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Article

Reactions of Cyclopalladated Complexes with Lithium Diphenylphosphide

Valeria A. Stepanova,[†] Valery V. Dunina,[‡] and Irina P. Smoliakova*[,†]

[†]*Chemistry Department, University of North Dakota, 151 Cornell Street, Stop 9024, Grand Forks, North Dakota 58202-9024, and* [‡]*Chemistry Department, M.V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation*

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Reactions of the cyclopalladated dimer $\{Pd(\eta^2\text{-}L^1)(\mu\text{-}Cl)\}_2$ (**7**) derived from *N*,*N*-dimethylbenzylamine (HL^1) with lithium diphenylphosphide were studied under varied conditions. The $LiPPh_2$ reagents used were purchased from Sigma-Aldrich Co. or synthesized from PPh_3, $ClPPh_2$, or $HPPh_2$ by known general methods. Depending on the source of lithium phosphide, solvent, and reagent ratio, reactions of $LiPPh_2$ with complex **7** resulted in the formation of different products. The commercial $LiPPh_2$ solutions reacted with compound **7** and several other cyclopalladated dimeric complexes in THF to form the corresponding mononuclear derivatives with $Ph_2P(CH_2)_4OH$ as an auxiliary ligand, $Pd(\eta^2\text{-}L)Cl\{PPh_2(CH_2)_4OH\}$. The monophosphido-bridged analogue of dimer **7**, $\{Pd(\eta^2\text{-}L^1)\}_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)$ (**17**), was the most common product of the 1:2 reactions of dimer **7** with other $LiPPh_2$ solutions in THF. *ortho*-(Diphenylphosphino)-*N*,*N*-dimethylbenzylamine (**20**) was obtained in the reactions of complex **7** with the synthesized solutions of $LiPPh_2$ using a 1:4.5 molar ratio of the reagents in THF or a 1:2 ratio in toluene. Possible mechanisms of these reactions are discussed.

I. Introduction

Since the discovery of cyclopalladated complexes (CPCs) a half a century ago, these organometallic compounds have found a plethora of applications.[1] In particular, CPCs can be used for ligand transformations using reactions of the Pd−C bond.[2] Almost all reported transformations of this type include reactions of alkenes, alkynes, allenes, carbon monoxide, isocyanides, acyl halides, or halogens.[2] We have been interested in studying reactions of CPCs with $LiPAr_2$. Insertion of the PAr_2 moiety into the Pd−C bond of *C,N*- or *C,P*-palladacycles would provide a general approach for synthesis of aminophosphines, diphosphines, and related ligands valuable in asymmetric reactions.

The idea of using CPCs in reactions with metal phosphides is not new; however, there are only four communications related to this research field. In 1980, the Sokolov group reported preparation of aminophosphines (S_{pl})-**2** and *rac*-**2** by reactions of CPCs (S_{pl},S_{pl})-**1** and *rac*-**1** with $LiPPh_2$ (Scheme 1).[3] The authors reported two different procedures. In one of them, $LiPPh_2$ was synthesized from PPh_3 and Li using an excess of the former reagent. In the other procedure, excess Li was used; however, (S_{pl},S_{pl})-**1** was added to $LiPPh_2$ along with PPh_3.

Later, the same group reported a reaction of (S_{pl},S_{pl})-**1** with the prochiral phosphide LiPMePh (Scheme 1).[4] The corresponding two diastereomers of aminophosphine **3** were obtained in 52% total yield and were separated using column chromatography on silica gel.

The Bolm group studied preparation of (S_C,R_{pl}) and (S_C,S_{pl}) diastereomers of the oxazolynyl[2.2]paracyclophane-derived phosphine **5** by reacting each of the two corresponding diastereomers of the mononuclear CPC **4** with $KPPh_2$ (Scheme 2).[5] Purification of phosphine **5** in the form of the BH_3 adduct followed by deprotection afforded two diastereomers in 67% and 61% yield. Surprisingly, the same group in a later paper did not apply this method for synthesis of the isopropyl analogue of phosphine **5**; instead, the compound was obtained using a multistep synthesis in a low overall yield.[6]

As a part of the study directed toward the development of new Pd-coordinated aminophosphine catalysts, Dunina et al. reported the NMR spectroscopic evidence of the in situ formation of Pd(0) complexes of the composition (aminophosphine)$Pd(PPh_3)_2$.[7] These complexes were prepared by

*To whom correspondence should be addressed. E-mail: ismoliakova@chem.und.edu.

(1) (a) *Palladacycles. Synthesis, Characterization and Applications*; Dupont, J.; Pfeffer, M., Eds.; Wiley-VCH Verlag GmbH: Weinheim, 2008. (b) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527–2571.

(2) Vila, J. M.; Pereira, M. T. The Pd−C Building Block of Palladacycles: A Cornerstone for Stoichiometric C−C and C−X Bond Assemblage. In *Palladacycles. Synthesis, Characterization and Applications*; Dupont, J.; Pfeffer, M., Eds.; Wiley-VCH Verlag GmbH: Weinheim, 2008; pp 87−108.

(3) Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organomet. Chem.* **1980**, *202*, C58–C60.

(4) Troitskaya, L. L.; Starikova, Z. A.; Demeshchik, T. V.; Sokolov, V. I. *Russ. Chem. Bull.* **1999**, 1738–1743.

(5) Bolm, C.; Wenz, K.; Raabe, G. *J. Organomet. Chem.* **2002**, *662*, 23–33.

(6) Whelligan, D. K.; Bolm, C. *J. Org. Chem.* **2006**, *71*, 4609–4618.

(7) (a) Dunina, V. V.; Kuz′mina, L. G.; Howard, J. A. K.; Kataeva, N. A.; Rubina, M. Y.; Parfyonov, A. G.; Veits, Y. A.; Grishin, Y. K., Direct Route from Chiral Palladacycles to Enantioselective Aminophosphine Palladium(0) Catalysts. In *10th IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis* (*OMCOS-10*); Versailles, France, 1999; p 124. (b) Grishin, Y. K.; Rubina, M. Y.; Kataeva, N. A.; Churakov, A. V.; Kuz′mina, L. G.; Howard, J. A. K.; Dunina, V. V. *CCDC, XOZPIL*, **2002**, private communication.

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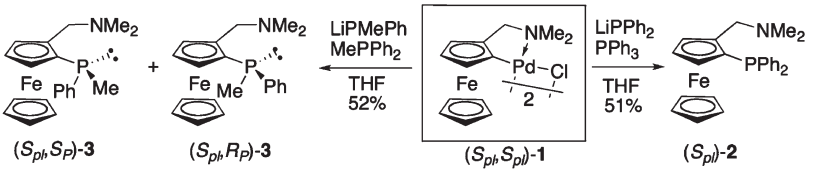
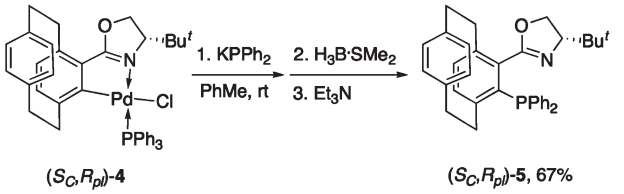
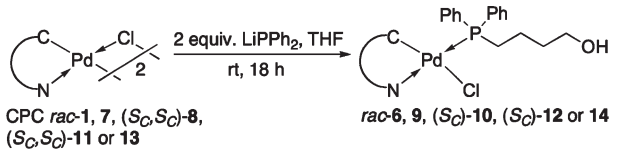
Scheme 1



Scheme 2



Scheme 3



reacting dimeric CPCs with $LiPPh_2$ in the presence of excess PPh_3. Inspired by the results of these groups, we undertook our study of the reactions of CPCs with $LiPPh_2$ under different conditions; the results are presented in this paper.

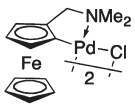
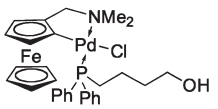
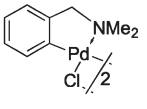
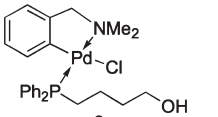
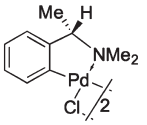
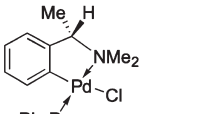
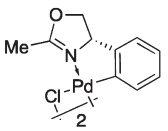
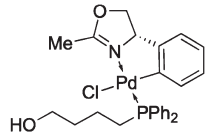
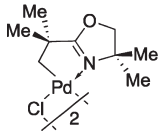
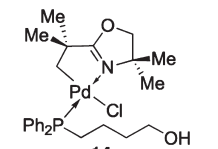
II. Results and Discussion

II.1. Reaction of μ-Cl Dimeric CPCs with a Commercial (Sigma-Aldrich Co.) Solution of $LiPPh_2$ in THF. This part of the study was conducted using a 0.5 M solution of $LiPPh_2$ in THF purchased from Sigma-Aldrich Co. We have found that, in the absence of PPh_3, reaction of 2 molar equiv of $LiPPh_2$ with dimeric CPC *rac*-**1** did not result in the insertion of the phosphide moiety into the Pd−C bond in the temperature range from −78 to +25 °C. Instead, the major product of the reaction was complex *rac*-**6**, in which the phosphide moiety was converted to a tertiary phosphine with one 4-hydroxybutyl group (Scheme 3 and Table 1, entry 1). The appearance of this alkyl fragment in the final product was a result of the formal insertion of the PPh_2 moiety in one of the two C−O bonds of THF used in the reaction as a solvent.

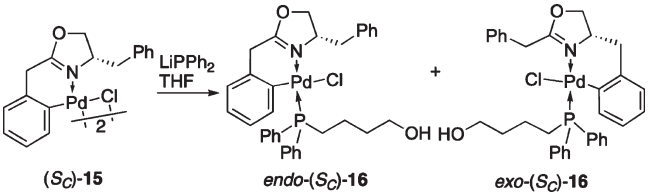
In order to determine whether this transformation is applicable to other cyclopalladated amines, two dimeric complexes, **7** and (S_C,S_C)-**8**, were also subjected to the same reaction conditions with the same solution of $LiPPh_2$. In both cases, the corresponding air- and moisture-stable mononuclear complexes **9** and (S_C)-**10** were isolated after purification of the crude mixtures using preparative column chromatography in 85% and 78%, respectively (Table 1, entries 2 and 3).

Two oxazoline-derived dimeric CPCs, (S_C,S_C)-**11**, with a five-membered exo-palladacycle containing the (sp^2)C−Pd bond, and complex **13**, with an aliphatic five-membered palladacycle and the (sp^3)C−Pd bond, were tested as well. As expected, the $PPh_2(CH_2)_4OH$ adducts (S_C)-**12** and **13** were obtained in good yield (Table 1, entries 4 and 5).

Table 1. Reactions of Dimeric CPCs with the $LiPPh_2$ Reagent Aldrich-1

Entry	CPC	Product	Yield, %
1	 *rac*-**1**	 *rac*-**6**	87
2	 **7**	 **9**	85
3	 (S_C,S_C)-**8**	 (S_C)-**10**	78
4	 (S_C,S_C)-**11**	 (S_C)-**12**, 67%	67
5	 **13**	 **14**	69

Scheme 4



Reaction of $LiPPh_2$ with the dimer **15**, containing a six-membered endo-palladacycle, provided *exo*-**16** in 61% yield. When the concentration of the complex was increased by 3-fold, a 1:1 mixture of two complexes, *exo*-**16** and *endo*-**16**, in a total yield of 20% was obtained (Scheme 4). The observed intramolecular trans-cyclopalladation is especially interesting considering that cyclopalladation of (S_C)-2,4-dibenzyl-2-oxazoline under different conditions results exclusively in the

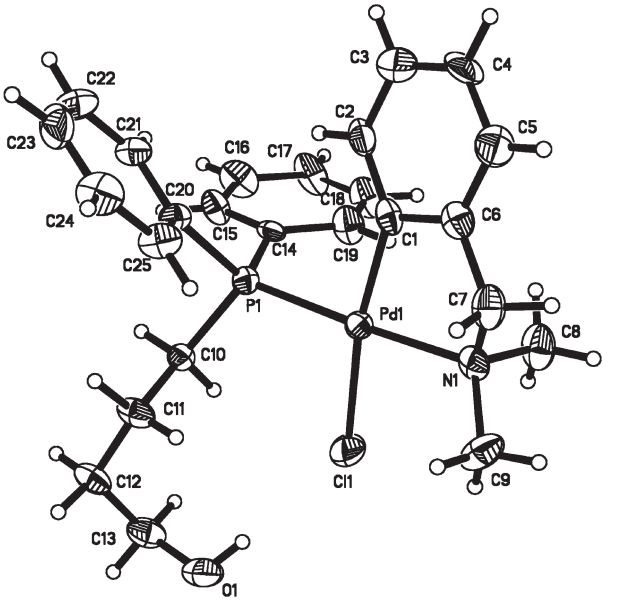


Figure 1. Molecular structure of complex **9**.

formation of CPC (S_C,S_C)-**15** with the endo-palladacycle.[8] However, this case of intramolecular trans-cyclopalladation is not unique; this type of transformation has been previously reported for other CPCs under different conditions.[9−13]

The structures of complexes **6**, **9**, **10**, **12**, **14**, *endo*-(S_C)-**16**, and *exo*-(S_C)-**16** were proven by IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy data, as well as by COSY, HMQC, and DEPT NMR spectra. Purity of all new complexes was confirmed by satisfactory elemental analyses. The ^{31}P NMR spectra of the complexes with the $Ph_2P(CH_2)_4OH$ ligand exhibited a single signal within the 13.1−20.1 ppm region. For comparison, the spectra of similar PPh_3 derivatives usually have signals around 30 ± 4 ppm.[8,10] The *trans*-{*N,P*} geometry of complexes **6**, **9**, **10**, **12**, **14**, *endo*-**16**, and *exo*-**16** in solutions is supported by the characteristic values of coupling constants in the ^{1}H and ^{13}C NMR spectra: (i) $^4J_{HP}$ = 1.6−2.9 Hz found for the NMe_2 group in the spectra of **6**, **9**, and **10**; (ii) $^3J_{HP}$ = 4.6 Hz for the $PdCH_2$ signal of **14**, and (iii) $^3J_{CP}$ 9.7−13.0 Hz for H(6) in the spectra of **6**, **9**, **10**, **12**, *endo*-**16**, and *exo*-**16**. The unambiguous proof of the proposed structure for complex **9** was obtained by the X-ray crystallographic study (Figure 1).

