Inorg. Chem. **2007**, *46*, 5100–5109

Cyclopalladation of the Prochiral (Di-*tert*-butyl)(diphenylmethyl)phosphine: Kinetic Lability of the Corresponding (+)-Phosphapalladacyclic Pd–C Bond and the Reluctance of the Phosphine to Bind in a Monodentate Fashion

Joseph Kok-Peng Ng,[†] Shuli Chen,[‡] Yongxin Li,[‡] Geok-Kheng Tan,[†] Lip-Lin Koh,[†] and Pak-Hing Leung*[,‡]

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, and Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore 637616

Received February 7, 2007

The ortho palladation of prochiral (di-*tert*-butyl)(diphenylmethyl)phosphine proceeded readily to give rise to the dimeric complex, di-μ-chlorobis{[(phenyl)(di-*tert*-butylphosphino)methyl]phenyl-C^2, P}dipalladium(II). The (*S*,*S*)-(+)-dimer was subsequently obtained by optical resolution with sodium (*S*)-prolinate. The absolute configuration of the optically resolved (+)-dimer was concluded from the X-ray diffraction studies of the derivatized *O*,*O*-acetylacetonate complex. The availability of the (+)-dimer is crucial to the study of the properties of the Pd–C bond. The phosphapalladacycle Pd–C bond exhibited a remarkable thermodynamic stability. It could not be permanently ruptured to give rise to the η^1–P monodentate even in a refluxing acetone solution containing concentrated hydrochloric acid. Instead, the phosphine was noted to fluctuate between the ring closed and opened states via the reversible Pd–C bond cleavage/formation under this condition. Inevitably, this resulted in the racemization of the five-membered organopalladium ring structure. In contrast, such bond cleavage was not observed at room temperature in the absence of HCl. In fact, the phosphine was observed to readily ortho palladate even under conditions not favorable to cyclopalladation. Indeed, the difficulty of isolating the phosphine as a simple η^1–P monodentate coordination complex was further noted by its lack of reactivity toward the *N*,*N*-dimethyl-1-(1′naphthyl)ethylaminate palladacycle μ-chloro dimer. Only by enhancing the Lewis acidity of the palladacycle in the form of the positively charged bis(acetonitrile) complex could the phosphine be encouraged to participate in monodentate η^1–P bonding. Even then, this form of coordination was weak and was only observed by NMR spectroscopy.

Introduction

Ever since the unprecedented ortho metalation of azobenzene was reported by Cope et al.,[1] the chemistry of cyclopalladated reagents (chiral and otherwise) has developed into a very rich one. Such complexes have generated interests for their many roles as catalysts,[2] agents for enantiomeric excess determinations,[3] resolving agents[4], and stoichiometric agents for the syntheses of organic compounds.[5] These agents have also gained attention for their photoluminescent behavior,[6] biological properties[7], and as liquid crystals.[8]

We have previously contributed to this field of interest by utilizing the chiral *N*,*N*-dimethyl-1-(1′-naphthyl)ethylaminate palladacycle for the syntheses of a number of optically active phosphorus-containing ligands.[9] It is well known that the chiral-inducing ability of this palladacycle derives from the transmission of vital stereochemical information originating from the conformationally robust five-membered palladacycle[9d,i,10] by (i) the dimethylamino group of the neighboring coordination site on the Pd atom[11] and

* To whom correspondence should be addressed. E-mail: pakhing@ntu.edu.sg.
† National University of Singapore.
‡ Nanyang Technological University, Singapore.

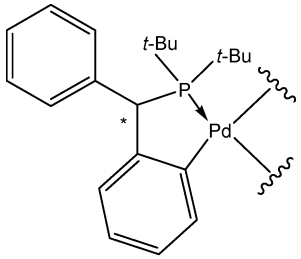
(1) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272–3273.

10.1021/ic0702320 CCC: $37.00
Published on Web 05/10/2007

(ii) the protruding aromatic proton H′ of the site adjacent to the Pd−C bond.[10e]

Encouraged by these results, we sought to develop new variants of this type.[12,13] Palladacycles containing phosphorus donors, or especially those of other heteroatoms such as arsenic,[13a,14] oxygen[15], and sulfur[16], are relatively limited with respect to their numerous nitrogen counterparts. Even among the *P*−donor palladacycles,[2c,d, 17] or aptly known as "phosphapalladacycles", those prepared in the optically active forms[13a,18] are a rarity. Also, with the very promising roles of phosphapalladacycles as catalysts,[2c,d,h,l] the development of new variants of these unique classes of organopalladium complexes seems necessary.

The delivery of new properties is expected with the replacement of the nitrogen atom with a congener. For instance, the phosphorus atom behaves as more than a σ donor, as, depending on the substituents available, it can possess various degrees of π-accepting properties as well.[19] This article describes the preparation of a novel phosphapalladacycle **1** in the optically active form and discusses the kinetic lability of the Pd−C bond from optical rotation data. The inclusion of the bulky *t*-butyl substituents was aimed at providing a greater stereochemical influence to the neighboring reaction sites on the Pd atom in all of the future applications of the palladacycle as a reaction promoter.



1

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of argon using standard Schlenk techniques. *R*-**11** was prepared from a reported procedure,[3220−32] but $AgPF_6$ was used in substitution of $AgClO_4$. Hexanes and toluene (analytical grade) were used without further purification. Dichloromethane was dried in the presence of calcium chloride and distilled under purified nitrogen before use. THF and diethyl ether were distilled from deep-purple solutions of sodium benzophenone ketyl under purified nitrogen. Routine ^{1}H NMR spectra were recorded at 300 or 500 MHz, respectively, on a Bruker ACF 300 or Bruker AMX 500 NMR spectrometer. All of the ^{31}P{^{1}H} NMR

(2) (a) Mitsudo, T.; Fischetti, W.; Heck, R. F. *J. Org. Chem.* **1984**, *49*, 1640−1646. (b) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743−749. (c) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Piermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844−1848. (d) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem.−Eur. J.* **1997**, *3*, 1357−1364. (e) Shaw, B. L.; Perera, S. D.; Staley, E. A. *Chem. Commun.* **1998**, 1361−1362. (f) Albisson, D. A.; Bedford, R. B.; Lawrence, S. E.; Scully, P. N. *Chem. Commun.* **1998**, 2095−2096. (g) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379−7383. (h) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23−41. (i) Beller, M.; Riermeier, T. H. *Eur. J. Inorg. Chem.* **1998**, 29−35. (j) Albisson, D. A.; Bedford, R. B.; Scully, P. N. *Tetrahedron Lett.* **1998**, *39*, 9793−9786. (k) Shaw, B. L. *New J. Chem.* **1998**, 77−79. (l) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848−1849. (m) Morales-Morales, D.; Redón R.; Yung, C.; Jensen, C. M. *Chem. Commun.* **2000**, 1619−1620. (n) Ohff, M.; Ohff, A.; Milstein, D. *Chem. Commun.* **1999**, 357−358. (o) Weissman, H.; Milstein, D. *Chem. Commun.* **1999**, 1901−1902. (p) Alonso, D. A.; Nájera, C.; Pacheco, M. C. *Org. Lett.* **2000**, *2*, 1823−1826. (q) Nowotny, M.; Hanefeld, U.; van Koningsveld, H.; Maschmeyer, T. *Chem. Commun.* **2000**, 1877−1878. (r) Gai, X.; Grigg, R.; Ramzan, M. I.; Sridharan, V.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 2053−2054. (s) Alonso, D. A.; Nejara, C.; Pacheco, M. C. *Adv. Synth. Catal.* **2002**, *344*, 172−183. (t) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y. S. *J. Am. Chem. Soc.* **1999**, *121*, 9531−9538. (u) Bergbreiter, D. E.; Osburn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058−9064. (v) Gruber, A. S.; Zim, D.; Ebeling, G.; Monteiro, A. L.; Dupont, J. *Org. Lett.* **2000**, *2*, 1287−1290. (w) Zim, D.; Gruber, A. S.; Ebeling, G.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2000**, *2*, 2881−2884. (x) Consorti, C. S.; Zanini, M. L.; Leal, S.; Ebeling, G.; Dupont, J. *Org. Lett.* **2003**, *5*, 983−986. (y) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207−3212. (z) Brody, M. S.; Finn, M. G. *Tetrahedron Lett.* **1999**, *40*, 415−418.

(3) (a) Böhm, A.; Seebach, D. *Helv. Chim. Acta* **2000**, *83*, 3262−3278. (b) Dunina, V. V.; Gorunova, O. N.; Livantsov, M. V.; Grishin, Y. K. *Tetrahedron: Asymmetry* **2000**, *11*, 2907−2916. (c) Levrat, F.; Stoeckli-Evans, H.; Engel, N. *Tetrahedron: Asymmetry* **2002**, *13*, 2335−2344. (d) Albert, J.; Granell, J.; Muller, G.; Sainz, D.; Font-Bardia, M.; Solans, X. *Tetrahedron: Asymmetry* **1995**, *6*, 325−328. (e) Dunina, V. V.; Golovan, E. B.; Gulyukina, N. S.; Buyevich, A. V. *Tetrahedron: Asymmetry* **1995**, *6*, 2731−2746. (f) Lopéz, C.; Bosque, R.; Sainz, D.; Solans, X.; Font-Bardía, M. *Organometallics* **1997**, *16*, 3261−3266. (g) Moncarz, J. R.; Laritcheva, N. F.; Glueck, D. S. *J. Am. Chem. Soc.* **2002**, *124*, 13356−13357. (h) Kyba, E. P.; Rines, S. P. *J. Org. Chem.* **1982**, *47*, 4800−4801.

