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ARTICLE *in* ORGANOMETALLICS · JANUARY 2009

Impact Factor: 4.13 · DOI: 10.1021/om800743r

Article

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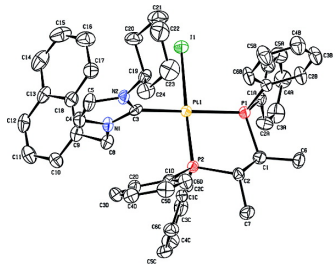
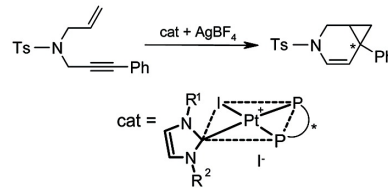
Organometallics, **2009**, 28 (1), 140-151 • DOI: 10.1021/om800743r • Publication Date (Web): 10 December 2008





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Platinum(II) Complexes Featuring Chiral Diphosphines and N-Heterocyclic Carbene Ligands: Synthesis and Evaluation as Cycloisomerization Catalysts

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Received August 1, 2008

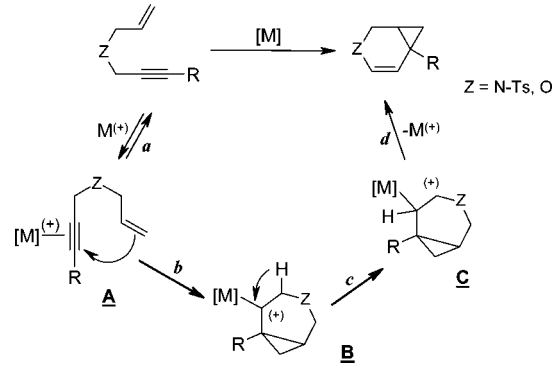
Square-planar platinum(II) complexes that combine chiral diphosphines and NHC ligands have been obtained in high yields from (NHC)$Pt^{(0)}$(dvtms) complexes, via an oxidative addition/ligand exchange sequence. The use of suitable carbene−diphosphine pairs allows axially chiral, configurationally stable platinum complexes to be isolated. The Pt(II) complexes have been evaluated as precatalysts for the cycloisomerization reaction of an allyl propargylamine derivative. Their catalytic properties have been examined as a function of structural variations on both the diphosphine and the NHC units. For axially chiral species possible epimerization pathways have been envisioned and the inversion barriers have been estimated through computational studies.

Introduction

Transition metal-promoted enyne cycloisomerizations have emerged as powerful synthetic tools that convert simple starting materials into diverse cyclic products of increased complexity.[1] The conversion of 1,6-enynes into bicyclo[4.1.0]heptenes shown in Scheme 1 belongs to this class. These last reactions are known to be promoted by highly electrophilic metal species such as Pt(II) halides[2] and complexes,[3] Pt(IV) halides,[4] Au(I) salts[5] and complexes,[6] and cationic Ir(I) complexes.[7] Allyl propargyl ethers and amine derivatives are common substrates whose cycloisomerizations afford 3-oxa- or 3-azabicyclo[4.1.0]hept-4-ene derivatives, respectively.

The $PtCl_2$-catalyzed process was first reported by Fürstner,[2a,8] who also proposed a mechanistic pathway based on the electrophilic activation of the alkyne via its Pt π-complex **A** (Scheme 1). The platinum-coordinated alkyne displays carbocationic character and undergoes nucleophilic attack by the tethered alkene following a 6-*endo-dig* cyclization mode. The resulting metal-stabilized bicyclic carbocation **B**[9] evolves then to **C** by hydride migration. The final step involves formation of the double bond of the bicyclic product and concomitant elimination of the Pt(II) catalyst. This postulated mechanistic pathway was supported later by theoretical studies from Soriano.[10a]

Scheme 1. Cycloisomerization of 1,6-Enynes into Bicyclo-[4.1.0]heptenes: Postulated Mechanism



According to the mechanistic proposal above, the observed rearrangement mainly results from the peculiar "π-acidic" properties of platinum(II)[1d] and its high affinity for the π-system of the acetylenic substrate. The whole catalytic cycle involves a single platinum−substrate bond, changing from π- to σ-bonds in the successive elementary steps, and consequently, simulta-

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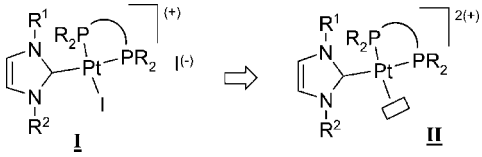
10.1021/om800743r CCC: $40.75
Publication on Web 12/10/2008

neous coordination of the alkyne and the alkene to the metal center is not required. It is thus conceivable that platinum complexes bearing modifiable ligands could be used as catalysts instead of platinum salts, provided that even a single coordination site would be available for substrate coordination. This working hypothesis led us to design precatalysts made of square-planar platinum(II) complexes bearing three strongly bound ligands,[11] including chiral diphosphines, and a halide as the only arguably labile group. Complexes **I** had been targeted, where an N-heterocyclic carbene (NHC) and a chelating diphosphine ligands are combined. They are expected to generate the tricoordinate species **II** as a potential catalyst. Their successful use as well-defined, phosphine-modified platinum precatalysts for the enantioselective cycloisomerization of 1,6-enynes has been mentioned in our preliminary communication.[12]



We report here extensive synthetic and structural studies on complexes **I**, as well as comparative tests showing the effects of the phosphine and carbene ligands on the catalytic behavior of **I** in a model cycloisomerization reaction. Theoretical investigations of the structural features of complexes **I** and **II** are also reported.

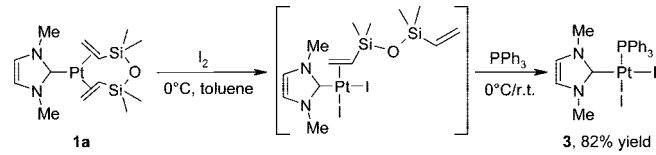
Results and Discussion

Synthesis and Structural Characterizations of Platinum(II) Complexes. With the aim of building tetracoordinated platinum(II) precatalysts for the cycloisomerization reactions shown in Scheme 1, we have targeted the mixed NHC/diphosphine complexes **I** as potentially suitable species. The choice of NHC ligands is a result of the high stability of their transition metal complexes and their excellent properties as supporting ligands in homogeneous catalysis,[13,14] while chelating diphosphines have been selected mainly because the diverse array of commercially available chiral compounds would offer the opportunity to develop an asymmetric version of these cycloisomerizations.

For the preparation of the mixed NHC/diphosphine platinum complexes **I** we have investigated a new sequence, which starts from the (NHC)$Pt^{(0)}$(dvtms) complexes (dvtms = divinyltetramethyldisiloxane, compounds **1** and **2** in Schemes 2−4) introduced by Markó et al.[14d] We reasoned that these stable and easily available Pt(0) compounds could represent versatile starting materials for the generation of Pt(II) derivatives through oxidative addition reactions. The labile alkene was expected to be then displaced rather easily by strongly coordinating ligands such as phosphines.

In order to check the approach, iodine was envisioned as a suitable reactant for the oxidation step and PPh_3 as a representative phosphorus ligand. The (NHC)Pt(dvtms) complex **1a** was reacted in toluene at 0 °C successively with I_2 and 1 equiv of triphenylphosphine (Scheme 2). The anticipated oxidation of Pt(0) into Pt(II) took place and the expected NHC/phosphine complex **3** was isolated in 82% yield after column chromatography.

Scheme 2. Synthesis of the Triphenylphosphine/NHC Platinum(II) Complex 3



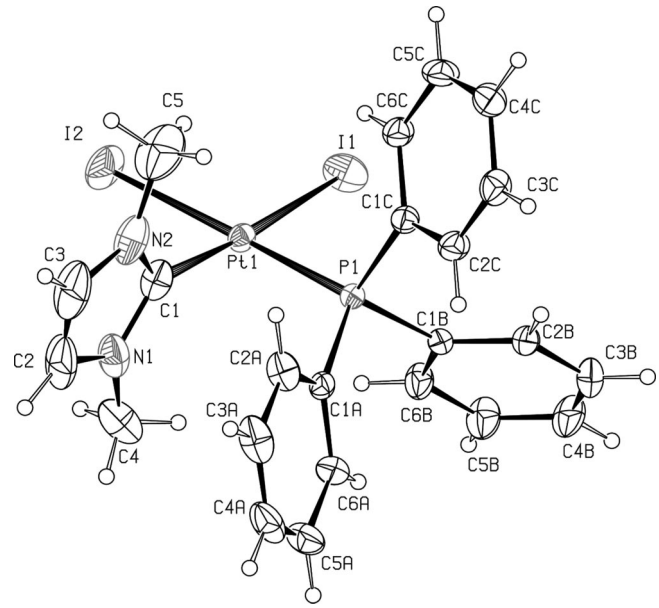


Figure 1. ORTEP drawing of the *cis*-(NHC)(triphenylphosphine)-PtI_2 complex **3**. Selected bond lengths [Å]: Pt−P = 2.2439(15), Pt−C(1) = 1.984(8), Pt−I(1) = 2.6517(7), Pt−I(2) = 2.6482(6), C(1)−N(1) = 1.351(11), C(1)−N(2) = 1.345(10). Selected bond angles [deg]: P−Pt−C(1) = 91.4(2), C(1)−Pt−I(2) = 84.8(2), I(1)−Pt−I(2) = 90.79(2), I(1)−Pt−P = 92.95(4). Torsion angle between the N−C(19)−N and P−Pt−I(2) mean planes: 89.1°.

Most notably, a single isomer of complex **3** was isolated, where the carbene and phosphine ligands occupy mutually *cis*-

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Table 1. Platinum(II)−Diphosphine Complexes Bearing Symmetrical Imidazolylidene Ligands

	compd	R^1	diphosphine	yield	^{31}P NMR: δ ($^1J_{P-Pt}$) [$^2J_{P-P}$]
1	**4a**	Me	(*R,R*)-MeDuPhos	84%	64.7 (2169 Hz) 63.7 (3229 Hz) [6 Hz]
2	**5a**	Me	(*R*)-Binap	47%	6.2 (2293 Hz) 5.1 (3370 Hz) [21 Hz]
3	**6a**	Me	(*R,R*)-Et-FerroTANE	95%	29.4 (3104 Hz) 26.4 (2191 Hz) [10 Hz]
4	**7a**	Me	(*S,S*)-Chiraphos	84%	37.8 (2170 Hz) 37.3 (3232 Hz) [17 Hz]
5	**7b**	C_6H_{11}	(*S,S*)-Chiraphos	96%	38.4 (2140 Hz) 37.0 (3255 Hz) [16 Hz]
6	**7c**	Ph	(*S,S*)-Chiraphos	70%	37.1 (2216 Hz) 34.9 (3278 Hz) [16 Hz]

positions. The *cis*-arrangement of **3** was supported by ^{31}P NMR data showing a signal at δ 8.5 ppm, with $^1J_{Pt-P}$ couplings of 3695 Hz. The $^1J_{Pt-P}$ coupling constant value lies in the range usually observed in platinum(II) complexes when iodide and phosphorus ligands are in *trans* relative positions.[15]

The molecular structure of **3** was then reliably assessed by single-crystal X-ray diffraction study. The corresponding ORTEP drawing is depicted in Figure 1.

