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Well-Defined BisMETAMORPhos Pd^{I}–Pd^{I} Complex: Synthesis, Structural Characterization, and Reactivity

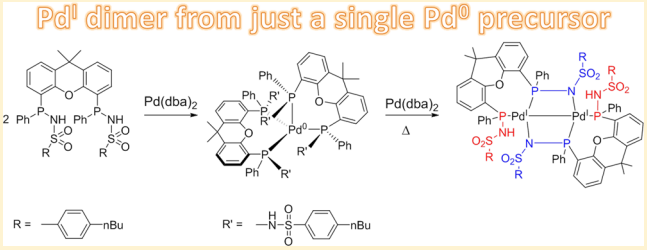
Sander Oldenhof,[†] Martin Lutz,[‡] Bas de Bruin,[†] Jarl Ivar van der Vlugt,[†] and Joost N. H. Reek*[,†]

[†]Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands

[‡]Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Supporting Information

ABSTRACT: The formation of a bisMETAMORPhos PN-bridged dimeric Pd^{I} complex (**3**) from ligand **1** and $Pd(dba)_2$ is described. The addition of **1** to $Pd(dba)_2$ initially leads to the formation of Pd^{0} complex **2**, which has a highly distorted tetrahedral environment and binds two neutral ligands **1**. Complex **2** converts to $\{Pd^{I}\}_2$ complex **3** upon heating. Complex **3** consists of a completely flat Pd–Pd core, with a Pd–Pd bond length of 2.6199(4) Å, and the Pd centers display a highly distorted square planar coordination environment. The formation of complex **3** from **2** is suggested to proceed via an *in situ* comproportionation pathway. Initial decoordination of one ligand from **2** followed by oxidative addition of one neutral coordinated ligand arm leads to a **1**-Pd^{II}H complex. Insertion of free dba into the Pd–H bond generates a **1**-Pd^{II}dba complex that releases 1,5-diphenylpent-1-en-3-one via intra- or intermolecular protonolysis. Concomitantly, comproportionation with **1**-Pd^{0} yields **3**. Complex **3** was found to function as a precatalyst in the Suzuki–Miyaura cross-coupling of *p*-chloroacetophenone with good conversions.



INTRODUCTION

Palladium is one of the most successfully applied transition metals in the field of homogeneous catalysis and is best known for its reactivity in cross-coupling involving C–C bond formation (for example in Suzuki–Miyaura and Sonogashira reactions).[1] The applied palladium (pre)catalysts typically are in the Pd^{0} or Pd^{II} oxidation states, while also complexes with Pd^{III} and Pd^{IV} oxidation states have recently received substantial attention.[2] Complexes with the interesting but relatively rare Pd^{I} oxidation state are stable only as closed-shell dinuclear $\{Pd^{I}\}_2$ complexes containing a Pd^{I}–Pd^{I} bond. The first $\{Pd^{I}\}_2$ complex was prepared in 1942 and fully characterized in 1981 by single-crystal X-ray diffraction.[3] These complexes are typically obtained via comproportionation of Pd^{II} and Pd^{0} precursors (Figure 1, route A).[4] Besides the simple combination of Pd^{II} and Pd^{0} precursors, *in situ* generation of the two oxidation states starting with a single Pd^{0} or Pd^{II} precursor has also been described. For instance, starting with a Pd^{0} precursor, the *in situ* oxidation of Pd^{II} with allyl halides or propargyl halides has successfully been applied to generate $\{Pd^{I}\}_2$ complexes.[4d,g,5] Also the *in situ* oxidation of Pd^{0} with Cu- or Ag-salts has been reported to lead to the formation of $\{Pd^{I}\}_2$ complexes.[5g] Other routes toward the formation of $\{Pd^{I}\}_2$ complexes involve bimetallic reductive elimination or radical-type reactions.[6] Brown et al. showed that bulky phosphine ligands ($P^{t}Bu_3$) coordinated to an iodide-bridged $\{Pd^{II}\}_2$ complex enforce the bimetallic reductive elimination of biphenyl and the formation of a $\{Pd^{I}\}_2$ complex (route B

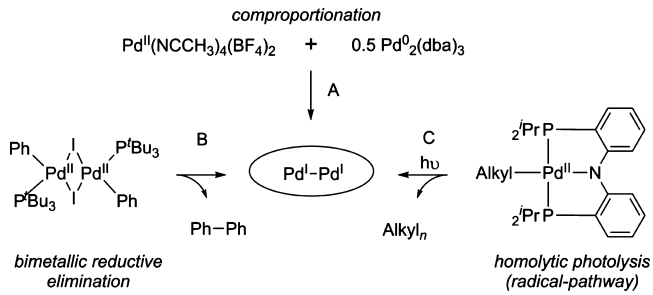


Figure 1. Formation of $\{Pd^{I}\}_2$ complexes via comproportionation of Pd^{II} with Pd^{0} (A), bimetallic reductive elimination (B), or photochemically induced Pd–C homolysis (C); dba = dibenzylideneacetone.

