The role of METAMORPhos ligands in transition metal complex formation and catalysis
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Chapter 5

A Well-Defined BisMETAMORPhos Pd\textsuperscript{1}-Pd\textsuperscript{1} complex: Synthesis, Structural Characterization and Reactivity*

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5.1 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).\textsuperscript{[1]} The applied palladium centers in these (pre)catalysts are typically in the Pd\textsuperscript{0} or Pd\textsuperscript{II} oxidation state. Also complexes with Pd\textsuperscript{III} and Pd\textsuperscript{IV} oxidation states have recently received substantial attention.\textsuperscript{[2]} Complexes with the interesting but relatively rare Pd\textsuperscript{I} oxidation state appear to be stable only as closed-shell dinuclear \{Pd\textsuperscript{I}\}_2 complexes containing a Pd\textsuperscript{I}-Pd\textsuperscript{I} bond. The first \{Pd\textsuperscript{I}\}_2 complex was prepared in 1942 and fully characterized in 1981 by single crystal X-ray diffraction.\textsuperscript{[3]} These complexes are typically obtained via comproportionation of Pd\textsuperscript{II} and Pd\textsuperscript{0} precursors (Figure 1, route A).\textsuperscript{[4]} Besides simply combining a Pd\textsuperscript{II} and Pd\textsuperscript{0} precursor, \textit{in situ} generation of the required secondary oxidation state species, starting from either solely Pd\textsuperscript{0} or Pd\textsuperscript{II} complex has also been described. For instance, starting with a Pd\textsuperscript{0} complex, the \textit{in situ} oxidation to Pd\textsuperscript{II} with allylic halides or propargylic halides has successfully been applied to generate \{Pd\textsuperscript{I}\}_2 complexes.\textsuperscript{[4d,4g,5]} Other routes toward the formation of \{Pd\textsuperscript{I}\}_2 complexes involve bimetallic reductive elimination or radical-type reactions.\textsuperscript{[6]} Brown et al. showed that bulky phosphine ligands \((P^t\text{Bu}_3)\) coordinated to an iodide-bridged \{Pd\textsuperscript{II}\}_2 complex enforce the bimetallic reductive elimination of biphenyl and the formation of a \{Pd\textsuperscript{I}\}_2 complex (Figure 1, route B). Ozerov et al. showed the formation of a \((PNP-Pd\textsuperscript{I})_2\) pincer complex via photochemically induced homolytic splitting of a Pd\textsuperscript{II}-alkyl bond, leading to the formation of alkyl radicals and mononuclear PNP-Pd\textsuperscript{I} species which undergo homocoupling to form higher alkyl chains and a \((PNP-Pd\textsuperscript{I})_2\) complex, respectively (Figure 1, route C).\textsuperscript{[6b]}

![Figure 1. Formation of \{Pd\textsuperscript{I}\}_2 complexes via comproportionation of Pd\textsuperscript{II} with Pd\textsuperscript{0} (A), bimetallic reductive elimination (B), or photochemically induced Pd-C homolysis (C), dba = dibenzylideneacetone.](image-url)
The Pd-Pd bond in this type of complexes has shown interesting reactivity, in particular toward the stoichiometric activation of small molecules, but catalytic applications of \{Pd\} complexes are rare. Only two examples* are known in which a \{Pd\} complex was found to be actively involved in a catalytic cycle. Allyl-bridged \{Pd\} complexes have been used in the catalytic carboxylation of allylstannanes and allylboranes. More recently, \{(P^tBu_3)PdBr\}_2 was applied in catalytic halide exchange of aryl iodides to bromides using tetrabutylammonium bromide (Bu_4NBr) as bromide source. In contrast to the scarce catalytic application of these complexes as intact entity, they have been often applied as efficient precatalysts for the in situ generation of highly reactive 12 electron LPd^0 species that are active in cross-coupling reactions. Two well-known \{Pd\} precatalysts are \{(P^tBu_3)PdBr\}_2 and Pd_2Cl(µ-Cl)P^tBu_2(Bph-Me), see Figure 2. Bromide-bridged complex \{(P^tBu_3)PdBr\}_2 was first prepared by Vilar and recently experimentally and computationally studied by Schoenebeck et al. in Suzuki cross-coupling reactions, while [Pd_2Cl(µ-Cl)P^tBu_2(Bph-Me)] was prepared by Vilar and applied in amination reactions of aryl chlorides.