When we were about to submit a manuscript describing these data, we learned that another 0.5 M solution of $LiPPh_2$ in THF (reagent **Aldrich-2**) also purchased from Sigma-Aldrich Co. did not react with dimeric CPC **7** to form complex **9**. A representative of Sigma-Aldrich Co. informed us that "the material continues to meet our specifications and is considered fine" and refused to provide any data on preparation of the $LiPPh_2$ samples. Interestingly enough,

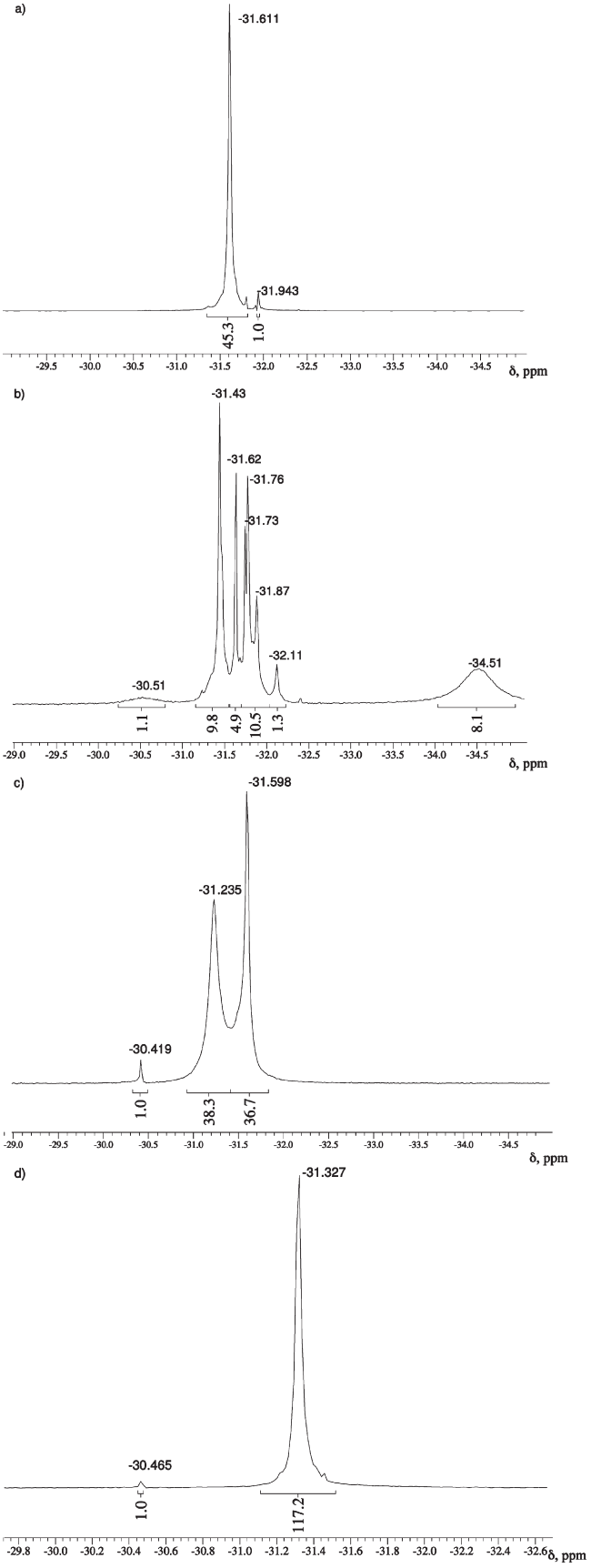


Figure 2. ^{31}P{^{1}H} NMR spectra the $LiPPh_2$ solutions in THF purchased from Sigma-Aldrich Co.: (a) **Aldrich-1**; (b) **Aldrich-2** upon receiving; (c) **Aldrich-2** after 12 months; and (d) **Aldrich-2** after 12 month and dilution (see the text for details).

(8) Mawo, R. Y.; Johnson, D. M.; Wood, J. L.; Smoliakova, I. P. *J. Organomet. Chem.* **2008**, *693*, 33–45.
(9) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252–1260.
(10) Mawo, R. Y.; Mustakim, S.; Young, V. G.Jr.; Hoffmann, M. R.; Smoliakova, I. P. *Organometallics* **2007**, *26*, 1801–1810.
(11) Dunina, V. V.; Gorunova, O. N.; Grishin, Y. K.; Kuz'mina, L. G.; Churakov, A. V.; Kuchin, A. V.; Howard, J. A. K. *Russ. Chem. Bull.* **2005**, 2073–2082.
(12) Kind, L.; Klaus, A. J.; Rys, P.; Gramlich, V. *Helv. Chim. Acta* **1998**, *81*, 307–316.
(13) Benito, M.; López, C.; Morvan, X. *Polyhedron* **1999**, *18*, 2583–2595.

Chart 1. Reported Structures of Lithium Phosphides

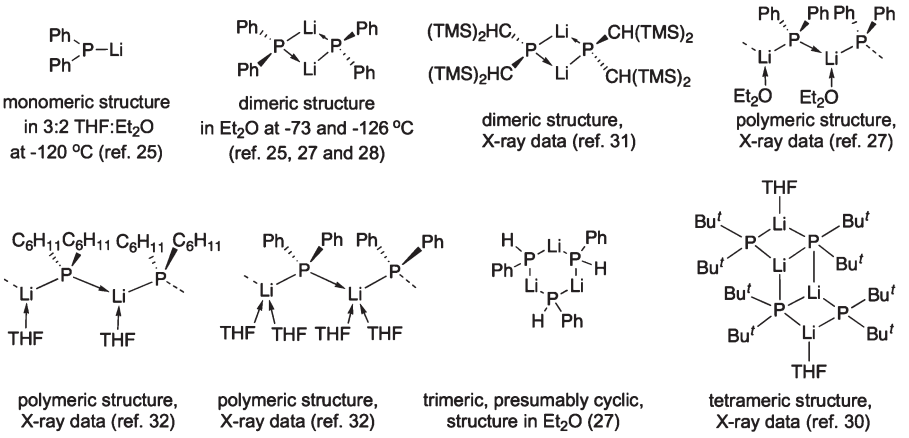
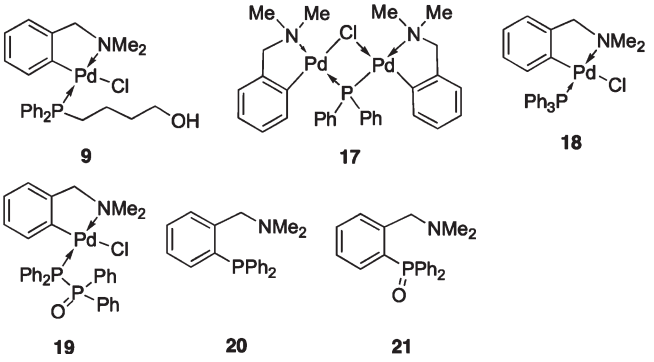


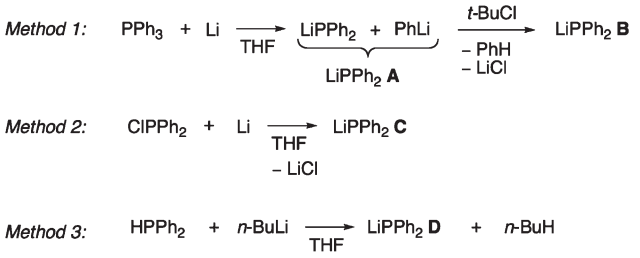
Chart 2. Structures of the Products Formed in the Reactions of CPC 7 with the $LiPPh_2$ Reagents



after one year, the $LiPPh_2$ reagent kept in the same bottle at rt did react with CPC **7** to give compound **9**. To attempt explaining these results, we synthesized $LiPPh_2$ by several methods and studied if preparation methods or other factors affect the structure of the phosphide as well as the products formed in reactions with dimeric CPCs.

II.2. $^{31}P\{^1H\}$ NMR Spectra of the Lithium Diphenylphosphide Reagents Obtained by Different Methods. Two $LiPPh_2$ solutions purchased from Sigma-Aldrich Co. have been analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. The first reagent, **Aldrich-1**, which reacted with CPC **7** to form complex **9**, had a single sharp $^{31}P\{^1H\}$ NMR signal at δ −31.6 ppm, $\omega/2$ = 8.5 Hz (Figure 2a). The second reagent, **Aldrich-2**, when purchased, showed several peaks in its $^{31}P\{^1H\}$ NMR spectrum (Figure 2b) and reacted with the dimeric CPC **7** to give several unidentified compounds with no traces of complex **9** (TLC and ^{31}P NMR data). In one year, the $LiPPh_2$ reagent **Aldrich-2** reacted with dimer **7** to yield complex **9** in 59% yield (along with 14% of complex **17**, see Part II.3 and Chart 2). The $^{31}P\{^1H\}$ NMR spectrum of this reagent changed significantly and had three signals, δ −30.4, −31.2 ppm ($\omega/2$ = 47.1 Hz) and −31.6 ($\omega/2$ = 6.3 Hz), in a ratio of ca. 1:38:37 (Figure 2c). After diluting the sample with THF-d_8 to a concentration of 0.35 M, the spectrum was quite different: the weak signal at δ −30.4 ppm remained unchanged, but two major signals became one, with the chemical shift, δ, −31.4 ppm; the signal ratio became 1:60. Diluting the sample again (0.27 M) gave a signal ratio of 1:62. When the $^{31}P\{^1H\}$ NMR spectra of the same sample were taken again in 24 and 48 h, the ratio changed to 1:78 and 1:117, respectively, and

Scheme 5



the chemical shift value of the major signal slightly moved to δ −31.3 ppm (Figure 2d). These data indicate that $LiPPh_2$ in THF solutions may form different structures, and these structures change upon both storing and diluting the reagents.

Since the method used by Sigma-Aldrich Co. for preparation of $LiPPh_2$ is proprietary knowledge, we synthesized this reagent by three different general methods (Scheme 5) and analyzed all samples by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of the $LiPPh_2$ reagent **A1** prepared by reacting PPh_3 with Li (1:2.2 molar ratio) in THF at rt for 18 h contained two signals, PPh_3 (δ −22.5 ppm) and $LiPPh_2$ (δ −39.1 ppm) in a ca. 2:1 ratio (signal delay, τ, was 2 s).[14−16] When this reaction mixture was treated with *t*-BuCl to remove PhLi,[17,18] the spectrum of the new $LiPPh_2$ reagent **B1** exhibited four signals assigned to PPh_3 (δ −20.4 ppm), $LiPPh_2$ (δ −30.4 and −31.4 ppm in a ratio of 2:1), and $HPPh_2$ (δ −55.4 ppm). The $LiPPh_2$ reagent **A2** was prepared by reacting PPh_3 with 6 equiv of Li. The spectrum of reagent **A2** contained only one signal at δ −37.4 in the range −30 to −40 ppm; however, a trace amount of PPh_3 was detected as well. After quenching PhLi in **A2** with *t*-BuCl, the new reagent **B2** exhibited two $^{31}P\{^1H\}$ NMR signals in the range −30 to −40 ppm, similar to reagent **B1**.

The $LiPPh_2$ reagent **C1** was obtained using method 2 (Scheme 5) by dropwise addition of $ClPPh_2$ to Li (1:3 molar

(14) According to our NMR experiments, the ratio of signals assigned to PPh_3 and $LiPPh_2$ species does not reflect the exact PPh_3:$LiPPh_2$ ratio when the signal delay, τ, is less than 10 s due to a diffrence in relaxation time for different P-containing species.

(15) Bianco, V. D.; Doronzo, S.; Chan, J.; Bennett, M. A. *Inorg. Synth.* **1976**, *16*, 161–163.
(16) Aguiar, A. M.; Beisler, J.; Mills, A. *J. Org. Chem.* **1962**, *27*, 1001–1005.
(17) Bianco, V. D.; Doronzo, S. *Inorg. Synth.* **1976**, *16*, 155–161.
(18) Luther, G. W. I.; Beyerle, G. *Inorg. Synth.* **1977**, *17*, 186–188.

ratio) in THF.[19−21] The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture had only one signal, δ −35.3 ppm. When a mixture of two $LiPPh_2$ reagents, **C1** and **Aldrich-1** (δ −31.6 ppm), was prepared, its $^{31}P\{^1H\}$ NMR spectrum contained two signals at δ −30.7 and −35.8 ppm, suggesting different structures of these two samples of the $LiPPh_2$ reagent. Interestingly, in two weeks, the $^{31}P\{^1H\}$ NMR spectrum of the $LiPPh_2$ reagent **C1**, which had one signal after its preparation, contained two peaks of an approximately equal intensity at δ −31.7 and −35.8 ppm. We also monitored the $^{31}P\{^1H\}$ NMR spectra of the $LiPPh_2$ reagent **C1** while heating it. Immediately after preparing reagent **C1**, a sample was taken and heated at 43 °C for 12 h. Its spectrum contained two signals, δ −31.8 and −36.2 ppm, in ca. 1:18 ratio. While keeping the sample at 43 °C, the $^{31}P\{^1H\}$ NMR spectra were measured every two hours, and the signal ratio gradually changed to 1:6.8 after 10 h. After storing the sample for an additional 12 h at rt, the signal ratio changed very slightly, 1:6.5. Finally, after 2 h at 7 °C and 6 h at 48−61 °C, the ratio became 1:3.3. Therefore, one can suggest that reagent **C1** changes its structure upon heating.