The crystal structure shows a square-planar coordination of the metal center. The heterocyclic carbene is perpendicular to the plane encompassing the four ligands (torsion angle = 89.1°). The Pt−C(1) bond length amounts to 1.984 Å and is in the expected range for Pt−imidazolylidene bonds.[16]

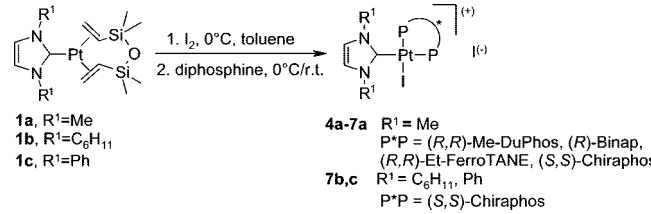
The formation of the *cis*-isomer of **3** as the unique product is consistent with the higher thermodynamic stability of *cis*-configurated carbene/phosphine complexes of platinum, highlighted recently by Huynh,[17] although a kinetic preference for the *cis*-isomer cannot be ruled out either.[18]

In order to achieve partial characterization of the intermediate olefin complex (Scheme 2), the oxidative addition of iodine to complex **1a** was monitored by ^1H NMR in toluene-d_8. The observed intermediate results from addition of I_2 and concomitant displacement of one of the coordinated olefin moieties: NMR signals for both the Pt-coordinated {δ 4.4−4.6 (m, 2H), 5.33 (d, J_{H-H} = 15 Hz, J_{H-Pt} = 62 Hz, 1H)} and unbound vinyl groups {δ 5.74 (dd, $^3J_{H-H}$ = 20.0 Hz, $^2J_{H-H}$ = 4.0 Hz, 1H), 5.95 (dd, $^3J_{H-H}$ = 15.0 Hz, $^2J_{H-H}$ = 4.0 Hz, 1H), 6.15 (dd, $^3J_{H-H}$ = 20.0 Hz, $^3J_{H-H}$ = 15.0 Hz, 1H) ppm} of the divinyldisiloxane moiety have been observed. The pairs of enantiotopic methyl groups on silicon display two separate signals each, at δ 0.16 (s, 3H), 0.17 (s, 3H), 0.40 (s, 3H), and 0.45 (s, 3H) ppm. The imidazolylidene ligand displays nonequivalent N-Me (δ 3.86 and 3.89 ppm) and CH groups at δ 6.96 and 7.00 ($^3J_{H-H}$ = 2.0 Hz) ppm. A structurally related (NHC)Pt(olefin)Cl_2 complex has been reported recently by Nolan.[19]

The reaction sequence above involving iodine oxidative addition to a Pt(0)-NHC complex and subsequent complexation of a phosphorus ligand was then performed by using symmetrically substituted carbenes and chiral chelating diphosphines (Scheme 3).

In a first series of experiments the (*N,N*-dimethylimidazolylidene)Pt^0 complex **1a** was oxidized with iodine and then

Scheme 3. Synthesis of the Imidazolylidene/Chiral Diphosphine Platinum(II) Complexes 4−7



combined with the commercially available diphosphines (*R,R*)-Me-DuPhos, (*R*)-Binap, (*R,R*)-Et-FerroTane, and (*S,S*)-Chiraphos (entries 1−4 in Table 1). Then, the *N,N*-dicyclohexyl- and *N,N*-diphenylimidazolylidene platinum(0) complexes were used as starting materials for the reaction with (*S,S*)-Chiraphos (entries 5 and 6). The corresponding cationic, diphosphine-containing complexes **4−7** were obtained in moderate to good yields as solids that separate directly from the reaction mixture. If necessary, additional purification of the final product was performed by column chromatography.

In their ^{31}P NMR spectra (see Table 1) these square-planar complexes display typical patterns: two nonequivalent phosphorus centers generate an AB system with $^2J_{P-P}$ = 6 to18 Hz, while $^{195}Pt-^{31}P$ couplings split the signals again into satellites. The $^1J_{P-Pt}$ couplings allow reliable assignment of the ^{31}P NMR signals to *cis*- and *trans*-phosphorus atoms, as larger couplings (>3000 Hz) are expected for phosphorus atoms *trans* to the halide ligand.

An X-ray diffraction study has been performed on the (*N,N′*-dicyclohexylimidazolylidene)Pt[(*S,S*)-Chiraphos] complex **7b** (Figure 2). The platinum center displays a perfect square-planar coordination of the four ligands, and the Pt−C(1) bond distance (2.063 Å) is similar to that found in other platinum(II)−NHC complexes. In chelate complexes, (*S,S*)-Chiraphos is known to preferentially adopt a δ-conformation since this allows the methyl groups to occupy pseudoequatorial positions.[20] The same preferred conformation of the diphosphine backbone has been noticed in complex **7b**. The higher steric hindrance is thus displayed in the bottom-left and upper-right quadrants of the coordination sphere of platinum (see sketch in Figure 2). Accordingly, the carbene ligand deviates from the expected arrangement, perpendicular to the coordination plane (90° dihedral angle, see Figure 1), to a tilt angle of 73.9° (dihedral angle between the P(1)−Pt−P(2) and N(1)−C(1)−N(2) mean planes) so as to minimize steric interactions between the bulky cyclohexyl group and the phosphine in the hindered bottom-left region. A similar distortion of the coordinated carbene from an orthogonal disposition was noticed in the crystal structure of a ((*R,R*)-Me-DuPhos)Pt(NHC)I_2 complex.[12]

The same synthetic procedure as above was then applied to the preparation of complexes **8** from the unsymmetrically substituted imidazolylidene-platinum(0) complexes **2a−k** ($R^1 \neq R^2$) and (*S,S*)-Chiraphos (Scheme 4). Square-planar complexes of this series featuring unsymmetrical carbene ligands are

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(17) Slow conversion of *trans*-configurated carbene/phosphine platinum(II) complexes into the thermodynamically favoured *cis*-isomers was observed: see ref 16b.

(18) For a detailed discussion on the mechanism and stereochemical outcome of ligand substitution on square-planar platinum complexes, see: Cross, R. J. *Chem. Soc. Rev.* **1985**, *14*, 197–223.

(19) Fantasia, S.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. *Organometallics* **2007**, *26*, 3286–3288.

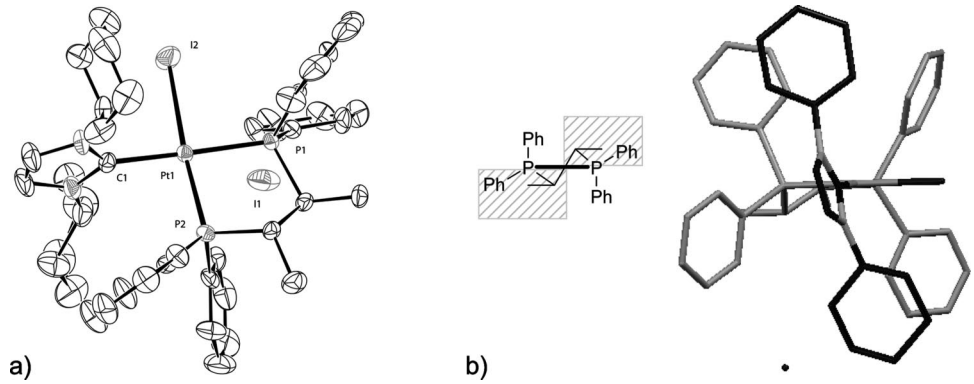
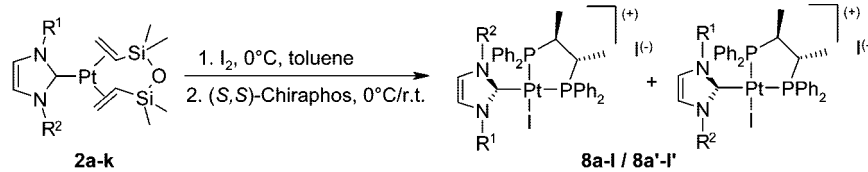


Figure 2. (a) ORTEP view of the (*N,N′*-dicyclohexylimidazolylidene)Pt[(*S,S*)-Chiraphos]I_2 complex **7b**. Selected bond distances (Å): Pt−C(1) = 2.062(9), C(1)−N(1) = 1.346(12), C(1)−N(2) = 1.336(12), Pt−P(1) = 2.286(2), Pt−P(2) = 2.236(2), Pt−I(2) = 2.6364(9). Selected bond angles (deg): P(1)−Pt−P(2) = 85.40(8), P(2)−Pt−C(1) = 95.2(3), C(1)−Pt−I(2) = 89.5(2), P(1)−Pt−I(2) = 89.91(6), N(1)−C(1)−N(2) = 104.7(8). (b) Schematic drawings of the (*S,S*)-Chiraphos complex highlighting the *δ*-conformation of the carbon backbone and the tilt angle of the imidazole ring with respect to the coordination plane.

Scheme 4. Synthesis of [(*S,S*)-chiraphos]Pt(II) Complexes 8 Bearing Unsymmetrical NHC Ligands



Comp	R^1, R^2	yield	Epimers ratio[a]	Comp	R^1, R^2	yield	Epimers ratio[a]
8a,a'[12]	Me, Ph	84%	1:1	**8g,g'**	CH_2Ph, Ph	63%	1:1
8b,b'	Me, CH_2Ph	90%	1:1	**8h,h'**	CH_2Ph, Cy	56%	1:1
8c,c'	Me, *t*-Bu	89%	1:1	**8i,i'**	NaphCH_2, Cy	76%	1:1
8d,d'	Me, 2,6-(*i*Pr)$_2$$C_6H_3$	71%	80:20[b]	**8j,j'**	NaphCH_2, *t*-Bu	53%	91:9
8e,e'	Me, Mes	72%	95:5[b]	**8k,k'**	Me, (*S*)-CH(Me)Ph	93%	70:30
8f,f'	CH_2Ph, *t*-Bu	80%	91:9	**8l,l'**	Me, (*R*)-CH(Me)Ph	92%	77:23

[a] The absolute axial configuration of the single epimers has not been assigned, except for **8i,i'**. [b] Kinetic products ratio

expected to display axial chirality[21,22] and, consequently, to generate diastereomeric pairs if rotation of the NHC ligand around the Pt−C bond is prevented by either steric hindrance or a multiple-bond character of the Pt−C bond.

Complexes **8a**−**l** have been obtained indeed as mixtures of epimers with opposite axial configurations. Assignment of the axial configurations has been done for **8i**,**i′** by X-ray diffraction studies on complex **8i′**. As shown in Figure 3, complex **8i′** displays an *R* configuration. The axial configuration of the other complexes **8** has not been assigned so far.

Reactions in Scheme 4 proceed with good diastereoselectivity only for Pt(0) complexes bearing very bulky imidazolylidene ligands. Thus for instance, use of the NHC ligand bearing a *t*-Bu and a CH_2Ph substituent on the nitrogen atoms affords the corresponding epimeric complexes **8j** and **8j′** in a 91:9 ratio, while the analogous complexes **8h**,**h′**, bearing the less hindered *N*-cyclohexyl substituent, are formed in 1:1 ratio. The absolute axial configuration of complexes **8j**,**j′** could not be unambiguously determined by crystallography. Nevertheless, based on the structural assignment for **8i′**, and by comparing the ^{1}H NMR data of these closely related complexes, we could tentatively assume that the major epimer **8j** displays an *S* axial configuration.[23] This is consistent with the expected trend by which, in the favored epimer **8j**, the bulkier *tert*-butyl substituent lies in the nonhindered upper-left quadrant of the (*S,S*)-Chiraphos platinum(II) complex.

The configurational stability of complexes **8a**,**a′** has been checked by ^{1}H NMR on enriched mixtures of **8a**+**8a′**: samples with **8a**:**8a′** ratios of 9:2 and 3:7, respectively, have been obtained by fractional crystallization. No interconversion of the epimers was observed, neither at room temperature nor after heating at 50 °C for 20 h.[24]

(20) (a) Brunkan, N. M.; White, P. S.; Gagné, M. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1579–1582. (b) Brunner, H.; Winter, A.; Breu, J. *J. Organomet. Chem.* **1998**, *553*, 285–306.

(21) For examples of axially chiral, square-planar complexes bearing NHC ligands see: (a) Enders, D.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3571–3574. (b) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, *91*, 3–919. (c) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*−*618*, 70–80. (d) Bolm, C.; Kesselgruber, M.; Raabe, G. *Organometallics* **2002**, *21*, 707–710. (e) Faller, J. W.; Fontaine, P. P. *Organometallics* **2006**, *25*, 5887–5893.

(22) The axis of chirality is represented by the carbene−Pt bond, whereas the two perpendicular planes contain this axis and either the two nitrogen atoms of the NHC ligand, for the first one, or the P and iodine atoms, for the second (see Figure 3).

(23) The N-CH_2 groups of complexes **8i** and **8i′** display typical ^{1}H NMR patterns made of two doublets. These doublets display a significantly larger $\Delta\delta$ shift for complex **8i** (1.94 ppm) than for **8i′** (0.61 ppm). The corresponding signals for complex **8j** have $\Delta\delta$ = 1.95 ppm. Thus, it is tentatively assumed that **8j** displays the same structural features as **8i**, i.e., an *S* axial configuration.

(24) Single epimers of analogous, configurationally stable, NHC−Pt complexes containing Me-DuPHOS or Me-BPE as the bidentate chiral phosphine have been characterized previously: see ref 12.