(4) (a) Chatterjee, S.; George, M. D.; Salem, G.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **2001**, 1890−1896. (b) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254−6260. (c) Roberts, N. K.; Wild, S. B. *J. Chem. Soc., Dalton Trans.* **1979**, 2015−2021. (d) He, G.; Mok, K. F.; Leung, P.-H. *Organometallics* **1999**, *18*, 4027−4031. (e) Dunina, V. V.; Golovan, E. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2747−2754. (f) Pabel, M.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1996**, *35*, 1244−1249. (g) Bader, A.; Pabel, M.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1996**, *35*, 3874−3877. (h) Pabel, M.; Willis, A. C.; Wild, S. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2369−2374. (i) Albert, J.; Granell, J.; Mínguez, J.; Muller, G.; Sainz, D.; Valerga, P. *Organometallics* **1997**, *16*, 3561−3564. (j) Albert, J.; Cadena, J. M.; Delgado, S.; Granell, J. *J. Organomet. Chem.* **2000**, *603*, 235−239. (k) Albert, J.; Cadena, J. M.; Granell, J.; Muller, G.; Panyella, D.; Sañudo, C. *Eur. J. Inorg. Chem.* **2000**, 1283−1286. (l) Albert, J.; Bosque, R.; Cadena, J. M.; Granell, J. R.; Muller, G.; Ordinas, J. I. *Tetrahedron: Asymmetry* **2000**, *11*, 3335−3343. (m) Kurita, J.; Usuda, F.; Yasuike, S.; Tsuchiya, T.; Tsuda, Y.; Kiuchi, F.; Hosoi, S. *Chem. Commun.* **2000**, 191−192. (n) Durán, E.; Gordo, E.; Granell, J.; Font-Bardía, M.; Solans, X.; Velasco, D.; López-Calahorra, F. *Tetrahedron: Asymmetry* **2001**, *12*, 1987−1997. (o) Durán, E.; Velasco, D.; López-Calahorra, F. *Heterocycles* **2002**, *57*, 825−855. (p) Tani, K.; Hironori, T.; Yoshida, M.; Yamagata, T. *J. Organomet. Chem.* **1994**, *469*, 229−236. (q) Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Manasserro, M. *Tetrahedron: Asymmetry* **1994**, *5*, 511−514. (r) Gladiali, S.; Pulacchini, S.; Fabbri, D.; Manasserro, M.; Sansoni, M. *Tetrahedron: Asymmetry* **1998**, *9*, 391−395. (s) Anderson, N. G.; Parvez, M.; Keay, B. A. *Org. Lett.* **2000**, *2*, 2817−2820. (t) Berens, U.; Brown, J. M.; Long, J.; Selke, R. *Tetrahedron: Asymmetry* **1996**, *7*, 285−292. (u) Kwong, F. Y.; Yang, Q.; Mak, T. C. W.; Chan, A. S. C.; Chan, K. S. *J. Org. Chem.* **2002**, *67*, 2769−2777. (v) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743−756. (w) Valk, J.-M.; Claridge, T. D. W.; Brown, J. M. B.; Hibbs, D.; Hursthouse, M. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2597−2610. (x) Lacey, P. M.; McDonnell, C. M.; Guiry, P. J. *Tetrahedron Lett.* **2000**, *41*, 2475−2478. (y) McCarthy, M.; Guiry, P. J. *Polyhedron* **2000**, *19*, 541−543.

(5) (a) van Baar, J. F.; Klerks, J. M.; Overbosch, P.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1976**, *112*, 95−103. (b) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229−232. (c) Vicente, J.; Saura-Llamas, I.; Turpín, J.; de Arellano, M. C. R.; Jones, P. G. *Organometallics* **1999**, *18*, 2683−2693. (d) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautisda, D. *Organometallics* **2002**, *21*, 3587−3595. (e) Lindsell, W. E.; Palmer, D. D.; Preston, P. N.; Rosair, G. M.; Jones, R. V. H.; Whitton, A. J. *Organometallics* **2005**, *24*, 1119−1133.

spectra were recorded at 121 or 202 MHz on the Bruker ACF 300 or Bruker AMX 500 NMR spectrometer, respectively. Unless stated otherwise, all of the NMR spectroscopic experiments were performed at room temperature (298 K). Melting points were determined on a Büchi melting point B-545 apparatus and were uncorrected. Optical rotations were measured on the specified solution in 1 or 0.1 dm cells at 25 °C with a Perkin-Elmer Model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

(Di-*tert*-butyl)(diphenylmethyl)phosphine (2). The synthesis of phosphine **2** was prepared according to the reported procedure[20]

(6) (a) Ghedini, M.; Pucci, D.; Calogeno, G.; Barigelletti, F. *Chem. Phys. Lett.* **1997**, *267*, 341−344. (b) Aiello, I.; Ghedini, M.; La Deda, M. *J. Lumin.* **2002**, *96*, 249−259. (c) La Deda, M; Ghedini, M.; Aiello, I.; Pugliese, T.; Barigelletti, F.; Accorsi, G. *J. Organomet. Chem.* **2005**, *690*, 857−861. (d) Ghedini, M.; Aiello, I.; La Deda, M; Grisolia, A. *Chem. Commun.* **2003**, 2198−2199. (e) Consorti, C. S.; Ebeling, G.; Rodembusch, F.; Stefani, V.; Livotto, P. R.; Rominger, F.; Quina, F. H.; Yihwa, C.; Dupont, J. *Inorg. Chem.* **2004**, *43*, 530−536. (f) Song, D.; Wu, Q.; Hook, A.; Kozin, L.; Wang, S. *Organometallics*, **2001**, *20*, 4683−4689. (g) Wu, Q.; Hook, A.; Wang, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3933−3935. (h) Neve, F.; Crispini, A.; Campagna, S. *Inorg. Chem.* **1997**, *36*, 6150−6156. (i) Neve, F.; Ghedini, M.; Crispini, A. *Chem. Commun.* **1996**, 2463−2464. (j) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153−8159.

(7) (a) Newkome, G. R.; Ornishi, M.; Puckett, W. E.; Deutsch, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4551−4552. (b) Suggs, J. W.; Dube, M. J.; Nichols, M. *J. Chem. Soc., Chem Commun.* **1993**, 307−309. (c) Navarro-Ranninger, C.; López-Solera, I.; González, V. M.; Pérez, J. M.; Alvarez-Valdés, A.; Martín, A.; Raithby, P. R.; Masaguer, J. R.; Alonso, C. *Inorg. Chem.* **1996**, *35*, 5181−5187. (d) Quiroga, A. G.; Pérez, J. M.; López-Solera, I.; Masaguer, J. R.; Luque, A.; Román, P.; Edwards, A.; Alonso, C.; Navarro-Ranninger, C. *J. Med. Chem.* **1998**, *41*, 1399−1408. (e) Higgins, J. D., III; Neely, L.; Fricker, S. *J. Inorg. Biochem.* **1993**, *49*, 149−156. (f) Navarro-Ranninger, C.; López-Solera, I.; Pérez, J. M.; Rodríguez, J.; García-Ruano, J. L.; Raithby, P. R.; Masaguer, J. R.; Alonso, C. *J. Med. Chem.* **1993**, *36*, 3795−3801. (g) Rodrigues, E. G.; Silva, L. S.; Fausto, D. M.; Hayashi, M. S.; Dreher, S.; Santos, E. L.; Pesquero, J. B.; Travassos, L. R.; Caires, A. C. F. *Int. J. Cancer* **2003**, *107*, 498−504. (h) Li, S. H.; Yu, C.-W.; Xu, J. G. *Chem. Commun*. **2005**, 450−452. (i) Guillena, G.; Kruithof, C. A.; Casado, M. A.; Egmond, M. R.; van Koten, G. *J. Organomet. Chem.* **2003**, *668*, 3−7. (j) Bezsoudnova, E. Y.; Ryabov, A. D. *J. Organomet. Chem.* **2001**, *622*, 38−42. (k) Kazankov, G. M.; Sergeeva, V. S.; Efremenko, E. N.; Alexandrova, L.; Varfolomeev, S. D.; Ryabov, A. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 3117−3119.

(8) (a) Baena, M. J.; Buey, J.; Espinet, P.; Kitzerow, H.-S.; Heppke, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1201−1203. (b) Espinet, P.; Etxebarría, J.; Marcos, M.; Pérez, J.; Rémon, A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1065−1066. (c) El-ghayoury, A.; Douce, L.; Skoulios, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1255−1258. (d) Hegmann, T.; Kain, J.; Diele, S.; Pelzl, G.; Tschierske, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 887−890. (e) Ghedini, M.; Morrone, S.; Francescangeli, O.; Bartolino, R. *Chem. Mater.* **1992**, *4*, 1119−1123.