Figure 1). Ozerov et al. showed the formation of a $(PNP\text{-}Pd^{I})_2$ pincer complex via photochemically induced homolytic splitting of a Pd^{II}–alkyl bond, leading to the formation of alkyl radicals and mononuclear PNP-Pd^{I}• species, which undergo homocoupling to form higher alkyl chains and a $(PNP\text{-}Pd^{I})_2$ complex (route C Figure 1).[6b]

The Pd–Pd bond in this type of complexes can infer interesting reactivity, in particular concerning the stoichiometric activation of small molecules,[6b,7] but catalytic applications of $\{Pd^{I}\}_2$ complexes are rare. To the best of our

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knowledge only two examples are known in which a $\{Pd^{I}\}_2$ complex was found to be actively involved in a catalytic cycle. Allyl-bridged $\{Pd^{I}\}_2$ complexes have been used in the catalytic carboxylation of allylstannanes and allylboranes,[8] and more recently $\{(P^tBu_3)Pd^{I}Br\}_2$ was applied in catalytic halide exchange of aryl iodides to bromides using tetrabutylammonium bromide ($Bu_4N^+Br^-$) as bromide source.[9] In contrast to the scarce catalytic application of these complexes they have been often applied as efficient precatalysts for the *in situ* generation of highly reactive 12-electron LPd^0 species active in cross-coupling reactions.[4d,10] Two well-known $\{Pd^{I}\}_2$ precatalysts are $\{(P^tBu_3)PdBr\}_2$ and $Pd_2Cl(\mu\text{-}Cl)P^tBu_2(Bph\text{-}Me)$; see Figure 2. Bromide-bridged complex $\{(P^tBu_3)PdBr\}_2$ was first

Figure 2. $\{Pd^{I}\}_2$ complexes $\{(P^tBu_3)PdBr\}_2$ and $Pd_2Cl(\mu\text{-}Cl)P^tBu_2(Bph\text{-}Me)$, two precatalysts applied in cross-coupling reactions.

prepared by Vilar, Mingos, et al.[6a] and recently experimentally and computationally studied by Schoenebeck et al. in Suzuki cross-coupling reactions,[11] while $[Pd_2Cl(\mu\text{-}Cl)P^tBu_2(Bph\text{-}Me)]$ was prepared by Vilar and applied in amination reactions of aryl chlorides.[4c,12]

We recently reported the reactivity of a xanthene-based bisMETAMORPhos ligand (**1**) toward low-valent Ir^{I}(acac)(cod) (see Figure 3a).[13] The initial formation of **1**-Ir^{I} involves

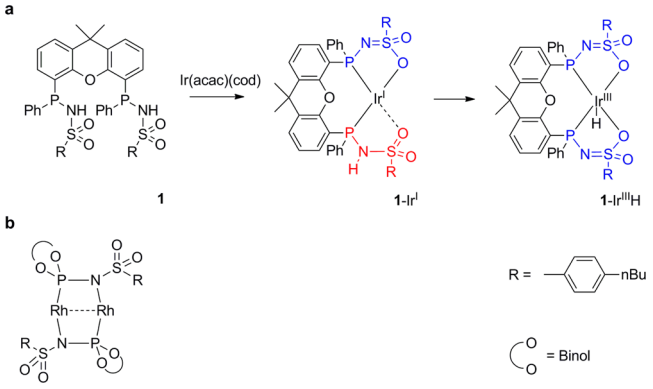


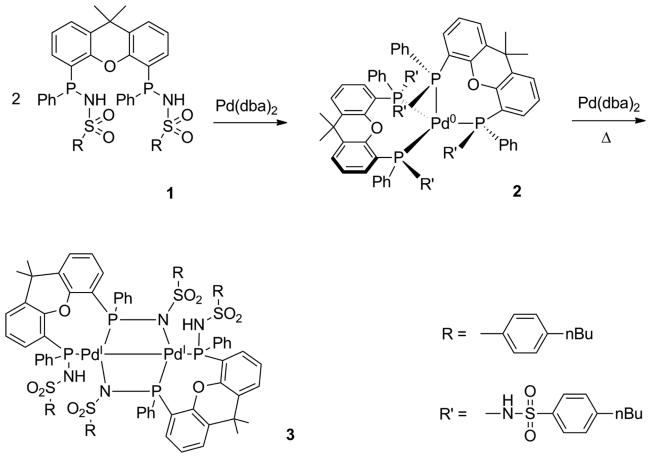
Figure 3. (a) Previously reported reactivity of bisMETAMORPhos **1** with Ir(acac)(cod) leading to the initial formation of **1**-Ir^{I} followed by oxidative addition of the ligand to generate a **1**-Ir^{III}-hydride complex. Red indicates a neutral sulfonamide ligand arm; blue indicates an anionic sulfonamide ligand arm. (b) Schematic presentation of a dinuclear Rh^{I} complex prepared with METAMORPhos ligands.