We also checked if the amount of Li used affected the structure of the $LiPPh_2$ reagent obtained by method 2. Addition of $ClPPh_2$ to excess Li (1:10 molar ratio) resulted in the formation of reagent **C2**, which, like reagent **C1**, exhibited one $^{31}P\{^1H\}$ NMR signal at δ −35.3. Therefore, there is no need to use more than a 3-fold excess of the metal for synthesis of $LiPPh_2$, and a large excess of Li appears to have no influence on the structure of the reagent obtained by this general method. In the case of the $ClPPh_2$ addition to 2 molar equiv of Li, the obtained reagent **C3** had three $^{31}P\{^1H\}$ NMR signals, −30.6 (broad), −31.2 (sharp), and −36.2 (broad), which points at a different structure of **C3** compared to other phosphides.

The $LiPPh_2$ reagent **D** was obtained using method 3 (Scheme 5) by adding *n*-BuLi to a solution of $HPPh_2$ in THF at −78 °C (4% excess of *n*-BuLi).[22,23] The obtained reagent had one rather broad $^{31}P\{^1H\}$ NMR signal of $LiPPh_2$ at δ −38.0 ppm.

There is some literature information about possible structures of alkali metal phosphides. First, it has been reported that solutions of these reagents can be paramagnetic or diamagnetic.[24] For example, reaction of PPh_3 with excess K in THF produces a red solution of the radical anion, $KPPh_2^{\bullet-}$, which has a characteristic ESP spectrum showing a triplet with a hyperfine constant of a_p = 8 G.[24] The same reaction in a dilute solution or without excess metal produces a yellow solution with no paramagnetic species.[24] According to Grim and Molenda, paramagnetic species present in metal phosphide solutions have no effect on the signal broadening in $^{31}P\{^1H\}$ NMR spectra.[24] The same authors reported that $KPPh_2^{\bullet-}$ is fairly unstable, while paramagnetic solutions of $LiPPh_2^{\bullet-}$ are stable at least for two weeks at rt under N_2.

Second, alkali metal phosphides in solutions can be monomeric, dimeric, trimeric, or even more complex. According to Reich and Dykstra, $LiPPh_2$ is dimeric in ether and monomeric in 3:2 THF−Et_2O (−120 °C); the reagent was obtained from $HPPh_2$ and *n*-BuLi.[25] Zschunke et al. reported a tetrameric structure of $LiPPh_2$ in THF, which was also prepared by the same general method.[26] The McFarlene group analyzed low-temperature (−73 °C) ^{31}P and ^7Li NMR spectra of the $LiPPh_2$ solution in THF also obtained from $HPPh_2$ and *n*-BuLi.[27] The authors concluded that the reagent had the symmetric dimeric structure (Chart 1). The same group proposed that PhMePLi in Et_2O solutions exists as a mixture of a dimer and a trimer, while PhHPLi in Et_2O has a trimeric structure.[27,28] Cryoscopic data for $LiPPh_2$ in 1,4-dioxane indicated the presence of both dimeric and monomeric structures in solution.[29]

Several crystallographic structures of lithium phosphides with coordinating ligands, including THF and Et_2O, have been reported as well. A crystal of a tetrameric complex with the unusual tricyclic Li_4P_4 core was obtained from $LiPBu^t_2$ in THF (Chart 1).[30] The dimeric structure of $LiP(CH(TMS)_2)_2$ in the solid state was confirmed by its X-ray analysis.[31] A polymeric structure was found for the solvate complex of $LiPPh_2$ obtained from $HPPh_2$ and *n*-BuLi in Et_2O/THF (Chart 1).[32]

Consideration of our $^{31}P\{^1H\}$ NMR data for all obtained samples of $LiPPh_2$ in THF indicates that the structure of $LiPPh_2$ in this solvent may depend on (i) preparation method, (ii) ratio of reagents, (iii) concentration, and (iv) length of storage. It is reasonable to suggest that the signal at δ −39.1 ppm observed only for the $LiPPh_2$ reagent **A1** is likely to belong to the $LiPPh_2 \cdot LiPh$ dimer because (i) this signal is not observed in the spectra of other $LiPPh_2$ reagents and (ii) it disappears after quenching this reagent with *t*-BuCl. Because of the specific reactivity of reagent **Aldrich-1**, giving one major $^{31}P\{^1H\}$ NMR signal at δ −31.6 ppm, one can suggest that the $LiPPh_2$ molecules in this reagent are coordinated to THF molecules. Also, because the reactivity of reagent **Aldrich-2** changed after one year and became similar to that observed for **Aldrich-1**, it is reasonable to suggest that both reagents, in addition to being coordinated to THF molecules, may have a polymeric structure similar to those reported for solid samples by Bartlett et al.[32] Other reagents are expected to be of a dimeric, trimeric, or even more complex structure of $LiPPh_2$ with or without coordinated THF molecules. Those more complex structures can be homoaggregates or mixed aggregates. Species of the latter type contain other lithium compounds, e.g., LiPh or LiCl. Broadening of many $^{31}P\{^1H\}$ NMR signals in the spectra of many reagents may suggest the presence of equilibria between different forms of $LiPPh_2$.

(19) Tamborski, C.; Ford, F. E.; Lehn, W. L.; Moore, G. J.; Soloski, E. J. *J. Org. Chem.* **1962**, *27*, 619–621.
(20) Clark, P. W. *Org. Prep. Proc. Int.* **1979**, *11*, 103–106.
(21) Singh, G.; Singh, A. K.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. *Polyhedron* **2006**, *25*, 2915–2919.
(22) Fries, G.; Wolf, J.; Stalke, D.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 564–566.
(23) Mansfield, N. E.; Coles, M. P.; Hitchcock, P. B. *Dalton Trans.* **2005**, 2833–2841.
(24) Grim, S. O.; Molenda, R. P. *Phosphorus* **1974**, *4*, 189–193.
(25) Reich, H. J.; Dykstra, R. R. *Organometallics* **1994**, *13*, 4578–4585.
(26) Zschunke, A.; Bauer, E.; Schmidt, H.; Issleib, K. *Z. Anorg. Chem.* **1982**, *115−119*, 115–119.
(27) Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. *Phosphorus Sulfur* **1983**, *18*, 61–64.
(28) Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1982**, 220–221.
(29) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 1118–1126.
(30) Jones, R. A.; Stuart, A. L.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7459–7460.
(31) Hitchcock, P. B.; Lappert, M. F.; Power, P. P.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1669–1700.
(32) Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243–1247.

II. 3. Reactions of CPC 7 with Different $LiPPh_2$ Reagents. The dimeric cyclopalladated complex **7** was used as a model compound to study reactions with the $LiPPh_2$ reagents obtained by different methods. In all reactions, unless specified, addition order, solvent, ratio of reagents, concentration of complex **7** in the reaction mixture, molarity of the $LiPPh_2$ solution, temperature, and reaction time were the same. Depending on the $LiPPh_2$ reagent and conditions used, one or more of six compounds **9** and **17**−**21** were isolated in each reaction (Chart 2 and Table 2).

Complex 9. One of the most unexpected results of this study was the isolation of complex **9** in good to excellent yield in the reactions of CPC **7** with **Aldrich-1** and aged **Aldrich-2** (see Part II.1 and entries 1−8 of Table 2). Insignificant amounts of **9** were also formed in the reactions of phosphides **B2** and **C2** (entries 15 and 17). It is noteworthy that reagent **A2** after storing at rt for 4.5 months reacted with CPC **7** to produce 14% of complex **9** and 34% of **17**, while freshly prepared phosphide **A2** provided only the latter product (entries 12 and 13). Reagent **C3** practically did not change its reactivity after 2.5 months in contrast to reagent **D**, which lost its reactivity after six months and reacted with dimer **7** to give only 3% of **17**.

The observed cleavage of a C−O bond in THF by $LiPPh_2$ is not unique. As early as 1962, Garner and Tedeschi reported that refluxing a 2:1 mixture of Li and Ph_2PCl in THF for 24 h furnished 44% of $Ph_2P(CH_2)_4OH$.[33] In a year, Mallion and Mann described the preparation of $Ph_2P(CH_2)_4OH$ in 22% yield by heating a 1:1 mixture of Ph_2PH and BuLi in THF for 7 h.[34] Similar results have also been disclosed by other groups, although heating time and yields of $Ph_2P(CH_2)_4OH$ vary.[35,36]

The $LiPPh_2$ solutions in THF purchased from Sigma-Aldrich Co. were checked for the presence of $Ph_2P(CH_2)_4OLi$ before reacting with a CPC. According to the $^{31}P\{^1H\}$ NMR data for the original $LiPPh_2$ solutions and the ^1H NMR data for the crude product obtained after quenching these solutions with H_2O, the reagents did not have even traces of $Ph_2P(CH_2)_4OLi$. Considering this information and the fact that the formation of complex **9** took place under much milder conditions than those reported for the formation of $Ph_2P(CH_2)_4OH$ from THF and $LiPPh_2$, one can conclude that cyclopalladated complexes act as promoters in this transformation. To the best of our knowledge, the use of any catalysts or promoters in the reaction of THF with $LiPPh_2$ has never been reported.

It is reasonable to suggest that molecules of $LiPPh_2$, at least in reagents **Aldrich-1** and aged **Aldrich-2**, are coordinated to THF molecules. A strong coordination of Li with THF is supported by obtaining complex **9** in 65% yield in the reaction of a solution of CPC **7** in C_6H_6 with the $LiPPh_2$ sample prepared by evaporating THF from **Aldrich-2** and drying the remaining solid in vacuum, 1 mbar, at 40 °C for 1.5 h (Table 2, entry 8). We propose that the reaction begins with the formation of the mononuclear CPC **F** with $PPh_2Li\cdot(THF)_n$ (Scheme 6; for simplicity, $n = 1$). It is worth mentioning that related phosphido complexes of the platinum group metals are considered to be active intermediates in a number of Pd(II)- and Pt(II)-catalyzed reactions leading to the formation of a P−C bond.[37,38] The next step of the reaction is likely to be the insertion of the Pd atom into the C−O bond of THF, resulting in the formation of the Pd(IV) intermediate, presumably **G**. Somewhat related Pd(IV) complexes with a palladacycle have been either synthesized or proposed as intermediates in catalytic processes.[39] In a reductive elimination step, complex **G** is expected to yield compound **H**. It is noteworthy that the cleavage of C−N and C−S bonds in the presence of Pd complexes has been reported; however, those reactions presumably take place through the oxidative addition of organic substrates to Pd(0).[40−42]

Complex 17. This complex was isolated from most of the reactions using a 1:2 molar ratio of dimeric CPC **7** and lithium phosphide (a 1:1 Pd:PPh_2 ratio). The best yield of 60% was obtained in the reaction of compound **7** with phosphide **D** at room temperature (Table 2, entry 23), although the transformation proceeded readily even at −78 °C (entry 22). Its formation can be attributed to exchange of one Cl ion in **7** for the PPh_2 moiety. It is noteworthy that μ-halogen-μ-PPh_2 Pd(II) complexes are very rare.[43−45] Isolation and X-ray data of the α-*tert*-butyl-substituted derivative $Pd_2(\eta^2\text{-}N^{\frown}C)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)$, the only known cyclopalladated complex of this type, have been reported by Dunina et al.[7]

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of this complex are consistent with the proposed structure. The ^1H NMR spectrum features four well-separated signals of the C_6H_4 fragment of the palladacycle. Integration of all aromatic signals in the spectrum suggests the presence of two C_6H_4Pd fragments per one PPh_2 moiety. The existence of the Pd−N bond in **17** is supported by the appearance of the NMe_2 signal in the $^{13}C\{^1H\}$ NMR spectrum as a doublet with $^3J_{CP} = 1.6$ Hz. One set of signals in both ^1H and $^{13}C\{^1H\}$ NMR spectra suggests the syn configuration of the dinuclear complex in $CDCl_3$ solutions. The signals of the C_6H_4 group have chemical shift values between 6.35 and 6.82 ppm due to magnetic anisotropy of the PPh_2 fragment. This suggests the cis position of the PPh_2 group with respect to both Pd-C_6H_4 moieties and, therefore, supports the syn configuration of the dimer. The only known μ-Cl-μ-PPh_2 cyclopalladated complex has the syn configuration in the solid state.[7] For

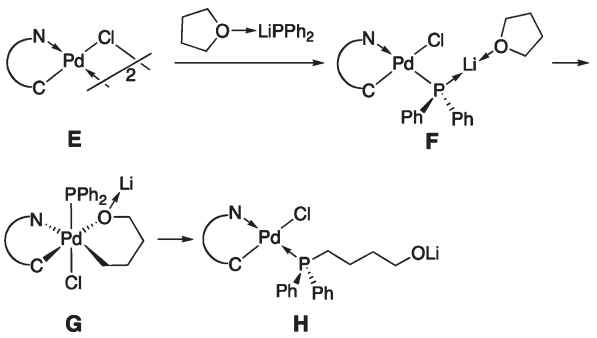
(33) Garner, A. Y.; Tedeschi, A. A. *J. Am. Chem. Soc.* **1962**, 4734–4737.
(34) Mallion, K. B.; Mann, F. G. *Chem. Ind.* **1963**, 654.
(35) Purdum, W. R.; Berlin, K. D. *J. Org. Chem.* **1975**, *40*, 2801–2806.
(36) Ushakov, N. V.; Vdovin, V. M.; Pozdnyakova, M. V.; Pritula, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 2125–2129.
(37) (a) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039–5040. (b) Schwan, A. L. *Chem. Soc. Rev.* **2004**, *33*, 218–224.
(38) Barañano, D.; Mann, G.; Hartwig, J. F. *Curr. Org. Chem.* **1997**, *1*, 287–305.
(39) (a) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; White, A. H. *Organometallics* **1996**, *15*, 5713–5722. (b) Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Organometallics* **2006**, *25*, 3996–4001. (c) Dick, A. R.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 12790–12791. (d) Whitfield, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 15142–15143. (e) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439–2463. (f) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924–1935.
(40) Kim, Y.-J.; Lee, S.-C.; Cho, M. H.; Lee, S.-W. *J. Organomet. Chem.* **1999**, *588*, 268–277.
(41) Ozerov, O. V.; Guo, C.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573–5580.
(42) Hernández, M.; Miralrio, G.; Arévalo, A.; Bernès, S.; García, J. J.; López, C.; Maitlis, P. M.; del Rio, F. *Organometallics* **2001**, *20*, 4061–4071.
(43) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Rosair, G. M.; Welch, A. J. *Inorg. Chem.* **1997**, *36*, 4426–4431.
(44) Cartwright, S. J.; Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* **1980**, *19*, 1120–1124.
(45) Chaouche, N.; Forniés, J.; Fortuño, C.; Kribii, A.; Martín, A.; Karipidis, P.; Tsipis, A. C.; Tsipis, C. A. *Organometallics* **2004**, *23*, 1797–1810.