* \{Pd\} complexes have been proposed as catalysts for cross-coupling reactions and several complexes have been isolated that implicate such reactivity, although conclusive evidence of direct involvement these species has, to the best of our knowledge, not been reported.
Figure 3. a) 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 dinuclear Rh$^I$-complex prepared with METAMORPhos ligands.$^{[14]}$

5.2 Results and discussion

5.2.1 Synthesis and characterization of {Pd$^I$}$_2$-complex 3

The preparation of bisMETAMORPhos ligand 1 has been described in chapter 2. Ligand 1 contains two stereogenic phosphorus centers and is obtained selectively as a single diastereomer (mesomeric form P$^R$/P$^S$). 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'BB' system) observed with $^{31}$P NMR spectroscopy (and 0.5 equivalent free {Pd(dba)$_2$}), see Scheme 1. MS data confirm the formation of 1$_2$-Pd$^0$ complex (2) as single species. This species is suggested to have a distorted tetrahedral geometry, but it is 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)$_2$Pd$^0$ complexes.$^{[15]}$ Upon heating this reaction mixture at 75 °C for 24 hours, complex 2 converted to a new species. Brown crystals of this species, suitable for single crystal X-ray diffraction, were
obtained and showed the formation of a dinuclear Pd complex (3) containing two anionic PN-bridging ligand moieties (see Figure 4 and Scheme 1).* Complex 3 is located on a crystallographic inversion center. The Pd-Pd bond length of 2.6199(4) Å is comparable with Pd-Pd bond lengths in other reported {Pd}$_2$ complexes.$^{[16]}$ As 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'XX' signals. The P-N bond length of the bridging P-N ligand moiety is slightly shorter [P$_1$-N$_1$: 1.670(2) Å] compared to the non-bridged P-N 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 non-bridging 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 in 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$_1$: 103.24(6); $\angle$N$_{1a}$-Pd$_1$-Pd$_{1a}$: 83.19(6); $\angle$Pd$_{1a}$-Pd$_1$-P$_1$: 71.34(2)$^\circ$] deviate significantly from 90$,^\circ$, indicating that the palladium atoms are in a highly distorted square planar geometry [$\Sigma$angles = 360.34(9)$^\circ$].

* Monitoring the reaction of 2 towards 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, another 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}'$_2$ product wherein the xanthene fragments are oriented in a mutual syn fashion, whereas complex 3 is the thermodynamic anti product (see Figure 5 and 6 in the experimental section for spectral data and structures).
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. The formation of 3 was also synthetically confirmed by a substitution reaction with \{Pd\}^2 precursor [Pd_2(CH_3CN)_6][BF_4]_2 and two equivalents of ligand 1 in the presence of a base (triethylamine or sodium acetate). Unlike other \{Pd\}^2 complexes reported in literature, complex 3 is remarkably stable toward O_2 in the solid state, and can be stored for days without decomposition.

Figure 4. Top: Molecular 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 disordered butylphenyl group on sulfonamide are omitted for clarity. Selected bond lengths (Å): Pd_1-Pd_1(α) 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 (°): P_1-Pd_1-P_2 102.57(3), P_2-Pd_1-N_1a 103.24(6), N_1a-Pd_1-P_1a 83.19(6), P_1a-Pd_1-P_1 71.34(2), P_2-Pd_1-P_1a 172.87(2), P_1-Pd_1-N_1a 153.74(7).
To investigate Pd-Pd interactions in complex 3, a computational study was performed using DFT [BP86, def2-SV(P)] on a slightly simplified model of ligand 1 (with R = Me instead of para-nBu-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. 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 non-bridged Pd-P bonds is also reflected by the calculated Pd-P bond orders. The bridging Pd-P1 bond has a bond order of 0.771, while the nonbridging Pd-P2 bond has a significantly lower bond order of 0.570 (see Table 1), in accordance with a longer Pd-P2 and shorter Pd-P1 bond (both calculated and experimental). Seven frontier molecular orbitals (FMOs) were found predominantly centered at the Pd atoms (see Figure 7a-g in the experimental section).

