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N-Heterocyclic Carbenes in the Synthesis of Axially Chiral Square-Planar Platinum Complexes

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Summary: A new synthetic approach allows access to axially chiral square-planar platinum(II) complexes by combining an enantiomerically pure diphosphine (DuPHOS, BPE, or Chiraphos) and an unsymmetric NHC ligand. The same approach proved to be highly stereoselective when applied to the synthesis of a chiral triazolylidene−dppe mixed complex.

Organometallic complexes with inherent chirality, including chiral-at-metal species, are actively sought as potential catalysts for enantioselective transformations.[1] Their use could represent an interesting alternative to the unique strategy developed so far, based on the association of a chiral organic ligand and a transition metal. Unlike chiral octahedral and tetrahedral complexes, which have been intensively investigated,[2] square-planar species are still rare. The achiral square-planar coordination mode may give rise to chiral structures[3] in special instances where the upper/bottom faces of the coordination plane are differentiated. This is the case for helically distorted complexes[4] and also for axially chiral complexes (Figure 1) where a planar, nonsymmetric ligand (**a**−**b**) is bound orthogonally to the coordination plane and two different ligands (L_1, L_2) are cis-coordinated to the first one. The most extensive work in this field has been performed by Enders,[5] by using nonsymmetric N-heterocyclic carbenes as the orthogonally oriented ligands in square-planar palladium and rhodium complexes (Figure 1).[6] The palladium complexes **B** bearing chiral NHC moieties were isolated as mixtures of epimers with moderate diastereomeric excess (de = 35%), while the rhodium complexes **C** could be formed in 36−97% de. The rhodium complexes were evaluated as catalysts in the hydrosilylation of ketones.

More recently, analogous square-planar rhodium and iridium complexes bearing carbene[7] or other[8] ligands have been mentioned briefly.

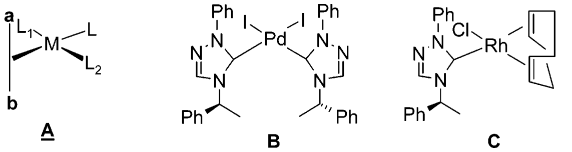

Figure 1. Square-planar, axially chiral complexes: general structural features and selected examples.[6a,b]

Herein, we report a new protocol for the synthesis of the first axially chiral square planar platinum(II) complexes of type **A** based on carbene−diphosphine pairs (M = Pt, **a**−**b** = unsymmetrically substituted NHC ligand, L_1−L = chelating diphosphine). The use of chelating diphosphines as ancillary ligands has been envisioned by considering that tightly bonded ligands may be a key feature to ensure, together with the hindered rotation around the carbene carbon−metal bond, the configurational stability of these axially chiral complexes.[9] The configurational stability of the metal center has been considered, as well as the potential use of these complexes as catalysts for a model enyne cycloisomerization reaction.[10]

Our straightforward synthetic approach to the desired NHC−diphosphine platinum(II) complexes is typified in Scheme 1. It starts from the well-known, easily available (NHC)Pt(divinyltetramethyldisiloxane) complexes,[11] which have been developed by Markó as efficient catalysts for hydrosilylation reactions.[12] Oxidative addition of iodine to these Pt(0) complexes in toluene at 0 °C generates Pt(II) complexes which are reacted in situ with bidentate phosphines[13] to afford the square-planar cationic complexes in high yields.

In the reaction of Scheme 1, after oxidation of the metal with iodine, the labile olefin is easily replaced by 1,2-bis(diphenylphosphino)ethane (dppe) and the desired complex **2** is obtained in 82% yield as a yellow solid which separates spontaneously from the reaction mixture. The ^{31}P NMR pattern is diagnostic of the given structure: two nonequivalent phosphorus signals at δ 39.5 and 40.1 ppm (J_{P-P} = 5 Hz) display

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(1) (a) Fontecave, M.; Hamelin, O.; Ménage, S. *Top. Organomet. Chem.* **2005**, *15*, 271−288. (b) Faller, J. W.; Fontaine, P. P. *J. Organomet. Chem.* **2006**, *691*, 5798−5803. (c) Faller, J. W.; Fontaine, P. P. *Organometallics* **2005**, *24*, 4132−4138. (d) Carmona, D.; Medrano, R.; Dobrinovich, I. T.; Lahoz, F. J.; Ferrer, J.; Oro, L. A. *J. Organomet. Chem.* **2006**, *691*, 5560−5566. (e) Corberan, R.; Lillo, V.; Mata, J. A.; Fernandez, E.; Peris, E. *Organometallics* **2007**, *26*, 4350−4353.