monodeprotonation of ligand **1** by $acac^-$ and displacement of acac*H* and cod, yielding a complex in which the ligand is monoanionic. Upon standing, oxidative addition of the neutral ligand arm occurs, generating a **1**-Ir^{III}-hydride complex wherein both ligand arms are deprotonated. Another interesting aspect of METAMORPhos-type ligands is their tendency to form dinuclear complexes, which has been shown by the generation of boat-shaped dinuclear Rh^{I} complexes (Figure 3b).[14] With these two characteristics of (bis)METAMORPhos ligands in mind we envisioned them to be suitable for the formation of $\{Pd^{I}\}_2$ complexes from a Pd^0 precursor. Here we report the formation of a dinuclear PN-bridged Pd^{I} complex from **1** and $Pd(dba)_2$ and propose a mechanism for its formation.

RESULTS AND DISCUSSION

Synthesis and Characterization of $\{Pd^{I}\}_2$ Complex 3. The preparation of bisMETAMORPhos ligand **1** has previously been reported.[13a] Ligand **1** contains two stereogenic phosphorus centers and is obtained selectively as a single diastereomer (mesomeric form $P^{R/S}$–$P^{S/R}$). Addition of an equimolar amount of **1** to a toluene suspension of bis(dibenzylideneacetone)palladium(0) {$Pd(dba)_2$} led to the formation of a single species with four nonequivalent phosphorus signals (AA′A″B system) observed with ^{31}P NMR spectroscopy; see Scheme 1. Note that 0.5 equiv of

Scheme 1. Procedure for the Synthesis of Dinuclear Complex 3, Involving Initial Formation of 2 from $Pd(dba)_2$ and Ligand 1



$Pd(dba)_2$ still remains unreacted as a 1:1 ligand to metal ratio was used, and thus a suspension of free $Pd(dba)_2$ and **2** was obtained. MS data confirm the formation of $\mathbf{1}_2$-Pd^0 complex **2** as the sole species. This species is suggested to have a distorted tetrahedral geometry, perhaps better described as a trigonal pyramidal geometry. Combined with the stereogenic nature of the P donors, this geometry explains the observation of four different P signals in the ^{31}P NMR spectrum (see Scheme 1). Similar distorted tetrahedral geometries were previously reported for $(Xantphos)_2Pd^0$ complexes.[15] Upon heating this reaction mixture at 75 °C for 24 h, species **2** converted to the new $\{Pd^{I}\}_2$ complex **3**. Brown crystals of **3**·1.7(CH_2Cl_2) suitable for single-crystal X-ray diffraction were obtained, which confirmed the formation of a dinuclear Pd^{I} complex containing two anionic PN bridging ligand moieties (see Figure 4 and Scheme 1). Monitoring the reaction of **2** toward **3** in time using ^{31}P and ^{1}H NMR spectroscopy revealed that complex **2** does not directly convert to **3**. Prior to the formation of **3** a complex (**3′**) is observed that shows very similar ^{31}P NMR and ^{1}H NMR signatures. Over time **3′** fully converts to complex **3**. Therefore, this intermediate **3′** is suggested to be a kinetic $\{Pd^{I}\}_2$ product wherein the xanthene fragments are oriented in a mutual *syn* fashion, whereas complex **3** is the thermodynamic *anti* product (see Supporting Information for spectral data and structures). Complex **3** is located on a crystallographic inversion center and has a Pd–Pd bond of 2.6199(4) Å, which is comparable with Pd–Pd bond lengths in other reported $\{Pd^{I}\}_2$ complexes.[16] As

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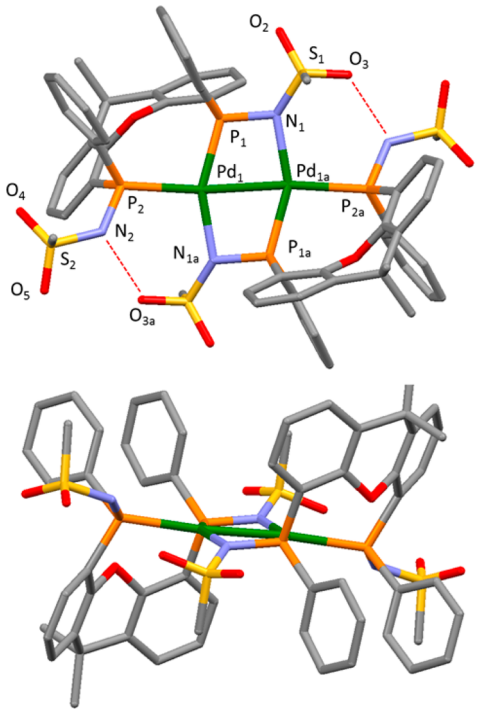