Table 1. Selected (DFT calculated\(^{(a)}\)) bond distances and Wiberg bond orders.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å) Exp. / DFT(^{(a)})</th>
<th>Wiberg B.O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Pd</td>
<td>2.6199(4) / 2.6910</td>
<td>0.274</td>
</tr>
<tr>
<td>Pd-N(_1) (bridging):</td>
<td>2.149(2) / 2.1556</td>
<td>0.450</td>
</tr>
<tr>
<td>Pd-P(_1) (bridging):</td>
<td>2.2273(7) / 2.2938</td>
<td>0.771</td>
</tr>
<tr>
<td>Pd-P(_2) (non-bridging):</td>
<td>2.4118(8) / 2.4624</td>
<td>0.571</td>
</tr>
</tbody>
</table>

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

5.2.2. Proposed mechanism for formation of complex 3

The formation of Pd\(^{1}\) 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\[^{[13]}\] the formation of a 1-Pd\(^{III}\)H species, via decoordination of one equivalent of 1 from 2 followed by oxidative addition of a neutral ligand arm, was initially hypothesized (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 observed in the \(^1\)H NMR spectrum down to -60 ppm in the temperature range of 213-363 K. The steady-state concentration of such a 1-Pd\(^{III}\)-hydride species might be too low to be detected, which could potentially be explained by a fast follow-up reaction of this species. Protonolysis of the Pd-H
bond by the NH of ligand 1 would lead 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 (Scheme 2).

Scheme 2. Speculated mechanism for formation of complex 3 from 2 via comproportionation of a transient 1-Pd$_{II}$H with Pd$^0$.

Notably, using an 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 dba, which hints to 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$_2$O$_5$P$_3$PdS$_2$ [M]$^+$: 1190.27199). $^1$H NMR spectroscopy of the reaction mixture also provided support for such a 1-Pd$_{II}$dba species (see Figure 8, experimental section). Furthermore, NMR analysis of the reaction mixture after prolonged heating (65 °C, 40 hours) showed the formation of 1,5-diphenylpent-1-en-3-one, which is the product of protonolysis of a Pd-dba bond (Figure 9, experimental section). 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 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.
Scheme 3. Proposed mechanism for the formation of complex 3.

5.2.3 Reactivity of complex 3

Dinuclear \{Pd\}$_2$ complexes have previously been successfully applied as precatalyst in Suzuki-Miyaura cross-coupling reactions of aryl chlorides. Also complex 3 shows activity in the Suzuki-Miyaura cross-coupling of \( p \)-chloroacetophenone with phenylboronic acid. In an isopropanol/THF mixture at 70 °C and 0.5 mol\% catalyst loading, 87% conversion was obtained after 6.5 hours with pre-formed complex 3 (Table 2, entry 1). \textit{In situ} formation of 3 resulted in a slightly lower conversion of 71% (entry 2). The difference in conversion between well-defined and \textit{in situ} generated catalyst is even more pronounced after 1 hour (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 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 would be directly involved as intact species during the catalysis, it is unlikely that the addition of exogenous ligand would inhibit the catalytic
activity. Therefore it is considered most likely that 3 acts as precatalyst for the generation of a mononuclear 1-Pd\(^0\) complex, concomitant with the formation of 1-Pd\(^{\text{II}}\).

### Table 2. Reaction conditions: Catalyst 0.5 mol\%, isopropanol (0.75 mL), 1.1 eq. KO\(\text{tBu}\) (1 M in THF), 6.5 h. at 70 °C, \(^a\)conversions were determined by GC-MC and \(^1\)H NMR, \(^b\)reaction was performed with the addition of one eq. 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion %(^a) (1h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>87 (25.1)</td>
</tr>
<tr>
<td>2</td>
<td>Pd(dba)(_2)/1</td>
<td>71 (11.2)</td>
</tr>
<tr>
<td>3(^b)</td>
<td>3/1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

#### 5.3 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\(^0\)) which contains four magnetically non-equivalent phosphorus atoms according to \(^{31}\)P NMR spectroscopy. In time, a unique PN-bridged dinuclear Pd\(^{\text{I}}\) complex (3) is obtained as the thermodynamic product. This species displays a completely flat Pd\(_2\)N\(_2\)P\(_2\) 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 \textit{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\(^{\text{II}}\)-hydride complex; 2) reaction of this 1-Pd\(^{\text{II}}\)-hydride species with free dba to yield a 1-Pd\(^{\text{II}}\)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 successfully applied in the Suzuki–Miyaura coupling reaction of \(p\)-chloroacetophenone with phenylboronic acid, resulting in good conversion to the hetero-coupled product. Complex 3 is most likely not directly involved as intact species during catalysis, but rather serves as a precatalyst for the catalytically active species.
5.4 Experimental Section

General procedures: All reactions were carried out in dry glassware under 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, CH$_2$Cl$_2$ was collected from an MB SPS-800. Deuterated solvents were degassed by four freeze-pump-thaw cycles and dried over molecular sieves (4Å). 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 recorded on an ESI (electrospray ionization) mass spectra were obtained on a time-of-flight JEOL AccuTOF LC-plus mass spectrometer equipped with a CSI and 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, coupled to the PQS Baker optimizer via the BOpt package, at the spin unrestricted ri-DFT level using the BP86 functional, the resolution-of-identity (ri) method, and the def2-SV(P) basis set for the geometry optimizations. Wiberg bond orders were calculated from the Turbomole output files using the AOMix program.