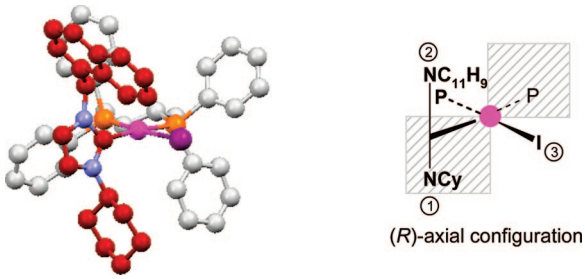


Figure 3. View of complex **8i′** from X-ray data.

In light of these data, an unexpected behavior was observed however for complexes **8e**,**e′** and **8d**,**d′**, which contain the bulky *N*-mesityl-*N*-methylimidazolylidene and *N*-(2,6-diisopropylphenyl)-*N*-methylimidazolylidene ligands, respectively. Complexes **8e**,**e′** were isolated as a 9:1 mixture of two compounds, which were tentatively assigned as the expected epimers with opposite axial configurations (72% total yield). When this mixture was stirred at room temperature in $CDCl_3$, slow isomerization was observed by ^{1}H NMR, which was then completed by heating at about 50 °C for 48 h. The final equilibrium mixture contains the isomeric derivative **8e′** as the major component, in 85% relative amount. In a similar way, the initial 7:3 mixture of complexes **8d**+**8d′** was slowly converted into pure **8d′** at room temperature in $CDCl_3$ solutions. The apparent facile isomerization of **8e** into **8e′**, or **8d** into **8d′**,[25] markedly contrasts with the observed configurational stability of complexes **8a**,**a′** and cannot be easily rationalized at present.

Catalysis and Computational Studies. As already mentioned in the Introduction, the NHC-diphosphine-Pt(II) complexes **I** have been designed as potential catalysts for a definite class of enyne cycloisomerization reactions, those proceeding through simple activation of the alkyne moiety by π-complexation on platinum. Thus, the cycloisomerization of the 1,6-enyne **9**, bearing a nitrogen-containing tether, into the 3-azabicyclo[4.1.0]-heptene **10**[2a] has been selected as the test reaction to evaluate the catalytic activity of complexes **I**.[26] To the best of our knowledge, no enantioselective synthesis of the bicyclic derivative **10** has been reported so far, although analogous asymmetric cycloisomerization reactions promoted by Ir complexes[7] have been described recently.

The standard protocol for catalytic reactions involves the use of a 9:1 toluene/dichloromethane mixture as the solvent,[27] a 4 mol % amount of catalyst, and heating at 90 °C for about 20 h. The catalytically active species have been generated from the Pt(II) complexes **4**−**7** by addition of $AgBF_4$ as a suitable halide scavenger. Conversion rates (from ^{1}H NMR) and enantioselectivities are given in Table 2. The enantiomeric excesses of **10** were measured by HPLC on samples that may contain some residual starting material, **9**.

In a preliminary screening, the relative efficiencies of various chiral diphosphines have been evaluated by comparing the catalytic behavior of the Pt complexes **4a**−**7a** bearing an *N*,*N*′-dimethylimidazolylidene ligand (entries 1−4 in Table 2). Clean reactions were usually observed, with the expected bicycle **10** being the only product. The highest catalytic activity and enantioselectivity levels were obtained with the Chiraphos

Scheme 5. Cycloisomerization Studies with Chiral Pt(II) Catalysts: Test Reaction

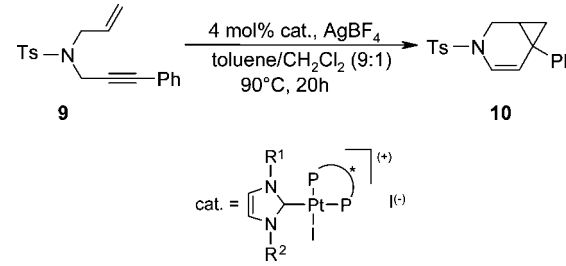


Table 2. Cycloisomerization Reactions Promoted by Chiral Pt Catalysts 4−7

entry	cat.	R^1, R^2	diphosphine	conv [%][a]	ee [%][b]
1	**4a**	Me	(*R*,*R*)-MeDuPhos	59	7
2	**5a**	Me	(*R*)-Binap	67	12
3	**6a**	Me	(*R*,*R*)-Et-FerroTANE	56	28
4	**7a**	Me	(*S*,*S*)-Chiraphos	100	58
5	**7b**	C_6H_{11}	(*S*,*S*)-Chiraphos	91	64
6	**7c**	Ph	(*S*,*S*)-Chiraphos	15	36

[a] By ^{1}H NMR of the crude reaction mixture. [b] HPLC: Chiracel OD, hexane/iPrOH, 99:1.

complex **7a** (entry 4), which gave total conversion and a 58% enantiomeric excess.

Following this preliminary screening, Chiraphos was selected as the preferred chiral diphosphine, and a second series of experiments was performed then with platinum complexes in which Chiraphos is combined with other symmetrically substituted NHC moieties (entries 5−7). Substitution of the nitrogen atoms by phenyl groups (complex **7c**) decreased both the catalytic activity and enantioselectivity (entry 6). The use of an imidazolylidene ligand bearing bulky cyclohexyl substituents afforded an active catalyst, **7b**, and allowed the enantiomeric excesses to be slightly improved from 58% to 64% (entry 5).

We next surveyed the catalytic properties of the (*S*,*S*)-Chiraphos complexes **8**, featuring unsymmetrically substituted NHC ligands, disregarding the fact that they have been isolated mainly as epimeric mixtures. Representative results are given in Table 3.

It appears that the nature of the nitrogen substituents of the imidazolylidene moiety modulates to some extent the enantioselectivity of the cycloisomerization reaction above. Carbenes bearing the rather bulky cyclohexyl or *tert*-butyl groups, combined with benzyl and 1-naphthylmethyl groups, respectively, allowed the highest enantioselectivities to be attained, with enantiomeric excesses up to 74% (entries **5** and **8**). The chiral induction did not improve significantly when complexes **8k** and **8l** were used, which display an additional stereogenic center on the nitrogen substituent (entries 9 and 10 vs 2).

All together these results show that the carbene ligands modulate to some extent both the yields and enantioselectivities of the cycloisomerization reaction promoted by the chiraphos-Pt complexes **7** and **8**. As an additional evidence of the essential role of the carbene ligand, it must be mentioned that a PtI_2(Chiraphos) complex afforded only trace amounts of the expected 3-azabicyclo[4.1.0]heptene, in the reaction conditions of Scheme 5.

When surveying the catalytic properties of the Pt complexes **8** made of N,N′-unsymmetrically substituted carbenes, a major question arose about the suitability of using the diastereomeric mixtures above as precatalysts. This procedure may be considered as convenient and adequate only if the epimeric platinum complexes interconvert during the catalytic cycle. Thus, to gain

(25) Unfortunately, crystals of **8e′** or **8d′** suitable for X-ray diffraction studies could not be obtained.

(26) (a) For previous examples of enyne cycloisomerization reactions promoted by ligand-modified platinum(II) see ref 3. (b) Fürstner, A.; Davies, P. W.; Gress, T. *J. Am. Chem. Soc.* **2005**, *127*, 8244–8245.

(27) Addition of a small amount of dichloromethane is required to produce, initially, a homogeneous solution of the catalyst.

Table 3. Cycloisomerization Reactions Promoted by Chiral (NHC)Pt-[(*S,S*)-Chiraphos] Complexes 8 (Scheme 5)

	Pre-catalyst	R^1,R^2	conv [%]	ee [%]
1	**8a,a'**	Me, Ph	90	57
2	**8b,b'**	Me, CH_2Ph	60	58
3	**8c,c'**	Me, *t*-Bu	91	62
4	**8d,d'**	Me, 2,6-di(*i*Pr)$_2$C$_6$H$_3$	90	60
5	**8f,f'**	**CH_2Ph, *t*-Bu**	**100**	**73**
6	**8g,g'**	CH_2Ph, Ph	100	48
7	**8h,h'**	CH_2Ph, Cy	100	70
8	**8i,i'**	**NaphCH_2, Cy**	91	**74**
9	**8k,k'**	Me, (*S*)-CH(Me)Ph	70	42
10	**8l,l'**	Me, (*R*)-CH(Me)Ph	81	61

insight into the configurational stability of the axially chiral platinum catalysts above during the cycloisomerization reaction, we compared the behavior of mixtures of the epimeric complexes **8i**,**i′** at different isomer ratios. Only minor variations of the enantiomeric excess have been observed, which cannot be ascribed to the catalytic activity of distinct epimeric catalysts. Thus, for instance, catalysts made from 1:1 and >95:5 mixtures of **8i**+**8i′** afforded the cyclization product **10** in 74% and 72% ee, respectively, in parallel experiments.

Thus, we came to the conclusion that the axial configuration of the platinum complexes **8i**,**i′** is likely to be lost during the cycloisomerization reaction. This is not inconsistent with the assessed configurational stability of the starting square-planar complexes **8**, since transient tricoordinated Pt complexes are expected to be involved in the process as the catalytically active species (see Introduction). Such tricoordinated complexes might display much lower epimerization barriers than the corresponding tetracoordinated species, due to peculiar isomerization mechanisms. This has been assessed through the experimental and theoretical studies above.

The epimerization process has been evidenced as follows: the iodide ligand has been removed from complex **8i′** (single diastereomer) by addition of 2 equiv of $AgBF_4$ in CH_2Cl_2 at room temperature. After about 10 min, an excess of KI was added and the mixture was stirred overnight. Monitoring the mixture by ^{1}H NMR showed the presence of a 60:40 mixture of the two epimeric complexes **8i**,**i′**.

A DFT study was carried out in order to enlighten and compare the structures and epimerization barriers of the tetracoordinated and tricoordinated platinum(II) complexes **I** and **II**, bearing a chelating diphosphine and an imidazolylidene ligand.[28] Calculations were carried out using simplified structures displaying the two-carbon bridge of (*S,S*)-Chiraphos. Methyl groups have been used as phosphorus substituents and the imidazolylidene ligands bear either two hydrogen atoms or a methyl group and a hydrogen atom as the N-substituents (Figure 4).

The optimized structures for complexes **Ia** and **IIa** are displayed in Figure 5. The calculated bond angles for the square-planar complex **Ia**, i.e., P−Pt−P = 85.7°, P−Pt−I = 90.9°, I−Pt−C = 87.0°, and C−Pt−P = 96.4°, fit well with the experimental values reported above for complex **7b** (P−Pt−P = 85.4°, P−Pt−I = 89.9°, I−Pt−C = 89.5°, and C−Pt−P = 95.2°). Furthermore, as in the crystal structure, the heterocyclic carbene is perpendicular to the P−Pt−P plane. This indicates that, in the absence of steric repulsion, the N- and P-substituents do not affect the geometrical features of these complexes.

The tricoordinated dicationic complex **IIa** adopts a T-shaped coordination with only minor variations of the bond angles with respect to complex **Ia**. Thus, for instance, the C−Pt−P bond angle increases by only 6.0° after removal of the iodide ligand, showing a very small shift of the carbene moiety from its initial position. The perpendicular conformation of the imidazolylidene ligand is also maintained, reflecting, as in **Ia**, a better electronic interaction between the ligand and the metal fragment in this arrangement.

We next considered the epimerization process, which could follow different pathways (Table 4). The conversion of complex (*R*)-**I** (or (*R*)-**II**) into complex (*S*)-**I** (or (*S*)-**II**) could take place through rotation of the carbene ligand around the Pt−C axis via **TS1**. Other possible epimerization pathways for complexes **I** and **II** involve a tetrahedral (**TS2**) and a Y-shaped achiral (**TS3**) transition state, respectively.[29]

For the epimerization processes of the tetracoordinated complexes **Ia**,**b**, our calculations reveal that rotation around the Pt−C bound axis is a low-energy-demanding process for carbene with low steric hindrance, i.e., with hydrogens as the N-substituents. The transition state **TS1** requires indeed only 15.6 kJ/mol free energy from **Ia**. The other pathway from **Ia**, which involves passage through a transient tetrahedral Pt(II) (**TS2**), has a much higher free energy barrier of 170.8 kJ/mol. This path is thus unlikely and has not been considered from **Ib**. Inclusion of steric hindrance with a *N*-methyl substituted carbene greatly increases the barrier to reach **TS1**. Indeed steric interaction between the N-methyl group and either the phosphine or the iodide ligand leads to transition states located respectively 61.7 and 74.6 kJ/mol higher in energy than **Ib**. It is noticeable that the iodide group induces a slightly more pronounced steric effect than the PMe_2 moiety. These results suggest that rotation around the Pt−C axis, and thus the epimerization process, could be easily prevented by the use of N,N′-disubstituted carbenes,

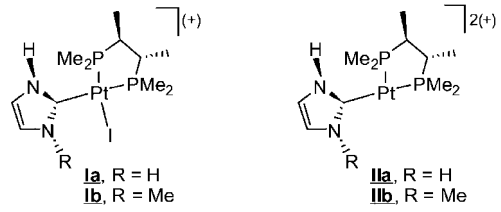


Figure 4. Calculated models of complexes **I** and **II**.