(2) (a) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194−1208. (b) Ganter, C. *Chem. Soc. Rev.* **2003**, *32*, 130−138.

(3) Cingi Biagini, M.; Ferrair, M.; Lanfranchi, M.; Marchiò, L.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1575−1580.

(4) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 303−322.

(5) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*−*618*, 70−80.

(6) (a) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483−1488. (b) Enders, D.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3571−3574. (c) Enders, D.; Gielen, H.; Runsink, J.; Breuer, K.; Brode, S.; Boehn, K. *Eur. J. Inorg. Chem.* **1998**, 913−919.

(7) (a) Bolm, C.; Kesselgruber, M.; Raabe, G. *Organometallics* **2002**, *21*, 707−710. (b) Chen, D.; Banphavichit, V.; Reibenspies, J.; Burgess, K. *Organometallics* **2007**, *26*, 855−859. (c) Bon, R. S.; de Kanter, F. J. J.; Lutz, M.; Spek, A. L.; Jahnke, M. C.; Hahn, F. E.; Groen, M. B.; Orru, R. V. A. *Organometallics* **2007**, *26*, 3639−3650. (d) Faller, J. W.; Fontaine, P. P. *Organometallics* **2006**, *25*, 5887−5893.

(8) Faller, J. W.; Milheiro, S. C.; Parr, J. *J. Organomet. Chem.* **2006**, *691*, 4945−4955.

(9) Alcock, N. W.; Brown, J. M.; Pérez-Torrente, J. J. *Tetrahedron Lett.* **1992**, *33*, 389−392.

(10) Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785−6786.

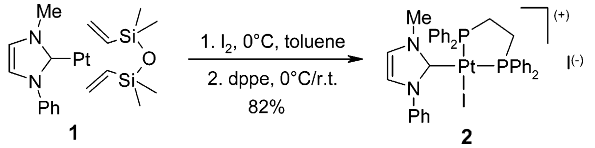
(11) (a) Buisine, O.; Berthon-Gelloz, G.; Brière, J.-F.; Stérin, S.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P.; Markó, I. E. *Chem. Commun.* **2005**, 3856−3858. (b) Berthon-Gelloz, G.; Buisine, O.; Brière, J.-F.; Michaud, G.; Stérin, S.; Mignani, G.; Tinant, B.; Declercq, J.-P.; Chapon, D.; Markó, I. E. *J. Organomet. Chem.* **2005**, *690*, 6156−6168.

(12) (a) Markó, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P. *Science* **2002**, *298*, 204−206. (b) De Bo, G.; Berthon-Gelloz, G.; Tinant, B.; Markó, I. E. *Organometallics* **2006**, *25*, 1881−1890.

(13) Monodentate phosphines also react with the Pt(II) complex to afford either *cis*-(NHC)Pt(phosphine)I_2 or (NHC)Pt(phosphine)$_2I_2$ complexes.

10.1021/om700839y CCC: $37.00

Scheme 1. Synthesis of the Square-Planar dppe−Pt(II) Complex 2

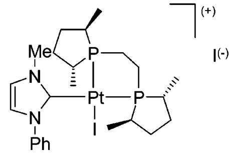
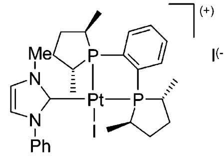
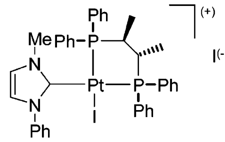


J_{P-Pt} couplings of 3311 and 2260 Hz, respectively. The larger coupling has been assigned to the phosphorus atom trans to iodine. These values are consistent with coupling trends noted for *cis*- and *trans*-PtI_2(phosphine)$_2$ complexes.[14] In the ^{13}C NMR spectrum, the carbene carbon at 164 ppm shows distinct couplings to the trans and cis phosphorus atoms, of 138[15] and 8 Hz, respectively.