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 literature procedure.$^{[13b]}$

Preparation of complex 2.

Pd(dba)$_2$ (16.9 mg, 1 eq.) and ligand 1 (50.0 mg, 2 eq.) were dissolved in toluene (2 mL) and stirred at room temperature for 30 minutes. The purple reaction mixture was filtered over Celite and concentrated to approximately 1 mL. Pentane (8 mL) was added to precipitate a yellow powder that was filtered, washed twice with pentane (5 mL) and collected (Yield: 69%). $^{31}$P$^{[1H]}$ 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, 8H), 2.42 – 2.29 (m, 4H), 2.21 (m, 2H), 1.85 (m, 3H), 1.63 (s, 3H), 1.49 – 1.05 (m, 22H), 0.96 – 0.85 (m, 12H); $^1$H$^{[31P]}$ NMR (400 MHz, toluene-d$_8$): δ 8.92 (s, 1H), 8.58 (d, $J = 7.7$ Hz, 1H), 7.91 (dd, $J =
Preparation of complex 3.
Pd(dbai)$_2$ (67.7 mg, 1 eq.) and ligand 1 (100 mg, 1 eq.) were dissolved in toluene (4 mL) and stirred at 75 °C for 24 hours. The brown reaction mixture was filtered over Celite and concentrated to approximately 1 mL. Pentane (10 mL) was added to precipitate a yellow powder that was filtered, washed twice with pentane (3 × 10 mL) and collected (Yield: 45%). $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ 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$_2$Cl$_2$): $\delta$ 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$_2$Cl$_2$): $\delta$ 8.92 $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ 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$_2$), 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$_{49}$N$_4$O$_{10}$P$_4$Pd$_2$S$_4$ [M]$^+$: 1931.30877, observed: 1931.31434. Anal. Calcd for C$_{94}$H$_{98}$N$_4$O$_{10}$P$_4$Pd$_2$S$_4$: C, 59.15; H, 5.17; N, 2.94. Found: C, 59.08; H, 5.21; N, 2.94. 
Complex 3 (1 µmol, 0.5 mol%) was dissolved in isopropanol (0.75 mL) and to this solution were added p-chloroacetophenone (0.2 mmol, 25.9 µL), phenylboronic acid (1.2 equivalent, 29.3 mg) and 1 M KOTBu in THF (0.22 mL, 1.1 equivalent). The reaction mixture was heated to 70 °C for 6.5 hours, 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 MgSO₄, filtered and concentrated. The biphenyl product was obtained as a light yellow solid. ¹H NMR (CDCl₃, 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]

Preparation of [Pd₂(CH₃CN)₆][BF₄]₂
To a solution of palladium(II)chloride (2.25 mmol, 400 mg) in dry MeCN (25 mL) was added AgBF₄ (4.5 mmol, 1.35 g). The reaction mixture was stirred for 2 hours and the formed precipitate was filtered over celite under an N₂ atmosphere. The volume of the filtrate was reduced to approximately 10 mL and dry Et₂O was added (75 mL) under rigorous stirring. The formed precipitate was filtered under N₂ atmosphere and washed with Et₂O (3 × 5 mL). The remaining solid was dried and collected as an off-yellow solid (Yield: 95%, 1.0 g). [Pd(CH₃CN)₄][BF₄]₂ was used without further purification or analysis for the preparation of [Pd₂(CH₃CN)₆][BF₄]₂, which was carried out according to a literature procedure.[21]

Monitoring the formation of 3 via 3’ starting from 2 using ³¹P NMR spectroscopy
Monitoring the reaction towards 3 in time showed the initial formation of 3’ from 2. Complex 3’ shows striking resemblance in ³¹P NMR to complex 3 and over time species 3’ converts into 3. Therefore 3’ is suggested to be a kinetic Pd₁-Pd₁ product with the xanthene backbones coordinated in a mutual syn fashion, while complex 3 is the thermodynamic product with a mutual anti alignment of the two ligand backbones, see Figure 5.