(9) (a) Qin, Y.; Lang, H.; Vittal, J. J.; Tan, G.-K.; Selvaratnam, S.; White, A. J. P.; Williams, D. J.; Leung, P.-H. *Organometallics* **2003**, *22*, 3944−3950. (b) He, G.; Loh, S. K.; Vittal, J. J.; Mok, K. F.; Leung, P.-H. *Organometallics* **1998**, *17*, 3931−3936. (c) Leung, P.-H.; Loh, S.-K.; Vittal, J. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem Commun.* **1997**, 1987−1988. (d) Leung, P.-H.; Loh, S.-K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem Commun.* **1996**, 591−592. (e) Siah, S. Y.; Leung, P.-H.; Mok, K. F.; Drew, M. G. B. *Tetrahedron: Asymmetry* **1996**, *7*, 357−360. (f) Leung, P.-H.; Loh, S.-K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1996**, 4443−4448. (g) Leung, P.-H.; He, G.; Lang, H.; Liu, A.; Loh, S.-K.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 7−15. (h) Song, Y.; Mok, K. F.; Leung, P.-H.; Chan, S.-H. *Inorg. Chem.* **1998**, *37*, 6399−6401. (i) Aw, B.-H.; Hor, T. S. A.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W.; Leung, P.-H. *Inorg. Chem.* **1997**, *36*, 2138−2146. (j) Liu, X.; Mok, K. F.; Leung, P.-H. *Organometallics* **2001**, *20*, 3918−3926. (k) Yeo, W.-C.; Tang, L.; Yan, B.; Tee, S.-Y.; Koh, L. L.; Tan, G.-K.; Leung, P.-H. *Organometallics* **2005**, *24*, 5581−5585. (l) Yeo, W. C.; Tee, S. Y.; Tan, H. B.; Tan, G. K.; Koh, L. L.; Leung, P. H. *Inorg. Chem.* **2004**, *43*, 8102−8109.

(10) (a) Siah, S. Y.; Leung, P. H.; Mok, K. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1747−1748. (b) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007−1014. (c) Leung, P. H.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1992**, *31*, 1406−1410. (d) Chooi, S. Y. M.; Hor, T. S. A.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494−1500. (e) Aw, B.-H.; Selvaratnam, S.; Leung, P. H.; Rees, N. H.; McFarlane, W. *Tetrahedron: Asymmetry* **1996**, *7*, 1753−1762.

(11) Chooi, S. Y. M.; Tan, M. K.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1994**, *33*, 3096−3103.

(12) (a) Leung, P.-H.; Ng, K. H.; Li, Y.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, *23*, 2435−2436. (b) Li, Y.; Ng, K.-H.; Selvaratnam, S.; Tan, G.-K.; Vittal, J. J.; Leung, P.-H. *Organometallics* **2003**, *22*, 834−842. (c) Li, Y.; Selvaratnam, S.; Vittal, J. J.; Leung, P.-H. *Inorg. Chem.* **2003**, *42*, 3229−3236.

(13) (a) Ng, J. K. P.; Tan, G. K.; Vittal, J. J.; Leung, P. H. *Inorg. Chem.* **2003**, *42*, 7674−7682. (b) Ng, J. K. P.; Li, Y.; Tan, G. K.; Koh, L. L.; Vittal, J. J. *Inorg. Chem.* **2005**, *44*, 9874−9886.

(14) (a) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Can. J. Chem.* **1988**, *66*, 3162−3165. (b) Dias, S. A.; Alyea, E. C. *Transition Met. Chem.* **1979**, *4*, 205−206. (c) Goel, R. G.; Ogini, W. O. *Inorg. Chim. Acta* **1980**, *44*, L165−L166. (d) Abicht, H.-P. *J. Organomet. Chem.* **1986**, *311*, 57−61.

(15) (a) Dehand, J.; Mauro, A.; Ossor, H.; Pfeffer, M.; Santos, R. H. de A.; Lechat, J. R. *J. Organomet. Chem.* **1983**, *250*, 537−550. (b) Fernández-Rivas, C.; Cárdenas, D. J.; Martín-Matute, B.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998−3006.

(16) (a) Dupont, J.; Gruber, A. S.; Fonseca, G. S.; Monteiro, A. L.; Ebeling, G.; Burrow, R. A. *Organometallics* **2001**, *20*, 171−176. (b) Vicente, J.; Abad, J. A.; Hernández-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848−3849. (c) Vicente, J.; Abad, J.-A.; Hernández-Mata, F. S.; Jones, P. G. *Organometallics* **2001**, *20*, 1109−1114. (d) Rüger, R.; Rittner, W.; Jones, P. G.; Isenberg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 382−383. (e) Hiraki, K.; Fuchita, Y.; Kage, Y. *J. Chem. Soc., Dalton Trans.* **1984**, 99−101. (f) Dupont, J.; Beydoun, N.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1989**, 1715−1720. (g) Fuchita, Y.; Hiraki, K.; Yamaguchi, T.; Maruta, T. *J. Chem. Soc., Dalton Trans.* **1981**, 2405. (h) Mizuno, H.; Nonoyama, M. *Polyhedron* **1990**, *9*, 1287−1292. (i) Nojima, Y.; Nonoyama, M.; Nakajima, K. *Polyhedron* **1990**, *15*, 3795−3809. (j) Davis, R. C.; Grinter, T. J.; Leaver, D.; O'Neil, R. M.; Thomson, G. A. *J. Chem. Res., Synop.* **1987**, 280−281.

(17) (a) Gill, D. F.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1972**, 65−66. (b) Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 270−278. (c) Alyea, E. C.; Malito, J. *J. Organomet. Chem.* **1988**, *340*, 119−126. (d) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Organometallics* **1989**, *8*, 1188−1191. (e) Herrmann, W. A.; Reisinger, C. P.; Öfele, K.; Brossmer, C.; Beller, M.; Fischer, H. *J. Mol. Catal. A: Chem.* **1996**, *108*, 51−56. (f) Hermann, W. A.; Böhm, V. P. W.; Reisinger, C. P. *J. Chem. Educ.* **2000**, *77*, 92−95. (g) Brunel, J. M.; Heumann, A.; Buono, G. *Angew. Chem., Intl. Ed.* **2000**, *39*, 1946−1949. (h) Albert, J.; Bosque, R.; Cadena, J. M.; Delgado, S.; Granell, J.; Muller, G.; Ordinas, J. I.; Font Bardia, M.; Solans, X. *Chem.—Eur. J.* **2002**, *8*, 2279−2287. (i) Zhuravel, M. A.; Glueck, D. S.; Zakharov, L. N.; Rheingold, A. L. *Organometallics*, **2002**, *21*, 3208−3214. (j) Hyde, E. M.; Shaw, B. L.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* **1978**, 1696−1705. (k) Shaw, B. L.; Truelock, M. M. *J. Organomet. Chem.* **1975**, *102*, 517−525. (l) Hiraki, K.; Fuchita, Y.; Uchimaya, T. *Inorg. Chim. Acta* **1983**, *69*, 187−190. (m) Castella, M.; Calahorra, F.; Sainz, D.; Velasco, D. *Org. Lett.* **2001**, *3*, 541−545. (n) Pereira, M. M.; Muller, G.; Ordinas, J. I.; Azenha, M. E.; Arnaut, L. G. *J. Chem. Soc. Perkin Trans. 2* **2002**, 1583−1588. (o) Dunina, V. V.; Gorunova, O. N.; Livantsov, M. V.; Grishin, Y. K.; Kuz'mina, L. G.; Kataeva, N. A.; Churakov, A. V. *Inorg. Chem. Commun.* **2000**, *3*, 354−357. (p) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687−11688. (q) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6351−6541. (r) Sjövall, S.; Wendt, O. F.; Andersson, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1396−1400. (s) Kiewel, K.; Liu, Y.; Bergbreiter, D. E.; Sulikowski, G. A. *Tetrahedron Lett.* **1999**, *40*, 8945−3948. (t) Albinati, A.; Affolter, S.; Pregosin, P. S. *Organometallics* **1990**, *9*, 379−387. (u) Albisson, D. A.; Bedford, R. B.; Lawrence, S. E.; Scully, P. N. *Chem. Commun.* **1998**, 2095−2096. (v) Sokolov, V. I.; Bulygina, L. A.; Borbulevych, O. Y.; Shishkin, O. V. *J. Organomet. Chem.* **1999**, *582*, 246−251. (w) Troitskaya, L. L.; Ovseenko, S. T.; Slovokhotov, Y. L.; Neretin, I. S.; Sokolov, V. I. *J. Organomet. Chem.* **2002**, *642*, 191−194.

and was isolated as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.98 (d, 18H, $^3J_{PH}$ = 10.0 Hz, *t*-Bu), 4.42 (d, 1H, $^2J_{PH}$ = 4.8 Hz, α-C*H*), 7.08−7.55 (m, 10H, aromatic protons). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ): 47.1 (s).

