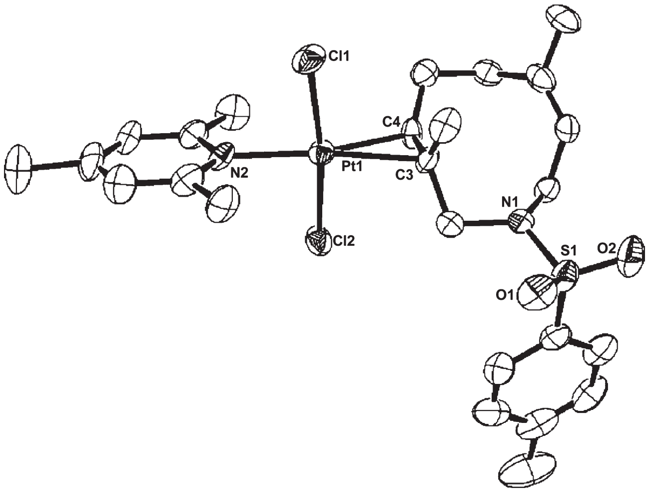


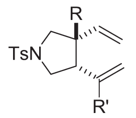
Figure 2. Molecular structure of (±)-**4b**. Thermal ellipsoids are drawn at the 40% probability level. The H atoms are omitted for clarity.

remaining (*Z*)-olefin to give the new platinum(II) complexes (±)-**4ax,** (±)-**4ay**, and (±)-**4bx** selectively. Furthermore, the treatment with PPh_3 of these complexes has caused the smooth liberation of their olefinic moieties. We will disclose these results herein.

Our initial experiments focused on the discrimination of two olefinic groups in (±)-**1a** by the complexation using **3**. The reaction of (±)-**1a** with an equimolar amount of **3** in CH_2Cl_2 at 30 °C for 21 h followed by chromatographic purification using silica gel allowed isolation of an air-stable yellow solid as a major product ((±)-**4a**). Recrystallization by diffusing *n*-hexane into the solution of this solid in a mixed solvent system of CH_2Cl_2 and diethyl ether gave single crystals that were subjected to an X-ray diffraction study, which determined the selective coordination of the *trans*-$PtCl_2$(2,4,6-trimethylpyridine) fragment at the (*E*)-olefin of (±)-**1a** (Figure 1). As the isolated yield of (±)-**4a** was moderate (60% yield), the fate of (±)-**1a** not being incorporated in (±)-**4a** merits specific mention. In addition to (±)-**4a**, the aforementioned chromatographic separation gave two minor fractions, whose ^1H NMR analysis indicated that one is a 44:56 mixture of (±)-**1a** and (±)-**6a** (25% yield; vide infra) and the other is the dinuclear complex (±)-**5a** (4% yield), whose identity was further established by $^{13}C\{^1H\}$ NMR and IR spectroscopy as well as elemental analysis (see the Supporting Information). It should be noted that (±)-**5a** was obtainable in 31% yield by a separate reaction of isolated (±)-**4a** with an equimolar amount of **3** in CH_2Cl_2 at 30 °C for 21 h. These results clearly demonstrated that the remaining (*Z*)-olefin in (±)-**4a** is also susceptible to coordination by the *trans*-$PtCl_2$(2,4,6-trimethylpyridine) fragment.

A similar reaction of (±)-**1b** with **3** proceeded rather sluggishly, but the corresponding mononuclear complex (±)-**4b** was obtained as the sole product after the chromatographic workup, albeit in modest yield (23%). Unlike the case of (±)-**1a,** no other product other than (±)-**1b** was isolable from the reaction mixture. The molecular structure of (±)-**4b** determined by an X-ray diffraction study is depicted in Figure 2.

The 2,4,6-trimethylpyridine ligand in **3** has turned out to be the ligand of choice, since it provides (±)-**4a** and (±)-**4b** as air-stable, easy-to-handle, crystalline compounds. In contrast, similar reactions with other $PtCl_2(\eta^2\text{-ethylene})$ complexes with less substituted pyridinic ligands, including pyridine, 2-picoline, and quinoline, gave less satisfactory results. For example, the reaction of (±)-**1b** with an equimolar amount of *trans*-$PtCl_2$(pyridine)(η^2-ethylene) at 0 °C for 20 min gave a complicated mixture containing a considerable amount of (±)-**6b**, from which the isolation of the desired platinum complex was difficult in our hands. Therefore, the 2,4,6-trimethylpyridine ligand in **3** should also contribute significantly to minimize the possible formation of (±)-**6a** or (±)-**6b**, which is explainable by a Cope-type rearrangement that is similar to the previously reported catalytic variant using $PdCl_2(PhCN)_2$.[1a,6]