Thus, reaction in Scheme 1 typifies a general and convenient approach to platinum(II)−NHC complexes, allowing the stepwise, controlled introduction of a carbene and a phosphine ligand. It complements previously known methods which mainly concern the synthesis of either bis-carbene platinum complexes[16] or complexes of carbenes bearing additional chelating phosphorus or nitrogen functions.[17] Some examples of Pt(II) complexes have been reported previously where both a carbene and a neutral two-electron ligand (olefin,[18] CO,[19] pyridine,[20] or phosphine[19b,20,21]) are present.[22]

With the aim of evidencing the possible configurational stability of Pt complexes of this class, we then carried out the reaction in Scheme 1 with several commercially available chiral bidentate phosphines, instead of dppe, in order to generate the corresponding platinum complexes as diastereomeric pairs. Selected representative examples are discussed hereafter: Table 1 summarizes the yields and ^{31}P NMR data for the complexes obtained by combining *N*-methyl-*N*-phenylimidazolylidene and (*R*,*R*)-Me-BPE, (*R*,*R*)-Me-DuPHOS, or (*S*,*S*)-Chiraphos.

Table 1. Platinum(II) Complexes Bearing NHC and Chiral Diphosphine Ligands[a]

Platinum complexes; yield			^{31}P NMR: δ (J_{P-Pt})[J_{P-P}]
	57%	(R_a)-**3a**	65.9 (2199 Hz) 68.6 (3209 Hz) [4 Hz]
		(S_a)-**3b**	60.3 (2210 Hz) 67.1 (3164 Hz) [5 Hz]
	58%	(R_a)-**4a**	64.3 (2194 Hz) 64.7 (3225 Hz) [6 Hz]
		(S_a)-**4b**	63.3 (2214 Hz) 64.4 (3233 Hz) [5 Hz]
	84%	**5a**	35.2 (3290 Hz) 37.1 (2180 Hz) [16 Hz]
		5b	37.1 (3237 Hz) 38.7 (2214 Hz) [16 Hz]

[a] NMR spectra in $CDCl_3$. Isomer ratios of about 1:1.

Under the same reaction conditions as in Scheme 1, (*R*,*R*)-Me-BPE afforded a mixture of two diastereomeric platinum complexes in a 1:1 ratio and 57% total yield. Diastereomer **3a** was obtained in pure form by crystallization from dichloromethane−ethyl acetate. Its structure was established by NMR and X-ray diffraction studies. An ORTEP drawing as well as selected bond angles and distances for complex **3a** are given in Figure 2. In the solid-state structure of complex **3a**, platinum displays a square-planar coordination, with the carbene ligand adopting a distorted orthogonal position with respect to the coordination plane: P(2)−Pt−C(3)−N(1) dihedral angle −106.2(5)°. The Pt−C(3) distance of 2.051(6) Å is similar to that found in other platinum(II)−NHC complexes.[17b,18b,19b]

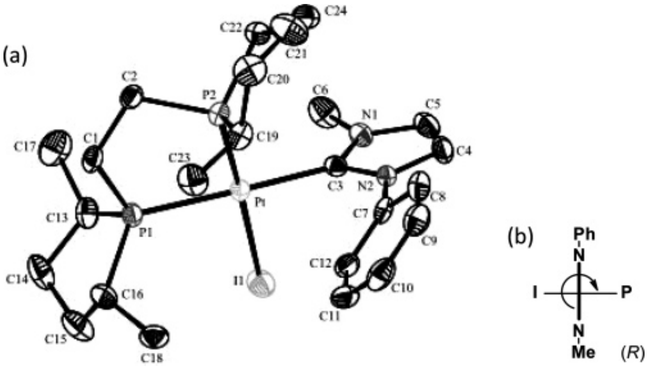


Figure 2. (a) ORTEP drawing of complex **3a**. The I^- counterion has been omitted for clarity. Selected bond distances (Å) for **3a** are as follows: Pt−C(3) = 2.051(6), Pt−P(1) = 2.2886(18), Pt−P(2) = 2.2466(19), Pt−I = 2.6745(12), C(3)−N(1) = 1.349(8), C(3)−N(2) = 1.352(8), C(3)−N(1) = 1.349(8). Selected bond angles (deg): P(2)−Pt−P(1) = 85.50(6), P(1)−Pt−I = 92.53(5), C(3)−Pt−I = 86.45(18), C(3)−Pt−P(2) = 95.55(18). (b) Stereochemical descriptor.

X-ray data allowed assignment of an *R* axial configuration (R_a) to the **3a** diastereoisomer. (*Note*: The stereochemistry has been defined by using the *R* and *S* descriptors as proposed by

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(14) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356−1365.