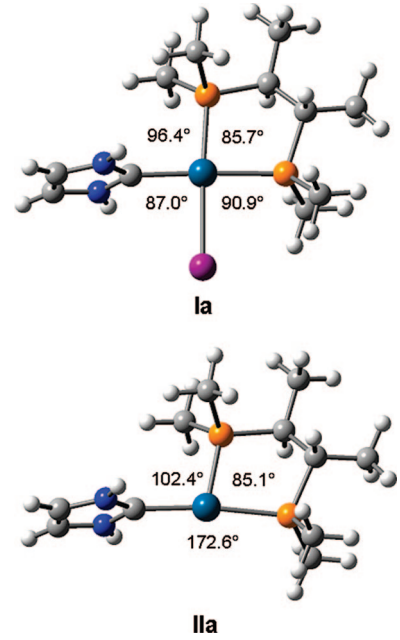
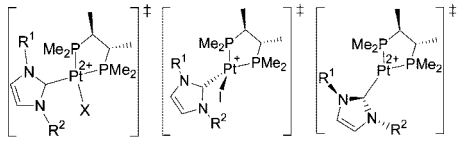


Figure 5. Geometrical structures of complexes **Ia** and **IIa**.

Table 4. Activation Free Energy Calculated at the B3LYP/6-31G(d,p)/LANL2DZ Level for the Epimerization Pathways for Complexes Ia,b and IIa,b (energies in kJ/mol)



	R^1	R^2	X	TS1	TS2	TS3
Ia	H	H	I^-	15.6	170.8	-
Ib	H	Me	I^-	74.6	-	-
Ib	Me	H	I^-	61.7	-	-
IIa	H	H	Ø	29.0	-	17.9
IIb	H	Me	Ø	27.7	-	18.3
IIb	Me	H	Ø	51.5	-	18.3

in agreement with the above experimental results indicating the configurational stability of complexes **I**.

The same trend is observed for the tricoordinated, T-shaped complexes **IIa**,**b**, revealing the possibility of preventing rotation around the Pt−C bond axis by using bulky N-substituted carbenes. Indeed, moving from **IIa** ($R^1 = R^2 = H$) to **IIb** ($R^1 = Me$, $R^2 = H$) induces an increase of the barrier from 29.0 to 51.5 kJ/mol to reach **TS1** when the methyl substituent is *cis* to the phosphine. We did however notice that (i) the increase is lower than that observed when moving from **Ia** to **Ib**, reflecting the possibility for the tricoordinated complexes to slightly open the C−Pt−P bond angle (C−Pt−P bond angles of 102.8° and 114.2° in **Ib-TS1** and **IIb-TS1**, respectively, for $R^1 = Me$), and (ii) steric hindrance is not observed when the methyl substituent is located *trans* to the phosphine ($R^2 = Me$). These results indicate that epimerization through rotation of the carbene moiety is easier for the tricoordinated complexes **II** than for tetracoordinated complexes **I**; an increase of the steric bulk of the phosphorus and/or the carbene substituents could nevertheless block this path. However, an alternative epimerization pathway can be envisioned for complexes **II** that involves a Y-shaped transition state **TS3** and swinging of the carbene ligand between two contiguous coordination sites. This is expected to be a low-energy pathway, irrespective of the nature and steric bulk of the carbene and phosphorus substituents. Our calculations confirm this hypothesis, **TS3** being located at ∼18 kJ/mol from both **IIa** and **IIb**.

Thus, the above computations afford some rationale to the observed easy epimerization of the tricoordinated platinum(II) complexes that are generated from **8** after removal of the halide ligand.

Conclusions

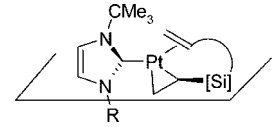
A general synthetic approach to platinum(II) complexes bearing both an NHC and a phosphine or a diphosphine ligand has been developed. The method involves oxidative addition of I_2 to the easily available (NHC)$Pt^{(0)}$(dvtms) complexes. When combining (*S,S*)-Chiraphos and unsymmetrically substituted carbenes, epimeric mixtures of axially chiral complexes of the general formula (NHC)PtI(Chiraphos)$^+I^-$ have been isolated, most of which display configurational stability. Experiments and DFT calculations suggest that epimerization of these tetracoordinated square-planar complexes is precluded mainly by the steric hindrance between the imidazolylidene N-substituent and the phosphine or the iodide ligands, which prevents rotation of the carbene around the Pt−C bond.

The Pt(II) complexes above represent suitable precatalysts for the enantioselective cycloisomerization reaction of *N*-allyl-*N*-(3-phenylpropyn-2-yl)-4-methylbenzenesulfonamide into the corresponding 3-azabicyclo[4.1.0]hept-4-ene. Tuning of the phosphine−NHC pair allows modulation of the catalytic properties and enantiomeric excesses up to 74% to be attained in this model reaction. These results support the postulated mechanism, which involves tricoordinated platinum complexes as the catalytically active species. Experiments and DFT calculations indicate that, in the case of unsymmetrically substituted NHC complexes, the T-shaped tricoordinated intermediates can easily epimerize through a Y-shaped transition state, allowing swinging of the carbene between the two available coordination sites. This epimerization process is broadly insensitive to the steric hindrance of the ligands.

Experimental Section

All reactions were run under an argon atmosphere, by using standard techniques for manipulating air-sensitive compounds. Anhydrous CH_2Cl_2 was obtained by filtration through drying columns. Toluene and all reagents were of commercial quality and were used without further purification. Flash column chromatography was performed using 40−63 mesh silica. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{31}P) were recorded on either Bruker AV 500 or AV 300 spectrometers. Optical rotations were determined with a JASCO P-1010 polarimeter. HPLC was performed at a column temperature of 20 °C on a Waters 2695 Separations Module equipped with a diode array UV detector.

Starting Materials: (NHC)Pt^0(dvtms) Complexes. Imidazolium salts have been prepared either by alkylation of 1-substituted imidazoles with alkyl halides or from primary amines, glyoxal, and formaldehyde according to the reported methods.[30] The Pt(0) complexes **1** and **2** have been prepared by the synthetic procedure described by Markó,[14d] which involves reaction of an imidazolium salt (1 equiv) with 1 equiv of the Karstedt's catalyst (Pt_2(dvtms)$_3$) (2% Pt in xylene solution) in xylene, in the presence of *t*-BuOK (1.4 equiv) at 0 °C to rt for several hours. Complexes **1a**, **1b**, **1d**,[14d] and **2a**[12] are known compounds. Spectral data for the Pt(0) complexes **1c** and **2b**−**k** are reported hereafter. Complexes **2c**, **2f**, and **2j**, bearing *N*-*t*-Bu-sustituted imidazolylidenes, display two separate series of NMR signals. This has been tentatively assigned to the presence of noninterconverting (or slowly interconverting) isomers due to hindered rotation of the NHC ligand around the Pt−C axis, combined with the metallacyclopropane-like character of the olefin−metal bonds, which differentiates the two faces of the coordination plane (see X-ray data in ref 14d).



(1,3-Diphenylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (1c). Complex **1c** was obtained in 20% yield (60 mg, 0.1 mmol) from 1,3-diphenylimidazolium chloride (130 mg, 0.5 mmol), after purification by chromatography with an 8:2 heptane/ethyl acetate mixture as the eluent ($R_f = 0.4$). ^1H NMR (300 MHz, $CDCl_3$): δ −0.61 (s, 6H, SiMe), 0.21 (s, 6H, SiMe), 1.5−1.7 (4H, H_2C=C*H*Si), 1.93 (dd, $J = 9.6$ Hz, $J = 1.8$ Hz, $^2J_{H-Pt} = 50$ Hz, 2H, H_2C=CHSi), 7.3 (6H), 7.43 (s, $^4J_{H-Pt} = 11.1$ Hz, 2H, NCH=), 7.5 (4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.8 (Me), 1.4 (Me), 33.8 ($^1J_{C-Pt} = 122$ Hz, H_2C=*C*HSi), 41.5 ($^1J_{C-Pt} = 163$ Hz, H_2C=CHSi), 122.3 ($^3J_{C-Pt} = 38$ Hz, NCH=), 124.6, 127.8, 128.6, 140.8 (C) ppm.

(1-Benzyl-3-methylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2b). Complex **2b**was obtained in 78% yield (73 mg, 0.13 mmol) from 1-benzyl-3-methylimidazolium

iodide[31] (50 mg, 0.17 mmol), after purification by chromatography with an 8:2 heptane/ethyl acetate mixture as the eluent ($R_f = 0.4$). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.06 (s, 6H, SiMe), 0.58 (s, 6H, SiMe), 2.0−2.3 (4H, H_2C═C*H*Si), 2.49 (br d, J = 10.5 Hz, $^2J_{H-Pt}$ = 52.8 Hz, 2H, H_2C═CHSi), 3.82 (s, $^4J_{H-Pt}$ = 2.7 Hz, 3H, NMe), 5.40 (s, $^4J_{H-Pt}$ = 5.4 Hz, 2H, NCH_2Ph), 7.16 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 11.7 Hz, 1H, NCH═), 7.28 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 12.0 Hz, 1H, NCH═), 7.4 (2H, Ph), 7.5−7.6 (3H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.9 (SiMe), 1.5 (SiMe), 34.5 ($^1J_{C-Pt}$ = 118 Hz, H_2C═*C*HSi), 36.9 ($^3J_{C-Pt}$ = 45.0 Hz, NMe), 40.3 ($^1J_{C-Pt}$ = 158 Hz, H_2C═CHSi), 53.3 ($^3J_{C-Pt}$ = 42 Hz, N*C*H_2Ph), 120.5 ($^3J_{C-Pt}$ = 36 Hz, NCH═), 122.5 ($^3J_{C-Pt}$ = 37 Hz, NCH═), 127.5, 127.8, 128.7, 136.8(C_{Ph}), 184.7 (Pt═C) ppm.

(1-*tert*-Butyl-3-methylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane) platinum(0) (2c). Complex **2c** was obtained in 41% yield (42 mg, 0.08 mmol) from 1-*tert*-butyl-3-methylimidazolium iodide[31] (58 mg, 0.2 mmol) after purification by chromatography with 9:1 heptane/ethyl acetate as the eluent. Due to hindered rotation of the carbene moiety, complex **2c** is formed as a 1:1 mixture of isomers. White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.28 (s, 6H, SiMe), −0.27 (s, 6H, SiMe), 0.33 (s, 12H, SiMe), 1.56 (s, 9H, CMe_3), 1.6 (s, 9H, CMe_3), 1.6−2.0 (8H), 2.14 (d, J = 9.9 Hz, $^2J_{H-Pt}$ = 52 Hz, 2H, H_2C═CHSi), 2.28 (d, J = 11.1 Hz, $^2J_{H-Pt}$ = 54 Hz, 2H, H_2C═CHSi), 3.45 (s, $^4J_{H-Pt}$ = 5.1 Hz, 3H, NMe), 3.50 (s, $^4J_{H-Pt}$ = 5.1 Hz, 3H, NMe), 6.96 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 10 Hz, 1H, NCH═), 6.97 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 11 Hz, 1H, NCH═), 7.20 (d, ^3J = 2 Hz, 1H, NCH═), 7.21 (d, ^3J = 2 Hz, 1H, NCH═) ppm.

