ORGANOMETALLICS

The First Carbodiphosphorane Complex with Two Palladium Centers Attached to the CDP Carbon: Assembly of a Single-Stranded di-Pd Helicate by the PCP Pincer ligand C(dppm)₂

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Supporting Information

ABSTRACT: The reaction of the protonated PCP pincer carbodiphosphorane (CDP) complex $[PdCl(CH(dppm)_2)]Cl_2$ (1) with $[PdCl_2(MeCN)_2]$ results in the opening of one ring of the pincer structure and affords the betaine $[Pd_2Cl_5(CH(dppm)_2)]$ (2). The $[CH(dppm)_2]^+$ ligand forms a five-membered chelate ring with the $Pd(1)Cl_2$ moiety via the protonated CDP carbon (positively charged) and one phosphine functionality and bridges to the anionic $Pd(2)Cl_3$ fragment via the second phosphine phosphorus. The complex is chiral due to a stereocenter at the



protonated CDP carbon atom. Treatment of **2** with water effects deprotonation of the CDP carbon, C–H activation at one methylene group, and the coordination of the second Pd to the CDP carbon. The resulting tricyclic complex $[Pd_2Cl_3(C(dppm)(Ph_2CHPh_2))]$ (**3**) is the first compound with two Pd centers coordinated to a CDP carbon. Compound **3** forms a single-stranded helicate structure and exhibits two interdependent carbon stereocenters, resulting in only two possible enantiomers. The complexes **2** · 2CH₂Cl₂ and **3** · 3CH₂Cl₂ crystallize in the chiral space group *P*2₁, whereby a spontaneous resolution of the enantiomers occurs in both cases.

INTRODUCTION

Carbodiphosphoranes (CDPs, C(PR₃)₂) are formally composed of one carbon atom and two tertiary phosphines.¹ In keeping with recent quantum chemical results,² the central carbon of CDPs behaves as a potential four-electron donor and may interact with one or two Lewis acids, e.g., with one or two protons, one or two metal centers, or one proton and one metal center.³ Complexes with a CDP/metal ratio of 1/2 have hitherto been seldom realized: two d¹⁰ gold atoms are coordinated by the CDP carbon in $[(AuMe)_2C(PMe_3)_2], [(AuPPh_3)_2C(PMePh_2)_2]$ $Br_{2,4}^{4}$ and $[(AuCl)_2C(PPh_3)_2]^{5}$ whereas one d^{10} gold and one d⁸ palladium are attached to the CDP functionality in $[PdAu(Cl)_2(C(dppm)_2)]Cl.^6$ Two of these compounds, namely, $[(AuCl)_2C(PPh_3)_2]$ and $[PdAu(Cl)_2(C(dppm)_2)]Cl$, have been structurally characterized.^{5,6} All these dinuclear CDP complexes involve at least one d¹⁰ gold center, whose sterically favorable linear coordination geometry and the ability to form tangential metallophilic interactions (e.g., $d^{10}-d^{10}$ or $d^{10}-d^8$) may stabilize the complexes. We were interested in the potential of CDPs for the coordination of two non-d¹⁰ metal centers in order to probe an extension of the chemistry of this class of ligands. The complex $[PdCl(CH(dppm)_2)]Cl_2(1)^7$ was chosen as a promising starting material for this purpose, since it contains one d⁸-Pd center, and its potential to form bimetallic complexes has been shown by the synthesis of [PdAu(Cl)₂(C(dppm)₂)]Cl.^o

In this paper we report on two homodinuclear palladium complexes of $[CH(dppm)_2]^+$ and the hitherto unknown

derivative $[C(dppm)(Ph_2CHPh_2)]^-$ including the first CDP complex with two Pd centers attached to the central carbon.

RESULTS AND DISCUSSION

Synthesis. Treatment of the protonated PCP pincer⁷ CDP complex $[PdCl(CH(dppm)_2)]Cl_2(1)^8$ with $[PdCl_2(MeCN)_2]$ in CH₂Cl₂ results in the opening of one five-membered ring of the pincer system and produces the dinuclear palladium complex $[Pd_2Cl_5(CH(dppm)_2)]$ (2) according to Scheme 1 in almost quantitative yield. The two MeCN ligands of $[PdCl_2(MeCN)_2]$ are substituted by one phosphine donor of the $[CH(dppm)_2]^+$ ligand and one Cl⁻. The ring-opening reaction may be initiated by Cl⁻ attack at the pincer complex 1, forming a pentacoordinated palladium intermediate, followed by the dissociation of one phosphine function, which is in turn coordinated by the second Pd center.⁹ The protonated CDP functionality carries a positive charge, which is compensated within the complex by the negatively charged PdCl₃ group in a betaine-type fashion. The complex is chiral due to a stereocenter at the protonated CDP carbon atom.