Complex 3’
This kinetic product is formed in the process of converting complex 2 into thermodynamic product 3 and this species has therefore not been isolated. ³¹P[¹H] NMR (162 MHz, CD₂Cl₂): δ = 37.70 (AA’BB’, J = 37.1, 10.0, 3.3 Hz, 2P), 17.89 (AA’BB’, J = 37.2, 10.2, 3.8 Hz, 2P).
Figure 5. $^{31}$P NMR spectra of the formation of 3 in time, starting with complex 2 followed by the formation of complex 3’ and 3.

Monitoring the formation of 3 via 3’ starting from 2 using $^1$H NMR spectroscopy

Concomitant with the formation of 2, the formation of free dba is observed by $^1$H NMR spectroscopy (Figure 6, bottom). The formation of 3’ and conversion toward 3 was also observed by $^1$H NMR spectroscopy, as the triplet at 10.5 ppm (indicative of complex 3’) decreases in time, while a similar triplet at 10.7 ppm increases (Figure 6, middle and top).
Figure 6. $^1$H NMR spectra of the formation of 3 in time, starting with complex 2 followed by the formation of complex 3’ and 3. 

Frontier molecular orbitals of complex 3 (simplified model with $R = \text{Me}$) 

Figure 7a. LUMO: -2.952 eV 
Figure 7b. HOMO: -5.020 eV
Figure 7c. HOMO-1: -5.192 eV
Figure 7d. HOMO-2: -5.389 eV
Figure 7e. HOMO-3: -5.410 eV
Figure 7f. HOMO-4: -5.532 eV
Figure 7g. HOMO-5: -5.637 eV
Monitoring the formation of a Pd\textsuperscript{II}-alkyl intermediate by \textsuperscript{1}H NMR spectroscopy

A solution of toluene-$d_8$ with 1 and Pd(dba)$_2$ was heated to 65 °C for 5 minutes, whereafter the mixture was immediately cooled to 0 °C. \textsuperscript{1}H NMR spectroscopy of the reaction mixture provided support for a 1-Pd\textsuperscript{II}dba species, as two doublets-of-doublets were observed (4.4 - 4.0 ppm; $J_{\text{P-H}}$ 10.0, 6.9 Hz) in the expected region for a benzylic protons of a Pd-alkyl species.

![Image of NMR spectra](image)

Figure 8. \textsuperscript{1}H NMR of reaction mixture, showing signals indicative for the formation of 1-Pd\textsuperscript{II}dba (*).

\textsuperscript{1}H NMR spectroscopic identification of the formation of 1,5-diphenylpent-1-en-3-one

![Image of NMR spectra](image)

Figure 9. \textsuperscript{1}H NMR showing the formation of 1,5-diphenylpent-1-en-3-one (●).
X-ray crystal structure determination of 3·1.7(CH₂Cl₂)

C₉₄H₉₈N₄O₁₀P₄Pd₂S₄ · 1.7(CH₂Cl₂), Fw = 2053.06, orange needle, 0.77 x 0.32 x 0.15 mm³, monoclinic, C2/c (no. 15), a = 29.7519(12), b = 15.2666(7), c = 22.4112(10) Å, β = 11321(2)°, V = 9482.7(7) Å³, Z = 4, Dₐ = 1.438 g/cm³, μ = 0.69 mm⁻¹. X-ray intensities were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) up to a resolution of (sin θ/λ)max = 0.65 Å⁻¹ at a temperature of 150(2) K. Integration was performed using the Eval15 software.²²a Absorption correction and scaling based on multiple measured reflections was performed with SADABS²²b (0.66-0.75 correction range). 84795 Reflections were measured, 10876 reflections were unique (Rint = 0.033), of which 8791 were observed [l>2σ(l)]. The structure was solved with Direct Methods using the program SHELXS-97²²c and refined with SHELXL-97²²d against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions. All hydrogen atoms were refined with a riding model. The dichloromethane molecule was refined with partial occupancy. Disorder models were used for one of the phenyl rings and one of the n-butyl groups. 609 Parameters were refined with 111 restraints (for distances, angles, displacement parameters and flatness in the disordered groups). R1/wR2 [l > 2σ(l)]: 0.0401 / 0.1105. R1/wR2 [all refl.]: 0.0530 / 0.1187. S = 1.038. Residual electron density between -0.76 and 1.04 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.
5.4 References