(1-(2,6-Diisopropylphenyl)-3-methylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2d). Complex **2d** was obtained in 34% yield (87 mg, 0.14 mmol) from 1-(2,6-diisopropylphenyl)-3-methylimidazolium chloride (0.15 mg, 0.41 mmol),[30c] after purification by chromatography with 95:5 heptane/ethyl acetate as the eluent ($R_f = 0.3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.41 (s, 6H, SiMe), 0.25 (s, 6H, SiMe), 1.06 (d, ^3J = 6.9 Hz, 6H, CH*Me*$_2$), 1.19 (d, ^3J = 6.6 Hz, 6H, CH*Me*$_2$), 1.5−2.1 (6H, H_2C═CHSi), 2.75 (m, 2H, *CH*Me_2), 3.71 (s, NMe), 7.02 (d, ^3J = 1.8 Hz, $^4J_{H-Pt}$ = 11 Hz, 1H, NCH═), 7.14 (d, ^3J = 7.7 Hz, 2H), 7.18 (d, ^3J = 1.8 Hz, $^4J_{H-Pt}$ = 10 Hz, 1H, NCH═), 7.32 (t, ^3J = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8 (SiMe), 1.5 (SiMe), 22.2 (Me), 26.2 (Me), 28.1 ($CHMe_2$), 34.7 ($^1J_{C-Pt}$ = 110 Hz, H_2C═*C*HSi), 37.4 (NMe), 40.4 ($^1J_{C-Pt}$ = 159 Hz, H_2C═CHSi), 120.9 (CH), 123.4 (CH), 124.8 (CH), 129.3 (CH), 146.0 (C) ppm.

(1-Mesityl-3-methylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2e). Complex **2e** was obtained in quantitative yield (130 mg, 0.22 mmol) from 1-mesityl-3-methylimidazolium iodide[32] (72 mg, 0.22 mmol), after purification by chromatography with 9:1 heptane/ethyl acetate as the eluent (R_f = 0.2). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.66 (s, 6H, SiMe), 0.23 (s, 6H, SiMe), 1.6−1.9 (4H, H_2C═CHSi), 2.03 (6H, Me), 2.20 (d, J = 11 Hz, $^2J_{H-Pt}$ = 51.6 Hz, 2H, H_2C═CHSi), 2.22 (3H, Me), 3.67 (s, 3H, NMe), 6.84 (s, 2H), 6.95 (d, ^3J = 1.8 Hz, $^4J_{H-Pt}$ = 10 Hz, 1H, NCH═), 7.20 (d, ^3J = 1.8 Hz, $^4J_{H-Pt}$ = 10 Hz, 1H, NCH═); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.4 (SiMe), 1.4 (SiMe), 17.9 (Me), 20.9 (Me), 34.7 ($^1J_{C-Pt}$ = 118 Hz, H_2C═*C*HSi), 37.2 (NMe), 40.3 ($^1J_{C-Pt}$ = 162 Hz, H_2C═CHSi), 121.8 (NCH═), 122.7 (NCH═), 128.8 (CH), 135.1 (C), 138.5 (C) ppm.

(1-Benzyl-3-*tert*-butylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2f). Complex **2f** was obtained in 31% yield (104 mg, 0.17 mmol) from 1-benzyl-3-*tert*-butylimidazolium chloride (140 mg, 0.56 mmol), after purification by chromatography with 9:1 heptane/ethyl acetate as the eluent. Colorless oil. Due to hindered rotation of the carbene moiety, complex **2f** is formed as a 1:1 mixture of isomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.47 (s, 6H, SiMe), −0.29 (s, 6H, SiMe), 0.27 (s, 6H, SiMe), 0.30 (s, 6H, SiMe), 1.59 (s, 9H, CMe_3), 1.62 (s, 9H, CMe_3), 1.7−2.3 (12H, H_2C═C*H*Si), 5.13 (s, 2H, NCH_2Ph), 5.25 (s, 2H, NCH_2Ph), 6.81 (d, ^3J = 1.8 Hz, 1H, NCH═), 6.88 (d, ^3J = 1.8 Hz, 1H, NCH═), 7.1 (4H), 7.2−7.3 (8H); ^{13}C NMR (75 MHz, $CDCl_3$, selected data) δ −2.6 (SiMe), −2.5 (SiMe), −1.50 (SiMe), 30.6 (CMe_3), 30.7 (CMe_3), 32.8 ($^1J_{C-Pt}$ = 123 Hz, H_2C═*C*HSi), 34.1 ($^1J_{C-Pt}$ = 119 Hz, H_2C═*C*HSi), 43.2 ($^1J_{C-Pt}$ = 169 Hz, H_2C═CHSi), 43.5 ($^1J_{C-Pt}$ = 168 Hz, H_2C═CHSi), 54.3 (NCH_2), 54.4 (NCH_2), 58.2 (N*C*Me_3) ppm.

(1-Benzyl-3-phenylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2g). Complex **2g** was obtained in 53% yield (98 mg, 0.16 mmol) from 1-benzyl-3-phenylimidazolium bromide, after purification by chromatography with 8:2 heptane/ethyl acetate as the eluent ($R_f = 0.3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.67 (s, 6H, SiMe), 0.12 (s, 6H, SiMe), 1.5−2.1 (6H, H_2C═CHSi), 5.10 (s, 2H, NCH_2), 6.91 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 11 Hz, 1H, NCH═), 7.0−7.2 (9H), 7.3−7.4 (2H); ^{13}C NMR (75 MHz, $CDCl_3$, selected data) δ −2.6 (SiMe), 1.4 (SiMe), 34.4 ($^1J_{C-Pt}$ = 121 Hz, H_2C═*C*HSi), 41.4 ($^1J_{C-Pt}$ = 162 Hz, H_2C═CHSi), 53.8 ($^3J_{C-Pt}$ = 44.7 Hz, NMe),120.9 ($^3J_{C-Pt}$ = 36.2 Hz, NCH═), 122.3 ($^3J_{C-Pt}$ = 37 Hz, NCH═), 136.4 (C), 140.6 (C), 185.1 (C−Pt) ppm.

(1-Benzyl-3-cyclohexylimidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2h). 1-Cyclohexylimidazole[33] was prepared from cyclohexylamine, glyoxal, and paraformaldehyde in dioxane/water in the presence of H_3PO_4 (63% yield after chromatography on silica gel with CH_2Cl_2/MeOH as the eluent). 1-Benzyl-3-cyclohexylimidazolium chloride was obtained in 96% yield by reacting 1-cyclohexylimidazole with benzyl chloride in dioxane at 100 °C. Complex **2h** was obtained in 39% yield (100 mg, 0.16 mmol) from 1-benzyl-3-cyclohexylimidazolium chloride (100 mg, 0.41 mmol), after purification by chromatography with 95:5 heptane/ethyl acetate as the eluent. ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.24 (s, 3H, SiMe), 0.08 (s, 3H, SiMe), 0.33 (s, 6H, SiMe), 1.0−2.0 (14H), 2.18 (d, J = 10.8 Hz, $^2J_{H-Pt}$ = 52.2 Hz, 2H, H_2C═CHSi), 4.4 (m, 1H, NCH), 5.10 (s, 2H, NCH_2), 6.91 (d, ^3J = 1.5 Hz, $^4J_{H-Pt}$ = 13 Hz, 1H, NCH═), 7.03 (d, ^3J = 1.5 Hz, $^4J_{H-Pt}$ = 12 Hz, 1H, NCH═), 7.1−7.3 (5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$, selected data) δ −1.8 (SiMe), 1.4 (SiMe), 25.3 (CH_2), 25.4 (CH_2), 33.9 (CH_2), 34.0 (CH_2═*C*HSi), 40.7 ($^1J_{C-Pt}$ = 162 Hz, *C*H_2═CHSi), 53.5 (NCH_2), 58.4 (NCH), 117.6 (NCH═), 120.7 ($^3J_{C-Pt}$ = 34 Hz, NCH═), 127.7, 128.6, 136.8 (C_{Ph}), 182.6 (C−Pt) ppm.

(1-Cyclohexyl-3-(1-naphthylmethyl)imidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum(0) (2i). 1-Cyclohexyl-3-(1-naphthylmethyl)imidazolium bromide was obtained in 88% yield by reacting 1-cyclohexylimidazole with 1-(bromomethyl)naphthalene in dioxane at 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1−1.5 (3H), 1.6−1.9 (5H), 2.0−2.1 (2H), 4.32 (tt, ^3J = 11.7, ^3J = 4.0 Hz, 1H, NCH), 5.95 (s, 2H, NCH_2), 7.5−7.7 (4H), 7.84 (t, J = 1.8 Hz, 1H, NCH═), 7.84 (t, J = 1.8 Hz, 1H, NCH═), 8.0−8.2 (3H), 9.45 (t, J = 1.8 Hz, 1H, NCHN) ppm. Complex **2i** was obtained in

(28) For recent computational studies on the NHC−metal bond see: (a) Green, J. C.; Herbert, B. J. *Dalton Trans.* **2005**, 1214–1220. (b) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407–5413. (c) Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350–4358, and references therein.

(29) The epimerization process could also be operative through dissociation/reassociation of the carbene ligand or be facilitated by dissociation of one arm of the diphosphine. These pathways are however unlikely due to the ability of these ligands to strongly bind the metal. The calculated dissociation energy of 329 and 241 kJ/mol for respectively the carbene and one phosphine of **Ia** confirms this hypothesis.

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66% yield (119 mg, 0.17 mmol) from 1-cyclohexyl-3-(1-naphthylmethyl)imidazolium bromide (100 mg, 0.27 mmol), after purification by chromatography with 9:1 heptane/ethyl acetate as the eluent (R_f = 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.20 (s, 6H, SiMe), 0.35 (s, 6H, SiMe), 1.0−2.0 (14H), 2.38 (d, J = 10.8 Hz, $^2J_{H-Pt}$ = 53.4 Hz, 2H, H_2C=CHSi), 4.44 (m, 1H, NCH), 5.53 (s, 2H, NCH_2), 6.78 (d, ^3J = 1.8 Hz, $^4J_{H-Pt}$ = 12 Hz, 1H, NCH=), 6.96 (d, ^3J = 1.8 Hz, $^4J_{H-Pt}$ = 10 Hz, 1H, NCH=), 7.2−7.5 (4H), 7.8−8.0 (3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8 (SiMe), 1.5 (SiMe), 25.3 (CH_2), 25.4(CH_2), 33.9 (CH_2), 34.2 (CH_2=*CH*Si), 40.6 ($^1J_{C-Pt}$ = 162 Hz, CH_2=CHSi), 51.6 (NCH_2), 58.5 (NCH), 117.4 (NCH=), 120.6 (NCH=), 123.5, 125.2, 126.0, 126.5, 127.1, 128.7, 128.9, 131.2 (C), 132.0 (C), 133.7 (C) ppm.

(1-*tert*-Butyl-3-(1-naphthylmethyl)imidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane)platinum (2j). 1-*tert*-Butyl-3-(1-naphthylmethyl)imidazolium bromide was obtained in 93% yield by reacting 1-*tert*-butylimidazole with 1-(bromomethyl)naphthalene in dioxane at 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 9H, CMe_3), 5.96 (s, 2H, NCH_2), 7.4−7.7 (5H), 7.79 (t, J = 1.8 Hz, 1H, NCH=), 8.0−8.1 (2H), 8.2 (1H), 9.67 (1H, NCHN) ppm. Complex **2j** was obtained in 47% yield (130 mg, 0.20 mmol) from 1-*tert*-butyl-3-(1-naphthylmethyl)imidazolium bromide (150 mg, 0.43 mmol), after purification by chromatography with 9:1 heptane/ethyl acetate as the eluent (R_f = 0.3). Due to hindered rotation of the carbene moiety, complex **2c** is formed as a 1:1 mixture of isomers. Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.57 (s, 6H, SiMe), −0.25 (s, 6H, SiMe), 0.27 (s, 6H, SiMe), 0.32 (s, 6H, SiMe), 1.63 (s, 9H, CMe_3), 1.66 (s, 9H, CMe_3), 1.9−2.1 (8H), 2.28 (d, J = 11.1 Hz, $^2J_{H-Pt}$ = 52.8 Hz, 2H, H_2C=CHSi), 2.40 (dd, J = 8.1 Hz, J = 2.7 Hz, $^2J_{H-Pt}$ = 54.6 Hz, 2H, H_2C=CHSi), 5.55 (s, $^4J_{H-Pt}$ = 6.0 Hz, 2H, NCH_2), 5.65 (s, $^4J_{H-Pt}$ = 5.7 Hz, 2H, NCH_2), 6.70 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 10.8 Hz, 1H, NCH=), 6.74 (d, ^3J = 2.1 Hz, $^4J_{H-Pt}$ = 10.2 Hz, 1H, NCH=), 7.1−7.2 (4H), 7.4−7.5 (6H), 7.8 (6H) ppm.