Upon reaction of 2 with water, two Cl⁻ ligands are substituted by two carbon centers with concomitant liberation of two equivalents of HCl. The product $[Pd_2Cl_3(C(dppm)(Ph_2CHPh_2))]$ (3) is composed of the hitherto unknown CDP ligand $[C(dppm)(Ph_2-CHPh_2)]^-$ and two palladium and three chlorine atoms

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Figure 1. Thermal ellipsoid plot of $2 \cdot 2$ CH₂Cl₂. The phenyl groups except for the *ipso* carbon atoms are omitted for clarity. Selected distances (Å) and angles (deg): Pd(1)-C(1) 2.115(8), Pd(1)-P(1) 2.241(2), Pd(1)-Cl(1) 2.311(2), Pd(1)-Cl(2) 2.375(2), Pd(2)-P(4) 2.227(2), Pd(2)-Cl(5) 2.273(3), Pd(2)-Cl(4) 2.280(3), Pd(2)-Cl(3) 2.359(3), P(2)-C(1) 1.786(9), P(3)-C(1) 1.806(8), C(1)-Pd(1)-P(1) 92.4(2), C-(1)-Pd(1)-Cl(1) 177.3(2), P(1)-Pd(1)-Cl(1) 90.21(9), C(1)-Pd(1)-Cl(2) 90.07(9), P(4)-Pd(2)-Cl(5) 90.54(11), P(4)-Pd(2)-Cl(4) 89.77(9), Cl(5)-Pd(2)-Cl(4) 176.84(19), P(4)-Pd(2)-Cl(3) 179.99(13), Cl(5)-Pd(2)-Cl(3) 89.45(13), Cl(4)-Pd(2)-Cl(3) 90.24(11), H(1)-C(1)-P(2) 106(5), H(1)-C(1)-P(3) 104(4), P-(2)-C(1)-P(3) 119.9(5), H(1)-C(1)-Pd(1) 109(5), P(2)-C-(1)-Pd(1) 103.6(4), P(3)-C(1)-Pd(1) 113.2(4).

(Scheme 1). The tricyclic structure incorporates a PCC pincer substructure consisting of a four-membered PdCPC ring and a five membered PdPCPC ring. The CDP complex **3** is the first example where the central carbon acts as a donor toward two metals without the involvement of gold.

The reaction is thought to be initiated by the deprotonation of the protonated CDP carbon atom C(1) of **2** in view of a related reaction of **1** with water resulting in the CDP complex $[PdCl(C(dppm)_2)]Cl.^7$ Subsequent steps—in unknown chronological order—comprise the coordination of the second Pd center at the CDP carbon and the cyclometalation at one methylene group, resulting in the formation of a tricyclic structure.¹⁰ The CH activation of the methylene group of coordinated dppm ligands is not uncommon, and predominantly coinage metals were attached to the carbon center.¹¹ Other CH



Figure 2. Thermal ellipsoid plot of $3 \cdot 3CH_2Cl_2$. The phenyl groups except for the ipso carbon atoms are omitted for clarity. Selected distances (Å) and angles (deg): Pd(1)-C(1) 2.145(3), Pd(1)-P(1) 2.2480(9), Pd(1)-Cl-(1) 2.3502(9), Pd(1)-Cl(2) 2.3657(8), Pd(1)-Pd(2) 3.0951(5), Pd-(2)-C(1) 2.088(3), Pd(2)-C(2) 2.177(3), Pd(2)-P(4) 2.2905(8), Pd(2)-Cl(3) 2.3556(9), P(2)-C(1) 1.776(3), P(3)-C(1) 1.763(3), P(1)-C(2) 1.782(3), P(2)-C(2) 1.762(3), P(3)-C(3) 1.808(3), P-(4)-C(3) 1.842(3), C(1)-Pd(1)-P(1) 87.81(8), C(1)-Pd(1)-Cl(1) 174.89(9), P(1)-Pd(1)-Cl(1) 88.62(3), C(1)-Pd(1)-Cl(2) 94.57(8), P(1)-Pd(1)-Cl(2) 172.55(3), Cl(1)-Pd(1)-Cl(2) 89.43(3), C(1)-Pd(2)-C(2) 74.33(12), C(1)-Pd(2)-P(4) 91.86(9), C(2)-Pd(2)-P-(4) 166.19(9), C(1)-Pd(2)-Cl(3) 171.51(9), C(2)-Pd(2)-Cl(3)97.32(9), P(4)-Pd(2)-Cl(3) 96.49(3), P(3)-C(1)-P(2) 125.39 (18), P(3)-C(1)-Pd(2) 110.69(15), P(2)-C(1)-Pd(2) 89.23(13),P(3)-C(1)-Pd(1) 121.87(15), P(2)-C(1)-Pd(1) 105.84(15), Pd-(2)-C(1)-Pd(1) 93.96(12).