(15) The value is consistent with previously reported data for nickel complexes: Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422−3427.

(16) (a) Muehlhofer, M.; Strassner, T.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *660*, 121−126. (b) Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Song, H.-B.; Zhang, Z.-Z. *Organometallics* **2004**, *23*, 610−614. (c) Baker, M. V.; Brown, D. H.; Simpson, P. V.; Skelton, B. W.; White, A. H.; Williams, C. C. *J. Organomet. Chem.* **2006**, *691*, 5845−5855. (d) Ahrens, S.; Herdtweck, E.; Sigrid, G.; Strassner, T. *Eur. J. Inorg. Chem.* **2006**, 1268−1274. (e) Quezada, C. A.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2003**, *671*, 183−186. (f) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Öfele, K. (Hoechst AG) Eur. Patent 0721953, 1995.

(17) (a) Hahn, C.; Jahnke, M. C.; Pape, T. *Organometallics* **2006**, *25*, 5927−5936. (b) Poyatos, M.; Maisse-François, A.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2006**, *25*, 2634−2641.

(18) (a) Hasan, M.; Kozhevnikov, I. V.; Siddiqui, M. R. H.; Femoni, C.; Steiner, A.; Winterton, N. *Inorg. Chem.* **2001**, *40*, 795−800. (b) Fantasia, S.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. *Organometallics* **2007**, *26*, 3286−3288.

(19) (a) Liu, S.-T.; Hsieh, T.-Y.; Lee, G.-H.; Peng, S.-M., *Organometallics* **1998**, *17*, 993−995. (b) Ku, R.-Z.; Huang, J.-C.; Cho, J.-Y.; Kiang, F.-M.; Reddy, K. R.; Chen, Y.-C.; Lee, K.-J.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1999**, *18*, 2145−2154.

(20) Han, Y. H.; H.V.; Tan, G. K. *Organometallics* **2007**, *26*, 4612−4617.

(21) (a) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F.; Manojlovic-Muir, L.; Muir, K. W. *Chem. Commun.* **1971**, 400−401. (b) McGuinness, D. S.; Cavell, K. J.; Yates, B. F. *Chem. Commun.* **2001**, 355−356. (c) McGuinness, D. S.; Cavell, K. J.; Yates, B. F.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 8317−8328. (d) Hahn, F. E.; Langenhahn, V.; Lügger, T.; Pape, T.; Le Van, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 3759−3763. (e) Duin, M. A.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J. *Chem. Commun.* **2003**, 400−401.

(22) Mixed NHC−phosphine complexes of palladium, nickel, and rhodium have also been reported. See: (a) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617−618*, 616−628. (b) Huynh, H. V.; Han, Y.; Ho, H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267−3274. (c) Reference 15. (d) Herrmann, W. A.; Frey, G.; Herdtweck, E.; Steinbeck, M. *Adv. Synth. Catal.* **2007**, *349*, 1677−1691.

Enders.[6a] The square-planar complexes are considered as axially chiral atropisomeric compounds, where the axis is represented by the metal−carbene bond and the two perpendicular planes are defined respectively by the coordination plane of platinum and the imidazolylidene ligand. The usual nomenclature rules then apply.[23])

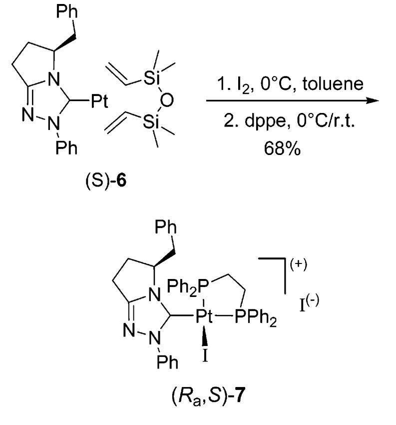
The synthetic procedure of Scheme 1 has been run also with (*R*,*R*)-Me-Duphos as the chiral diphosphine. It afforded a 58% yield of a 1:1 diastereomeric mixture, from which the pure complex **4b** was isolated by crystallization. The absolute axial configuration of complex **4b** has been established to be *S* by X-ray crystallography (see the Supporting Information). The structural parameters of complex **4b** are roughly the same as for complex **3a** with a Pt−C distance of 2.060(6) Å and a dihedral angle of 90.6(5)° between the carbene heterocycle and the platinum coordination plane.