Di-μ-chlorobis{1-[(di-*tert*-butylphosphino)(phenyl)methyl]-phenyl-*C*^{2},*P*}dipalladium(II) ((±)-3). Method A: Prepared phosphine **2** (2.8 g, 8.9 mmol) and palladium(II) acetate (2.0 g, 8.9 mmol) were suspended in degassed toluene (100 mL), and the reacting mixture was stirred at 50 °C for 6.5 h to give a yellow solution. The excess solvents were evaporated from the mixture to give a yellow-orange oil, which was then dissolved in acetone (15 mL). A solution of lithium chloride (0.76 g, 17.8 mmol) in acetone/methanol (5:15, v/v) was added, and the mixture was then stirred for 90 min, evaporated to dryness, and suspended in dichloromethane. The suspension was then washed with water (50 mL), and the aqueous layer was removed. The organic extract was concentrated and chromatographed on a silica gel column using dichloromethane/hexanes (1:2, v/v) from which chloro-dimer **3** was eluted as a pale yellowish-green fraction. Crystallization from acetone/diethylether yielded pale-yellow blocks, 3.34 g (82.7% yield). Method B: A dichloromethane solution (5 mL) of prepared phosphine **2** (0.241 g, 0.770 mmol) was added via cannular into a freshly deoxygenated aqueous solution (3 mL) of $Li_2[PdCl_4]$ (0.39 mmol; prepared in-situ from $PdCl_2$ (0.068 g, 0.39 mmol) and excess LiCl (0.032 g, 0.77 mmol) in water) followed by rapid stirring at room temperature for 30 min. The organic layer was separated, washed with water (2 × 10 mL), dried with $MgSO_4$, and chromatographed in a short silica gel column using CH_2Cl_2/hexanes (in increasing polarities from 1:4 to 1:1, v/v). Purified chloro dimer **3** was eluted from the column and was crystallized as pale-yellow blocks from acetone/ether, mp (dec) 243.9−248.9 °C; 0.107 g (61.6% yield). Anal. Calcd for $C_{42}H_{56}Cl_2P_2Pd_2$: C, 55.7; H, 6.2. Found: C, 55.8; H, 6.4. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.33−1.43 (br d, 18H, *t*-Bu), 4.51 (d, 1H, $^2J_{PH}$ = 11.2 Hz, *t*-Bu_2PC*H*), 6.70−7.95 (br m, 9H, aromatic protons). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ): 111.5, 111.8, 111.9 (br s), (223 K, δ): 110.0 (s), 110.2 (s), 110.3 (s), 110.5 (s).

[(*S*)-Prolinato-*N*,*O*] {1-[(di-*tert*-butylphosphino)(phenyl)-methyl]phenyl-*C*^{2},*P*}palladium(II) (4). A methanol solution (2 mL) of potassium (*S*)-prolinate (0.12 g, 0.78 mmol) was added to chloro-dimer (±)-**3** (0.23 g, 0.25 mmol) dissolved in dichloromethane (2 mL), and the mixture was stirred vigorously at room temperature for 30 min. The resulting white suspension was evaporated to dryness, washed with water (10 mL), and was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried with $MgSO_4$ to give a colorless solution, which was evaporated to dryness to yield **4** as a white solid, mp (dec) 262−264 °C, $[\alpha]_D$ +105°, $[\alpha]_{578}$ +110°, $[\alpha]_{546}$ +128°, $[\alpha]_{436}$ +250°, $[\alpha]_{365}$ +541° (c, 1.0, CH_2Cl_2); 0.25 g (92.6% yield). Anal. Calcd for $C_{39}H_{43}ClP_2Pd$: C, 58.7; H, 6.8; N, 2.6. Found: C, 58.9; H, 6.8; N, 2.4. ^{1}H NMR (500 MHz, $CDCl_3$), two sets of signals corresponding to the (*R*,*S*) and (*S*,*S*) diastereomers. Assignment of signals to either diastereomer was made by comparison with the ^{1}H NMR spectrum of the isolated (*S*,*S*)-**4** diastereomer (below), δ, 1.24 (d, 9H, $^3J_{PH}$ = 13.8 Hz, *t*-Bu of (*R*,*S*)-diastereomer), 1.25 (d, 9H, $^3J_{PH}$ = 14.2 Hz, *t*-Bu of (*S*,*S*)-diastereomer), 1.26 (d, 9H, $^3J_{PH}$ = 12.9 Hz, *t*-Bu of (*S*,*S*)-diastereomer), 1.36 (d, 9H, $^3J_{PH}$ = 13.2 Hz, *t*-Bu of (*R*,*S*)-diastereomer), 1.75−4.15, (*S*)-prolinate signals: δ, 1.75−1.87 (m, 2H, γ-*H* of both diastereomers), 2.02−2.21 (m, 3H, β- and γ-*H* of (*R*,*S*)-diastereomer, γ-*H* of (*S*,*S*)-diastereomer), 2.29−2.42 (m, 2H, both β-*H* of (*S*,*S*)-diastereomer), 2.54 (m, 1H, β-*H* of (*R*,*S*)-diastereomer), 3.33−3.50 (m, 5H, all δ-*H* of both diastereomers and N-*H* of (*S*,*S*)-diastereomer), 3.60 (m, 1H, N-*H* of (*R*,*S*)-diastereomer), 4.07−4.14 (m, 2H, α-*H* of both diastereomers), 4.54 (d, 1H, $^2J_{PH}$ = 11.3 Hz, palladacycle α-C*H* of (*S*,*S*)-diastereomer), 4.64 (d, 1H, $^2J_{PH}$ = 11.6 Hz, palladacycle α-C*H* of (*R*,*S*)-diastereomer), 6.73−7.57, aromatic signals: δ, 6.75 (m, 1H, H^5 of (*R*,*S*)-diastereomer), 6.80 (m, 1H, H^5 of (*S*,*S*)-diastereomer), 6.91−6.96 (m, 4H, H^3 and H^4 of both diastereomers), 7.07−7.12 (m, 2H, H^2 of both diastereomers), 7.18−7.22 (m, 4H, Ph ring *m*- and *p*-*H* of both diastereomers), 7.27−7.31 (m, 2H, Ph ring *m*-*H* of both diastereomers), 7.34−7.36 (br d, 2H, Ph ring *o*-*H* of both diastereomers), 7.50 (m, 1H, Ph ring *o*-*H* of (*R*,*S*)-diastereomer), 7.56 (m, 1H, Ph ring *o*-Ph of (*S*,*S*)-diastereomer). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) four sets of signals in 99.0, 98.0, 1.0, 2.0; relative intensities, δ: 108.2 (s), 109.8 (s), 110.1 (s), 111.2 (s).

Optical Resolution of Di-μ-chlorobis{1-[(di-*tert*-butylphosphino)(phenyl)methyl]phenyl-*C*^{2}, *P*}dipalladium(II). Isolation of (+)-[(*S*)-Prolinato-*N*,*O*]{(*S*)-1-[(di-*tert*-butylphosphino)(phenyl)-methyl]phenyl-*C*^{2},*P*}palladium(II) ((*S*,*S*)-4). A dichloromethane solution (10 mL) of the 1:1 diastereomeric mixture of (*R*,*S*)- and (*S*,*S*)-prolinate **4** (1.18 g, 2.2 mmol) was diluted with toluene of the same volume, and the colorless solution was concentrated in vacuo. The resulting solution was mainly enriched in toluene as the solvent was left to stand at room temperature, from which a white solid that was 71% de enriched in favor of the (*S*,*S*) isomer was obtained. The obtained white solid was recrystallized twice from the above solvent system to yield the (*S*,*S*)-**4** isomer as a white solid with a final optical purity of 98.1% de, mp (dec) 287−288 °C; $[\alpha]_D$ +287°, $[\alpha]_{578}$ +307°, $[\alpha]_{546}$ +353°, $[\alpha]_{436}$

(18) (a) Longmire, J. M.; Zhang, X.; Shang, M. *Organometallics* **1998**, *17*, 4374−4379. (b) Dunina, V. V.; Gorunova, O. N.; Kuz'mina, L. G.; Livantsov, M. V.; Grishin, Y. K. *Tetrahedron: Asymmetry* **1999**, *10*, 3951−3961. (c) Dunina, V. V.; Gorunova, O. N.; Livantsov, M. V.; Grishin, Y. K.; Kuz'mina, L. G.; Kataeva, N. A.; Churakov, A. V. *Tetrahedron: Asymmetry* **2000**, *11*, 3967−3984. (d) Williams, B. S.; Dani, P.; Lutz, M.; Spek, A. L.; van Koten, G. *Helv. Chim. Acta* **2001**, *84*, 3519−3530. (e) Morales-Morales, D.; Cramer, R. E.; Jensen, C. M. *J. Organomet. Chem.* **2002**, *654*, 44−50.

(19) (a) Romeo, R.; Arena, G.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4879−4884. (b) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391−4398.

(20) Grüetzmacher, H. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Phosphorus Arsenic Antimony and Bismuth; Thieme Medical Publishers: New York, 1996; Vol. 3, pp 85−88.

(21) (a) Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307−318. (b) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. D* **1970**, 1176−1177.

(22) (a) Clark, H. C.; Goel, A. B.; Goel, R. G.; Goel, S.; Ogini, W. O. *Inorg. Chim. Acta* **1978**, *31*, L441−L442. (b) Cheney, A. J.; Shaw B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 860−865.

(23) (a) Dehand, J.; Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1981**, *209*, 255−270. (b) Hiraki, K.; Fuchita, Y.; Takakura, S. *J. Organomet. Chem.* **1981**, *210*, 273−280. (c) Hiraki, K.; Fuchita, Y.; Maruta, T. *Inorg. Chim. Acta* **1980**, *45*, L205−L206. (d) Mutet, C.; Pfeffer, M. *J. Organomet. Chem.* **1979**, *171*, C34−C36.

(24) Clark, H. C.; Goel, A. B.; Goel, S.; Ogini, W. O. *Inorg. Chem*. **1979**, *18*, 2803−2808.

(25) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229−266.

(26) Dunina, V. V.; Razmyslova, E. D.; Kuz'mina, L. G.; Churakov, A. V.; Rubina, M. Y.; Grishin, Y. K. *Tetrahedron: Asymmetry* **1999**, *10*, 3147−3155.