activation reactions in complexes of Pd, Pt, and Rh with the CDP ligand $C(PPh_3)_2$ concern the phenyl groups and afford CCC pincer complexes, if two phenyl rings are orthometalated.^{12–14} The CDP and the methine carbon atoms in **3** are stereogenic, and in view of their interdependence, which is caused by the tricyclic ring system, only two enantiomers are expected.

Crystallography. The complexes $2 \cdot 2 \text{CH}_2 \text{Cl}_2$ and $3 \cdot 3 \text{CH}_2 \text{Cl}_2$ crystallize in the chiral space group $P2_1$, whereby a spontaneous resolution of the enantiomers occurs in both cases. The enantiomers with the absolute CIP configuration $C(1) \ \text{R} \ (2 \cdot 2 \text{CH}_2 \text{Cl}_2)$ and $3 \cdot 3 \text{CH}_2 \text{Cl}_2$) and $C(2) \ \text{R} \ (3 \cdot 3 \text{CH}_2 \text{Cl}_2)$ have been investigated by SCD. No substantial interaction with the corrystallized solvent molecules has been detected in both structures.

In $2 \cdot 2CH_2Cl_2$ (Figure 1) the coordination spheres of Pd(1) and Pd(2) are quadratic planar (sum of angles around Pd(1): 360.2°; sum of angles around Pd(2): 360.0°). The environment around C(1) is distorted tetrahedral (angles ranging from 103.6(4)° for P(2)-C(1)-Pd(1) to 119.9(5)° for P(2)-C(1)-P(3); sum of angles around C(1) including Pd(1), P(2), and P(3): 336.7°). The five-membered ring Pd(1)P(1)C(2)P(2)C(1) displays an envelope conformation with P(2) at the flap; the bridging arm of the ligand backbone consisting of C(1)P(3)C(3)P(4) adopts a zigzag chain structure. The Pd(1)-C(1) distance (2.115(8) Å) as well as the P(2)-C(1)-P(3) angle $(119.9(5)^{\circ})$ are very similar to the respective values in the protonated pincer CDP complex 1 $(2.102(2) \text{ Å and } 121.9(2)^{\circ})$.⁷ The P–C distances (P(2)-C(1))1.786(9), P(3)-C(1) 1.806(8) Å) indicate P-C single bonds, as do those of 1 (P(2)-C(1) 1.804(3), P(3)-C(1) 1.801(3) Å). The Pd-P distances are in a narrow range (2.227(2) - 2.241(2) Å), whereas the Pd-Cl distances show substantial dependence on the

respective *trans*-ligand (*trans*-Cl: 2.273(3)–2.280(3) Å; *trans*-C: 2.311(2) Å; *trans*-P: 2.359(3)–2.375(2) Å).

In $3 \cdot 3CH_2Cl_2$ (Figure 2) the ligand $[C(dppm)(Ph_2PCHP-Ph_2)]^-$ forms a single-stranded helicate wrapped around the two Pd centers. The screw angle from P(1) along the ligand backbone to P(4) amounts to ca. 180° imposed by the bridging carbon atom, leading to approximately orthogonal square-planar coordination geometries of the Pd centers with a Pd(1)-C(1)-Pd(2) angle of 93.96(12)°. In this context it is interesting to note that compound 3 shows spontaneous resolution of the enantiomers, whereas single-stranded helicates usually tend to form racemic mixtures in the solid state; one chiral single-stranded dipalladium helicate has been synthetized by use of an enantiopure chiral ligand.¹⁵