When chiraphos was used as the bidentate phosphine, complex **5** was obtained in high yields; however, separation of the 1:1 mixture **5a** + **5b** could not be achieved. Thus, spectroscopic characterization of **5a** and **5b** has been performed on enriched samples only.

Complexes **3**−**5** are configurationally stable at room temperature, and no isomer interconversion was observed when heating pure **3a** or **5a** + **5b** mixtures in $CDCl_3$ at 50 °C for 12 h. The observed configurational stability can be ascribed to the presence of the tightly bonded chelating phosphorus ligands, which prevents isomerization through dissociative pathways.[24] It also implies hindered rotation of the carbene moiety around the Pt−C bond, which can be related to steric constraints. For comparison, it may be recalled here that, in the work of Enders, the configurational stability of square-planar (diene)(NHC)RhCl complexes had been ascribed mainly to the steric hindrance of the molecule, given that epimerization was observed when decreasing the steric bulk of the diene ligand.[6a,25]

As a complement to the strategy above involving chiral diphosphines and achiral NHC ligands, an axially chiral platinum complex has been prepared by combining a chiral NHC moiety and the achiral diphosphine dppe. The bicyclic triazolylidene described by Rovis[26] has been selected as a representative example of chiral carbene. The platinum(II) complex **7** bearing the *S*-configured triazolylidene ligand has been obtained in 68% yield via a two step procedure involving iodine addition to the corresponding Pt^0(dvtms)(NHC) complex, as shown in Scheme 2.

Scheme 2. Synthesis of the Triazolylidene(dppe)platinum Diiodide Complex 7



^{31}P NMR : 40.5 ($J_{P\text{-}Pt}$ = 2315 Hz)
41.4 ($J_{P\text{-}Pt}$ = 3203 Hz) [$J_{P\text{-}P}$ = 4 Hz)]

A single diastereoisomer of complex **7** has been observed in the final reaction mixture. In order to unambiguously characterize this complex, NMR and X-ray diffraction studies were performed. X-ray data allowed assignment to complex **7** of an axial (R_a) configuration (Figure 3). The R_a configuration minimizes steric interactions between dppe and the benzyl substituent of the (*S*)-pyrrolidine ring, since the benzyl group points to the iodide ligand. The dppe ligand adopts a distorted envelope conformation.[27]

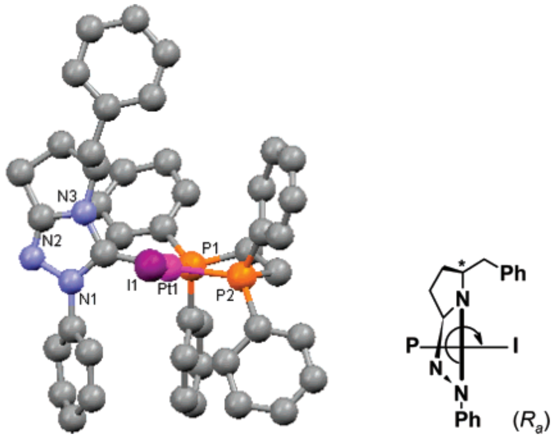


Figure 3. View of complex (R_a,*S*)-**7** from X-ray data (see the ORTEP drawing in the Supporting Information). I^- and crystallization solvents are omitted for clarity.

The preliminary results disclosed above demonstrate a highly suitable synthetic protocol to new axially chiral platinum complexes which combine NHC and diphosphine ligands. Although the reactions take place with various degrees of diastereoselection as a function of the carbene−diphosphine pair involved, diastereomerically pure compounds can be isolated in most instances. The last step of our work has been then to investigate possible uses of these new platinum complexes in enantioselective catalysis,[28] whereby the cycloisomerization of the 1,6-enyne-containing sulfonamide shown in Scheme 3 was targeted. $PtCl_2$[10,29] as well as gold complexes[30] have been used before as rather efficient catalysts for this and analogous reactions leading to azabicyclo[4.1.0]heptene derivatives. To the best of our knowledge, however, no enantioselective versions of this platinum-catalyzed reaction[31] have been reported to date.[32]

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(23) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed.* **1966**, *34*, 385−415.

(24) Configurational stability also implies that transient pentacoordinate (diphosphine)(NHC)PtI_2 complexes either do not form or do not undergo pseudorotation processes.