(27) Chooi, S. Y. M.; Siah, S. Y.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812−4818.

(28) McFarlane, W.; Swarbrick, J. D.; Bookham, J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 3233−3238.

(29) Leung, P. H.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.* **1986**, *25*, 3396−3400.

(30) (a) Pearson, R. G. *Inorg. Chem*. **1973**, *12*, 712−713. (b) Jørgensen, C. K. *Inorg. Chem.* **1964**, *3*, 1201−1202.

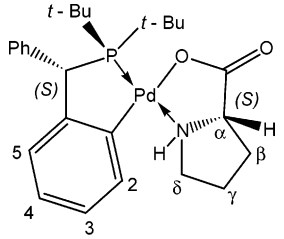
(31) (a) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127−2138. (b) Vicente, J.; Abad, J. A.; Frankland, A. D.; de Arellano, M. C. R. *Chem.*—*Eur. J.* **1999**, *5*, 3066−3075.

(32) Chooi, S. Y. M.; Leung, P.-H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529−532.

Table 1. Selected Bond Lengths (angstroms) and Angles (degrees) of (*S*)-**5**

Pd(1)−C(1)	1.997(4)	Pd(1)−P(1)	2.2172(11)
Pd(1)−O(1)	2.106(3)	Pd(1)−O(2)	2.084(3)
P(1)−C(7)	1.880(4)	C(1)−C(6)	1.403(5)
C(6)−C(7)	1.523(5)	C(7)−C(8)	1.521(5)
P(1)−C(14)	1.881(4)	P(1)−C(18)	1.883(4)
C(1)−Pd(1)−O(1)	178.6(2)	C(1)−Pd(1)−O(2)	92.0(1)
O(2)−Pd(1)−O(1)	87.7(1)	C(1)−Pd(1)−P(1)	81.6(1)
O(2)−Pd(1)−P(1)	173.46(8)	O(1)−Pd(1)−P(1)	98.84(9)
Pd(1)−C(1)−C(6)	122.9(3)	C(1)−C(6)−C(7)	119.3(3)
C(6)−C(7)−P(1)	102.9(3)	Pd(1)−P(1)−C(7)	104.8(1)

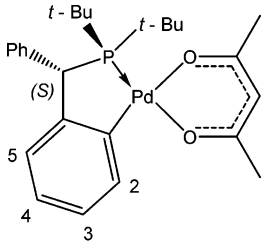
+650°, $[\alpha]_{365}$ +1200° (c, 0.3, CH_2Cl_2); 0.281 g (47.8%). Anal. Calcd for $C_{39}H_{43}ClP_2Pd$: C, 58.7; H, 6.8; N, 2.6. Found: C, 58.8; H, 6.9; N, 2.6. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.25 (d, 9H, $^3J_{PH}$ = 14.0 Hz, *t*-Bu), 1.26 (d, 9H, $^3J_{PH}$ = 13.2 Hz, *t*-Bu), 1.83 (m, 1H, γ-*H*′), 2.13 (m, 1H, γ-*H*″), 2.29−2.43 (m, 2H, both β-*H*), 3.40−3.51 (m, 3H, N-*H* and both δ-*H*), 4.09 (m, 1H, prolinate α-*H*), 4.54 (d, 1H, $^2J_{PH}$ = 11.4 Hz, palladacycle α-C*H*), 6.80 (m, 1H, *H*^{5}), 6.91−6.96 (m, 2H, *H*^{4}, *H*^{3}), 7.09 (m, 1H, *H*^{2}), 7.18−7.21 (m, 2H, Ph ring *m*- and *p*-*H*), 7.27 (m, 1H, Ph ring *m*-*H*), 7.35 (br d, 1H, J_{HH} = 7.4 Hz, Ph ring *o*-*H*), 7.56 (m, 1H, Ph ring *o*-*H*). ^{31}P-{^{1}H} NMR (202 MHz, $CDCl_3$): three sets of signals in 100, 0.97, 1.93; relative intensities, δ: 108.2 (s, *Z*-(*S*,*S*)-isomer), 109.8 (s, (*R*,*S*)-isomer), 110.1 (s, *E*-(*S*,*S*)-isomer).



Z-(S, S)-**4**

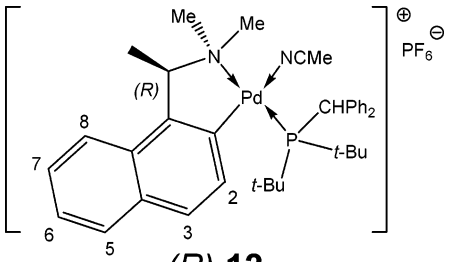
(+)-(*S*,*S*)-Di-μ-chlorobis{1-[(di-*tert*-butylphosphino)(phenyl)-methyl]phenyl-*C*^{2}, *P*}dipalladium(II) ((*S*,*S*)-3). HCl (10 mL, 1 M) was added to a CH_2Cl_2 solution (12 mL) of resolved (*S*,*S*)-**4** prolinate (0.23 g, 0.43 mmol), and the two-phase mixture was vigorously stirred for 5 min at room temperature. The aqueous layer was separated, and the procedure was repeated once using the same amount of HCl. The organic layer was removed, and it was washed with water (2 × 10 mL), dried with $MgSO_4$, and evaporated to dryness in vacuo to afford the optically active dimer (*S*,*S*)-**3** as a pale-yellow amorphous powder, mp (dec) 274−275 °C, $[\alpha]_D$ +342°, $[\alpha]_{578}$ +358°, $[\alpha]_{546}$ +412°, $[\alpha]_{436}$ +723° (c, 0.5, CH_2Cl_2); 0.193 g (99.0%). Anal. Calcd for $C_{42}H_{56}Cl_2P_2Pd_2$: C, 55.7; H 6.2. Found: C, 55.2; H, 6.3. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.28−1.42 (m, 18H, *t*-Bu), 4.51 (d, 1H, $^2J_{PH}$ = 11.4 Hz, α-C*H*), 6.70 (m, 1H, aromatic), 6.85−6.94 (br m, 2H, aromatic protons), 7.04−7.33 (br m, 4H, aromatic protons), 7.81−7.97 (br m, 2H, aromatic protons). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) two sets of closely spaced signals at δ: 111.8 (s), 112.2 (s), (223 K) δ: 110.5 (s) and 110.0 (s).

(Acetylacetonato-*O*,*O*′){(*S*)-1-[(di-*tert*-butylphosphino)(phenyl)-methyl]phenyl-*C*^{2},*P*}palladium(II) ((*S*)-5). Na(acac)·H_2O (0.029 g, 0.21 mmol) was added to an acetone solution (2 mL) of the resolved dimer (*S*,*S*)-**3** (0.095 g, 0.11 mmol), and the mixture was stirred vigorously for 2 h at room temperature. The resulting white suspension was filtered through a plug of celite to give a clear and colorless solution, which was concentrated. The optically active product was isolated as colorless blocks upon slow crystallization, mp (dec) 245−248 °C; $[\alpha]_D$ +267°, $[\alpha]_{578}$ +282°, $[\alpha]_{546}$ +327°, $[\alpha]_{436}$ +645°, $[\alpha]_{365}$ +1337° (*c* 0.5, CH_2Cl_2); 0.059 g (54.4%). Anal. Calcd for $C_{26}H_{35}O_2PPd$: C, 60.4; H, 6.8. Found: C, 60.5; H, 7.0. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.27 (d, 9H, $^3J_{PH}$ = 13.8 Hz, equatorial *t*-Bu), 1.33 (d, 9H, $^3J_{PH}$ = 13.0 Hz, axial *t*-Bu), 1.90 (s, 3H, acac−Me), 2.14 (s, 3H, acac−Me), 4.54 (d, 1H, $^2J_{PH}$ = 11.5 Hz, α-C*H*), 5.37 (s, 1H, acac−C*H*), 6.71 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.57 Hz, *H*^{5}), 6.88 (dddd, 1H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{PH}$ = 2.1 Hz, *H*^{4}), 6.98 (ddd, 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.6 Hz, *H*^{3}), 7.15−7.18 (m, 2H, *m*-Ph, α-*p*-Ph), 7.24 (m, 1H, α-*m*-Ph), 7.33 (br d, 1H, $^3J_{HH}$ = 8.4 Hz, α-*o*-Ph), 7.69 (m, 1H, α-*o*-Ph), 7.91 (ddd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 3.9 Hz, *H*^{2}). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, δ): 107.5 (s).