Table 2. Reactions of Dimeric CPC 7 with the $LiPPh_2$ Reagents[a]

entry	$LiPPh_2$	Pd:PPh_2 ratio[b]	temp., °C	time, h	product	yield, %
1	**Aldrich-1**	1:1	rt	18	**9**	85
2	**Aldrich-1**	1:1	rt	3	**9**	53
3	**Aldrich-1**	1:1	0, then 0 → rt	0.1 1	**9**	66
4	**Aldrich-1**[c]	1:1	−78, then −78 → rt	0.5 2.5	**9**	28
5	**Aldrich-1**[c]	1:1	rt	0.4	**9**	58
6	**Aldrich-2** (after one year)	1:1	rt	18	**9** **17**	59 14
7	**Aldrich-2** (after one year)	1:2.25	rt	4	**9** **20**	85 traces
8	**Aldrich-2**[d] (after one year)	1:1	rt	18	**9** **17** **20**	65 22 traces
9	**A1**	1:1	rt	18	**18** **17**	81 traces
10	**A1**	1:1	rt	5	**18** **17**	58 17
11	**B1**	1:1	rt	6	**18** **17**	52 12
12	**A2**	1:1	rt	18	**17**	62
13	**A2** after 4.5 months	1:1	rt	18	**17** **9**	34 14
14	**A2**	1:2.25	rt	18	**20**	35
15	**B2**	1:1	rt	18	**17** **18** **9**	32 9 4
16	**C1**	1:1	rt	4	**17** **19**	23 traces
17	**C2**	1:1	rt	7	**17** **19** **9**	28 12 traces
18	**C3**	1:1	rt	3	**17** **21** **19**	55 5 traces
19	**C3**	1:2.25	rt	18	**20**	49
20	**C3**[e]	1:2.25	rt	18	**20**	28
21	**C3**[d]	1:1	rt	18	**20** **17**	81 17
22	**D**	1:1	−78	4	**17**	40
23	**D**	1:1	rt	4	**17**	60
24	**D**	1:2.25	rt	18	**20**	27
25	**D**[e]	1:2.25	rt	18	**20**	35

[a] Unless otherwise noted, a 0.5 M solution of $LiPPh_2$ in THF was added dropwise to a solution of CPC **7** in THF (the total volume of THF was 1.0 mL per 0.017−0.020 mmol of CPC). [b] Here and later, Pd:PPh_2 ratios are given instead of molar ratios. [c] Reverse addition order. [d] Prior to the reaction, a THF solution of $LiPPh_2$ was evaporated and the obtained residue was kept under vacuum (< 1 mbar) at 40 °C for 1.5 h. The reaction of CPC **7** with the obtained solid sample of $LiPPh_2$ was done in toluene (entry 21) or benzene (entry 8). [e] The total volume of THF in the reaction mixture was 10 times higher than in other reactions.

Scheme 6



comparison, the ^{31}P NMR signals of **17**, its α-*tert*-butyl-substituted analogue $Pd_2(\eta^2\text{-}N^{\frown}C)_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)$, and the related dinuclear complex $Pd_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(C_6F_5)_2Py_2$ appear at 21.5 ppm [in $CDCl_3$ relative to $P(OEt)_3$], 34.6 ppm (in $CDCl_3$ relative to H_3PO_4),[7] and 23.8 ppm (in acetone-d_6 relative to H_3PO_4).[43]

Complex 18. This previously reported complex[46] was one of the products obtained in the reactions of CPC **7** with the $LiPPh_2$ reagents **A1** and **B1**,**2** synthesized from PPh_3 and Li (Table 2, entries 9−11 and 15). It is assumed that complex **18** is formed as a result of the reaction of dimeric CPC **7** with PPh_3, which was spectroscopically detected in these solutions of lithium phosphide.

Complex 19. This compound was isolated in 12% yield in the reaction of dimeric CPC **7** with 2 molar equiv of the $LiPPh_2$ reagent **C2** (Table 2, entry 17). Traces of complex **19** were also detected among the products formed in reactions of the $LiPPh_2$ reagents **C1** and **C3** (entries **16** and **18**). Interestingly, this complex was also isolated in 25% yield after storing a solution of complex **17** in CH_2Cl_2 at rt for two months; Pd(0) was formed as well.

Surprisingly, little is known about complexes of Pd(II) with PPh_2PPh_2 or its oxide;[47−50] none of them contain a palladacycle. The structure of compound **19** as a mononuclear cyclopalladated complex with $PPh_2P(O)Ph_2$ as an auxiliary ligand is proposed on the basis of the ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and 2D NMR spectra. In the ^1H NMR spectrum of **19**, there are four Ph groups per one cyclopalladated C_6H_4 fragment. In contrast to the ^1H NMR spectra of **17** and **18**, signals of the PPh hydrogens of complex **19** are not well resolved, which may suggest nonequivalence of four Ph rings. The chemical shift values, 6.09−6.73 ppm, of four well-resolved signals of the PdC_6H_4 moiety and the appearance of the H(6) signal at δ 6.09 ppm as a dd (J_{HH} = 7.5, J_{HP} = 4.2) suggests that the PPh fragment is in close proximity to the cyclopalladated aromatic ring and cis to the Pd−C bond. The $^{31}P\{^1H\}$ NMR spectrum of **19** exhibited two broadened nonsymmetrical doublets, δ 23.5 and 102.6 ppm, with the large coupling constant $J_{PP} \approx 203$ Hz, suggesting two nonequivalent PPh_2 fragments. The value of this constant is such that, in general, it can be attributed to either $^1J_{PP}$ or *trans*-$^2J_{PP}$.[47,51,52] For comparison, the coupling constant $^1J_{PP}$ for the free ligand $PPh_2P(O)PPh_2$ is 224 Hz.[48] For the recently reported trinuclear cluster $Ar_2Pt(\mu\text{-}PPh_2)(\mu\text{-}Br)Pd(\mu\text{-}PPh_2PPh_2)PtAr_2$ (Ar = C_6F_5), the coupling constant $^1J_{PP}$ was 191 Hz, whereas $^2J_{PP}$ for the *trans*-$Ph_2P-Pd-PPh_2PPh_2$ fragment was larger, 296 Hz.[47]

The ^{31}P NMR chemical shift of 23.5 ppm observed for **19** is ordinary for the P atoms in tertiary phosphines bonded to Pd(II),[53] whereas the value of 102.6 ppm is rather unusual. We suggest that this signal belongs to the $POPh_2$ fragment of the $PPh_2P(O)Ph_2$ ligand. This is supported by the presence of an intense signal at ν 1261 cm^{-1} in the IR spectrum of

(46) (a) Crociani, B.; Boschi, T.; Pietropaolo, R.; Belluco, U. *J. Chem. Soc. A* **1970**, 531–535. (b) Ryabov, A. D.; Yatsimirskii, A. K.; Berezin, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1378–1383.
(47) Forníes, J.; Fortuño, C.; Ibáñez, S.; Martín, A. *Inorg. Chem.* **2008**, *47*, 5978–5987.
(48) Forníes, J.; Fortuño, C.; Ibáñez, S.; Martín, A.; Tsipis, A. C.; Tsipis, C. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2407–2410.
(49) Shmidt, F. K.; Belykh, L. B.; Goremyka, T. V. *Russ. J. Coord. Chem.* **2002**, *28*, 92–103.
(50) Issleib, K.; Schwager, G. *Z. Anorg. Chem.* **1961**, *310*, 43–49.
(51) Fluck, E.; Binder, H. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 307–313.
(52) Ogilvie, F. B.; Jenkins, J. M.; Vercade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 1916–1923.
(53) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979.

complex **19** in a benzene solution, which can be assigned to the P=O group.[54]

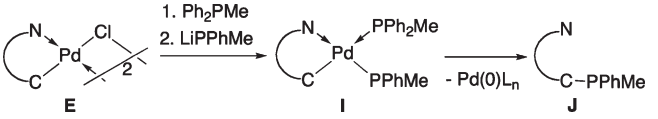
No signal of PPh_2PPh_2 was detected in the ^{31}P NMR spectra of the $LiPPh_2$ reagents used in this study. Also, attempts to generate complex **19** by reacting dimer **7** with PPh_2PPh_2 followed by oxidation using different conditions and varied reagent ratios failed. According to ^{31}P NMR spectra of the reaction mixtures, numerous species are formed in these reactions; moreover, it appears that tetraphenyldiphosphine undergoes a P−P bond cleavage. Therefore, direct reaction of CPC **7** with PPh_2PPh_2 followed by oxidation can be ruled out as a possible route for the formation of **19**.

Formation of **19** in the reaction of dimer **7** with the $LiPPh_2$ reagent **C2** in THF (Table 2, entry 17) can be explained by the attack of $LiPPh_2$ on the Pd atom of **17** (the major product of this reaction) followed by elimination of LiCl, producing $\{(\eta^2\text{-}N^{\cap}C)Pd(\kappa^1\text{-}PPh_2)_2\}^-$. This intermediate can undergo reductive elimination of PPh_2PPh_2 with the formation of Pd(0). A similar intermediate, *cis*-$\{(PPh_3)_2Pd(\kappa^1\text{-}PPh_2)_2\}$, was postulated by Stille in the Pd(II)-catalyzed coupling of ArHal with Me_3SnPPh_2 and Me_3SiPPh_2,[38,55] and a related complex, $\{Pd(PPh_2)_2\}_n$, was isolated by Abel.[56] Formation of the dimeric di-μ-PPh_2 derivative $\{(\eta^2\text{-}N^{\cap}C)Pd(\mu\text{-}PPh_2)\}_2$ as an intermediate in the reaction of **17** with $LiPPh_2$ cannot be ruled out either. Although cyclopalladated dinuclear diphosphido-bridged complexes are unknown, a crystal structure of the Pt complex $\{Pt(bzq)(\mu\text{-}PPh_2)\}_2$ was recently reported.[57] The Pd(II)-bonded PPh_2PPh_2 along with Pd(0) can be released from this intermediate as a result of reductive elimination. According to the $^{31}P\{^1H\}$ NMR data ($CDCl_3$, τ = 8 s), the reaction mixture obtained by reacting complex **17** with 3.5 molar equiv of the $LiPPh_2$ reagent **C3** in C_6H_6 at rt for 18 h contained a number of compounds including unreacted complex **17** (ca. 24%), compound **9** (ca. 16%), and, presumably, free $PPh_2P(O)Ph_2$ (ca. 8%). The last compound provided two doublets, δ 21.4 and −36.1 ppm, with J_{PP} = 228 Hz (cf. δ 32.7 and −24.9, J_{PP} = 220 Hz, in C_6D_6 for a sample of $PPh_2P(O)Ph_2$ obtained using a published procedure[58]). Unfortunately, attempts to isolate $PPh_2P(O)Ph_2$ were unsuccessful.

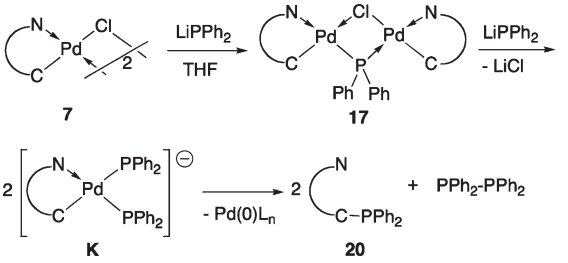
The fact that decomposition of complex **17** in CH_2Cl_2 provided **19** and Pd(0) suggests that, under these conditions, complex **17** can be transformed to either the μ-di-PPh_2 analogue or $\{(\eta^2\text{-}N^{\cap}C)Pd(\kappa^1\text{-}PPh_2)_2\}^-$. These intermediates can undergo reductive elimination with the formation of PPh_2PPh_2 (cf. Scheme 8).

Aminophosphine 20. This compound is perhaps the most desirable product of the reaction of CPC **7** with $LiPPh_2$. As mentioned in the Introduction, there have been three reports of the reactions between CPCs and $LiPR_2$, in which either aminophosphines were synthesized[3,4] or their Pd(0) complexes were detected spectroscopically.[7] In these studies, reactions were carried out in the presence of PPh_3; this means that the corresponding mononuclear cyclopalladated

Scheme 7



Scheme 8



complexes with PPh_3 as an auxiliary ligand were actual reactants. A mechanism of the aminophosphine formation in the reaction of dimeric CPCs with LiPPhMe in the presence of 2 equiv of PPh_2Me in THF was proposed by Troitskaya et al.[4] The authors suggested the formation of intermediate **I**, which is transformed to aminophosphine **J** as a result of reductive elimination (Scheme 7).[4,59]

All reactions of CPCs with lithium phosphide reported in this study were carried out without addition of PPh_3, although reagents **A1** and **B1** contained a significant amount of triphenylphosphine (see Section II.2). Phosphides **A2** and **B1** contained only trace amounts of PPh_3 (see Section II.2). Reagents **C1**−**3** and **D** were obtained from $ClPPh_2$ and $HPPh_2$, respectively, and could not contain PPh_3.