(25) To the best of our knowledge, no data are available in the literature concerning analogous chiral platinum−carbene complexes.

(26) (a) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2002**, *124*, 10298−10299. (b) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Org. Chem.* **2005**, *70*, 5725−5728.

(27) Brunner, H.; Winter, A.; Breu, J. *J. Organomet. Chem.* **1998**, *553*, 285−306.

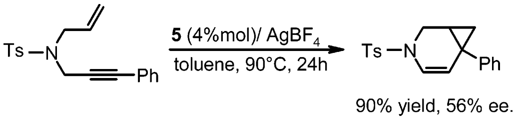
(28) The use of Pt(II)−NHC complexes in catalysis has not often been reported: (a) Reference 17b. (b) Jung, I. G.; Seo, J.; Lee, S. I.; Choi, S. Y.; Chung, Y. K. *Organometallics* **2006**, *25*, 4240−4242.

(29) (a) Cho, E. J.; Kim, M.; Lee, D. *Org. Lett.* **2006**, *8*, 5413−5416. (b) Hercouet, A.; Berrée, F.; Lin, C. H.; Toupet, L.; Carboni, B. *Org. Lett.* **2007**, *9*, 1717−1720.

(30) (a) Lee, S. I.; Kim, S. M.; Choi, M. R.; Kim, S. Y.; Chung, Y. K.; Han, W.-S.; Kang, S. O. *J. Org. Chem.* **2006**, *71*, 9366−9372. (b) Lee, S. I.; Kim, S. M.; Kim, S. Y.; Chung, Y. K. *Synlett* **2006**, 2256−2260.

(31) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271−2296.

Scheme 3. Platinum-Catalyzed Cycloisomerizations



The preliminary tests performed so far show that the platinum carbene−diphosphine complexes are able to promote this reaction after being activated by addition of $AgBF_4$. Activation by $AgBF_4$ is expected to result from abstracting the iodide ligand and increasing the positive net charge of the complex.[33] In comparison to $PtCl_2$ itself, the catalytic activity is somewhat lower; however, significant chiral induction with an enantiomeric excess up to 56% has been obtained by using the chiraphos complex **5** (mixture of isomers). Other chiral phosphines as well as the triazolylidene complex **7** gave uniformly low enantioselectivities (ee < 15%).

According to the assumed mechanism for these platinum-promoted enyne cycloisomerizations,[34] the catalytic activity of $PtCl_2$ (or platinum complexes) should arise from simple π-complexation of the alkyne moiety, which triggers the rearrangement process. The catalytic cycle might thus involve a single vacant coordination site on platinum, which would then retain both the NHC and the diphosphine ligands throughout the catalytic cycle.[35] If this is the case, this catalytic reaction might take place with retention of configuration at the chiral square-planar complex, in some instances at least. We therefore envision the use of these cycloisomerization reactions as hopefully suitable probes to investigate the configurational stability of the axially chiral platinum complexes above, and other analogues, throughout a catalytic process.

Supporting Information Available: Text, tables, and figures giving experimental procedures for the synthesis of complexes **2**−**7** and crystallographic data for complexes **3a**, **4b**, and **7**; the crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray data have also been deposited at the CCDC, Cambridge, U.K., with deposit numbers 655409, 655409, and 655408, respectively.

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(32) Related cycloisomerizations of nitrogen-bridged enynes are known to be promoted by chiral iridium complexes with moderate to good enantioselectivity: Shibata, T.; Kobayashi, Y.; Maekawa, S.; Toshida, N.; Takagi, K. *Tetrahedron* **2005**, *61*, 9018−9024.

(33) Hahn, C. *Chem. Eur. J.* **2004**, *10*, 5888−5899.

(34) (a) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863−11869. (b) Soriano, E.; Ballesteros, P.; Marco-Contelles, J. *Organometallics* **2005**, *24*, 3172−3181. (c) Soriano, E.; Marco-Contelles, J. *J. Org. Chem.* **2005**, *70*, 9345−9353.

(35) A related example of catalytic processes involving tricoordinated platinum(II) catalysts is the enantioselective cycloisomerization of dienes described by Gagné et al.: Feducia, J. A.; Campbell, A. N.; Doherty, M. Q.; Gagné, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 13290−13297. A chiral bidentate phosphine and trimethylphosphine are simultaneously used as the platinum ligands.