Figure 4. Top: X-ray structure of **3** top view; dotted lines indicate hydrogen bonds. Bottom: Molecular structure of **3** side view. Partially occupied CH_2Cl_2 solvent molecules, hydrogen atoms, and a disordered butylphenyl group on sulfonamide are omitted for clarity. Symmetry operation a: $0.5 - x$, $1.5 - y$, $1 - z$. Selected bond lengths (Å) Pd_1–$Pd_{1(a)}$ 2.6199(4), Pd_1–P_1 2.2273(7), Pd_1–N_1 2.149(2), P_1–N_1 1.670(2), N_1–S_1 1.588(2), Pd_1–P_2 2.4118(8), P_2–N_2 1.709(3), N_2–S_2 1.639(3), S_1–O_2 1.437(2), S_1–O_3 1.452(2), S_2–O_4 1.435(3), S_2–O_5 1.430(3), N_2···O_{3a} 2.677(4). Selected angles (deg): P_1–Pd_1–P_2 102.57(3), P_2–Pd_1–N_{1a} 103.24(6), N_{1a}–Pd_1–Pd_{1a} 83.19(6), Pd_{1a}–Pd_1–P_1 71.34(2), P_2–Pd_1–Pd_{1a} 172.87(2), P_1–Pd_1–N_{1a} 153.74(7).

a consequence of its centrosymmetry, the two xanthene fragments are in a mutual *anti* configuration. This symmetry is retained in solution on the NMR time scale, leading to a relatively simple ^{31}P NMR spectrum with two AA′BB′ signals. The P–N bond length of the bridging P–N ligand moiety is slightly smaller [P_1–N_1: 1.670(2) Å] compared to the nonbridged P–N^H bond [P_2–N_2: 1.709(3) Å]. A significant difference in bond length between Pd_1–P_1 and Pd_1–P_2 (2.2273(7) and 2.4118(8) Å, respectively) was observed, which is ascribed to the *trans* influence of the Pd–Pd bond.[16d,17] The short interatomic distance between the nitrogen of the nonbridging ligand arm (N_2) and the oxygen of the bridging sulfonamide unit [$O_{3(a)}$] suggests the presence of an intramolecular N–H···O hydrogen bond (red dotted line at the top of Figure 4). The angles in the core bimetallic skeleton ($\angle P_1$–Pd_1–P_2 102.57(3)°; $\angle P_2$–Pd_1–N_{1a} 103.24(6)°; $\angle N_{1a}$–Pd_1–Pd_{1a} 83.19(6)°; $\angle Pd_{1a}$–Pd_1–P_1 71.34(2)°) deviate significantly from 90°, indicating that the palladium atom is in a highly distorted square planar geometry [$\sum_{angles}$ = 360.34(9)°]. The six-membered Pd–P–N–Pd–P–N ring is essentially flat with a puckering amplitude of only 0.1801(16) Å. This is in sharp contrast with dinuclear rhodium complexes with bisMETAMORPhos that display boat-like-shaped geometries.[14] The formation of **3** was also synthetically confirmed by a substitution reaction with $\{Pd^I\}_2$ precursor $[Pd_2(CH_3CN)_6][BF_4]_2$ and with two equivalents of ligand **1** in the presence of a base (triethylamine or sodium acetate). Unlike many other $\{Pd^I\}_2$ complexes reported in the literature, complex **3** is remarkably stable toward O_2 in the solid state and can be stored for days without decomposition.[18]

To investigate Pd–Pd interactions in complex **3**, a computational study was performed using DFT [BP86, def2-SV(P)] using a slightly simplified model of ligand **1** (having R = Me instead of para-^{n}Bu-Ph; see Figure 3). The DFT structure is very similar to the molecular structure determined by X-ray diffraction (Figure 4). The calculated Pd–Pd and Pd–P bond lengths of the optimized structure are only slightly longer (~0.05–0.07 Å) than the corresponding experimental values (commonly observed). The DFT-calculated Pd–Pd Wiberg bond order of 0.274 suggests a rather weak Pd–Pd bond, in agreement with the rather long Pd–Pd bond length (see Table 1). The difference in bridged and nonbridged Pd–P bonds is also reflected by the Pd–P bond orders found.

Table 1. Selected (DFT-Calculated[a]) Bond Distances and Wiberg Bond Orders

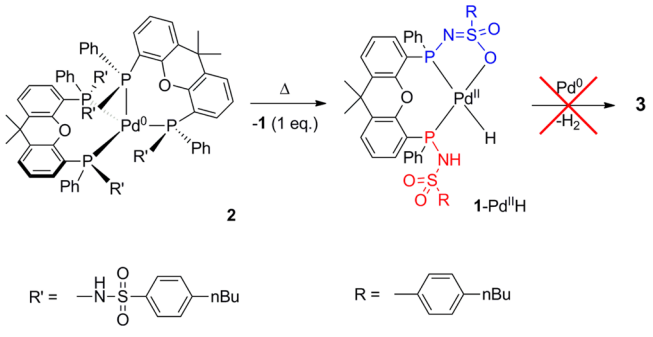
	distance (Å), exptl/DFT	Wiberg BO
Pd–Pd	2.6199(4)/2.6910	0.274
Pd–N_1 (bridging)	2.149(2)/2.1556	0.450
Pd–P_1 (bridging)	2.2273(7)/2.2938	0.771
Pd–P_2 (nonbridging)	2.4118(8)/2.4624	0.571

[a]Turbomole BP86, def2-SV(P), analyzed with AOMix.