(1-Methyl-3-(1-phenylethyl)imidazol-2-ylidene)(1,3-divinyltetramethyldisiloxane) platinum(0) ((*S*)-2k, (*R*)-2k). (*S*)-1-(1-Penylethyl)imidazole was prepared from (*S*)-α-methylbenzylamine (3 mmol), glyoxal (7.5 mmol), and paraformaldehyde (7.5 mmol) in the presence of H_3PO_4. Yield: 430 mg, (83%) after chromatography on silica gel with 5:95 EtOH/CH_2Cl_2 as the eluent. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88 (d, ^3J = 6.9 Hz, 3H, Me), 5.37 (q, ^3J = 6.9 Hz, 1H, N*CH*Me), 6.95 (t, J = 2 Hz, 1H, NCH=), 7.10 (t, J = 2 Hz, 1H, NCH=), 7.15−7.20 (2H), 7.3−7.4 (3H), 7.61 (1H, NCHN) ppm. ((*S*)-1-methyl-3-(1-phenylethyl)imidazolium iodide was obtained in 66% yield by reaction of (*S*)-1-(1-phenylethyl)imidazole and MeI in acetonitrile at 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (d, ^3J = 6.9 Hz, 3H, Me), 4.14 (s, 3H, Me), 5.86 (q, ^3J = 6.9 Hz, 1H, N*CH*Me), 7.18 (1H), 7.37 (1H), 7.4−7.5 (5H), 10.3 (1H, NCHN). Complex (*S*)-**2k** was obtained in 78% yield (141 mg, 0.24 mmol) from (*S*)-1-methyl-3-(1-phenylethyl)imidazolium iodide, after purification by chromatography with 8:2 heptane/ethyl acetate as the eluent. (*S*)-**2k**: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.25 (s, 6H, SiMe), 0.35 (s, 6H, SiMe), 1.71 (d, ^3J = 7.0 Hz, 3H, NCH*Me*), 1.8−2.1 (4H, H_2C=CHSi), 2.3 (br, 2H, H_2C=CHSi), 3.54 (3H, NMe), 5.86 (br, 1H, N*CH*Me), 6.87 (br, 1H, NCH=), 7.01 (s, $^4J_{H-Pt}$ = 11.5 Hz, 1H, NCH=), 7.2−7.4 (5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.0 (SiMe), 1.4 (SiMe), 20.5 (NCH*Me*), 34.4 ($^1J_{C-Pt}$ = 117 Hz, H_2C=*CH*Si), 36.8 ($^3J_{C-Pt}$ = 45.0 Hz, NMe), 40.1 (H_2C=CHSi), 57.4 (N*CH*Me), 117.8 ($^3J_{C-Pt}$ = 36 Hz, NCH=), 122.5 ($^3J_{C-Pt}$ = 37 Hz, NCH=), 126.6, 127.6, 128.5, 140.9 (C_{Ph}), 183.5 (Pt=C) ppm. $[\alpha]_D$ = −116 (*c* 0.6, $CHCl_3$). The enantiomeric complex (*R*)-**2k** was obtained by the same reaction starting from (*R*)-1-methyl-3-(1-phenylethyl)imidazolium iodide.

***cis*-(*N*,*N*′-Dimethylimidazolylidene)Pt(triphenylphosphine)diiodide (3).** A solution of I_2(25 mg, 0.1 mmol) in toluene (3 mL) was added at 0 °C to a solution of (*N*,*N*-dimethylimidazolylidene)Pt^0(dvtms) complex **1a** (50 mg, 0.1 mmol) in 2 mL of toluene under argon. To the resulting mixture was then added at 0 °C a solution of PPh_3 (30 mg, 0.11 mmol) in toluene (1 mL). The reaction mixture was stirred at room temperature for 4 h. After evaporation of the solvent, the final product was purified by chromatography with a 1:1 heptane/ethyl acetate mixture as the eluent (R_f = 0.2). Yield of **3**: 66 mg (82%). Yellow solid. ^{31}P NMR ($CDCl_3$) δ 8.5 (J_{P-Pt} = 3695 Hz); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (6H, NMe), 6.51 (s, J_{H-Pt} = 10.2 Hz, 2H, NCH=), 7.2−7.6 (15H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.5 (NMe), 121.7 (NCH=), 128.1 (d, J_{C-P} = 11 Hz, CH), 130.8, 134.2 (d, J_{C-P} = 10 Hz, CH) ppm; MS (^{195}Pt) calcd for $C_{23}H_{23}I_2N_2PPtNa$ 829.9234, found 829.9274. Crystals suitable for X-ray diffraction studies were obtained from a CH_2Cl_2/Et_2O solution.

Synthesis of the (Diphosphine)(NHC)PtI_2 Complexes. Typical Procedure: Synthesis of (*N*,*N*′-Dimethylimidazolylidene)-Pt((*R*,*R*)-MeDuPhos))I_2 (4a). A solution of I_2 (25 mg, 0.1 mmol) in toluene (4 mL) was added at 0 °C to a solution of (*N*,*N*-dimethylimidazolylidene)Pt^0(dvtms) complex **1a** (50 mg, 0.1 mmol) in 3 mL of toluene under argon. The resulting mixture was then added at 0 °C to a solution of (*R*,*R*)-MeDuPhos in toluene (3 mL). The reaction mixture was stirred overnight at room temperature, during which time the desired product separated from the mixture as a pale yellow solid. Yield: 84% (72 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (dd, $^3J_{H-P}$ = 16.5 Hz, ^3J = 7.0 Hz, 3H, Me), 1.01 (dd, $^3J_{H-P}$ = 17.0 Hz, ^3J = 7.0 Hz, 3H, Me), 1.1−1.2 (m, 1H, CH_2), 1.21 (dd, $^3J_{H-P}$ = 19.0 Hz, ^3J = 7.0 Hz, 3H, Me), 1.46 (dd, $^3J_{H-P}$ = 19.0 Hz, ^3J = 7.0 Hz, 3H, Me), 1.8−2.0 (m, 2H, CH_2), 2.2−2.6 (5H), 2.7−2.8 (2H), 2.98 (m, 1H, P*CH*Me), 3.79 (s, 3H, NMe), 3.85 (m, 1H, P*CH*Me), 3.89 (s, 3H, NMe), 7.22 (s, 1H, NCH=), 7.50 (s, 1H, NCH=), 7.7−7.8 (3H), 7.99 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (Me), 14.3 (Me), 16.8 (Me), 17.0 (Me), 35.7 (d, J_{C-P} = 7.4 Hz, CH_2), 36.0 (d, CH_2), 36.2 (CH_2), 37.4 (J_{C-Pt} = 16 Hz, CH_2), 38.0−38.5 (P*CH*Me + NMe), 39.3 (J_{C-Pt} = 24 Hz, N-Me), 41.2 (d, $^1J_{C-P}$ = 35 Hz, P*CH*Me), 42.9 (d, $^1J_{C-P}$ = 35 Hz, P*CH*Me), 123.9 (N-CH=), 125.7 (N-CH=), 132.8−133.5 (Ar) ppm; HRMS (^{195}Pt) calcd for $C_{21}H_{37}IN_2P_2PtNa$ 724.1022, found 724.1025. $[\alpha]_D$ = −15 (*c* 0.5, $CHCl_3$).

(*N*,*N*′-Dimethylimidazolylidene)Pt((*R*)-Binap))I_2 (5a). A pale yellow solid was obtained in 47% yield (54 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 3H, NMe), 4.02 (s, 3H, NMe), 6.52 (d, J = 8.5 Hz, 1H), 6.7 (3H), 6.8 (2H), 6.9−7.1 (5H), 7.14 (2H), 7.21 (2H), 7.28 (2H), 7.3−7.4 (7H), 7.47 (d, J = 10 Hz, 1H), 7.5−7.7 (7H), 8.00 (dd, J = 8.5 Hz, J = 2 Hz, 1H), 8.14 (dd, J = 10.5 Hz, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, selected data) δ 38.2 (N-Me), 38.9 (NMe) ppm; HRMS (^{195}Pt) calcd for $C_{49}H_{40}IN_2P_2Pt$ 1040.1359, found 1040.1292. $[\alpha]_D$ = +225 (*c* 0.5, $CHCl_3$).

(*N*,*N*′-Dimethylimidazolylidene)Pt((*R*,*R*)-Et-FerroTane))I_2 (6a). **6a** was isolated as an orange oil that spontaneously separates from the crude reaction mixture and solidifies on standing (94 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.61 (t, ^3J = 7.5 Hz, 3H, Me), 0.78 (t, ^3J = 7.5 Hz, 3H, Me), 1.1−1.3 (m, 4H, CH_2), 1.16 (t, ^3J = 7.5 Hz, 3H, Me), 1.30 (t, ^3J = 7.5 Hz, 3H, Me), 1.7 (m, 1H), 1.9 (m, 2H), 2.2 (m, 1H), 2.2−2.4 (m, 3H), 2.50 (m, J_{H-P} = 38.5 Hz, 1H), 2.6 (m, 1H), 2.75 (m, 1H), 2.95 (m, 1H, PCH), 3.77 (s, 3H, NMe), 3.97 (s, 3H, NMe), 4.14 (m, 1H), 4.24 (1H, CH_{Cp}), 4.36 (1H, CH_{Cp}), 4.64 (1H, CH_{Cp}), 4.66 (1H, CH_{Cp}), 4.70 (1H, CH_{Cp}), 4.84 (2H, CH_{Cp}), 4.94 (1H, CH_{Cp}), 7.42 (s, 1H, NCH=), 7.54 (s, 1H, NCH=); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.7 (d, $^3J_{C-P}$ = 9 Hz, Me), 12.0 (d, $^3J_{C-P}$ = 15 Hz, Me), 13.6 (d, $^3J_{C-P}$ = 13 Hz, Me), 13.8 (d, $^3J_{C-P}$ = 13 Hz, Me), 24.7 (d, $^2J_{C-P}$ = 5 Hz, CH_2), 24.9 (d, $^2J_{C-P}$ = 2 Hz, CH_2), 26.7 (CH_2), 26.8 (CH_2), 34.6 (d, $^2J_{C-P}$ = 17 Hz, CH_2), 35.8 (d, $^2J_{C-P}$ = 16 Hz, CH_2), 38.0, 38.2, 38.4 (PCH), 38.5 (NMe), 39.6 (NMe), 39.6 (d, $^1J_{C-P}$ = 38 Hz, PCH), 42.4 (d, $^1J_{C-P}$ = 40 Hz, PCH), 73.5−76.0 (CH_{Cp}), 124.6

(NCH═), 125.1 (NCH═) ppm; HRMS (^{195}Pt, ^{57}Fe) calcd for $C_{29}H_{44}FeIN_2P_2Pt$ 860.1005, found 860.0983. $[\alpha]_D = -203$ (*c* 0.5, $CHCl_3$).

(*N*,*N*′-Dimethylimidazolylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (7a). 7a was obtained as a colorless solid that precipitates from the crude reaction mixture (81 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04−1.13 (6H, Me), 2.3 (m, 1H, PCH), 2.8 (m, 1H, PCH), 2.90 (s, 3H, NMe), 3.47 (s, 3H, NMe), 6.83 (s, 1H, NCH═), 7.1−7.8 (m, 19H), 7.9 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.4 (d, $^2J_{C-P} = 16$ Hz, Me), 14.0 (d, $^2J_{C-P} = 16$ Hz, Me), 34.3 (dd, $^1J_{C-P} = 37$ Hz, $^2J_{C-P} = 12$ Hz, PCH), 36.9 (NMe), 37.0 (dd, $^1J_{C-P} = 38$ Hz, $^2J_{C-P} = 15$ Hz, PCH), 38.0 ($J_{C-Pt} = 25$ Hz, NMe), 123.9 ($J_{C-Pt} = 27$ Hz, NCH═), 124.0 ($J_{C-Pt} = 27$ Hz, NCH═) ppm; HRMS (^{195}Pt) calcd for $C_{33}H_{36}IN_2P_2Pt$ 844.1046, found 844.1021. $[\alpha]_D = +142$ (*c* 0.5, $CHCl_3$).