6a: R = R' = H
6b: R = R' = CH_3

While the stabilizing effect of complexation with the $Pt(PPh_3)_2$ fragment on torsionally strained olefins[7] such as bicyclo[2.2.0]hexene,[8a] bicyclo[4.2.1]non-1-ene,[8b] and bicyclo[3.3.1]non-1-ene[8c] has been well-documented in several reports,[8] similar studies using a $PtCl_2$ fragment have been rather limited. The most notable among them is a report by Godleski and co-workers in 1983, demonstrating that thermally unstable bicyclo[3.3.1]non-1-ene can be effectively trapped upon treatment with *trans*-$PtCl_2$(pyridine)(η^2-ethylene) to afford *trans*-$PtCl_2$(pyridine)(η^2-bicyclo[3.3.1]non-1-ene) (**7**), whose structure was characterized on the basis of ^1H

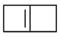
---

(6) For a review on the electrophilic activation of alkenes by Pt(II), see: Chianese, A. R.; Lee, S. J.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 4042–4059.

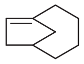
(7) (a) Luef, W.; Keese, R. *Top. Stereochem.* **1991**, *20*, 231–318. (b) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067–1093. (c) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683–1715.

(8) (a) Jason, M. E.; McGinnety, J. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1974**, *96*, 6531–6532. (b) Stamm, E.; Becker, K. B.; Engel, P.; Ermer, O.; Keese, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 685–686. (c) Godleski, S. A.; Gundlach, K. B.; Valpey, R. S. *Organometallics* **1985**, *4*, 296–302. (d) Nicolaides, A.; Smith, J. M.; Kumar, A.; Barnhart, D. M.; Borden, W. T. *Organometallics* **1995**, *14*, 3475–3485. (e) The pyramidalized alkenes are predicted to be much more strongly bonded to the $Pt(PPh_3)_2$ fragment than is ethylene. Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 1912–1914.

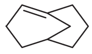
and $^{13}C\{^1H\}$ NMR spectroscopic analysis.[9] Since this bridgehead alkene with a unique nonplanar π system can be regarded as a bicyclic analogue of (*E*)-cyclooctene, which has been the legendary prototypical example of planar chiral cyclic compounds, it is of interest to compare the NMR data of (±)-**4b** with the reported data of **7**.



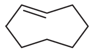
bicyclo[2.2.0]hexene



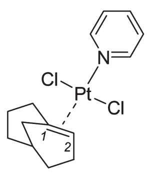
bicyclo[4.2.1]non-1-ene



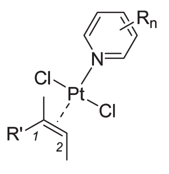
bicyclo[3.3.1]non-1-ene



(*E*)-cyclooctene



7

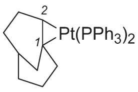


8a: R$_n$ = 2,4,6-(CH$_3$)$_3$, R' = H
8b: R$_n$ =H, R' = CH$_3$

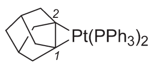
Table 1 gives select $^{13}C\{^1H\}$ NMR data for (±)-**4a** and (±)-**4b** along with those for related platinum complexes. Noteworthy are the large upfield shifts on coordination ($\Delta\delta$) for disubstituted carbons C(3) and C(4) in (±)-**4a** (41.0 and 41.3 ppm, respectively) as well as C(4) in (±)-**4b** (40.9 ppm), which are very similar to that for C(2) in **7** (41.5 ppm). Also, the upfield shift for trisubstituted carbon C(3) in (±)-**4b** (29.4 ppm) is also similar to that for C(1) in **7** (27.8 ppm). Moreover, the $^1J_{Pt-C}$ coupling constants ((±)-**4a**, 193.1 and 170.0 Hz; (±)-**4b**, 175.7 and 162.6 Hz) far exceeding those for **8a** or **8b** around 150 Hz are indicative of a stronger interaction of the (*E*)-olefin in (±)-**1a** and (±)-**1b**, with the platinum center arising from more pronounced rehybridization relative to ordinary unstrained olefins, while the degree of contribution of a platinacyclopropane structure in (±)-**4a** or (±)-**4b** may be less prominent than that in **7** with $^1J_{Pt-C}$ values over 200 Hz or in a series of Pt(PPh$_3$)$_2$ complexes **A**−**D** with much larger $^1J_{Pt-C}$ values.[11]