The bridging Pd–P_1 bond has a bond order of 0.771, while the nonbridging Pd–P_2 bond has a significantly lower bond order of 0.570 (see Table 1), in accordance with a longer Pd–P_2 and shorter Pd–P_1 bond (both calculated and experimental). Seven frontier molecular orbitals (FMOs) were found predominately centered at the Pd atoms; see Supporting Information.

Proposed Mechanism for Formation of Complex 3. The formation of Pd^I dimer **3** solely from a Pd^0 precursor strongly suggests the *in situ* generation of a transient **1**-Pd^{II} species, followed by comproportionation with a suitable Pd^0 complex. In line with previously observed reactivity for Ir,[13] we hypothesized the formation of a **1**-$Pd^{II}H$ species via the decoordination of one equivalent of neutral ligand **1** from complex **2**, followed by oxidative addition of a neutral ligand arm; see Scheme 2. Variable-temperature NMR experiments were performed with complex **2** in toluene-d_8 to investigate whether a Pd-hydride species could be detected. However, no hydride signal was detected in the ^1H NMR spectrum down to −60 ppm in the temperature range 213–363 K. The steady-

Scheme 2. Formation of Complex 3 from 2 via Comproportionation of Transient 1-Pd^{II}-H with Pd^0



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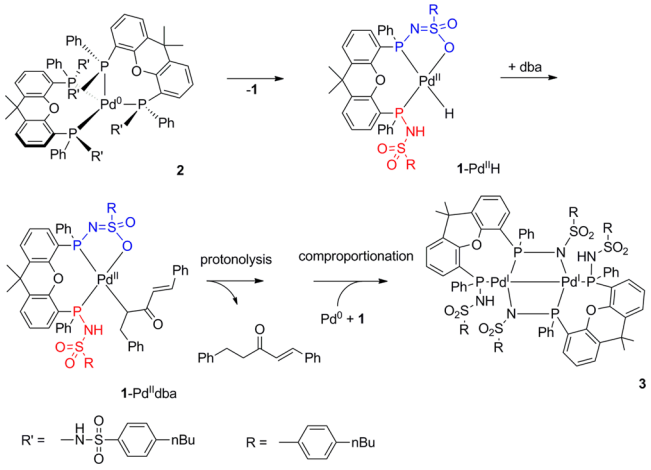
state concentration of such a 1-Pd^{II}-hydride species might be too low to be detected, which could potentially be explained by an immediate follow-up reaction of the formed 1-Pd^{II}-hydride species. Protonolysis of the Pd−H bond by the NH of ligand **1** leads to the formation of H_2; such reactivity was previously described with 1-Ir^{III}H.[13a,b] However, when **3** was prepared in a sealed NMR tube, no H_2 could be observed by ^{1}H NMR spectroscopy, which rules out the direct protonolysis of the Pd−H bond with the ligand; see Scheme 2.

Notably, using the alternative Pd^0 precursor tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, also generated species **2** upon reaction with two equivalents of **1**, but in this case the formation of **3** could not be observed upon heating. Interestingly, **3** was formed when the reaction of **1** with $Pd(PPh_3)_4$ was performed in the presence of one equivalent of dba, which hints at an important role of dba in the sequence of reaction steps leading to formation of complex **3**. Analysis of the crude reaction mixture by mass spectrometry (CSI+) indicates the presence of a 1-Pd^{II}dba intermediate at m/z 1190.30727 (m/z calcd for $C_{64}H_{64}N_2O_5P_2PdS_2$ $[M]^+$: 1190.271 99). ^{1}H NMR spectroscopy of the reaction mixture also provided support for such a 1-Pd^{II}dba species (see Supporting Information).[19] Furthermore, NMR analysis of the reaction mixture after prolonged heating (65 °C, 40 h) showed the formation of 1,5-diphenylpent-1-en-3-one, which is the product of protonolysis of a Pd−dba bond; see Supporting Information. This compound was also detected by GC-MS, with an overall conversion of 20% dba (theoretical yield: 25%). These combined observations are in agreement with the proposed reaction mechanism shown in Scheme 3. Initial

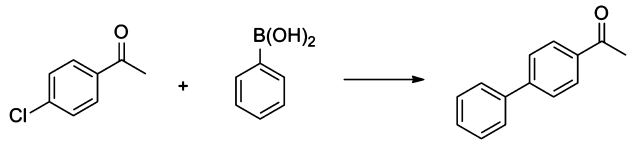
Scheme 3. Proposed Mechanism for the Formation of Complex 3



decoordination of one equivalent of **1** from complex **2** and subsequent oxidative addition of one ligand arm leads to formation of the transient 1-Pd^{II}-hydride species. Immediate insertion of dba into the Pd−H bond generates 1-Pd^{II}dba. Protonolysis (intra- or intermolecular) of the Pd−dba bond by the acidic sulfonamide N−H of the bis-METAMORPhos ligand generates 1,5-diphenylpent-1-en-3-one and a coordinately unsaturated Pd^{II} species, which couples with (**1**)Pd^0 (liberated from **2**) to produce the final $\{Pd^I\}_2$ complex **3**.