Aminophosphine **20** was isolated in the reactions using a 1:4.5 molar ratio of dimeric CPC **7** and the $LiPPh_2$ reagents **A2**, **C3**, and **D** (1:2.25 Pd:PPh_2 ratio); all these reactions were performed in THF (Table 2, entries 14, 19, 20, 24, and 25). Formation of Pd(0) black was observed in these reactions. It is notable that (i) the lithium phosphide reagents purchased from Sigma-Aldrich Co. provided, at best, only traces of the aminophosphine (entry 7) under the same conditions and (ii) reagents **A2**, **C3**, and **D** did not contain PPh_3.

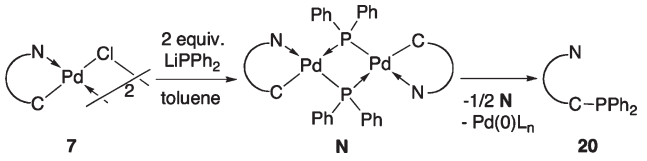
When a 1:1 Pd:PPh_2 ratio was used in THF, no aminophosphine was formed; instead, μ-Cl-μ-PPh_2 complex **17** was furnished (entries 18, 22, and 23). Remarkably, when the reaction of dimeric CPC **7** and 2 equiv of reagent **C3** (a 1:1 Pd:PPh_2 ratio) was performed in toluene, aminophosphine **20** was obtained in 81% (solvent THF was removed under vacuum prior to the reaction; see entry 21). It is noteworthy that reagent **Aldrich-2** used instead of **C3** in benzene with the same reagent ratio provided only traces of aminophosphine **20** (entry 8). Therefore, the reaction direction depends on the preparation method of lithium phosphide, reagent ratio, and the nature of the solvent used.

It appears that mechanisms of the reactions between CPC **7** and reagent **C3** in THF and toluene are different. In the reactions occurring in THF, a 1:2 Pd:PPh_2 ratio was essential

(54) Hesse, M.; Meier, H.; Zeeh, B. *Spectroscopic Methods in Organic Chemistry*; Georg Thieme Verlag: Stuttgart, 1997; p 54.
(55) Tunney, S. E.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 748–753.
(56) Abel, E. W.; McLean, R. A. N.; Sabherwal, I. H. *J. Chem. Soc. A* **1968**, 2371–2373.
(57) (a) Díez, A.; Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2005**, *44*, 2443–2453. (b) Mastrorilli, P. *Eur. J. Inorg. Chem.* **2008**, 4835–4850.
(58) McKechnie, J.; Payne, D. S.; Sim, W. *J. Chem. Soc.* **1965**, 3500–3501.

(59) In the original paper,[4] the authors proposed the *trans*-(C^-, $PhMeP^-$) geometry of intermediate **I**. According to the transphobia concept, the *cis*-(C^-,$PhMeP^-$) geometry should be expected. For the concept of transphobia, see: (a) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127–2138. (b) Vicente, J.; Arcas, A.; Gálvez-López, M.-D.; Juliá-Hernández, F.; Bautista, D.; Jones, P. G. *Organometallics* **2008**, *27*, 1582−1590, and references therein.

Scheme 9



for the aminophosphine formation (entries 19 and 20), while using a 1:1 ratio in the same solvent (entry 18), μ-Cl-μ-PPh_2 complex **17** was isolated as the major compound. This may suggest that complex **17** is an intermediate of the aminophosphine formation in THF. To confirm this hypothesis, two identical reactions of μ-Cl-μ-PPh_2 complex **17** with 1 equiv of $LiPPh_2$ reagent **C3** were carried out (THF, rt, 18 h). The ^{31}P NMR spectrum of the first reaction mixture contained signals of aminophosphine **20** and $PPh_2P(O)Ph_2$ in ca. 2:1 ratio. The second reaction was used to isolate products formed. Aminophosphine **20** was obtained from this reaction in 38% yield, backing up the idea that compound **17** is an intermediate of the aminophosphine formation in THF. Because Pd(0) was formed in all reactions in THF leading to compound **20**, the last step of the aminophosphine formation in this solvent is expected to be reductive elimination. On the basis of these considerations and the fact that 2 equiv of $LiPPh_2$ are necessary for each palladacycle, we propose that the reaction begins with the formation of **17** followed by the attack of $LiPPh_2$ on the Pd(II) atom and LiCl elimination to afford the intermediate $\{(\eta^2\text{-}N^{\frown}C)Pd(\kappa^1\text{-}PPh_2)_2\}^-$ (**K**, Scheme 8). The reductive elimination step brings the reaction to its end, producing Pd(0) and aminophosphine **20**.

The reaction of CPC **7** with the $LiPPh_2$ reagent **C3** in toluene furnishing aminophosphine **20** required only 1 equiv of the PPh_2 ion per palladacycle. This difference must be related to the noncoordinating nature of this solvent and, as one of the consequences, to a change in structure and reactivity of $LiPPh_2$ reagents in THF and toluene. The μ-Cl-μ-PPh_2 complex **17** is an unlikely candidate for an intermediate in the reactions in toluene or benzene leading to compound **20**, because no aminophosphine is formed in the reaction of complex **17** with 3.5 molar equiv of the $LiPPh_2$ reagent **C3** in benzene. A possible mechanism of the reaction in a noncoordinating solvent includes the formation of the intermediate $\{(\eta^2\text{-}N^{\frown}C)Pd(\mu\text{-}PPh_2)\}_2$ (**N**, Scheme 9) directly from $\{(\eta^2\text{-}N^{\frown}C)Pd(\mu\text{-}Cl)\}_2$ through a simple anion metathesis well known for dinuclear cyclopalladated complexes.[1] Formation of different intermediates in toluene and THF (Scheme 8) can be explained by a different structure and, therefore, reactivity of the phosphide ion in a noncoordinating solvent and THF.[60] One can also hypothesize that in a noncoordinating solvent such as toluene the neutral dimer $\{(\eta^2\text{-}N^{\frown}C)Pd(\mu\text{-}PPh_2)\}_2$ may be more stable than the anionic complex $\{(\eta^2\text{-}N^{\frown}C)Pd(\kappa^1\text{-}PPh_2)_2\}^-$. For example, $Pd(PPh_2)_2$ is apparently tetrameric in benzene.[56] Reductive elimination as the final step is to afford the aminophosphine, Pd(0), and a new portion of **N**, which is to undergo reductive elimination again.

(60) For the conversion of mononuclear terminal phosphido complexes to the corresponding dinuclear bridged phosphido derivatives of Pt(II), see: (a) Scriban, C.; Wicht, D. K.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2006**, *25*, 3370–3378. (b) Maassarani, F.; Davidson, M. F.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, M. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Inorg. Chim. Acta* **1995**, *235*, 327–338.

The structure and composition of aminophosphine **20** and its oxide **21** were proven by ^1H, ^{13}C, ^{31}P, and 2D NMR spectra, as well as HRMS data.

Conclusions

Cyclopalladated complexes react with commercial $LiPPh_2$ reagents and lithium phosphide solutions synthesized in our lab to furnish different types of products. The difference in the ^{31}P NMR spectra of the $LiPPh_2$ reagents obtained from Sigma-Aldrich Co. and those synthesized in our lab by different methods suggests their different structures in THF. Reaction of the dimeric CPC **7** with $LiPPh_2$ is highly sensitive to reaction conditions, especially to the reagent ratio, addition order, solvent, and source of lithium phosphide. The major pathway of the reactions in THF between dinuclear CPCs and the lithium phosphide purchased from Sigma-Aldrich Co. is the formation of the corresponding mononuclear complexes with $Ph_2P(CH_2)_4OH$ as an auxiliary ligand. Reactions of dimeric CPC **7** in THF with the lithium phosphide reagents synthesized in our lab from PPh_3, $ClPPh_2$, or $HPPh_2$ lead to the formation of either μ-Cl-μ-PPh_2 complex **17** using 1 equiv of $LiPPh_2$ per palladacycle or aminophosphine **20** using 2.25 equiv of the phosphide. Aminophosphine **20** can also be obtained in toluene using 1 equiv of $LiPPh_2$ per palladacycle. Preparation of aminophosphine **20** in either THF or toluene does not require the presence of PPh_3 and cannot be accomplished with the $LiPPh_2$ reagents in THF purchased from Sigma-Aldrich Co. The mechanisms of the aminophosphine formation in THF and toluene appear to be different.

Currently, we are studying stoichiometric and catalytic reactions of mono- and dinuclear cyclopalladated complexes with other phosphides under different conditions in order to shed more light on possible mechanisms of these transformations and synthesize a set of structurally different P*- and C*P*-chiral aminophosphines, potential catalysts in asymmetric transformations.

Experimental Section

General Methods and Materials. All reactions of $LiPPh_2$ were carried out under a positive pressure of argon using the Schlenk technique. Purifications by column chromatography were carried out using Natland silica gel 60 (230 mesh). Preparative thin-layer chromatography (TLC) was carried out using 200 × 250 mm glass plates with an unfixed layer of Natland or Merck silica gel 60 (230 mesh). Analytical TLC was performed on Whatman silica gel 60 (F_{254}) 250 μm precoated plates. Compounds were visualized on TLC plates using UV light (254 nm) and/or iodine stain. Routine ^1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz), and $^{31}P\{^1H\}$ (202 MHz) as well as DEPT, COSY, and HSQC spectra were recorded on a Bruker AVANCE 500 NMR spectrometer. Chemical shifts are reported in ppm with $SiMe_4$ as an internal standard (^1H and ^{13}C) or $P(OEt)_3$ as an external standard (^{31}P). Spin−spin coupling constants, *J*, are given in Hz. Spectra of the products obtained in reactions of the $LiPPh_2$ reagents with CPCs were recorded in $CDCl_3$ unless otherwise stated. Melting points were measured on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Optical rotations were measured at room temperature on a Rudolph Autopol III automatic polarimeter. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA. Benzene and toluene were dried by refluxing over K/benzophenone ketyl, distilled under Ar, and kept over potassium. Tetrahydrofuran and THF-d_8 were distilled over K/benzophenone ketyl under Ar immediately before starting a reaction. Acetone was purified by distillation over $KMnO_4$. Other

solvents were distilled over CaH_2. $ClPPh_2$ and $HPPh_2$ were distilled in vacuum prior to use. *tert*-BuCl was distilled over $CaCl_2$. Other chemicals were used as purchased without further purification. Lithium used was obtained from Acros, granules 99.9 +%, unless stated otherwise. Two 0.5 M solutions of $LiPPh_2$ used this study, **Aldrich-1** and **Aldrich-2**, were purchased from Sigma-Aldrich Co., lot # 00111CD and 17309MH, respectively.

Synthesis of $LiPPh_2$ Using PPh_3 and Li.[15,16] Reagent **A1**: Granules of Li (61.1 mg, 8.8 mmol) were placed into an Ar-filled 10 mL Schlenk flask followed by addition of THF (2 mL). In another Ar-filled flask, PPh_3 (655.7 mg, 2.5 mmol) was dissolved in THF (3 mL). Then the PPh_3 solution was added dropwise to the metal through a septum during 3−4 min. The reaction mixture was stirred overnight for 18 h. Then the solution was filtered to remove excess Li. The solution's color was dark brown-red. To take a ^{31}P NMR spectrum of the reaction mixture, 0.01 mL of THF-d_8 and 0.25 mL of the prepared solution were used. $^{31}P\{^1H\}$ NMR (δ, ppm): two signals, −22.4 (PPh_3) and −39.1 ($\omega/2$ = 28.6 Hz, $LiPPh_2$), with a relative intensity of 2:1 (τ = 2 s). Reagent **A2** was obtained using 6 equiv of Li following the same procedure. $^{31}P\{^1H\}$ NMR (δ, ppm): −37.4.

Synthesis of $LiPPh_2$ Using PPh_3 and Li Followed by Quenching of PhLi.[17,18] Reagent **B1**: A solution of the $LiPPh_2$ reagent **A1** in THF (1 mL, 0.5 mmol) obtained as described above was placed into an Ar-filled 10 mL Schlenk flask followed by dropwise addition of *t*-BuCl (0.05 mL, 0.5 mmol) using a syringe. The resulting solution was stirred at rt under Ar for 1.5 h and slowly filtered (at normal pressure and in inert atmosphere) prior to further use. $^{31}P\{^1H\}$ NMR (δ, ppm): four signals, −20.4 (PPh_3), −30.4 and −31.4 ($\omega/2$ = 4.0 and 9.2 Hz, respectively, $LiPPh_2$), and −55.4 ($HPPh_2$). Reagent **B2** was obtained from **A2** using the same procedure. $^{31}P\{^1H\}$ NMR (δ, ppm): −30.2 and −31.1 (signal ratio 1:2.3).

Preparation of $LiPPh_2$ Using $ClPPh_2$ and Li.[19−21] Reagent **C3**: Li pieces (37.2 mg, 5.4 mmol) and THF (5.4 mL) were placed into an Ar-filled Schlenk flask. Then $ClPPh_2$ (0.50 mL, 2.7 mmol) was added dropwise in 6 min. In ca. 30 min, the reaction mixture turned bright orange. The reaction was slightly exothermic. The reaction was stirred overnight and slowly filtered (at normal pressure and in inert atmosphere) prior to further use. Complete conversion of $ClPPh_2$ was confirmed by ^{31}P NMR data. $^{31}P\{^1H\}$ NMR (δ, ppm): overlap of −30.6 (broad) and −31.2 (sharp), −36.2 (broad). Reagent **C1** was synthesized using a 1:3 molar ratio of $ClPPh_2$ and Li following the same procedure. $^{31}P\{^1H\}$ NMR (δ, ppm): −35.3 ppm, $\omega/2$ = 14.6 Hz. Reagent **C2** was obtained using a 1:10 molar ratio of $ClPPh_2$ and Li following the same procedure. $^{31}P\{^1H\}$ NMR (δ, ppm): −35.3 ppm.