(*N*,*N*′-Dicyclohexylimidazolylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (7b). 7b was isolated as a pale yellow solid that spontaneously separates from the crude reaction mixture (105 mg, 96% yield). The solid was recrystallized from a dichloromethane/ether mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.14 (1H, NCH*CH*$_2$), 0.7−1.8 (m, 17H), 1.08 (dd, $^3J_{H-P} = 15$ Hz, $J = 7$ Hz, 3H, Me), 1.20 (dd, $^3J_{H-P} = 12.9$ Hz, $J = 6.9$ Hz, 3H, Me), 2.25 (m, 2H), 2.49 (d, $J = 12$ Hz, 1H), 3.03 (m, 1H), 3.91 (m, 1H, NCH), 4.23 (m, 1H, NCH), 6.88 (s, 1H, NCH═), 7.10 (s, 1H, NCH═), 7.1−7.2 (2H), 7.5−8.0 (18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 (d, $^2J_{C-P} = 17$ Hz, Me), 13.9 (d, $^2J_{C-P} = 17$ Hz, Me), 24.7 (CH_2), 25.0 (CH_2), 25.3 (CH_2), 25.6 (CH_2), 26.1 (CH_2), 31.1 (CH_2), 33.1 (CH_2), 33.5 (CH_2), 34.8 (dd, $^1J_{C-P} = 33$ Hz, $^2J_{C-P} = 10$ Hz, PCH), 37.2 (dd, $^1J_{C-P} = 40$ Hz, $^2J_{C-P} = 16$ Hz, PCH), 59.8 (NCH), 60.3 (NCH), 119.5 (d, $^4J_{C-P} = 5.7$ Hz, NCH═), 119.9 (d,$^4J_{C-P} = 5.6$ Hz, NCH═), 160.7 (dd, $^2J_{C-P} = 139$ Hz, $^2J_{C-P} = 10$ Hz, *C*═Pt) ppm; HRMS (^{195}Pt) calcd for $C_{43}H_{52}IN_2P_2Pt$ 980.2298, found 980.2073. $[\alpha]_D = +90$ (*c* 0.5, $CHCl_3$). Crystals suitable for X-ray diffraction studies have been grown from CH_2Cl_2/AcOEt.

(*N*,*N*′-Diphenylimidazolylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (7c). The synthesis of **7c** was performed at a 0.05 mmol scale. **7c** was obtained in 70% yield (38 mg) after chromatography on silica gel with 95:5 CH_2Cl_2/MeOH as the eluent ($R_f = 0.3$). Colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (dd, $^3J_{C-P} = 15.0$ Hz, $J = 6.5$ Hz, 3H, Me), 0.94 (dd, $^3J_{C-P} = 12.5$ Hz, $J = 6.5$ Hz, 3H, Me), 1.90 (m, 1H, PCH), 2.33 (m, 1H, PCH), 6.9−7.0 (4H), 7.1 (4H), 7.2−7.4 (11H), 7.5−7.7 (6H), 7.7−7.8 (5H), 7.81 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, selected data) δ 13.3 (d, $^2J_{C-P} = 16$ Hz, Me), 13.7 (br d, Me), 34.4 (br dd, PCH), 36.6 (br dd, PCH), 125.3 (NCH═), 125.5 (NCH═), 125.8 (CH), 126.6 (CH), 128.6−135.8, 138.0 (C), 138.7 (C) ppm; HRMS (^{195}Pt) calcd for $C_{43}H_{40}IN_2P_2Pt$ 968.1359, found 968.1266. $[\alpha]_D = +349$ (*c* 0.5, $CHCl_3$).

(1-Benzyl-3-methylimidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8b,b′). Complex **8** was obtained as a 1:1 mixture of epimers. It was isolated as a pale yellow solid that spontaneously separates from the crude reaction mixture (94 mg, 90% yield). ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.1 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 2177$ Hz), 38.0 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 2169$ Hz), 37.7 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 3217$ Hz), 37.4 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 3225$ Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.1−1.2 (Me), 2.34 (m, PCH), 2.93 (m, PCH), 2.98 (NMe), 3.11 (d, $^2J = 14.0$ Hz, CH_2Ph), 3.55 (NMe), 4.62 (d, $^2J = 14.0$ Hz, CH_2Ph), 5.19 (d, $^2J = 14.5$ Hz, CH_2Ph), 5.28 (d, $^2J = 14.5$ Hz, CH_2Ph), 6.44 (s), 6.63 (s), 6.87 (s), 7.0−8.0 (Ar) ppm; HRMS (^{195}Pt) calcd for $C_{39}H_{40}IN_2P_2Pt$ (M − I) 920.1359, found: 920.1282.

(1-*tert*-Butyl-3-methylimidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8c,c′). A 1:1 mixture of the diastereomeric **8c** and **8c′** was obtained after separation of the crude reaction mixture by column chromatography (CH_2Cl_2/EtOH, 98:2, $R_f = 0.2$). Yield: 90 mg, 89%. ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.3 (d, $J_{P-P} = 15$ Hz, $J_{P-Pt} = 2165$ Hz), 37.1 (d, $J_{P-P} = 15$ Hz, $J_{P-Pt} = 3393$ Hz) and 37.0 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 2199$ Hz), 36.0 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 3310$ Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.1−1.4 (MeCH), 1.23 (s, CMe_3), 1.53 (s, CMe_3), 2.02 (m, CHMe), 2.22 (m, CHMe), 3.22 (s, NMe), 3.52 (CHMe), 3.60 (m, CHMe), 3.63 (s, NMe), 6.70 (NCH═), 7.00 (NCH═), 7.11 (NCH═), 7.19 (NCH═), 7.3−7.7 (Ph), 8.2 (Ph) ppm; HRMS (^{195}Pt) calcd for $C_{36}H_{42}IN_2P_2Pt$ (M − HI) 886.1516, found 886.1508.

(1-(2,6-Diisopropylphenyl)-3-methylimidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8d,d′). This compound was obtained in 71% yield (79 mg) as a yellow solid that separates from the reaction mixture. The solid contains a 8:2 mixture of **8d**+**8d′**. The filtrate contains small amounts of **8d**+**8d′**, with **8d′** being the major epimer. MS (ESI) *m*/*z* 991 (M − I + H, 86), 748 (100). Spectral data for **8d** (from the mixture): ^{31}P NMR (121 MHz, $CDCl_3$) δ 36.3 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 2110$ Hz), 32.0 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 3390$ Hz); ^{1}H NMR (500 MHz, $CDCl_3$, selected data) δ 0.36 (d, $^3J = 7.0$ Hz, 3H, Me), 1.0 (6H, Me), 1.1−1.2 (6H, Me), 1.32 (d, $^3J = 5.5$ Hz, 3H, Me), 3.65 (3H, NMe) ppm.

Stirring of the **8d**+**8d′** mixture at room temperature for 48 h in $CDCl_3$ led to conversion of **8d** into **8d′** (>9:1). Spectral data for **8d′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.6 (d, $J_{P-P} = 17$ Hz, $J_{P-Pt} = 2182$ Hz), 36.6 (d, $J_{P-P} = 17$ Hz, $J_{P-Pt} = 3368$ Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (d, $^3J = 6.6$ Hz, 3H, Me), 0.49 (d, $^3J = 6.6$ Hz, 3H, Me), 0.72 (d, $^3J = 6.6$ Hz, 3H, Me), 0.86 (dd, $^3J_{H-P} = 12.9$ Hz, $^3J = 6.9$ Hz, 3H, Me), 0.95 (dd, $^3J_{H-P} = 14.7$ Hz, $^3J = 6.9$ Hz, 3H, Me), 1.01 (d, $^3J = 6.6$ Hz, 3H, Me), 1.8−2.0 (2H), 2.57 (m, 1H, PCHMe), 3.32 (s, 3H, NMe), 3.68 (m, 1H, $CHMe_2$), 6.77 (d, $^3J = 0.9$ Hz, 1H, NCH═), 6.92 (1H, NCH═),6.9−7.8 (Ar); ^{13}C NMR (75 MHz, $CDCl_3$, selected data) δ 13.6 (PCH*Me*), 21.9 (Me), 22.6 (Me), 25.4 (Me), 27.6 (Me), 28.0 (Me), 28.7 (Me), 39.7 (NMe) ppm. $[\alpha]_D = +135$ (*c* 0.5, $CHCl_3$).

(1-Mesityl-3-methylimidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8e,e′). This compound was obtained in 88% yield (94 mg) as a pale yellow solid that separates from the reaction mixture. The solid contains a 95:5 mixture of **8e**+**8e′**. MS (ESI) *m*/*z* 949 (M − I + H, 100%). Spectral data for **8e** (from the 95:5 mixture with **8e′**): ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.4 (d, $J_{P-P} = 17$ Hz, $J_{P-Pt} = 2216$ Hz), 35.3 (d, $J_{P-P} = 17$ Hz, $J_{P-Pt} = 3373$ Hz); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.0−1.1 (6H, PCHMe), 1.25 (3H, Me), 1.95 (s, 3H, Me), 2.28 (2H, PCHMe), 2.35 (s, 3H, Me), 3.58 (s, 3H, NMe), 6.79 (s, 1H), 6.84 (s, 1H), 6.94 (s, 1H), 7.1−7.8 (20H, Ph), 7.94 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, recorded at −20 °C) δ 13.5−13.9 (Me), 18.4 (Me), 21.1 (Me), 21.5 (Me), 33.9 (PCHMe), 35.3 (CHMe), 39.4 (NMe), 164.4 ($J_{Pt-C} = 153$ Hz, Pt═C) ppm. When the sample of **8e** (+**8e′**) was heated at 50 °C in $CDCl_3$, clean conversion of **8e** into **8e′** was observed. After 48 h heating, a 15:85 mixture of **8e**+**8e′** was obtained. Spectral data for **8e′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.8 (d, $J_{P-P} = 17$ Hz, $J_{P-Pt} = 2161$ Hz), 36.4 (d, $J_{P-P} = 17$ Hz, $J_{P-Pt} = 3350$ Hz); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (dd, $^3J_{H-P} = 14.7$ Hz, $J = 6.9$ Hz, 3H, Me), 1.00 (dd, $^3J_{H-P} = 12.9$ Hz, $^3J = 6.9$ Hz, 3H, Me), 1.19 (s, 3H, Me), 1.89 (m, 1H, PCHMe), 2.17 (s, 3H, Me), 2.35 (s, 3H, Me), 2.88 (m, 1H, PCHMe), 3.14 (s, 3H, NMe), 6.42 (s, 1H), 6.83 (s, 1H), 6.89 (s, 1H), 7.0−7.8 (Ar) ppm.

(1-Benzyl-3-*tert*-butylimidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8f,f′). The solid that separates from the reaction mixture was filtered and purified by filtration through a short silica gel column with CH_2Cl_2/EtOH as the eluent. Yield: 87 mg (80%) of a 91:9 mixture of **8f**+**8f′**. Spectral data for the major epimer **8f** are the following: ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.8 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 2198$ Hz), 36.0 (d, $J_{P-P} = 16$ Hz, $J_{P-Pt} = 3306$ Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (dd, $^3J_{H-P} = 15.0$ Hz, $J = 6.0$ Hz, 3H, Me), 1.23 (m, 3H, Me), 1.57 (s, 9H, CMe_3), 2.28 (m, 1H, PCHMe), 3.43 (d, $^2J = 14.0$ Hz, 1H, CH_2Ph), 3.55 (m, 1H, PCHMe), 5.74 (d, $^2J = 14.0$ Hz, 1H, CH_2Ph), 6.35 (s, 1H, NCH═), 7.12 (2H), 7.16 (s, 1H), 7.25 (3H), 7.4−7.8 (18H, Ph), 8.22 (2H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3 (d, $^2J_{C-P} = 17$ Hz, Me), 15.0 (d, $^2J_{C-P} = 20$ Hz, Me), 32.2 (C*Me*$_3$), 35.8 (dd, $^1J_{C-P} = 35$ Hz, $^2J_{C-P} = 13$ Hz,

PCH), 40.2 (dd, $^1J_{C-P}$ = 38 Hz, $^2J_{C-P}$ = 14 Hz, PCH), 54.8 (*CH*$_2$Ph), 59.3 (N*C*Me$_3$), 121.0 (NCH), 121.6 (NCH) ppm; HRMS (^{195}Pt) calcd for $C_{42}H_{46}IN_2P_2Pt$ (M − I) 962.1829, found 962.1838. Minor epimer **8f′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 39.8 (d, J_{P-P} = 15 Hz), 37.6 (d, J_{P-P} = 15 Hz) ppm.