Reactivity of Complex 3. Dinuclear $\{Pd^I\}_2$ complexes have previously been successfully applied as precatalysts in Suzuki−Miyaura cross-coupling reactions of aryl chlorides. Also complex **3** shows activity in the Suzuki−Miyaura cross-coupling of *p*-chloroacetophenone. In a 2-propanol/THF mixture at 70 °C and 0.5 mol % catalyst loading, 87% conversion was obtained after 6.5 h with preformed complex **3** (Table 2, entry

Table 2. Suzuki-Miyaura Cross-coupling with Various Pd-complexes[a]



entry	catalyst	conversion %[b] (1 h)
1	**3**	87 (25.1)
2	Pd(dba)$_2$/**1**	71 (11.2)
3[c]	**3**/**1**	<1

[a]Reaction conditions: catalyst 0.5 mol %, 2-propanol (0.75 mL), 1.1 equiv of KO^{t}Bu (1 M in THF), 6.5 h at 70 °C. [b]Conversions were determined by GC-MC and ^{1}H NMR. [c]Reaction was performed with the addition of 1 equiv of **1**.

1). *In situ* formation of **3** resulted in slightly lower conversion (71%), Table 2, entry 2. The difference in conversion between well-defined and *in situ* generated catalyst is even more pronounced after 1 h (25.1% vs 11.2% for **3** and Pd(dba)$_2$/**1**, respectively). This suggests that the initial formation of **3** is required to obtain high catalytic activities. Addition of one equivalent of **1** to the reaction mixture led to complete loss of catalytic activity. This inhibition effect was previously observed for the (Xantphos)Pd-catalyzed amination of aryl bromides due to the formation of (Xantphos)$_2$Pd.[15] If complex **3** is directly involved in the catalysis, it is unlikely that the addition of exogenous ligand would inhibit the catalytic activity. Therefore, we consider it most likely that **3** acts as precatalyst for the generation of a mononuclear 1-Pd^0 complex, concomitant with the formation of 1-Pd^{II}. Further studies on the reactivity of complex **3** are currently ongoing.

CONCLUSIONS

The versatile coordination chemistry of bisMETAMORPhos ligand **1** with the Pd^0 precursor Pd(dba)$_2$ is discussed. Initially, displacement of the dba ligand results in formation of Pd^0 complex **2** (**1**$_2$-Pd^0)$_2$, which contains four magnetically inequivalent phosphorus atoms according to ^{31}P NMR spectroscopy. In time, a unique PN-bridged dinuclear Pd^I complex (**3**) is obtained as the thermodynamic product. This species displays a completely flat Pd−Pd core, with a Pd−Pd bond length of 2.6199(4) Å. The formation of complex **3** from **2** is suggested to proceed via an *in situ* comproportionation pathway. This route involves (1) decoordination of one ligand in **2**, followed by oxidative addition of one coordinated ligand arm to generate a 1-Pd^{II}-hydride complex; (2) reaction of this 1-Pd^{II}-hydride species with free dba to yield a 1-Pd^{II}dba complex, which was detected by ^{1}H NMR and mass spectrometry; (3) intra- or intermolecular protonolysis of the Pd−dba bond to release 1,5-diphenylpent-1-en-3-one, which is observed by ^{1}H NMR and GC-MS, concomitant with comproportionation with 1-Pd^0 to generate **3**. Complex **3** was applied in the Suzuki−Miyaura coupling reaction of *p*-chloroacetophenone, and good conversion was obtained. Complex **3** is most likely not directly involved in catalysis but serves as a precatalyst for the catalytically active species.

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EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in dry glassware under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Toluene, pentane, and THF were distilled from sodium under dinitrogen, ACN was distilled from CaH_2 under nitrogen, and CH_2Cl_2 was collected from an MB SPS-800. Deuterated solvents were degassed by four freeze−pump−thaw cycles and dried over molecular sieves (4 Å). NMR spectra were measured on a Bruker AMX 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, and ^{31}P: 162.0 MHz) or on a Varian Mercury 300 (^{1}H: 300.1 MHz) spectrometer. High-resolution mass spectra were obtained on a time-of-flight JEOL AccuTOF LC-plus mass spectrometer (JMS-T100LP) equipped with a CSI or ESI source. Calculated spectra were obtained with JEOL Isotopic Simulator (version 1.3.0.0). Geometry optimizations were carried out with the Turbomole program package,[21a] coupled to the PQS Baker optimizer[21b] via the BOpt package,[21c] at the spin unrestricted ri-DFT level using the BP86[21d,e] functional, the resolution-of-identity (ri) method,[21f] and the def2-SV(P) basis set[21g] for the geometry optimizations. Wiberg[21h] bond orders were calculated from the Turbomole output files using the AOMix program.[21i,j]