(S)-**5**

Attempted Isolation of (Acetonitrile){(*R*)-1-[1′-(*N*,*N*-dimethyl-amino)ethyl]naphthyl-*C*^{2},*N*}[(di-*tert*-butyl)(diphenylmethyl)-phosphine]palladium(II) Hexafluorophosphate(V) ((*R*)-12). A dichloromethane solution (5 mL) of **2** (0.12 g, 0.38 mmol) was transferred via cannular under argon to crystalline (*R*)-**11** (0.20 g, 0.38 mmol) with stirring, which led to the immediate formation of a golden-yellow solution. Attempts made to isolate the product by crystallization have been unsuccessful. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.41 (d, 9H, $^3J_{PH}$ = 14.4 Hz, *t*-Bu), 1.60 (d, 9H, $^3J_{PH}$ = 14.4 Hz, *t*-Bu), 1.82 (d, 3H, $^3J_{HH}$ = 6.6 Hz, α-CMe), 1.85 (d, 3H, $^4J_{PH}$ = 3.8 Hz, equatorial NMe), 2.11 (br s, NCMe), 2.42 (d, 3H, $^4J_{PH}$ = 1.8 Hz, axial NMe), 4.07 (dq, 1H, $^3J_{HH}$ = 6.6 Hz, $^4J_{PH}$ = 5.0 Hz, α-C*H*), 5.27 (d, 1H, $^2J_{PH}$ = 11.4 Hz, phosphine α-C*H*), 7.23−7.26 (m, 3H, aromatic protons), 7.29−7.32 (m, 2H, aromatic protons), 7.37 (d, 1H, $^3J_{HH}$ = 8.8 Hz, *H*^{3}), 7.44−7.46 (m, 2H, aromatic protons), 7.58 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, J_{PH} = 5.6 Hz , *H*^{2}), 7.60 (m, 1H, *H*^{8}), 7.71 (m, 1H, aromatic proton), 7.76−7.80 (m, 3H, aromatic protons), 8.21 (d, 2H, $^3J_{HH}$ = 7.9 Hz, α-*o*-Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, δ): 54.6 (s, phosphine *P*), −143.9 (septet, $^1J_{PF}$ = 711 Hz, PF_6^-).



(R)-**12**

Crystal Structure Determination of (*S*)-5. Crystal data for the complex and a summary of the crystallographic analyses are given in Table 2. Diffraction data were collected on a Siemens SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. SADABS absorption corrections were applied, and refinements by full-matrix least-squares were based

Table 2. Crystallographic Data for Complexes of (*S*)-**5**

formula	$C_{26}H_{35}O_2PPd$
mol wt	516.91
No.	*P*2(1)2(1)2(1)
cryst syst	orthorhombic
a (Å)	9.9659(15)
b (Å)	15.391(2)
c (Å)	16.128(2)
V (Å^3)	2473.9(6)
Z	4
T (K)	223(2)
λ (Å)	0.71073
μ (mm^{-1})	0.834
R1 (obs. data)[a]	0.0434
wR2 (obs. data)[b]	0.0801
flack parameter	−0.03(3)

on SHELXL 93.[3333] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at a fixed distance from carbon and nitrogen atoms and were assigned fixed thermal parameters.

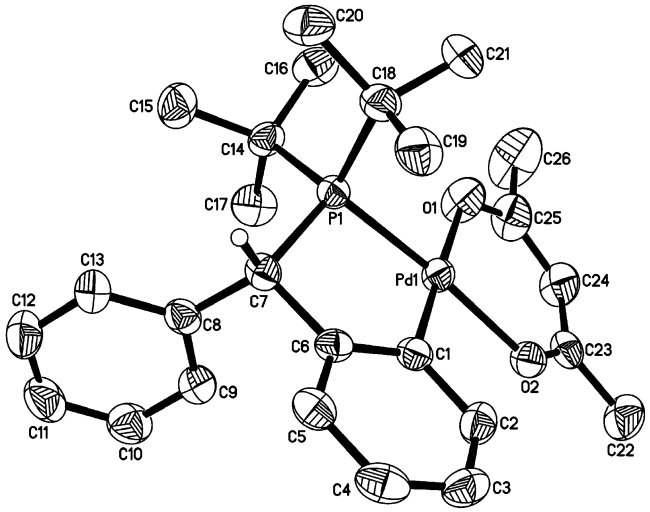


Figure 1. Molecular structure of (*S*)-**5**.

Results and Discussion

Synthesis of the Optically Active Phosphapalladacycle. As illustrated in Scheme 1, the synthesis of the phosphapalladacycle was readily achieved by the direct treatment of the prochiral phosphine (**2**)[20] and palladium(II) acetate in 1:1 stoichiometry followed by a chloride ion metathesis reaction using lithium chloride to arrive at the chloro-bridged dimer **3** as an air-stable yellow solid in 82.7% yield. The ease of cyclopalladation can be attributed to the steric stimulation presented by bulky substituents available on the donor,[21]which in the case of **2**, corresponds to the *t*-butyl groups. This is in general agreement with previous observations,[17k,22] in which enhancement to cyclopalladation was accredited to the presence of such bulky groups. In fact, the fluency of cyclopalladating **2** was manifested by employing the even weaker cyclopalladating agent,[17l,23] $[PdCl_4]^{2-}$ in a 2:1 (ligand:Pd(II)) stoichiometric ratio in the absence of an external Brønsted base, albeit a lower yield of 61.6%. Despite the use of such a reaction stoichiometry to encourage the formation of the bis(phosphine) complex of the type $[PdCl_2L_2]$ (L = **2**), such a product was not observed at the end of the reaction. Notably, the reaction was completed within 5 min at room temperature. As demonstrated in preceding examples,[14b,17c,22,24] the (ligand:Pd(II)) stoichiometry becomes rather inconsequential in such systems when bulky substituents are present.

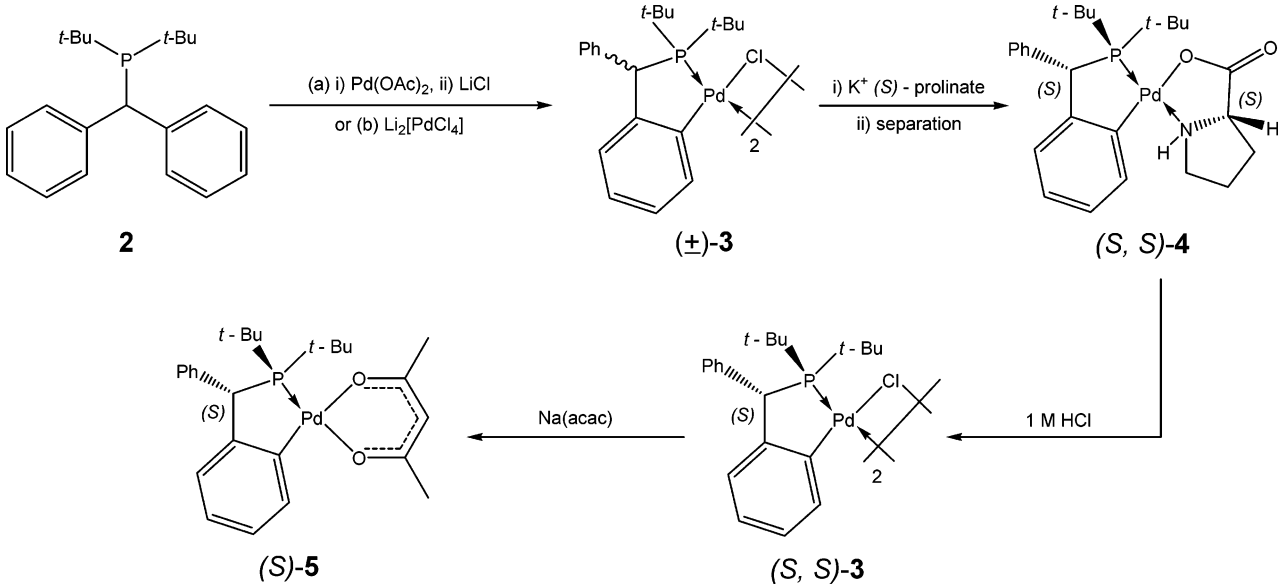
Whereas dimeric **3** was represented as a poorly resolved resonance at ca. δ 112 from the $^{31}P\{^1H\}$ NMR spectrum in ($CDCl_3$), signal resolution could be improved upon cooling the NMR sample to 223 K, such that the appearance of four singlet peaks at δ 110.0, 110.2, 110.3 and 110.5 became apparent. These four peaks must reflect the existence of the dimer as a mixture of six possible isomers in solution, namely the chiral syn- and anti-(R,R)/(S,S) as well as the meso syn- and anti-(R,S) isomers, which is therefore evident of the chiral nature of the palladacycle. Moreover, the formation of the palladacycle as a five-membered ring structure was supported by a coordination shift ($\Delta\delta$) value of about +65,[25] when comparing the $^{31}P\{^1H\}$ NMR chemical shifts of the free phosphine (δ 47.1) and the dimer.

A very high regioselectivity was noted in the reaction of the dimer with the chelating ligand, (*S*)-prolinate. Two pairs of geometric isomers, **4**, were observed. These were presented as four singlet peaks from the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of the crude product at δ 108.2, 109.8, 110.1, and 111.2 in a relative ratio of 99:98:1:2. The isolation of the (*S*,*S*) isomer with 98.1% de (from $^{31}P\{^1H\}$ NMR spectroscopic data) in 47.8% yield with $[\alpha]_D$ +287° (CH_2Cl_2) from the mixture was achieved via an optical resolution procedure of repeated fractional crystallization from the mother liquor that was enriched in toluene. A standard two-phase treatment of the isolated prolinate derivative (*S*,*S*)-**4** with dilute HCl (1 M) readily led to its conversion to the optically resolved dimer (*S*,*S*)-**3** as an amorphous yellow-green powder in the optically active form with $[\alpha]_D$ +342° (CH_2Cl_2). In $CDCl_3$, the optically resolved (*S*,*S*)-**3** was displayed as two sufficiently resolved singlet peaks from $^{31}P\{^1H\}$ NMR spectra at δ 111.8 and 112.2 at room temperature and δ 110.5 and 110.0 at 223 K, which support the existence of the dimer as a mixture of anti and syn regioisomers. Notably, the absence of the extra NMR signals that corresponded to the meso syn- and anti-(R,S)/(S,R) isomers (present in the unresolved parent dimer) must also point to the optically active form of the phosphapalladacycle complex. This method of optical resolution, that is, by the use of chiral amino acidates, has been previously applied to the isolation of optically active palladacycles.[3c,12c,18b,c,26] No loss in optical purity was detected from this transformation. This was verified from the $^{31}P\{^1H\}$ NMR data of the prolinate derivative (*S*,*S*)-**4** obtained from the rederivatization of the resolved dimer (*S*,*S*)-**3** by treatment with potassium (*S*)-prolinate in excess.