The Pd(1)–Pd(2) separation of 3.0951(5) Å is within the van der Waals limit of 3.26 Å;¹⁶ however no strong bond is assumed to be present, in particular since the d^8-d^8 interaction in Pd complexes is generally weaker than for other metals (e.g., Rh, Ir, Pt).¹⁷ The Pd–Pd distance and the coordination geometries might be mainly determined by the rigid ligand backbone so that a conclusion is difficult. The corresponding Pd(1)-C-(1)-Pd(2) angle $(93.96(12)^\circ)$ is distinctly smaller than the value of 98.44(11)° reported for the Au-C-Au element in $[C(AuCl)_2(PPh_3)_2]$, which is not constrained by any cyclic ligand backbone.⁵ An even smaller angle was observed for the cationic complex $[PdAuCl_2(C(dppm)_2)]Cl (86.80(11)^\circ).^6$ The corresponding intermetallic separations are 3.1432(2)Å for $[C(AuCl)_2(PPh_3)_2]^5$ and 2.8900(3) Å for $[PdAuCl_2]$ $(C(dppm)_2)$]Cl.⁶ The environment of both Pd(1) and Pd(2) is planar (sum of angles around Pd(1): 360.4°; around Pd(2): 360.0°). The *cis* angles involving Pd(1) ranging from 87.81(8)° to $94.57(8)^{\circ}$ show a nearly quadratic coordination geometry, whereas major distortions around Pd(2), most pronounced in the C(1)Pd(2)C(2) angle of 74.33(12)°, seem to be caused by the strain of the four-membered Pd(2)C(1)P(2)C(2) ring. This might also play a significant role for distortions in the tetrahedral geometries of the other ring members C(1), C(2), and P(2), being evident from the relatively small angles of P(2)-C-(1)-Pd(2) (89.23(13)°), P(2)-C(2)-Pd(2) (86.80(13)°), and C(2)-P(2)-C(1) (93.55(14)°). The sum of these inner angles of the four-membered ring is 343.91°, demonstrating that the ring is substantially bent. The transannular Pd(2)-P(2)distance in this ring amounts to 2.7229(9) Å and is thought to be imposed by the geometry of the small ring rather than indicating any interaction. The arrangement of the atoms surrounding the CDP carbon C(1) differs markedly from a regular tetrahedral geometry, as can be seen from the angles around C(1) ranging from $125.39(18)^{\circ}$ for P(3)-C(1)-P(2) to $89.23(13)^{\circ}$ for P(2)-C(1)-Pd(2). Whereas C(1) is nearly in plane with P(2), P(3), and Pd(1) according to a sum of angles of 353.1°, the sum of the angles around C(1) formed with the sets P(2)P-(3)Pd(2) and Pd(1)Pd(2)P(3) amounts to 325.3° and 326.5° , corresponding to a tetrahedral geometry. The sum of angles around C(1) including Pd(1)Pd(2)P(2) is as small as 289.0° . The five-membered ring Pd(2)C(1)P(3)C(3)P(4) being part of the PCC pincer substructure exhibits a twist conformation. The second five-membered ring involving Pd(1) (Pd(1)C(1)P(2)) C(2)P(1) displays an envelope conformation with the P(2)atom at the flap. The three Pd-C separations of 3 vary between 2.088(3) and 2.177(3) Å. The distances between the two palladium centers and the CDP carbon C(1) are significantly different (2.145(3) Å (Pd(1)) and 2.088(3) Å (Pd(2))), although there is a diagonal C-Pd-Cl bond sequence in both