Not surprisingly, the C(3)−C(4) units of (±)-**4a** and (±)-**4b** adopt an upright geometry with respect to the square plane surrounding the platinum in the solid state, as shown in Figures 1 and 2.[12] Their pyridine nuclei also adopt an almost perpendicular arrangement with respect to the coordination plane.[3d,13] These features are interpreted as a result of a steric repulsion between the two *o*-methyl groups and the two chloro ligands, which should provide an opportunity for the 5d orbitals of platinum to overlap with the two π* molecular orbitals at the pyridine nucleus and olefin (i.e., back-donation). The overlap should be positioned trans but orthogonal to each other. We believe that the two *o*-methyl groups should contribute to the reduction of the lability of ligands around the central platinum in (±)-**4a** and (±)-**4b** (vide infra).[14]

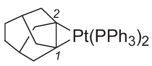
Table 1. $^{13}C\{^1H\}$ **Chemical Shifts and** $^1J_{Pt-C}$ **Coupling Constants**[a]



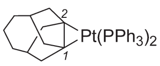
A



B



C



D

	$\delta_{C(1)}$, ppm	$\Delta\delta_{C(1)}$, ppm	$^1J_{Pt-C(1)}$, Hz	$\delta_{C(2)}$, ppm	$\Delta\delta_{C(2)}$, ppm	$^1J_{Pt-C(2)}$, Hz	ref
PtCl$_2$							
(±)-**4a**	83.2[b]	41.0[c]	193.1[d]	95.7[e]	41.3[f]	170.0[g]	this work
(±)-**4b**	105.1[b]	29.4[c]	175.7	92.7[e]	40.9[f]	162.6	this work
7	120.4	27.8	211.6	84.3	41.5	202.9	9
8a	92.5	29.0	155				10
8b	116.0	14.7	143.6	84.7	34.0	147.2	9
Pt(PPh$_3$)$_2$							
A	61.4	86.6	320	52.5	73.5	220	8c
B	66.9[h]		407[h]				8d
C	74.9[h]		343[h]				8d
D	78.8[i]		296[i]				8d
Pt(C$_2$H$_4$)(PPh$_3$)$_2$	39.6	88	194				8c

[a] In CDCl$_3$ unless otherwise noted. [b] $\delta_{C(3)}$. [c] $\Delta\delta_{C(3)}$. [d] $^1J_{Pt-C(3)}$. [e] $\delta_{C(4)}$. [f] $\Delta\delta_{C(4)}$. [g] $^1J_{Pt-C(4)}$. [h] C$_6$D$_6$, 298 K. [i] In toluene-d_8, 338 K.

The selected bond lengths for the coordinated C(3)−C(4) unit in the solid-state structure of (±)-**4a** and (±)-**4b** are summarized in Table 2. However, distinctive features for our complexes cannot be fully extracted, due to the paucity of data for the solid-state structures of PtCl$_2$ complexes having a multisubstituted olefin or an originally distorted olefinic ligand, except for the well-known *trans*-PtCl$_2$((*E*)-cyclooctene)[(*R*)-(+)-PhCH(NH$_2$)CH$_3$] (**9**).[15] It has been claimed that the magnitude of back-donation in Pt(η^2-olefin) complexes may be more appreciably manifested in the solid-state structures at the C−C bond length rather than at the Pt−C bond length, which can greatly hinge on steric requirements.[8c,16] However, we note that the C(3)−C(4) bond

---

(9) Godleski, S. A.; Valpey, R. S.; Gundlach, K. B. *Organometallics* **1983**, *2*, 1254–1257.

(10) (a) van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941–2950. (b) Erdogan, G.; Grotjahn, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 10354–10355.

(11) A slight decrease in the olefinic $^1J_{C-H}$ value upon complexation was commonly observed in the case of torsionally strained olefin complexes such as **7** (from 160.6 to 159.8 Hz)[9] or RuCl$_2$(pybox-*ip*)-[(−)-(*E*)-cyclooctene] (from 150.6 to 148.7 Hz); see: Nishiyama, H.; Naitoh, T.; Motoyama, Y.; Aoki, K. *Chem. Eur. J.* **1999**, 3509–3513. Similar changes for (±)-**4a**, (±)-**4b**, and their congeners will be measured and reported separately.