(1-Benzyl-3-phenylimidazoly-2-lidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8g,g′). A 1:1 mixture of **8g**+**8g′** was obtained after chromatography on a silica gel column with 98:2 CH_2Cl_2/EtOH as the eluent: 70 mg, 63% yield. ^{31}P NMR (121 MHz, $CDCl_3$, selected data) δ 39.2 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2213 Hz), 37.5 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2190 Hz), 37.2 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3227 Hz), 35.6 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3278 Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (dd, $^3J_{H-P}$ = 15.0 Hz, J = 6.5 Hz, 2 Me), 1.04 (dd, $^3J_{H-P}$ = 12.5 Hz, J = 6.5 Hz, Me), 1.10 (dd, $^3J_{H-P}$ = 13.0 Hz, J = 7.0 Hz, Me), 2.01 (m, PCH), 2.22 (m, PCH), 2.37 (m, PCH), 3.07 (m, PCH), 3.28 (d, ^2J = 14.0 Hz, CH_2Ph), 4.78 (d, ^2J = 14.0 Hz, CH_2Ph), 5.53 (d, ^2J = 14 Hz, CH_2Ph), 5.60 (d, ^2J = 14 Hz, CH_2Ph); MS(ESI) *m*/*z* 982 (M − I, 100%).

(1-Benzyl-3-cyclohexylimidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8h,h′). This compound was obtained in 56% yield (62 mg) as a 1:1 mixture of diastereomers after column chromatography with CH_2Cl_2/EtOH as the eluent (R_f = 0.3). Colorless solid. ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.8 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2168 Hz), 38.4 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2152 Hz), 37.8 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3218 Hz), 36.8 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3250 Hz); ^{1}H NMR (500 MHz, $CDCl_3$, selected data) δ −0.01 (br d, J = 11 Hz), 2.96 (m, PCH), 3.02 (d, ^2J = 14.0 Hz, CH_2Ph), 3.12 (m, PCH), 3.98 (NCH), 4.32 (NCH), 4.64 (d, ^2J = 14.5 Hz, CH_2Ph), 5.20 (d, ^2J = 14.5 Hz, CH_2Ph), 5.31 (d, ^2J = 14.0 Hz, 1H, CH_2Ph), 6.58 (s, 1H), 6.70 (s, 1H), 6.83 (s, 1H) ppm; HRMS (^{195}Pt) calcd for $C_{44}H_{48}IN_2P_2Pt$ (M − I) 988.1985, found 988.1987.

(1-Cyclohexyl-3-(1-naphthylmethyl)imidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8i,i′). This compound was obtained in 76% yield (88 mg) as a 1:1 mixture of epimers. The yellow solid separates from the crude reaction mixture. Pure (R_a)-**8i′** was isolated by slow crystallization in $CHCl_3$. Spectral data for **8i′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.1 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2157 Hz), 36.3 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3259 Hz); ^{1}H NMR (500 MHz, CD_2Cl_2) δ −0.1 (br s, 1H), 0.98 (dd, $^3J_{H-P}$ = 15.0 Hz, J = 6.5 Hz, 3H, Me), 1.05 (dd, $^3J_{H-P}$ = 12.5 Hz, J = 6.5 Hz, 3H, Me), 0.9−1.1 (4H), 1.2 (m, 1H), 1.60−1.65 (2H), 1.79 (br d, $J \approx$ 12 Hz, 1H), 2.28 (m, 1H, PCH), 2.52 (br d, $J \approx$ 12 Hz, 1H), 2.61 (m, 1H, PCH), 3.98 (br, 1H, NCH), 5.00 (d, ^2J = 15.0 Hz, 1H, CH_2Naph), 5.61 (d, ^2J = 14.5 Hz, 1H, CH_2Naph), 6.44 (s, 1H), 6.74 (s, 1H), 6.91 (d, J = 7.0 Hz, 1H), 7.2−7.8 (Ar); ^{13}C NMR (125 MHz, CD_2Cl_2, selected data) δ 13.4−13.9 (CHMe), 25.4 (CH_2), 26.1 (CH_2), 26.6 (CH_2), 31.6 (CH_2), 33.8 (CH_2), 34.7 (P*C*HMe), 37.1 (P*C*HMe), 53.3 (NCH_2), 61.2 (NCH), 119.6 (NCH═), 122.4 (NCH═) ppm; HRMS (^{195}Pt) calcd for $C_{48}H_{50}IN_2P_2Pt$ (M − I): 1038.2142. Found: 1038.2115. $[\alpha]_D$ = +18 (*c* 0.5, $CHCl_3$). Crystals suitable for X-ray diffraction studies have been obtained from $CHCl_3$. **8i′** displays an (*R*)-axial configuration. A small amount of pure **8i** (3 mg) was isolated from the filtrate by crystallization. Spectral data for **8i**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.6 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2168 Hz), 37.1 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3220 Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.8−1.9 (16H), 2.4 (br m, 1H, PCH), 3.00 (br m, 1H, PCH), 3.65 (d, ^2J = 14.5 Hz, 1H, CH_2Naph), 4.37 (1H, NCH), 5.62 (d, ^2J = 14.5 Hz, 1H, CH_2Naph), 6.42 (s, 1H), 7.0−8.0 (Ar) ppm.

(1-*tert*-Butyl-3-(1-naphthylmethyl)imidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8j,j′). This complex was obtained in 53% yield (60 mg) as a 91:9 mixture of two epimers. The solid that separates from the reaction mixture was purified by column chromatography with 95:5 CH_2Cl_2/EtOH as the eluent. Pale yellow solid. Spectral data for the major epimer **8j** (from the mixture): ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.4 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2195 Hz), 36.0 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3298 Hz); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (dd, $^3J_{H-P}$ = 15.0 Hz, J = 6.5 Hz, 3H, Me), 1.23 (dd, $^3J_{H-P}$ = 14 Hz, J = 7.0 Hz, 3H, Me), 1.59 (9H, CMe_3), 2.34 (1H, PCH), 3.48 (1H, PCH), 4.05 (d, ^2J = 14.5 Hz, 1H, CH_2Naph), 6.00 (d, ^2J = 14.5 Hz, 1H, CH_2Naph), 6.24 (s, 1H), 6.99 (d, J = 7.0 Hz, 1H), 7.1−7.9 (Ar), 8.19 (2H); ^{13}C NMR (125 MHz, $CDCl_3$, selected data) δ 14.4 (d, $^2J_{C-P}$ = 16 Hz, Me), 14.8 (d, $^2J_{C-P}$ = 13 Hz, Me), 32.2 (C*Me*$_3$), 35.8 (dd, $^1J_{C-P}$ = 35 Hz, $^2J_{C-P}$ = 11 Hz, PCH), 39.7 (dd, $^1J_{C-P}$ = 40 Hz, $^2J_{C-P}$ = 14 Hz, PCH), 52.7 (CH_2Naph), 59.4 (*C*Me$_3$) ppm; HRMS (^{195}Pt) calcd for $C_{46}H_{48}IN_2P_2Pt$ 1012.1985, found 1012.2053. Minor epimer **8j′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 40.2 (d, J_{P-P} = 15 Hz), 37.8 (d, J_{P-P} = 15 Hz) ppm.

((*S*)-1-Methyl-3-(1-phenylethyl)imidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8k,k′). This compound was obtained in 93% yield (98 mg of an orange solid that spontaneously separates from the reaction mixture) from (*S*)-**2k**, as a 70:30 mixture of two epimers. Spectral data for the major epimer **8k** (from the mixture): ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.1 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2162 Hz), 37.8 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3213 Hz); ^{1}H NMR (500 MHz, $CDCl_3$, selected data) δ 1.04 (d, ^3J = 7.0 Hz, 3H, *Me*CHPh), 1.1−1.2 (6H, Me), 2.38 (1H, PCH), 3.00 (s, 3H, NMe), 3.0 (1H, PCH), 5.70 (q, ^3J = 6.5 Hz, 1H, NCHPh), 6.79 (s, 1H), 6.88 (s, 1H) ppm; HRMS (^{195}Pt) calcd for $C_{40}H_{42}IN_2P_2Pt$ 934.1516, found 934.1490. Minor epimer **8k′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.5 (d, J_{P-P} = 16 Hz), 35.4 (d, J_{P-P} = 16 Hz) ppm; ^{1}H NMR (500 MHz, $CDCl_3$, selected data) δ 1.63 (d, ^3J = 7.0 Hz, 3H, *Me*CHPh), 2.3 (1H, PCH), 2.8 (1H, PCH), 3.49 (s, 3H, NMe), 5.62 (br q, 1H, NCHPh) ppm.

((*R*)-1-Methyl-3-(1-phenylethyl)imidazol-2-ylidene)Pt((*S*,*S*)-Chiraphos))I$_2$ (8l,l′). This compound was obtained from (*R*)-**2k** in 90% yield (95 mg) as a yellow solid that separates from the reaction mixture. The solid contains a 77:23 mixture of **8l**+**8l′**. Spectral data for the major epimer **8l** (from the mixture): ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.1 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 2150 Hz), 36.5 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3228 Hz); ^{1}H NMR (500 MHz, $CDCl_3$, selected data) δ 0.88 (d, ^3J = 7.0 Hz, 3H, *Me*CHPh), 1.0−1.3 (6H, Me), 2.13 (m, 1H, *CH*Me), 3.24 (m, *CH*Me), 3.57 (s, 3H, NMe), 5.33 (br q, NCHPh) ppm. Minor epimer **8l′**: ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.1 (d, J_{P-P} = 13 Hz), 37.8 (d, J_{P-P} = 13 Hz); ^{1}H NMR (300 MHz, $CDCl_3$, selected data) δ 1.0−1.2 (6H, Me), 1.75 (d, ^3J = 7 Hz, 3H, MeCHPh), 2.30 (m, 1H, *CH*Me), 3.00 (NMe), 5.66 (br q, 1H, NCHPh); HRMS (^{195}Pt) calcd for $C_{40}H_{42}IN_2P_2Pt$ 934.1516, found 934.1464.

Enyne Cycloisomerization Reaction. *N*-Allyl-*N*-(3-phenylpropyn-2-yl)-4-methylbenzenesulfonamide was prepared as described.[34]

The (NHC)(diphosphine)PtI$_2$ complex **I** (6.4×10^{-3} mmol) was dissolved in 0.5 mL of CH_2Cl_2. $AgBF_4$ (3 mg, 0.016 mmol), *N*-allyl-*N*-(3-phenylpropyn-2-yl)-4-methylbenzenesulfonamide **9** (52 mg, 0.16 mmol), and toluene (4.5 mL) were added successively. The resulting mixture was heated at 90 °C for 20 h. After evaporation of the solvents, conversion rates were measured by ^{1}H NMR on the crude mixture. 6-Phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[4.1.0]hept-4-ene, **10**,[2a] was isolated by flash chromatography on a silica gel column (heptane/ethyl acetate, 90:10). Enantiomeric excesses were determined by HPLC: Chiralpak IC column, eluent hexane/methyl *tert*-butyl ether/2-propanol (75/20/5); flow 1 mL/min, retention times 20.0 and 21.4 min (major). Samples for HPLC may contain some residual starting material, which elutes with a retention time of 25.1 min under these conditions. **10**: $[\alpha]_D$ = −67 (*c* 0.5, $CHCl_3$) for a 70% ee sample.

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Computational Methods. Calculations have been carried out with the Gaussian03 package of programs.[35] Full geometry optimizations for all compounds were carried out with the use of the B3LYP[36] density functional level of theory and with the following basis set. A 6-31G(d,p) basis set was employed for the first- (H), second- (C, N), and third-row (P) elements. The standard LANL2DZ small-core relativistic effective-core potential with a valence shell of double-ζ quality was used on platinum[37] and iodine.[38] The validity of this level of calculation has been demonstrated before in studies on Pt(II) complexes.[10] Each stationary point has been characterized with frequency analysis and shows the correct number of negative eigenvalues (0 for a local minimum and one for a transition state). The Gibbs free energy corresponding to a given pathway was deduced from the equation

$$\Delta G = \Delta E_{\text{elec}} + \Delta \text{ZPE} + \Delta E_{\text{T}} - T\Delta S \qquad (1)$$

with ΔE_{elec}, ΔZPE, ΔE_{T}, and ΔS being the differences in the electronic energy, zero-point vibrational energy, thermal energy, and entropy between the products and the reactants, respectively.

Supporting Information Available: ^{13}C NMR or ^{1}H NMR spectra for the new Pt(0) complexes **1** and **2**. ^{31}P, ^{1}H, and ^{13}C NMR spectra for the Pt(II) complexes **3**−**8**. X-ray crystallographic data (CIF files) for complexes **3a**, **7b**, and **8i′**. Chiral HPLC traces for the starting materials and products of the cycloisomerization reaction. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as nos. CCDC-696746 (**3a**), CCDC-696747 (**7b**), and CCDC-696748 (**8i′**). Detailed optimized geometries and free energies for the calculated structures (Table 4). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800743R

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