Whereas the isolated prolinate derivative (*S*,*S*)-**4** could not be obtained as single crystals of a satisfactory quality to allow a determination of the phosphapalladacycle absolute configuration by X-ray crystallography, this problem was readily circumvented by the use of the β-diketonate derivative (*S*)-**5** instead. This was obtained as white crystals with $[\alpha]_D$

(33) Sheldrick, G. M. *SHELXL 93, Program for Crystal Structure*; University of Gottingen: Gottingen, Germany, 1993.

Scheme 1



2 (±)-**3** (*S, S*)-**4** (*S, S*)-**3** (*S*)-**5**

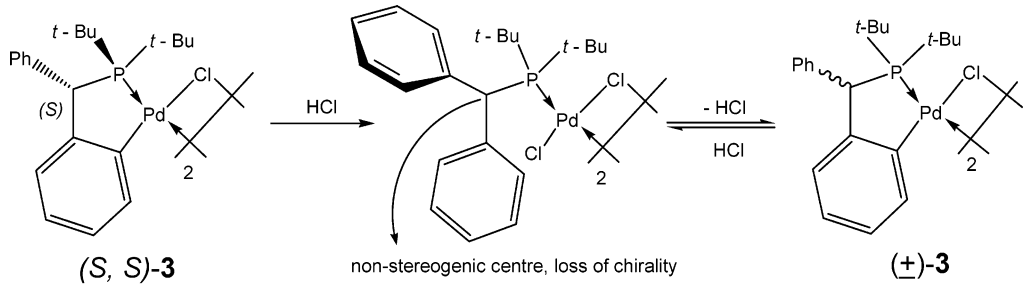
+267° (CH_2Cl_2) by the direct treatment of the optically resolved (*S,S*)-**3** with sodium acetylacetonate. The molecular structure and numbering scheme of (*S*)-**5** are presented in Figure 1, and selected bond lengths and bond angles are given in Table 1. Importantly, the (*S*) absolute configuration at the stereogenic α-C center of the optically resolved phosphapalladacycle was confirmed by the Flack parameter [−0.03(3)]. Notably, the five-membered palladacycle ring was noted to adopt a puckered conformation, and the nonplanarity of the ring was given by the mean intrachelate torsion angle of 18.3°. This value is comparable to those of the ortho-palladated 1-(1′-naphthyl)ethyldiphenylphosphine (16.7−21.0°) and 1-(1′-naphthyl)ethyldiphenylarsine (16.0−20.3°) systems[13a] but is weak with respect to that obtained from the phosphapalladacycle chloro dimer of 1-[(2′, 5′-dimethyl)-1-phenyl]ethyldiphenylphosphine (31.4°).[13b] The α-C phenyl substituent takes up the axial disposition. This was inferred from the angle of 11.0° between the C(8)−C(7) bond to the normal of the mean coordination plane surrounding the central Pd atom.

Kinetic Lability of the Phosphapalladacycle Pd−C Bond. In many publications devoted to the chemistry of palladacycles, much has been investigated about the stability and therefore the Pd−C bond reactivity. In particular, this bond was known to be reactive toward various nucleophiles.[5] In fact, one of the other main interests of cyclopalladated complexes was based on the exploitation of the reactivity of this bond as a means of functionalizing the metalated chelate so that a plethora of organic molecules could be derived thereafter. For the palladacycles of the 1-(1′-napthyl)-ethyldiphenylphosphine/arsine[13a] and later, 1-(2′,5′-dimethylphenyl)ethyldiphenylphosphine[13b] that we have developed, the Pd−C bonds of such systems were found to be unstable in the presence of concentrated HCl, so that the addition of one drop of the latter to NMR samples of the $CDCl_3$ solutions of their chloro-bridged dimers at room temperature was sufficient to bring about the immediate rupture of these Pd−C bonds. In all the three cases, the palladacycles could not survive and were dechelated instantaneously to the η^1−P (or η^1−As) monodentate dimers via Pd−C bond cleavage and protonation.

In contrasting fashion, $^{31}P\{^1H\}$ NMR spectroscopy revealed no chemical transformation when the same test was applied to the current phosphapalladacycle dimer, (±)-**3**. To determine if the phosphapalladacycle was able to withstand an even harsher reaction condition, the same complex was subsequently treated with excess concentrated HCl in refluxing acetone for 2 h. Quite remarkably, a similar $^{31}P\{^1H\}$ NMR spectral picture of the original dimer was observed, suggesting that no reaction had taken place and that the Pd−C bond had remained intact in spite of such harsh conditions. However, it has to be emphasized that the above treatment was applied to **3** in the racemic form because repeating the above experiment using the optically active (*S,S*)-**3** led unexpectedly to the racemization of the phosphapalladacycle. This important fact was established from two experimental observations. First, dimer **3** was no longer optically active, with $[\alpha] = 0$ determined at various wavelengths. Additionally, treatment of the product with excess potassium (*S*)-prolinate revealed the presence of two sets of diastereomers in equal intensities from the $^{31}P\{^1H\}$ NMR spectrum of the obtained prolinate derivatives **4**, that is, an identical spectral pattern that was also obtained from (±)-**3**. Racemization must have proceeded via a Pd−C bond cleavage because this generates symmetry on the η^1−P coordinated phosphine ligand. It then follows that either one of the available two enantiotopic phenyl rings could ortho palladate thereafter (Scheme 2).

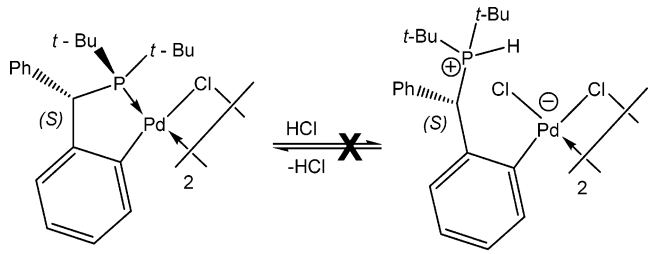
The above results seemed to suggest that the phosphapalladacycle was undergoing reversible ring opening/closing via the repeated Pd−C bond cleavage/re-formation under the above reflux condition. Such an activity could not have been detected from the racemic dimer alone because no change in optical activity could be anticipated before and after the experiment. In other words, in such acidic medium, the

Scheme 2

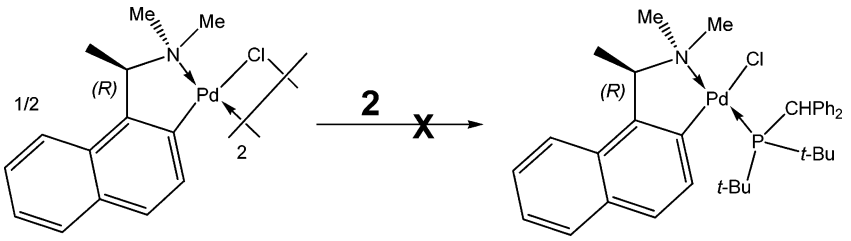


6

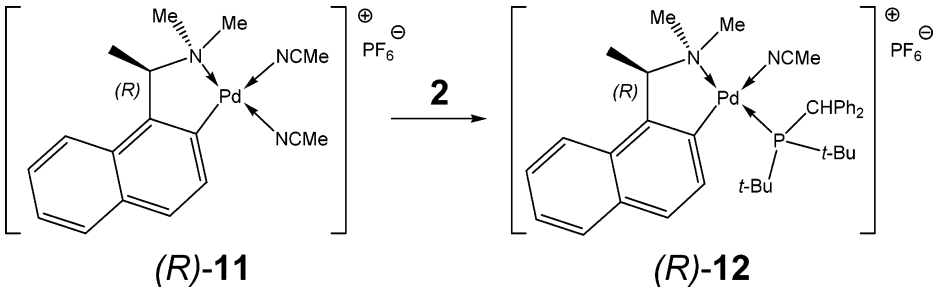
Scheme 3



Scheme 4



Scheme 5

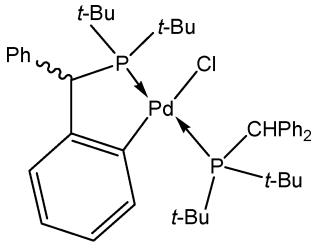


phosphapalladacycle is unstable kinetically, but is itself the thermodynamically stable product. The strong tendency of the phosphine to undergo ring closure from the η^1−P monodentate state, after hydrolysis by HCl, is therefore obvious here. This inclination is most probably stimulated by the steric effects of the bulky *t*-butyl substituents. This tendency was so strong that the presence of concentrated HCl was only sufficient to labilize the Pd−C bond and not bring about its permanent dissection.