(12) (a) Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799–844. (b) Hartley, F. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 596–606. (c) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801–3812. (d) Tsipis, A. C. *Organometallics* **2008**, *27*, 3701–3713 and references therein.

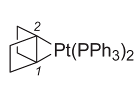
(13) Either the (*E*)-olefin or 2,4,6-trimethylpyridine ligand of (±)-**4a** and (±)-**4b** should rotate freely in solution, at least at ambient temperature, since the two methyl groups at the 2,6-position of the pyridine ring were observed as equivalent signals in NMR spectra of their CDCl$_3$ solution, despite the unsymmetrical structure of their olefinic units (see the Supporting Information).

(14) As early as 1969, Orchin and co-workers reported[14a] that pyridinic ligands undergo more rapid ligand exchange with solvent molecules than olefinic ligands in this class of compounds, but the anomalous feature of **3** arising from 2,6-disubstitution at the pyridine nuclei has been documented later by a number of research groups[3b−f] including themselves.[14b] (a) Kaplan, P. D.; Schmidt, P.; Brause, A.; Orchin, M. *J. Am. Chem. Soc.* **1969**, *91*, 85–88. (b) Pesa, F.; Spaulding, L.; Orchin, M. *J. Coord. Chem.* **1975**, *4*, 225–230.

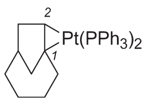
(15) (a) Cope, A. C.; Ganellin, C. R.; Johnson, H. W., Jr.; van Auken, T. V.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1963**, *85*, 3276–3279. (b) Monor, P. C.; Shoemaker, D. P.; Parkes, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5260–5262.

(16) (a) Evans, A.; Mortimer, C. T.; Puddephatt, R. J. *J. Organomet. Chem.* **1974**, *72*, 295–297. (b) Tsuchiya, K.; Kondo, H.; Nagashima, H. *Organometallics* **2007**, *26*, 1044–1051 and references therein.

Table 2. Selected Bond Lengths (Å)



E



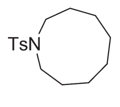
F

	Pt−C(1), Å	Pt−C(2), Å	C(1)−C(2), Å	Δ(C−C),[a] Å	ref
$PtCl_2$					
(±)-**4a**	2.172(11)[b]	2.166(15)[c]	1.364(19)[d]		this work
(±)-**4b**	2.266(10)[b]	2.137(10)[c]	1.400(16)[d]	0.07	this work
9	2.11		1.35		15b
$Pt(PPh_3)_2$					
B	2.068(8)	2.056(8)	1.475(11)		8d
C	2.105(9)[e]	2.115(8)[e]	1.441(9)[e]		8d
D	2.129(4)	2.113(4)	1.421(7)		8d
E	2.07	2.14	1.55		8a
F	2.16	2.11	1.41		8b

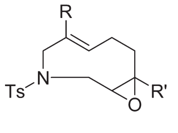
[a] Difference between the coordinated and noncoordinated forms of the alkene ligand. [b] Pt−C(3). [c] Pt−C(4). [d] C(3)−C(4). [e] Data for the other independent molecule of the two are 2.086(8), 2.095(8), and 1.467(9) Å, respectively.

length in (±)-**4b** was elongated by 0.07 Å from that of (±)-**1b**[1a] and that the dihedral angle C(2)−C(3)−C(4)−C(5) in (±)-**4b** (38.8°) was remarkably increased from that in (±)-**1b** (29.5°). These results indicated that the inherent olefinic strain[17] of **1** can be effectively released by the complexation, which should be a critical beneficial factor in the formation and the stability of **4**.