Materials. All reagents were purchased from commercial suppliers and used without further purification: $Pd(dba)_2$ (Sigma-Aldrich), $Pd(PPh_3)_4$ (Strem Chemicals), *trans,trans*-dibenzylideneacetone (Sigma-Aldrich), palladium(II)chloride (Sigma-Aldrich). Ligand **1** was prepared according to a literature procedure.[13b]

Preparation of Complex 2. $Pd(dba)_2$ (16.9 mg, 1 equiv) and ligand **1** (50.0 mg, 2 equiv) were dissolved in toluene (2 mL) and stirred at room temperature for 30 min. The purple reaction mixture was filtrated over Celite and concentrated to approximately 1 mL. Pentane (8 mL) was added to precipitate out a yellow powder, which was filtrated, washed twice with pentane (5 mL), and collected (yield: 69%). ^{31}P{^{1}H} NMR (162 MHz, toluene-d_8): δ 53.31 (ddd, J = 99.5, 35.1, 20.1 Hz, 1P), 49.73 (ddd, J = 100.4, 96.9, 42.0 Hz, 1P), 45.61 (br dd, J = 97.5, 35.2 Hz, 1P), 33.74 (ddd, J = 41.8, 20.4, 19.5, Hz, 1P). ^{1}H NMR (400 MHz, toluene-d_8): δ 8.92 (d, J = 25.6 Hz, 1H), 8.58 (m, 1H), 7.91 (dd, J = 11.1, 8.3 Hz, 4H), 7.47 (d, J = 8.2 Hz, 4H), 7.39−7.29 (m, 4H), 7.17−7.06 (m, 6H), 7.00−6.92 (m, 6H), 6.92−6.69 (m, 3H), 6.64−6.52 (m, 4H), 6.54−6.43 (m, 8H), 6.15−6.06 (m, 4H), 5.93 (t, J = 7.3 Hz, 2H), 5.49 (br s, 1H), 5.42 (t, J = 8.4 Hz, 2H), 5.18 (br s, 1H), 3.48 (d, J = 22.8 Hz, 1H) 2.63 (m, 2H), 2.42−2.29 (m, 4H), 2.21 (m, 2H), 1.85 (s, 3H), 1.63 (s, 3H), 1.49−1.05 (m, 22H), 0.96−0.85 (m, 12H). ^{1}H{^{31}P} NMR (400 MHz, toluene-d_8): δ 8.92 (s, 1H), 8.58 (d, J = 7.7 Hz, 1H), 7.91 (dd, J = 11.1, 8.3 Hz, 4H), 7.47 (d, J = 8.2 Hz, 4H), 7.39−7.29 (m, 4H), 7.17−7.06 (m, 6H), 7.00−6.92 (m, 6H), 6.92−6.69 (m, 3H), 6.64−6.52 (m, 4H), 6.54−6.43 (m, 8H), 6.15−6.06 (m, 4H), 5.93 (t, J = 7.3 Hz, 2H), 5.49 (br s, 1H), 5.42 (d, J = 8.2 Hz, 2H), 5.18 (br s, 1H), 3.48 (s, 1H) 2.63 (m, 2H), 2.42−2.29 (m, 4H), 2.21 (m, 2H), 1.85 (s, 3H), 1.63 (s, 3H), 1.49−1.05 (m, 22H), 0.96−0.85 (m, 12H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 148.67 (s, C_{quat}), 147.68 (s, C_{quat}), 140.80 (s, C_{quat}), 136.17 (s, C_{quat}), 135.29 (s, C_{quat}), 131.63 (s, CH), 131.31 (s, CH), 131.18 (s, CH), 130.84 (s, CH), 129.64 (s, CH), 129.58 (s, CH), 129.52 (s, CH), 129.43 (s, CH), 129.36 (s, CH), 129.30 (s, CH), 129.26 (s, CH), 129.06 (s, CH), 128,75 (s, CH), 128.56 (s, CH), 128.49 (s, CH), 128.37 (s, CH), 127. 55 (s, CH), 127. 36 (s, CH), 126.91 (s, CH), 126.70 (s, CH), 126.67 (s, CH), 126.52 (s, CH), 126.12 (s, CH), 125.90 (s, CH), 124.86 (s, C_{quat}), 124.47 (s, C_{quat}), 124.18 (s, CH), 123.88 (s, CH), 123.64 (s, CH), 123.44 (s, CH), 123.23 (s, C_{quat}), 122.82 (s, CH), 122.66 (s, C_{quat}), 36.26 (s, C_{quat}), 35.99 (s, C_{quat}), 35.85 (s, CH_2), 35.81 (s, CH_2), 35.74 (s, CH_2), 33.76 (s, CH_2), 33.65 (s, CH_2), 33.18 (s, CH_2), 30.90 (s, CH_3), 22.98 (s, CH_2), 22.75 (s, CH_2), 22.64 (s, CH_2), 14.16−13.98 (m, CH_3s). HR MS (CSI$^+$): m/z calcd for $C_{94}H_{100}N_4O_{10}P_4Pd_1S_4$ $[M]^+$ 1801.432 35, obsd 1801.440 59.