It is important to understand that the racemization process could not have proceeded via the alternate P → Pd dative bond cleavage as illustrated in Scheme 3. This process is immediately ruled out because ring opening of the phosphapalladacycle by acid protonation of the P donor would not have led to a symmetrization of the phosphine ligand but would preserve the stereogenic integrity of the α-C atom and hence the overall chirality of the Pd−C-bonded phosphonium ligand in the intermediate (*S*,*S*)-**7**, by the continued presence of four different substituents on the α-C atom.

The phosphine has therefore displayed a very strong tendency to remain in the ortho-palladated state and that this mode of coordination is much preferred over the simple η^1−P monodentate. In fact, the strong inclination of the phosphine toward the ortho-palladated state over the latter coordination mode was earlier exemplified from its reaction with the agent $Li_2[PdCl_4]$ in 2:1 (ligand/metal) stoichiometry in the absence of any external Brønsted base. Notably, neither the formation

of the coordinated complex, dichlorobisphosphinepalladium-(II), nor the adduct of the type **8** was isolated, in which both



8

complexes contain at least one simple P-coordinated monodentate unit of the phosphine ligand. Their formations may not be ruled out given the initial 2:1 (ligand/metal) stoichiometry. Clearly, the strong tendency of the phosphine to achieve an ortho-palladated structure and its difficulty to remain in a simple η^1-P monodentate coordination bonding as a consequence of the stimulating effect of the bulky *t*-butyl groups is again manifested here. Therefore, the η^1-P monodentate type of coordination alone does not impart improved stability to the free, uncoordinated ligand. As such, the ortho-palladated mode of coordination can be seen as the more-stable mode of coordination over the former η^1-P monodentate type, so that it converts spontaneously to the cyclopalladated mode whenever pathways leading to the latter are available. This behavior is further supported by the observations in the following.

It is well-known that μ-chloro dimers of cyclopalladated amines such as the chiral *N*,*N*-dimethylamino-1-(1′-naphthyl)ethylaminate system react rather easily with a wide range of monodentate phosphines and arsines via the cleavage of the chloro bridges to form trans-(N,E) mononuclear adducts (where E = P/As). These contain the stable Pd−Cl bond, both thermodynamically and kinetically.[27] The stability of this bond was exemplified from the possibility to isolate the optically resolved forms of the mononuclear compounds of 1-(1′-napthyl)ethyldiphenylphosphine/arsine[13a] and 1-(2′,5′-dimethylphenyl)ethyldiphenylphosphine[13b] in the η^1-E coordination modes despite their abilities to ortho palladate. Given the restriction (to cyclopalladate) imposed by the Pd−Cl bond, it was therefore of little surprise when no reaction was observed (from ^{31}P NMR spectroscopy) when phosphine **2** was treated with the chloro dimer of (*R*,*R*)-*N*,*N*-dimethylamino-1-(1′-naphthyl)ethylaminate in the usual 2:1 stoichiometry. Here, the transformation of the phosphine from the monodentate mode to the cyclopalladated mode becomes remote because of the presence of the Pd−Cl bond. Because the monodentate η^1-P coordination presents little incentive over the free ligand in the uncoordinated state, the phosphine remains uncoordinated.

However, phosphine **2** could be coerced to bind in the η^1-P coordination mode when an extra stimulus was provided by the improved Lewis acidity of the Pd(II) center in the form of positively charged complex (*R*)-**11**. This was observed from the presence of the ^{1}H−^{31}P spin−spin couplings for the axial and equatorially disposed NMe

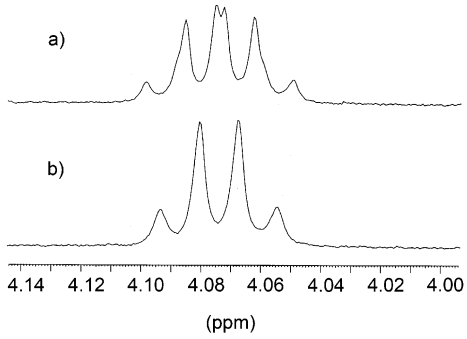


Figure 2. Spectroscopic evidence for phosphine coordination in (*R*)-**12** by comparison of (a) ^{1}H and (b) ^{1}H{^{31}P} spectra for the signals of the (*R*)-1-(1′-naphthyl)ethylaminate palladacycle α-CH proton.

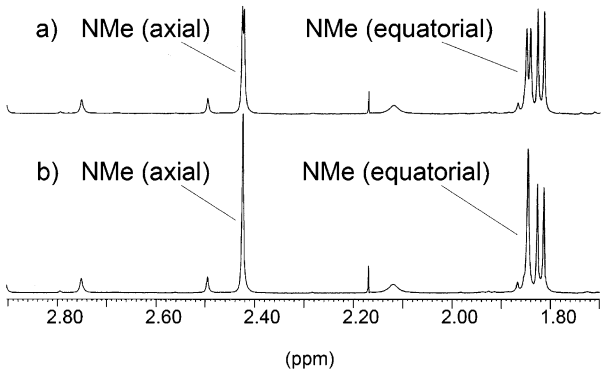


Figure 3. Spectroscopic evidence for phosphine coordination in (*R*)-**12**: by comparison of (a) ^{1}H and (b) ^{1}H{^{31}P} spectra for the signals of the (*R*)-1-(1′-naphthyl)ethylaminate palladacycle axial and equatorial NMe protons.

protons and the α-C methine proton of the *N*,*N*-dimethylamino-1-(1′-naphthyl)ethylaminate palladacycle in the ^{1}H NMR spectrum of the crude compound. These were determined to be 5.0, 1.8, and 3.8 Hz, respectively. Moreover, the existence of $^4J_{PH}$ coupling as the only observed ^{1}H−^{31}P spin−spin coupling for the palladacycle α-C methine proton is also indicative of the usual trans-(P, N) geometry of the complex. This conclusion was made on the basis of a previous report of similar complexes of C_2-symmetric chiral diphosphine ligands chelated to the *N*,*N*-dimethylamino-1-(1′-phenyl)ethylamine palladacycle. It revealed that the palladacycle α-C methine proton had spin-coupled to only one of the two ^{31}P nuclei and, specifically, the ^{31}P nucleus cis to the adjacent Pd−C bond.[28] This trans-(P, N) arrangement was dictated by the electronic directing effects of the hard/soft natures of the N and C$^-$ donors of the aminate palladacycle[10c,11,29] and is attributed to the result of "anti-symbiosis".[30] Support for the direct phosphine attachment was adequately provided by a comparison of the ^{1}H and ^{1}H-{^{31}P} NMR spectra for the resonance of these three sets of protons (Figures 2 and 3). The ^{31}P{^{1}H} NMR spectroscopic chemical shift of the observed complex, at δ 54.6 ($CDCl_3$) only indicates a monodentate η^1-P coordination mode of the phosphine. This is because the rather small value of the coordination shift, $\Delta\delta$, at 7.5 ppm with respect to the chemical shift of the free ligand, does not justify the formation of a five-membered ring that is satisfied by the ortho palladated structure.[25] Even then, the monodentate η^1-P coordination was only detected in solution spectro-

scopically, as attempts made to isolate the complex by slow crystallization have led to the isolation of the starting material (*R*)-**11** in almost quantitative yield. The gradual de-coordination of the phosphine ligand is therefore evident, which once again points to the low thermodynamic stability of complex (*R*)-**12** and therefore, the continued difficulty of the phosphine to be engaged in a simple η^1-P monodentate coordination. Ring closure following the monodentate coordination in this case was probably prohibited by the unfavorable trans-(aryl, aryl) arrangement known as the phenomenon of "transphobia",[31] notwithstanding the possible coordination vacancy that could be generated by the withdrawal of the rather weakly coordinated acetonitrile ligand from the Pd(II) center.

Conclusions

Direct ortho palladation of the title phosphine was readily accomplished by the use of palladium(II) acetate or even the less effective metallating agent $Li_2[PdCl_4]$,[17l,23] despite employing 1:2 (metal/ligand) stoichiometry. The resulting phosphapalladacycle was then obtained in the optically active form by optical resolution involving the separation of the (*S*)-prolinate diastereomeric derivatives. Racemization of the optically active phosphapalladacycle was noted in refluxing acetone/HCl. This was the result of the lability of the Pd−C bond, which was undergoing reversible cleavage under this condition. Notably, in contrast to previous experiences involving other similar palladacycles, a permanent rupture of the Pd−C bond and therefore the transformation of the phosphine from the cyclopalladated state to the monodentate η^1-P state was not observed. The ortho-palladated state, rather than the monodentate η^1-P state, was the more-favored choice of coordination, so that whenever the formation of the former was rendered impossible, the phosphine would preferably remain in the free, uncoordinated state. This was supported by its lack of reactivity toward the μ-chloro dimer of the *N*,*N*-dimethyl-1-(1′naphthyl)ethylaminate palladacycle. The tendency of the phosphine to cyclopalladate is attributed to the stimulating steric effect presented by the bulky *t*-butyl substituents at the P donor.

It is noteworthy that the kinetic lability of the Pd−C bond in the phosphapalladacycle could not have been discovered in the absence of the resolved form of the complex. At the time of writing, investigations related to the asymmetric ortho palladation of the phosphine and the synthetic applications of the enantiomeric form of the newly prepared phosphapalladacycle are in progress.

Acknowledgment. We thank the National University of Singapore and Nanyang Technological University for the awards of the research scholarships to J.K.P.N. and S.C., respectively.

Supporting Information Available: Crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters for (*S*)-**5**. This material is available free of charge via the Internet at http://pubs.acs.org

IC0702320