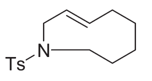
The stability of (±)-**4a** and (±)-**4b** caused their (*Z*)-olefin moiety to undergo further functionalization, as long as it proceeds under conditions milder than those for a Cope-type rearrangement.[18] For example, the reactions of (±)-**4a** and (±)-**4b** with an excess amount of *m*-CPBA in CH_2Cl_2 at 0−30 °C followed by an extractive workup with aqueous $Na_2S_2O_3$ selectively furnished corresponding complexes having an epoxide moiety, (±)-**4ax** and (±)-**4bx**, in 32 and 86% yields, respectively. Also, the hydrogenation of (±)-**4a** in toluene containing Pd/C as a catalyst ($P(H_2)$ = 1 atm, 30 °C) for a very short period provided (±)-**4ay** in 80% yield, although the fully saturated *N*-tosylcycloazanonane (**10**) was detectable in the crude reaction mixture. Notwithstanding the masked reactivity of the (*E*)-olefin moiety in a series of platinum complexes, all of the platinum complexes obtained in this study were susceptible to smooth liberation of the corresponding olefinic ligands upon treatment with an excess amount of PPh_3. The high efficiency in the recovery of (±)-**1ax**, (±)-**1bx**, and (±)-**1ay** from (±)-**4ax**, (±)-**4bx**, and (±)-**4ay** (85%, 85%, and 78% yields, respectively) has strengthened the synthetic utility of these reactions, since these products are otherwise difficult to obtain.[19]



10



1ax: R = R' = H
1bx: R = R' = CH_3



1ay

Moreover, the aforementioned attachment and detachment of olefins onto the *trans*-$PtCl_2$(2,4,6-trimethylpyridine) fragment was characterized by high stereospecificity, which was confirmed by separate experiments starting from optically active **1a** or **1b**. For example, the reaction of (*R*)-(−)-**1a** or (*R*)-(−)-**1b** with > 98% ee with **3** gave the optically active complexes (+)-**4a** and (+)-**4b**, displaying a specific rotation of +150.3° (*c* = 1.20, $CHCl_3$) or +119.3° (*c* = 0.46, $CHCl_3$), both of which were proven to be > 98% ee, as evidenced by HPLC analysis using a Daicel Chiralcel OD-H column.

On the other hand, the PPh_3-induced liberation of (−)-**4b** with 34% ee afforded (*S*)-(+)-**1b** without any loss of enantiopurity. We have also confirmed that the hydrogenation of (+)-**4a** with > 98% ee afforded (+)-**4ay**, displaying a specific rotation of +112.2° (*c* = 1.10, $CHCl_3$), which was confirmed to be > 98% ee by HPLC analysis using a Daicel Chiralpak AS-H column. It is worth noting that the recovered **1ay** from an optically pure (+)-**4ay** turned out to be completely racemic, possibly due to the insufficient stability of the planar chirality of **1ay** at ambient temperature.

In summary, we have found that the (*E*)-olefin moiety in a series of planar chiral diolefinic organonitrogen cycles undergoes selective complexation with the *trans*-$PtCl_2$(2,4,6-trimethylpyridine) fragment to give novel chiral platinum complexes, whose structural feature and reactivities have been clarified.[20] Of particular note was the robustness of their coordinated moiety, which allowed further functionalizations at the untouched olefin to furnish new platinum complexes. Several unique synthetic fabrications could be attained with a combination of these results and the PPh_3-induced liberation of their coordinated olefin. These results should open up a deeper understanding of the molecular topological constraints, which should allow us to manipulate tailor-made planar chiral molecules. Further studies toward this final goal are actively underway in our laboratory.

Acknowledgment. This research was supported by the MEXT (Nos. 22350019 and 21550096) and the Global COE Program (Kyushu University). We are grateful to Professor Hiroharu Suzuki (Tokyo Institute of Technology) for valuable discussions.

Supporting Information Available: Text, tables, figures, and CIF files giving experimental procedures and X-ray crystallographic data for (±)-**4a**, (±)-**4b**, (±)-**4bx**, and (±)-**5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(17) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891–1900.

(18) The thermolysis of (±)-**4b** in toluene at 80 °C for 1.5 h resulted in its complete consumption to give a mixture, from which (±)-**6b** was isolated in 54% yield.

(19) The newly obtained (±)-**1ay** is not obtainable by a Mitsunobu-type reaction of $HO(CH_2)_5CH{=}CHCH_2NHTs$ in refluxing THF containing PPh_3 and $C_2H_5O_2CN{=}NCO_2C_2H_5$, although similar reaction conditions have been very effective for the preparation of the series (±)-**1a**−**d**.

(20) (a) $^{13}C\{^1H\}$ NMR data for the coordinated olefinic parts of (±)-**4ax**, (±)-**4bx**, (±)-**4ay**, and (±)-**5a** are compiled in the Supporting Information. (b) The solid-state structures of (±)-**4bx** and (±)-**5a** were also determined by X-ray diffraction. See the Supporting Information.