cases. Distances similar to the mean (2.117 Å) are observed for related complexes in which two Lewis acids interact with the CDP carbon center: 2.115(8) Å for 1, in which the CDP carbon atom interacts with one palladium and one proton, and 2.128(3) Å observed for $[PdAu(Cl)_2(C(dppm)_2)]Cl$, in which a gold and a palladium center are attached to the CDP carbon.⁶ A smaller value of 2.062(2) Å has been reported for the PCP pincer complex $[PdCl(C(dppm)_2)]Cl$, involving a three-coordinate central CDP carbon.⁷ The Pd–C distance in an orthometalated palladium complex of the CDP ligand $C(PPh_3)_2$ is 2.127(7) Å,¹⁴ and a similar Pd-C distance (2.120(2) Å) was observed for a complex of a P-heterocyclic carbodiphosphorane.¹⁴ The longest Pd-C bond in 3 (2.177(3) Å) connects Pd(2) with the methine carbon atom C(2). A similar value (2.153(8) Å) has been reported for a complex involving the substructure PPh₂CH- $(Pd)P(O)Ph_2$.¹⁸ The C(1)-P distances in 3 amount to 1.776(3) and 1.763(3) Å, which is close to the values reported for other CDP complexes in which two metals are attached to the central carbon: 1.776(3) Å for $[(AuCl)_2(CPPh_3)_2]^3$ and 1.786(3) Å for $[PdAuCl_2(C(dppm)_2]Cl.^6$ This is slightly shorter than expected for P-C single bonds and indicates a partial delocalization of a negative charge on the central carbon atom. The same effect also applies for the cyclometalated dppm fragment of 3, exhibiting $\overline{C(2)}$ – P distances of 1.782(2) and 1.762(3) Å, compared to the distinctly longer C(3)–P distances (1.808(3) and 1.842(3) Å) involving the other dppm set including the methylene group. The axial H atom of the dppm-CH2 group shows a weak intramolecular contact toward Cl(2) (H(3a)-Cl(2) 2.566 Å; C(3)-H(3a)-Cl(2) 132°), in line with the observation that dppm and related ligands are capable of acting as $C-H \cdots X$ hydrogen bond donors.

NMR Spectroscopy. The ³¹P chemical shifts of **2** and **3** show the phosphines at high field (**2**: 6.0, 10.2 ppm; **3**: -3.9, 12.5 ppm) and the phosphoranes at low field (**2**: 27.7, 15.6 ppm; **3**: 29.0, 51.5 ppm). The largest ³¹P-³¹P couplings (**2**: 41 Hz; **3**: 49, 56 Hz) are typical for the five-membered ring substructures, in line with the NMR parameters of the related compounds **1** and [PdAuCl₂(C(dppm)₂)]Cl.^{6,7} The ²*J*(P2P3) are only small in both cases (**2**: 6 Hz; **3**: 13 Hz). The P1-P4 and P2-P4 couplings in **3** display relatively large values (both 16 Hz), which are attributed to the ³*J*(P-Pd-C-P)_{trans} pathway along Pd2.

The ¹H NMR spectrum of 3 shows the methine proton at highest field (2.59 ppm) and the methylene protons at lower field. An unusually large chemical shift difference of 2.69 ppm is observed between the CH₂ atoms H3a (6.23 ppm) and H3b (3.54 ppm). Significantly smaller differences were found in compounds containing methylene groups, e.g., in cyclohexane or in metal complexes ($\Delta \delta = 0.5-1.5$ ppm).²⁰ Moreover it is interesting to note that metal complexes of dppm and related ligands show the resonances of equatorial protons at lower field than the axial ones.²⁰ In contrast to that, an inverted pattern is observed for the axial H3a (6.23 ppm) and the equatorial H3b (3.54 ppm) in 3. A tentative explanation for the extreme low-field resonance of the axial proton in 3 could be its spatial proximity to the CDP-Pd₂ core: A considerable magnetic anisotropy of the bonding system might account for this striking feature. Furthermore the intramolecular contact of H3a toward Cl2 (see Crystallography section) is also expected to contribute to the deshielding in the proton NMR spectrum.

The ¹³C signal of the central carbon atom of 3 shows a chemical shift at even higher field (-8.8 ppm) than values reported for other CDP metal complexes derived from C(PPh₃)₂ (15.13–6.94 ppm).¹³

CONCLUSION

The formation of compound 3 shows that the ligand C- $(dppm)_2$ is able to stabilize complexes with two d⁸-metals at the CDP carbon, leading to the first example for this class of ligands. An extended synthetic potential was revealed by C–H activation of C(dppm)₂, which not only behaves as a PCP ligand but may form additional bonds to metal centers via the aliphatic carbons of the dppm subunits.