Preparation of Complex 3. $Pd(dba)_2$ (67.7 mg, 1 equiv) and ligand **1** (100 mg, 1 equiv) were dissolved in toluene (4 mL) and stirred at 75 °C for 24 h. The brown reaction mixture was filtered over Celite and concentrated to approximately 1 mL. Pentane (10 mL) was added to precipitate out a yellow powder, which was filtrated, washed twice with pentane (3 × 10 mL), and collected (yield: 45%). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 39.62 (AA′BB′, J = 37.1, 10.0, 3.3 Hz, 2P), 22.27 (AA′BB′, J = 37.2, 10.2, 3.8 Hz, 2P). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.26 (t, J = 8.5 Hz, 2H), 8.24−8.13 (m, 2H), 7.81−7.42 (m, 2H), 7.63−7.50 (m, 4H), 7.30−6.55 (m, 24H), 6.92−6.70 (m, 8H), 6.70−6.57 (m, 6H), 6.39 (m, 4H), 6.16 (t, J = 7.6 Hz, 2H), 4.5 (br s, 1H), 2.72−2.60 (m, 4H), 2.61−2.52 (m, 4H), 1.75 (s, 6H), 1.67−1.48 (m, 8H), 1.46−1.26 (m, 8H), 1.20 (s, 6H), 1.00−0.92 (m, 12H). ^{1}H{^{31}P} NMR (400 MHz, CD_2Cl_2): δ 8.92. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 154.44 (d, J = 4.7 Hz, C_{quat}), 152.85 (d, J = 7.4 Hz, C_{quat}), 148.38 (s, C_{quat}), 146.28 (s, C_{quat}), 142.31 (s, C_{quat}), 140.55 (s, C_{quat}), 134.75 (s, C_{quat}), 134.13 (s, C_{quat}), 130.86 (s, CH), 130.04 (s, CH), 129.87 (s, CH), 129.71 (s, C_{quat}), 129.47 (s, CH), 129.05 (s, CH), 128.86 (s, CH), 128.77 (s, CH), 128.51 (s, CH), 128.38 (s, CH), 128.18 (s, CH), 127.92 (s, CH), 127.42 (s, CH), 126.86 (s, CH), 126.69 (s, CH), 126.51 (s, CH), 126.31 (s, CH), 125.81 (s, CH), 125.45 (s, CH), 125.16 (s, CH), 124.18 (s, CH), 122.91 (d, J = 24.14 Hz, C_{quat}), 122.53 (d, J = 16.67 Hz, C_{quat}), 35.98 (s, C_{quat}), 35.88 (s, CH_2), 35.71 (s, CH_2), 35.71 (s, CH_2), 33.85 (s, CH_2), 33.79 (s, CH_2), 31.15 (s, CH_3), 22.93 (s, CH_3), 22.73 (s, CH_2), 22.64 (s, CH_2), 14.08 (s, CH_3), 14.02 (s, CH_3). HR MS (CSI$^+$): m/z calcd for $C_{94}H_{98}N_4O_{10}P_4Pd_2S_4$ $[M + Na]^+$ 1931.308 77, obsd 1931.314 34. Anal. Calcd for $C_{94}H_{98}N_4O_{10}P_4Pd_2S_4$: C, 59.15; H, 5.17; N, 2.94. Found: C, 59.08; H, 5.21; N, 2.94.

Suzuki−Miyaura Coupling. Complex **3** (1 μmol, 0.5 mol %) was dissolved in 2-propanol (0.75 mL), and to this solution were added *p*-chloroacetophenone (0.2 mmol, 25.9 μL), phenylboronic acid (1.2 equiv, 29.3 mg), and 1 M KO^{t}Bu (0.22 mL, 1.1 equiv) in THF. The reaction mixture was heated to 70 °C for 6.5 h, whereafter it was cooled to room temperature and concentrated. Water (2 mL) was added, and the product was extracted with diethyl ether (3 × 2 mL). The organic fractions were combined and dried with $MgSO_4$, filtered, and concentrated. The biphenyl product was obtained as a light yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.65−7.62 (m, 2H), 7.52−7.40 (m, 3H), 2.65 (s, 3H). MS (EI, m/z): 196 (M^+). These assignments matched with previously reported literature data.[20]

ASSOCIATED CONTENT

Supporting Information

CIF file, ^{1}H and ^{31}P NMR of formation of **3** from **2** with intermediate product **3′**, preparation of $[Pd_2(CH_3CN)_6][BF_4]_2$, xyz/pbd file of **3**, Wiberg bond orders, FMOs. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: j.n.h.reek@uva.nl.

Notes

The authors declare no competing financial interest.

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