Preparation of the $LiPPh_2$ Reagent D Using $HPPh_2$ and Li.[22,23] In the Ar atmosphere, $HPPh_2$ (0.48 mL, 2.8 mmol) and THF (5 mL) were placed into a 10 mL Schlenk flask. The solution was cooled to −75 °C and stirred for about 20 min. Then a 0.25 M solution of *n*-BuLi in hexane (1.0 mL, 2.5 mmol) was added dropwise in 5 min. During the addition, the color of the reaction mixture changed from colorless to orange. The mixture was stirred at −75 °C for 30 min and then was left to warm to rt within several hours. To take a $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, 0.01 mL of THF-d_8 and 0.25 mL of the prepared solution were used. $^{31}P\{^1H\}$ NMR (δ, ppm): −38.0 ppm ($\omega/2$ = 21.4 Hz).

Preparation of ^{31}P NMR Samples of the $LiPPh_2$ Reagents. For the collection of $^{31}P\{^1H\}$ NMR spectra, 0.25 mL of 0.5 M solutions of $LiPPh_2$ in THF were mixed with 0.01 mL of THF-d_8 at rt, so the estimated concentration of the reagents in NMR samples was 0.48 M. The $^{31}P\{^1H\}$ NMR spectra were taken at rt unless otherwise noted. In some cases, concentration of the obtained reagents was also evaluated using $^{31}P\{^1H\}$ NMR spectroscopy. An exact volume of the reagent's solution was mixed with a known amount of PPh_3, and a $^{31}P\{^1H\}$ NMR spectrum was run with a signal delay, τ, of 10 s. (When shorter signal delays were applied, signal ratios for the same sample varied due to changes in relaxation time for different P-containing species.)

Preparation of Dimeric CPCs. Complex *rac*-di(μ-chloro)bis[1-(*N*,*N*-dimethylamino)methylferrocenyl-*C*,*N*]dipalladium(II) (*rac*-**1**) was synthesized in 84% following a published procedure.[61] Compounds di(μ-chloro)bis[2-(*N*,*N*-dimethylamino)-methyl]phenyl-*C*,*N*]dipalladium(II) (**7**) and (S_C,S_C)-di(μ-chloro)-bis{2-[1-(*N*,*N*-dimethylamino)ethyl]phenyl-*C*,*N*}dipalladium(II) ((S_C,S_C)-**8**) were obtained from the corresponding benzylamines in 95% and 98% yield, respectively, using a reported procedure.[62] Complex (S_C,S_C)-di(μ-chloro)bis[2-(2-methyl-2-oxazolin-4-yl)-phenyl-*C*,*N*]dipalladium(II) ((S_C,S_C)-**11**) was synthesized in 92% yield by cyclopalladation of (*S*)-2-methyl-4-phenyl-2-oxazoline with $Pd(OAc)_2$ in AcOH followed by reaction with LiCl.[63] Complex di(μ-chloro)bis[2-methyl-2-(4,4-dimethyloxazolin-2-yl)propyl-*C*,*N*]dipalladium(II)[64] (**13**) was synthesized in 76% yield by cyclopalladation of 2-*tert*-butyl-4,4-dimethyl-2-oxazoline with $Pd(OAc)_2$ in AcOH followed by treatment with LiCl using a procedure described for cyclopalladation of other oxazolines.[10] Complex (S_C)-di(μ-chloro)bis{[2-(4-benzyl-2-oxazolin-2-yl)methyl]-phenyl-*C*,*N*}dipalladium(II) ((S_C)-**15**) was obtained in 78% yield following a published procedure.[8]

General Procedure for Preparation of Complexes 6, 9, (S_C)-10, (S_C)-12, 14, and *exo*-(S_C)-16. In the atmosphere of Ar, a 0.5 M solution of $LiPPh_2$ in THF (**Aldrich-1**, δ −31.6 ppm, 0.39 mL, 0.20 mmol) was introduced into a 15 mL Schlenk flask using a syringe. Then a solution of a dimeric CPC (0.096 mmol) in 5.3 mL of absolute THF was added dropwise during 5 min. The yellow solution turned red-orange after stirring for 8 h at rt. After removal of THF using a rotavapor, the crude product was dissolved in ca. 0.5 mL of CH_2Cl_2 and purified by preparative TLC (8:1 benzene−acetone). Pure complexes **6**, **9**, (S_C)-**10**, (S_C)-**12**, **14**, and *exo*-(S_C)-**16** were obtained after crystallization from CH_2Cl_2−hexane.

Chloro-{2-(*N*,*N*-dimethylamino)methyl]ferrocenyl-*C*,*N*}[(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) (6). Compound **6** was obtained from *rac*-**1** in 87% yield as orange-red crystals. Mp: 156−157 °C (dec); R_f 0.60 (5:1 benzene−acetone). ^1H NMR (δ, ppm): 1.13 (m, 1H, PCH_2CH^A), 1.40 (m, 1H, $PCH_2CH_2CH^B$), 1.96 (m, 1H, $^3J_{HP}$ = 4.3, $PCH_2CH_2CH^A$), 1.96 (m, 1H, PCH^A), 2.04 (m, 1H, PCH_2CH^B), 2.93 (s, 1H, H(5) ferrocenyl), 2.97 (d, 3H, $^4J_{HP}$ = 2.1, NCH_3^A), 3.04 (m, 2H, OH and PCH^B), 3.18 (d, 3H, $^4J_{HP}$ = 1.8, NCH_3^B), 3.40 (dd, 1H, $^4J_{HP}$ = 2.4, $^2J_{HH}$ = 14.4, NCH^A), 3.57 (m, 2H, NCH^B, CH^AOH), 3.71 (s, 5H, C_5H_5), 3.76 (m, 2H, CH^BOH and H(3) ferrocenyl), 3.96 (s, 1H, H(4) ferrocenyl), 7.40 (m, 2H, *m*-PPh^A), 7.47 (m, 1H, *p*-PPh^A), 7.55 (m, 3H, *m*- and *p*-PPh^B), 7.75 (m, 2H, *o*-PPh^A), 7.98 (m, 2H, *o*-PPh^B). $^{13}C\{^1H\}$ NMR (δ, ppm): 20.3 (d, $^2J_{CP}$ = 2.4, PCH_2CH_2), 30.3 (d, $^1J_{CP}$ = 32.6, PCH_2), 32.6 (d, $^3J_{CP}$ = 16.4, $PCH_2CH_2CH_2$), 51.2 (d, $^3J_{CP}$ = 2.5, NCH_3), 52.7 (d, $^3J_{CP}$ = 1.9, NCH_3), 59.8 (CH_2OH), 60.5 (C(4) ferrocenyl), 65.1 (d, $^3J_{CP}$ = 1.8, NCH_2), 65.5 (d, $^4J_{CP}$ = 3.8, C(3) ferrocenyl), 69.1 (C_5H_5), 71.3 (d, $^3J_{CP}$ = 9.7, C(5) ferrocenyl, 97.02 (d, $^3J_{CP}$ = 1.7, C(2) ferrocenyl), 97.17 (d, $^2J_{CP}$ = 2.1, PdC(1) ferrocenyl), 128.1 (d, $^3J_{CP}$ = 10.6, *m*-PPh^A), 128.7 (d, $^3J_{CP}$ = 9.8, *m*-PPh^B), 129.07 (d, $^1J_{CP}$ = 48.2, *ipso*-C of PPh^A), 130.3 (d, $^4J_{CP}$ = 3.1, *p*-PPh^A), 131.0 (d, $^4J_{CP}$ = 1.4, *p*-PPh^B), 132.3 (d, $^2J_{CP}$ = 10.8, *o*-PPh^A), 133.26 (d, $^1J_{PC}$ = 45.0, *ipso*-C of PPh^B), 135.4 (d, $^2J_{PC}$ = 11.8, *o*-PPh^B). $^{31}P\{^1H\}$ NMR (δ, ppm): 20.09. Anal. Calcd for $C_{29}H_{34}ClNOPPd$: C, 54.32; H, 5.34; N, 2.18. Found: C, 54.95; H, 5.59; N, 2.15.

(61) Gaunt, J. C.; Shaw, B. L. *J. Organomet. Chem.* **1975**, *102*, 511–516.

(62) Zalevskaya, O. A.; Dunina, V. V.; Potapov, V. M.; Kuz'mina, L. G.; Struchkov, Y. T. *Zh. Obshch. Khim.* **1985**, *55*, 1332–1341.

(63) Gorunova, O. N.; Keuseman, K. J.; Goebel, B. M.; Kataeva, N. A.; Churakov, A. V.; Kuz'mina, L. G.; Dunina, V. V.; Smoliakova, I. P. *J. Organomet. Chem.* **2004**, *689*, 2382–2394.

(64) Balavoine, G.; Clinet, J. C. *J. Organomet. Chem.* **1990**, *390*, C84–C88.

Chloro-{[2-(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}[(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) (9). Complex **9** was obtained from dimer **7** in 79% yield as pale yellow crystals. Mp: 154−155 °C (dec); R_f 0.61 (5:1 benzene−-acetone). ^{1}H NMR (δ, ppm): 1.57 (m, 2H, $PCH_2CH_2CH_2$), 1.81 (m, 2H, PCH_2CH_2), 2.43 (m, 2H, $^2J_{HP}$ = 2.6, PCH_2), 2.81 (d, 6H, $^4J_{HP}$ = 2.4, NCH_3), 2.99 (br s, 1H, OH), 3.65 (t, 2H, $^3J_{HH}$ = 5.8, CH_2O), 4.03 (d, 2H, $^4J_{HP}$ = 2.4, NCH_2), 6.40 (m, 2H, H(5,6) arom), 6.82 (t, 1H, $^3J_{HH}$ = 7.2, H(4) arom), 7.24 (d, 1H, $^3J_{HH}$ = 7.2, H(3) arom), 7.39 (m, 4H, *m*-PPh), 7.44 (m, 2H, *p*-PPh), 7.81 (m, 4H, *o*-PPh). ^{13}C{^{1}H} NMR (δ, ppm): 20.7 (d, $^2J_{CP}$ = 2.8, PCH_2CH_2), 29.3 (d, $^1J_{CP}$ = 33.8, PCH_2), 32.8 (d, $PCH_2CH_2CH_2$, $^3J_{CP}$ = 16.4), 50.3 (d, $^3J_{CP}$ = 2.4, NCH_3), 59.8 (CH_2OH), 72.9 (d, $^3J_{CP}$ = 3.1, NCH_2), 122.4 (C(3) arom), 123.9 (C(4) arom), 125.2 (d, $^4J_{CP}$ = 5.9, C(5) arom), 128.4 (d, $^3J_{CP}$ = 10.2, *m*-PPh), 130.3 (d, $^1J_{CP}$ = 48.1, *ipso*-C of PPh), 130.7 (d, $^4J_{CP}$ = 1.4, *p*-PPh), 134.5 (d, $^2J_{CP}$ = 12.3, *o*-PPh), 137.5 (d, $^3J_{CP}$ = 11.2, C(6) arom), 148.4 (d, $^2J_{CP}$ = 2.3, PdC(1) arom), 150.4 (C(2) arom). ^{31}P{^{1}H} NMR (δ, ppm): 21.83. Anal. Calcd for $C_{25}H_{31}ClNOPPd$: C, 56.19; H, 5.85; N, 2.62. Found: C, 56.08; H, 5.90; N, 2.59.

(*S*$_C$)-Chloro-{2-[1-(*N*,*N*-dimethylamino)ethyl]phenyl-*C*,*N*}[(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) ((*S*$_C$)-10). Compound (S_C)-**10** was synthesized from (S_C,S_C)-**8** as pale yellow crystals in 79% yield. [α]$_D$ +22 (*c* 0.0034, CH_2Cl_2). Mp: 60−61 °C; R_f 0.71 (5:1 benzene−acetone). ^{1}H NMR (δ, ppm): 1.49 (m, 1H, $PCH_2CH_2CH^AH^A$), 1.64 (m, 2H, $PCH_2CH^AH^BH^B$), 1.78 (d, 3H, $^3J_{HH}$ = 6.5, $CHCH_3$), 2.04 (m, 1H, $PCH_2CH^BH^B$), 2.22 (m, 1H, PCH^AH^A), 2.70 (m, 1H, PCH^BH^B), 2.74 (d, 3H, $^4J_{HP}$ = 2.9, $NCH_3{}^A$), 2.77 (d, 3H, $^4J_{HP}$ = 1.6, $NCH_3{}^B$), 3.02 (br s, 1H, OH), 3.62 (m, 1H, CH^AOH), 3.68 (m, 1H, CH^BOH), 3.79 (m, 1H, $CHCH_3$), 6.40 (m, 2H, H(5,6) arom), 6.82 (dt, 1H, J_{HP} = 4.5, $^3J_{HH}$ = 7.6, H(4) arom), 6.93 (d, 1H, $^3J_{HH}$ = 7.2, H(3) arom), 7.32 (m, 2H, *m*-PPh^A), 7.39 (m, 1H, *p*-PPh^A), 7.46 (m, 3H, *m*- and *p*-PPh^B), 7.68 (m, 2H, *o*-PPh^A), 7.92 (m, 2H, *o*-PPh^B). ^{13}C{^{1}H} NMR (δ, ppm): 20.5 (d, $^2J_{CP}$ = 3.0, PCH_2CH_2), 21.5 ($CHCH_3$), 29.1 (d, $^1J_{CP}$ = 33.6, PCH_2), 33.6 (d, $^3J_{CP}$ = 16.6, $PCH_2CH_2CH_2$), 46.2 (d, $^3J_{CP}$ = 1.7, $NCH_3{}^A$), 50.1 (d, $^3J_{CP}$ = 2.7, $NCH_3{}^B$), 59.6 (CH_2OH), 74.9 (d, $^3J_{CP}$ = 2.9, $CHCH_3$), 122.3 (C(3) arom), 123.9 (C(4) arom), 125.1 (d, $^4J_{CP}$ = 5.8, C(5) arom), 128.2 (d, $^3J_{CP}$ = 10.3, *m*-PPh^A), 128.5 (d, $^3J_{CP}$ = 10.4, *m*-PPh^B), 130.5 (d, $^4J_{CP}$ = 1.9, *p*-PPh^A), 130.6 (br d, $^1J_{CP}$ = 45.2, *ipso*-C of PPh^A and PPh^B), 130.7 (d, $^4J_{CP}$ = 2.3, *p*-PPh^B), 134.3 (d, $^2J_{CP}$ = 10.9, *o*-PPh^A), 134.4 (d, $^2J_{CP}$ = 11.1, *o*-PPh^B), 137.5 (d, $^3J_{CP}$ = 11.7, C(6) arom), 150.1 (C(2) arom), 154.3 (d, $^2J_{CP}$ = 2.1, PdC(1) arom). ^{31}P{^{1}H} NMR (δ, ppm): 21.83. Anal. Calcd for $C_{26}H_{33}ClNOPPd$: C, 56.94; H, 6.07; N, 2.55. Found: C, 56.74; H, 6.07; N, 2.43.