EXPERIMENTAL SECTION

The complexes 1^7 and $[PdCl_2(MeCN)_2)]^{21}$ were prepared by literature procedures; all other reagents were obtained from commercial suppliers. The solvents were not dried. All operations were carried out under atmospheric conditions. X-ray data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods.²²

³¹P, ¹H, and ¹³C NMR spectra were recorded on Bruker DPX 300 and Avance 600 NMR spectrometers and were referenced against solvent peaks or external 85% H₃PO₄. In the NMR data, the atoms are labeled as in the crystal structures. The ³¹P resonances of **2** and **3** were assigned on the basis of the ³¹P shifts found for 1 as well as by use of the large ${}^{2}J(PP)$ coupling in the five-membered ring.^{6,7} Additional ³¹P-¹H correlation experiments were performed, which support the assignments in 3. The ¹H resonances in **3** could be unambiguously assigned to the methine and methylene protons by a ${}^{1}H{}^{31}P{}$ experiment. The axial and equatorial protons of the CH2 group were assigned due to their different coupling pattern, in particular due to observation of the favorable long-range coupling of the equatorial H3b toward P2 along the W-type ligand backbone. No ¹H NMR data could be obtained for 2 due to massive line broadening at room temperature and immediate precipitation of $2 \cdot 2 CH_2 Cl_2$ during cooling experiments. The ¹³C shifts in 3—in particular the CDP carbon-could be observed only indirectly by use of ${}^{13}C-{}^{1}H$ correlation due to the limited solubility of this compound.

 $[Pd_2Cl_5(CH(dppm)_2)]$ (2): Compound 2 precipitates upon heating a mixture of $PdCl_2(MeCN)_2$ (13.0 mg, 0.05 mmol) and 1 (49.7 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) to 60 °C for 24 h. The brownish microcrystalline material is separated and dried in vacuo (55 mg, 94%). Single crystals of the composition $C_{51}H_{45}Cl_5P_4Pd_2 \cdot 2CH_2Cl_2$ were obtained upon standing of a mixture of $PdCl_2(MeCN)_2$ and 1 in CH_2Cl_2 at ambient temperature for several days.

 ${}^{31}P{}^{1}H}$ NMR (CD₂Cl₂): δ 6.0 (*J*(P1P2) = 41, P1), 27.7 (*J*(P2P3) = 6, *J*(P2P4) = 5, P2); 15.6 (*J*(P3P4) = 5, P3), 10.2 (P4). Anal. Calcd for C₅₁H₄₅Cl₅P₄Pd₂: C, 52.27; H, 3.87. Found: C, 52.0; H, 3.7.

 $[Pd_2Cl_3(C(dppm)(Ph_2CHPh_2))]$ (3): A mixture of 2 (58.6 mg, 0.05 mmol), CH_2Cl_2 (0.5 mL), and water (0.5 mL) is stirred for one week. The solid is separated, washed with CH_2Cl_2 , and dried in vacuo. Yield: 48 mg (82%). Single crystals of composition $C_{51}H_{43}Cl_3P_4Pd_2 \cdot 3CH_2Cl_2$ were obtained upon layering a supersaturated solution of 2 in CH_2Cl_2 with water.

³¹P{¹H} NMR (CD₂Cl₂): δ -3.9 (*J*(P1P2) = 49, *J*(P1P3) = 3, *J*(P1P4) = 16, P1), 29.0 (*J*(P2P3) = 13, *J*(P2P4) = 16, P2), 51.5 (*J*(P3P4) = 56, P3), 12.5 (P4). ¹H NMR (CD₂Cl₂/MeOH) δ 2.59 (*J*(P1H2) = 9.7, *J*(P2H2) = 10.5, *J*(P3H2) = 9.7, *J*(P4H2) = 4.1, H2), 3.54 (*J*(H3aH3b) = 14.5, *J*(P2H3b) = 4.2, *J*(P3H3b) = 6.2, *J*(P4H3b) = 9.5, H3b), 6.23 (*J*(P3H3a) = 19.3, *J*(P4H3a) = 10.6, H3a), 6.45-8.37 (m, ca. 40H, Ph). ¹³C{¹H} NMR (CD₂Cl₂/MeOH): δ -8.8 (C1), 6.3 (C2), 34.3 (C3). Anal. Calcd for C₅₁H₄₃Cl₃P₄Pd₂: C, 55.74; H, 3.94. Found: C, 55.4; H, 3.7.

ASSOCIATED CONTENT

Supporting Information. CIF data of $2 \cdot 2CH_2Cl_2$ and $3 \cdot 3CH_2Cl_2$. Schemes of potential reaction pathways for the formation of 2 and 3; crystal data table of $2 \cdot 2CH_2Cl_2$ and

 $3 \cdot 3 CH_2 Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) A scheme of the described mechanism as well as another potential reaction pathway for the formation of 2 is shown in the Supporting Information.

(10) A scheme of potential reaction pathways for the formation of **3** is shown in the Supporting Information.

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