(*S*$_C$)-Chloro-[2-(2-methyl-2-oxazolin-4-yl)phenyl-*C*,*N*][(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) ((*S*$_C$)-12). Compound (S_C)-**12** was synthesized from (S_C,S_C)-**11** as a pale yellow powder in 67% yield. [α]$_D$ +58 (*c* 0.0030, CH_2Cl_2). Mp: 96−97 °C; R_f 0.61 (5:1 benzene−acetone). ^{1}H NMR (δ, ppm): 1.45 (m, 2H, $PCH_2CH^AH^AH^A$), 1.69 (m, 1H, $PCH_2CH_2CH^BH^B$), 2.10 (m, 2H, $PCH^AH^BH^B$), 2.49 (s, 3H, CH_3), 2.72 (br s, 1H, OH), 2.91 (m, 1H, PCH^BH^B), 3.61 (m, 1H, CH^AOH), 3.68 (m, 1H, CH^BOH), 4.31 (m, 1H, OCH^AH^A), 4.88 (m, 1H, OCH^BH^B), 5.82 (m, 1H, CHN), 6.44 (m, 2H, H(5,6) arom), 6.70 (d, 1H, $^3J_{HH}$ = 7.3, H(3) arom), 6.87 (m, 1H, H(4) arom), 7.26 (m, 2H, *m*-PPh^A), 7.37 (m, 1H, *p*-PPh^A), 7.53 (m, 3H, *m*- and *p*-PPh^B), 7.59 (m, 2H, *o*-PPh^A), 8.12 (m, 2H, *o*-PPh^B). ^{13}C{^{1}H} NMR (δ, ppm): 14.1 (CH_3), 20.9 (PCH_2CH_2), 28.8 (d, $^1J_{CP}$ = 34.5, PCH_2), 32.8 (d, $^3J_{CP}$ = 16.4, $PCH_2CH_2CH_2$), 60.3 (CH_2OH), 73.6 (OCH_2), 74.0 (NCH), 120.4 (C(3) arom), 125.0 (C(4) arom), 125.7 (d, $^4J_{CP}$ = 6.1, C(5) arom), 128.5 (d, $^3J_{CP}$ = 12.3, *m*-PPh^A), 128.8 (d, $^3J_{CP}$ = 13.0, *m*-PPh^B), 130.1 (d, $^1J_{CP}$ = 46.9, *ipso*-C of PPh^A), 130.3 (d, $^1J_{CP}$ = 45.9, *ipso*-C of PPh^B), 130.5 (*p*-PPh^A), 131.0 (*p*-PPh^B), 134.1 (two overlapping d, *o*-PPh^A and *o*-PPh^B), 138.12 (d, $^3J_{CP}$ = 12.2, C(6) arom), 147.2 (C(2) arom), 149.1 (PdC(1) arom), 171.1 (d, $^3J_{CP}$ = 6.7, NCO). ^{31}P{^{1}H} NMR (δ, ppm): 20.28. Anal. Calcd for $C_{27}H_{31}ClNO_2PPd$: C, 56.36; H, 5.64; N, 2.43. Found: C, 56.11; H, 5.46; N, 2.46.

Chloro-[2-methyl-2-(4,4-dimethyloxazolin-2-yl)propyl-*C*,*N*]-[(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) (14). Compound **14** was obtained from CPC **13** as a pale yellow powder in 92% yield. Mp: 58−60 °C; R_f 0.26 (5:1 benzene−acetone); ^{1}H NMR (δ, ppm) 1.08 (s, 6H, CH_3), 1.22 (d, 2H, $^3J_{HP}$ = 4.6, $PdCH_2$), 1.58 (s and m, 8H, two CH_3 groups and $PCH_2CH_2CH_2$), 1.74 (m, 2H, PCH_2CH_2), 2.45 (m, 2H, PCH_2), 3.20 (br s, 1H, OH), 3.69 (m, 2H, CH_2OH), 4.11 (s, 2H, OCH_2), 7.41 (m, 6H, *m*- and *p*-PPh), 7.65 (m, 4H, *o*-PPh). ^{13}C{^{1}H} NMR (δ, ppm): 20.3 (PCH_2CH_2), 26.5 (d, $^1J_{PC}$ = 30.8, PCH_2), 27.6 and 27.9 (two CH_3 groups), 32.8 (d, $^2J_{CP}$ = 15.5, $PdCH_2$), 35.2 ($PCH_2CH_2CH_2$), 41.6 (Me_2CN), 59.8 (CH_2OH), 67.0 (d, $^3J_{CP}$ = 3.2, Me_2CCH_2Pd), 82.2 (d, $^4J_{CP}$ = 3.7, OCH_2), 128.3 (d, $^3J_{CP}$ = 10.2, *m*-PPh), 130.2 (d, $^4J_{CP}$ = 1.9, *p*-PPh), 132.0 (d, $^1J_{CP}$ = 46.4, *ipso*-C of PPh), 133.2 (d, $^2J_{CP}$ = 10.8, *o*-PPh), 182.2 (d, $^3J_{CP}$ = 2.7, NCO). ^{31}P{^{1}H} NMR (δ, ppm): 15.72. Anal. Calcd for $C_{25}H_{35}ClNO_2PPd$: C, 54.16; H, 6.36; N, 2.53. Found: C, 53.89; H, 6.34; N, 2.69.

(*S*$_C$)-Chloro-{[2-(4-benzyl-2-oxazolin-2-yl)methyl]phenyl-*C*,*N*}-[(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) (*endo*-(*S*$_C$)-16). Compound *endo*-(S_C)-**16** was synthesized from (S_C,S_C)-**15** following the general procedure except for using 1/3 of the THF amount for dissolving CPC (S_C,S_C)-**15**. The complex was isolated as a pale yellow powder in 10% yield. Mp: 98−100 °C; R_f 0.14 (5:1 benzene−acetone). ^{1}H NMR (δ, ppm): 1.32 (m, 2H, $PCH_2CH^AH^AH^A$), 1.63 (m, 2H, $PCH_2CH^BH^BH^B$), 2.00 (m, 2H, PCH^AH^A, OH), 2.40 (m, 1H, PCH^BH^B), 2.68 (m, 1H, $PhCH^AH^A$), 3.36 (m, 1H, CH^AOH), 3.43 (m, 1H, CH^BOH), 3.58 (dd, 1H, $^2J_{HH}$ = 12.1, $^3J_{HH}$ = 8.7, OCH^AH^A), 3.66 (d, 1H, $^2J_{HH}$ = 14.1, $C_6H_4CH^AH^A$), 3.90 (dd, 1H, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 6.3, $PhCH^BH^B$), 4.10 (d, 1H, $C_6H_4CH^BH^B$), 4.50 (m, 1H, OCH_2), 4.74 (m, 1H, CHN), 6.35 (m, 2H, H(5,6) of C_6H_4Pd), 6.68 (m, 2H, H(3,4) of C_6H_4Pd), 6.90 and 7.01 (two m, 5H, C_6H_5 of 4-Bn), (m, 2H, *m*-PPh^A), 7.20−7.40 (m, 6H, *m*- and *p*-PPh_2), 7.57 (m, 2H, *o*-PPh^A), 7.69 (m, 2H, *o*-PPh^B). ^{13}C{^{1}H} NMR (δ, ppm): 19.9 (PCH_2CH_2), 26.3 (d, $^1J_{CP}$ = 33.2, PCH_2), 31.8 (d, $^3J_{CP}$ = 16.4, $PCH_2CH_2CH_2$), 33.7 ($C_6H_4CH_2$), 39.6 ($PhCH_2$), 59.2 (NCH), 59.5 (CH_2OH), 71.5 (OCH_2), 122.7 and 125.8 (C(3) and C(4) of C_6H_4Pd), 124.6 (d, $^4J_{CP}$ = 6.3, C(5) of C_6H_4Pd), 127.0 (*p*-C of 4-Bn), 127.2 (two overlapping d, *m*-PPh), 128.1 (*o*-C of 4-Bn), 129.3 (*m*-C of 4-Bn), 129.7 (d, $^1J_{CP}$ = 47.3, *ipso*-C of PPh^A), 130.5 (d, $^1J_{CP}$ = 47.4, *ipso*-C of PPh^B), 132.6 (three overlapping d, *o*- and *p*-PPh), 134.1 (d, $^3J_{CP}$ = 10.7, C(6) of C_6H_4Pd), 134.9 (PdC(1) arom), 149.1 (C(2) of C_6H_4Pd), 170.6 (d, $^3J_{CP}$ = 5.0, NCO). ^{31}P{^{1}H} NMR (δ, ppm): 13.05. Anal. Calcd for $C_{33}H_{35}ClNO_2PPd$: C, 60.93; H, 5.42; N, 2.15. Found: C, 60.57; H, 5.72; N, 2.11.

(*S*$_C$)-{[2-(2-Benzyl-2-oxazolin-4-yl)methyl]phenyl-*C*,*N*}[(4-hydroxybutyl)diphenylphosphine-*P*]palladium(II) (*exo*-(*S*$_C$)-16). Compound *exo*-(S_C)-**16** was obtained from (S_C,S_C)-**15** as a pale yellow powder in 61% yield. Mp: 152−154 °C; R_f 0.25 (5:1 benzene−acetone). ^{1}H NMR (δ, ppm): 1.40 (m, 2H, $PCH_2CH^AH^ACH^AH^A$), 1.78 (m, 2H, $PCH_2CH^BH^BCH^BH^B$), 2.10 (m, 1H, PCH^AH^A), 2.17 (br s, OH), 2.48 (m, 1H, PCH^BH^B), 2.74 (dd, 1H, $^2J_{HH}$ = 13.7, $^3J_{HH}$ = 7.6, $C_6H_4CH^ACH$), 3.18 (dd, 1H, $^3J_{HH}$ = 4.2, $C_6H_4CH^BCH$), 3.40 (d, 1H, $^2J_{HH}$ = 16.4, $C_6H_4CH^ACN$), 3.47 (m, 1H, CH^AOH), 3.53 (m, 1H, CH^BOH), 4.14 (d, 1H, $C_6H_4CH^BCN$), 4.26 (m, 1H, OCH^AH^A), 4.51 (m, 1H, OCH^BH^B), 5.30 (m, 1H, CHN), 6.55 (m, 1H, H(6) of C_6H_4Pd), 6.81 (m, 1H, H(5) of C_6H_4Pd), 6.86 (m, 2H, H(3,4) of C_6H_4Pd), 6.98 (m, 2H, *o*-CH of 2-Bn), 7.02 (m, 2H, *m*-CH of 2-Bn), 7.08 (m, 1H, *p*-CH of 2-Bn), 7.20−7.55 (m, 6H, *m*- and *p*-PPh), 7.62 (m, 2H, *o*-PPh^A), 7.79 (m, 2H, *o*-PPh^B). ^{13}C{^{1}H} NMR (δ, ppm): 21.0 (PCH_2CH_2), 28.5 (d, $^1J_{CP}$ = 33.3, PCH_2), 33.4 (d, $^3J_{CP}$ = 15.6, $PCH_2CH_2CH_2$), 38.8 ($C_6H_4CH_2CN$), 40.6 ($PhCH_2$), 60.7 (CH_2OH), 63.6 (NCH), 74.9 (OCH_2), 123.7 (C(4) of C_6H_4Pd), 125.8 (d, $^4J_{CP}$ = 4.7, C(6) of C_6H_4Pd), 126.4 (*p*-CH of 2-Bn), 127.0 (C(3) of C_6H_4Pd), 128.3 (overlap of one s and two d, CH of 2-Bn, *m*-PPh^A and *m*-PPh^B), 129.8 (CH of 2-Bn), 130.3 (d, $^3J_{CP}$ = 15.1, *p*-PPh_2), 130.6 (d, $^1J_{CP}$ = 47.3, *ipso*-C of PPh^A), 131.5 (d, $^1J_{CP}$ = 47.0, *ipso*-C of PPh^B), 133.8 (two overlapping d, *o*-PPh_2), 135.9 and 136.0 (*ipso*-C of 2-Bn and PdC(1) arom), 137.7 (d, $^4J_{CP}$ = 13.0, C(5) of C_6H_4Pd), 149.1 (C(2) of C_6H_4Pd), 171.6

(NCO). $^{31}P\{^1H\}$ NMR (δ, ppm): 14.91. Anal. Calcd for $C_{33}H_{35}ClNO_2PPd$: C, 60.93; H, 5.42; N, 2.15; Cl, 5.45. Found: C, 61.22; H, 5.67; N, 2.23; Cl, 5.59.

μ-Chloro-μ-diphenylphosphido-{[2-(*N*,*N*-dimethylamino)methyl]-phenyl-*C*,*N*}dipalladium(II) (17). Method I. Complex CPC **7** (21.0 mg, 0.0380 mmol) was placed into an Ar-filled 10 mL Schlenk flask. The flask was vacuumed and THF (2.1 mL) was added. Then a 0.5 M solution of $LiPPh_2$ in THF (reagent **D**) was added dropwise in 8 min. The colorless mixture turned red. The reaction mixture was stirred in Ar at rt for 4 h. After solvent removal, the crude product was dissolved in CH_2Cl_2 and the solution was filtered through a layer of Celite. The filtrate was concentrated and the crude product was purified using preparative TLC (silica gel, 6:1 benzene−acetone). Complex **17** was isolated in 60% yield as a yellow solid. Method II. A solution of $LiPPh_2$ in THF (0.14 mL, 0.068 mmol) obtained from PPh_3 and Li (reagent **A1**) was placed into an Ar-filled 10 mL Schlenk flask. Then a solution of CPC **7** (18.3 mg, 0.0340 mmol) in THF (1.8 mL) was added dropwise to the $LiPPh_2$ solution in 4 min. During the addition, the color of the mixture changed from dark brown to dark red. The reaction mixture was stirred at rt in Ar for 5 h. After solvent evaporation using a rotavapor, the crude product was dissolved in CH_2Cl_2 and filtered through a layer of Celite. The filtrate was concentrated and the crude product was purified using preparative TLC (silica gel, 6:1 benzene−acetone). Complex **17** was obtained in 17% yield along with 58% of compound **18**. Method III. Complex **7** (20.0 mg, 0.0371 mmol) was placed into an Ar-filled 10 mL Schlenk flask. The flask was vacuumed and filled with Ar followed by addition of THF (3 mL). Then a 0.5 M solution of $LiPPh_2$ in THF (reagent **B1**, 0.15 mL, 0.074 mmol) was added dropwise in 2 min. The color of the mixture changed from yellow to orange-red. The reaction mixture was stirred in Ar at rt for 6 h. After solvent removal, the residue was dissolved in CH_2Cl_2 and filtered through a layer of Celite. The filtrate was concentrated and purified using preparative TLC (silica gel, 6:1 benzene−acetone). Complex **17** was obtained in 12% yield, compound **18** in 52% yield. Mp: 165−168 °C; R_f 0.91 (5:1 benzene−acetone). ^1H NMR (δ, ppm): 2.59 (s, 6H, $N(CH_3)_2$), 3.78 (s, 2H, CH_2N), 6.35 (dd, 1H, $^3J_{HH}$ = 7.5, J_{HP} = 4.2, C(6)H arom), 6.42 (t, 1H, $^3J_{HH}$ = 7.5, C(5)H arom), 6.72 (t, 1H, $^3J_{HH}$ = 7.5, C(4)H arom), 6.82 (d, 1H, $^3J_{HH}$ = 7.5, C(3)H arom), 7.17 (m, 3H, *p*- and *m*-PPh), 7.79 (m, 2H, *o*-PPh). $^{13}C\{^1H\}$ NMR (δ, ppm): 48.2 (d, $^3J_{CP}$ = 1.6, NCH_3), 69.9 (d, $^3J_{CP}$ = 2.0, NCH_2), 121.2 (C(3) arom), 122.3 (C(4) arom), 124.1 (d, $^4J_{CP}$ = 4.5, C(5) arom), 126.7 (d, $^3J_{CP}$ = 10.2, *m*-PPh), 127.7 (d, $^4J_{CP}$ = 2.5, *p*-PPh), 134.4 (d, $^2J_{CP}$ = 12.2, *o*-PPh), 134.7 (d, $^1J_{CP}$ = 28.4, *ipso*-PPh), 136.5 (d, $^3J_{CP}$ = 8.5, C(6) arom), 147.1 (d, $^2J_{CP}$ = 2.9, PdC(1) arom), 147.3 (d, $^3J_{CP}$ = 1.8, C(2) arom). $^{31}P\{^1H\}$ NMR (δ, ppm): 25.1. Anal. Calcd for $C_{66}H_{74}Cl_2N_4P_2Pd_4$ (2 molecules of **17** and 1 of benzene): C, 53.49; H, 5.03; N, 3.78. Found: C, 53.64; H, 5.08; N, 3.62 (the benzene signal was present in both the ^1H and ^{13}C spectra of the sample used for the analysis).

Chloro-{[2-(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}(triphenylphosphine-*P*)palladium(II) (18). This previously reported complex was a side product in reactions of CPC **7** with the $LiPPh_2$ reagents synthesized using PPh_3. Mp: 158−160 °C; R_f 0.82 (5:1 benzene−acetone). ^1H NMR (δ, ppm): 2.85 (s, 6H, $N(CH_3)_2$), 4.07 (s, 2H, CH_2N), 6.32 (dd, 1H, $^3J_{HH}$ = 7.3, J_{HP} = 6.6, C(6)H arom), 6.37 (t, 1H, $^3J_{HH}$ = 7.3, C(5)H arom), 6.82 (t, 1H, $^3J_{HH}$ = 7.3, C(4)H arom), 6.99 (d, 1H, $^3J_{HH}$ = 7.3, C(3)H arom), 7.34 (m, 6H, *m*-PPh), 7.41 (m, 3H, *p*-PPh), 7.72 (m, 6H, *o*-PPh). $^{13}C\{^1H\}$ NMR (δ, ppm): 50.5 (d, $^3J_{CP}$ = 2.4, NCH_3), 73.2 (d, $^3J_{CP}$ = 2.9, NCH_2), 122.3 (C(3) arom), 123.8 (C(4) arom), 124.9 (d, $^4J_{CP}$ = 5.8, C(5) arom), 128.0 (d, $^3J_{CP}$ = 10.7, *m*-PPh), 130.5 (d, $^4J_{CP}$ = 2.4, *p*-PPh), 131.4 (d, $^1J_{CP}$ = 49.9, *ipso*-PPh), 135.3 (d, $^2J_{CP}$ = 11.9, *o*-PPh), 137.9 (d, $^3J_{CP}$ = 10.8, C(6) arom), 148.5 (d, $^2J_{PC}$ = 1.9, PdC(1) arom), 150.8 (C(2) arom). $^{31}P\{^1H\}$ NMR (δ, ppm): 27.3.

Chloro{[2-(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}(tetraphenyldiphosphine oxide-*P*)palladium(II) (19). Complex **19** was formed from complex **17** after storing in CH_2Cl_2 for two months in 25% yield. Compound **19** was also obtained from complex **17** while heating in toluene at 60 °C for a week in 12% yield. This complex was also isolated from the reaction of CPC **7** with 2 molar equiv of reagent **C2** (THF, rt, 7 h) in 12% yield. The complex was isolated from reaction mixtures using preparative TLC (silica gel, benzene). Mp: 156−157 °C (dec); R_f 0.17 (5:1 benzene−acetone). ^1H NMR (δ, ppm): 2.68 (s, 6H, $N(CH_3)_2$), 3.76 (s, 2H, CH_2N), 6.09 (dd, 1H, $^3J_{HH}$ = 7.4, J_{HP} = 5.3, C(6)H arom), 6.24 (t, 1H, $^3J_{HH}$ = 7.4, C(5)H arom), 6.61 (t, 1H, $^3J_{HH}$ = 7.4, C(4)H arom), 6.73 (d, 1H, $^3J_{HH}$ = 7.4, C(3)H arom), 6.96 (br m, 4H, *p*-PPh), 7.08 (br m, 8H, *m*-PPh), 7.44 (m, 4H, *o*-PPh), 7.69 (m, 4H, *o*-PPh). $^{13}C\{^1H\}$ NMR (δ, ppm): 49.4 (d, $^3J_{CP}$ = 1.5, NCH_3), 69.9 (d, $^3J_{CP}$ = 2.5, NCH_2), 120.7 (C(3) arom), 122.0 (C(4) arom), 123.8 (d, $^4J_{CP}$ = 4.8, C(5) arom), 126.1 (d, $^3J_{CP}$ = 10.4, *m*-PPh), 127.1 (s, *p*-PPh), 130.4 (d, $^2J_{CP}$ = 11.4, *o*-PPh), 134.1 (br m, *o*-PPh and C(6) arom), 139.5 (d, $^1J_{CP}$ = 58.4, *ipso*-PPh), 146.3 (s, PdC(1) arom), 147.4 (C(2) arom). $^{31}P\{^1H\}$ NMR (δ, ppm): PPh_2 23.2 (d, $^1J_{PP}$ = 203.1), P(O) 103.2 (d, $^1J_{PP}$ = 203.1), and the other isomer PPh_2 23.8, P(O) 103.0. Anal. Calcd for $C_{34}H_{32}DCl_4NOP_2Pd$ (1 molecule of **19** and 1 of $CDCl_3$): C, 52.17; H, 4.38; N, 1.79. Found: C, 51.63; H, 4.53; N, 1.78.

***ortho*-(Diphenylphosphino)-*N*,*N*-dimethylbenzylamine (20).** Method I. A 0.5 M solution of $LiPPh_2$ in THF (reagent **C3**) was placed into an Ar-filled 10 mL Schlenk flask. Then THF was removed using a pump, and the formed pale yellow solid was kept under vacuum (< 1 mbar) for 1.5 h at 40 °C. A solution of CPC **7** (25.7 mg, 0.0465 mmol) in toluene (9.1 mL) was added dropwise in 4 min. The yellow reaction mixture was stirred in Ar at rt for 18 h. After solvent removal, a solid residue was dissolved in CH_2Cl_2 and purified using preparative TLC (silica gel, 8:1 benzene−acetone). Aminophosphine **20** was obtained in 81% yield, complex **17** was isolated in 17% yield. Method II. In the Ar atmosphere, $HPPh_2$ (0.015 mL, 0.084 mmol) was placed into a 10 mL Schlenk flask followed by addition of THF (0.25 mL). The solution was cooled to −78 °C, and then a 0.25 M solution of *n*-BuLi in hexane (0.034 mL, 0.084 mmol) was added dropwise in 5 min. During the addition, the colorless reaction mixture turned first yellow, then orange and finally back to colorless. The mixture was stirred at −78 °C for 30 min. Then it was slowly (within several hours) warmed to rt and stirred for 30 min. The estimated molarity of the obtained reagent was 0.3 M. Then a solution of CPC **4** (22.6 mg, 0.0409 mmol) in THF (3.5 mL) was added dropwise in 5 min. During the addition, the color of the mixture changed to bright red. The reaction mixture was stirred at rt in Ar for 18 h. In the end of the reaction, the mixture became dark red. After solvent removal, the solid residue was dissolved in CH_2Cl_2 and purified using preparative TLC (silica gel, 7:1 benzene−acetone). Aminophosphine **20** was obtained in 37% yield as a pale yellow syrup: R_f 0.61 (7:1 benzene−acetone). ^1H NMR (δ, ppm): 2.05 (s, 6H, $N(CH_3)_2$), 3.61 (d, 2H, $^4J_{HP}$ = 1.6, NCH_2), 6.90 (ddd, 1H, $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 4.3, $^4J_{HH}$ = 1.0, C(6)H arom), 7.14 (dt, 1H, $^3J_{HH}$ = 7.5, $^4J_{HP}$ = 1.0, C(5)H arom), 7.25 (m, 4H, *o*-PPh), 7.30 (m, 6H, *m*- and *p*-PPh), 7.34 (br m, 1H, C(4)H arom), 7.46 (br dd, $^4J_{HP}$ = 4.3, $^3J_{HH}$ = 7.3, C(3)H arom). $^{13}C\{^1H\}$ NMR (δ, ppm): 44.5 (s, NCH_3), 62.0 (br s, NCH_2), 127.2 (C(4) arom), 128.3 (br s, *m*-PPh), 128.5 (d, $^1J_{CP}$ = 39.0, *ipso*-PPh), 129.2 (d, $^3J_{CP}$ = 2.9, C(5) arom), 131.7 (d, $^3J_{CP}$ = 9.3, C(3) arom), 133.7 (d, $^2J_{CP}$ = 5.7, *o*-PPh), 133.8 (s, *p*-PPh), 136.7 (d, $^1J_{CP}$ = 15.3, C(1) arom), 137.7 (br s, C(2) arom). $^{31}P\{^1H\}$ NMR (δ, ppm): −30.3. HRMS: $[M + H]^+$ calcd for $C_{21}H_{23}NP$ 320.1523, found 320.1565.

***ortho*-(Diphenyloxophosphino)-*N*,*N*-dimethylbenzylamine (21).** This compound was obtained as a slightly yellow sticky oil in 5% yield in the reaction of CPC **7** with reagent **C3** (1:2 molar ratio) in THF at rt for 3 h: R_f 0.23 (7:1 benzene−acetone). ^1H NMR (δ, ppm): 1.99 (s, 6H, $N(CH_3)_2$), 3.78 (br s, 2H, NCH_2), 7.02 (dd, 1H, $^3J_{HH}$ = 7.3, $^3J_{HP}$ = 14.1, C(6)H arom), 7.18 (t, 1H, $^3J_{HH}$ = 7.3, C(5)H arom), 7.46 (m, 4H, *o*-PPh), 7.5 (br m, 1H, C(4)H arom), 7.53 (m, 2H, *p*-PPh), 7.62 (m, 4H, *m*-PPh), 7.76 (br m, 1H, C(3)H arom). $^{13}C\{^1H\}$ NMR (δ, ppm): 44.9 (s, NCH_3), 61.3 (br s, NCH_2), 126.2 (d, $^3J_{CP}$ = 13.8, C(5) arom), 128.4 (d, $^2J_{CP}$ = 15.1, *o*-PPh), 130.2 (br s, C(3) arom), 130.7 (d, $^1J_{CP}$ = 100.6, *ipso*-PPh), 131.5 (s, *p*-PPh), 131.7 (d, $^3J_{CP}$ = 8.8, *m*-PPh), 132.1 (br s, C(4)

arom), 133.1 (br s, C(1) arom), 133.6 (d, $^2J_{CP}$ = 13.8, C(6) arom), 134.0 (br s, C(2) arom). $^{31}P\{^1H\}$ NMR (δ, ppm): 16.6. HRMS: $[M + H]^+$ calcd for $C_{21}H_{23}NOP$ 336.1517, found 336.1522.

Crystallographic data for 9 have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-736136. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of compounds *rac*-**6**, **9**, (S_C)-**10**, (S_C)-**12**, **14**, *endo*-(S_C)-**16**, *exo*-(S_C)-**16**, and **17**−**21** and the CIF file with the data of the X-ray crystallographical analysis of complex **9**. This material is available free of charge via the Internet at http://pubs.acs.org.