Supplementary Materials for

Dinuclear Pd(I) Complexes – Solely Precatalysts? Demonstration of Direct Reactivity of a Pd(I) Dimer with an Aryl Iodide

Karl J. Bonney,[a,b] Fabien Proutiere[a,b] and Franziska Schoenebeck[a,b]*

[a] *Laboratory for Organic Chemistry, ETH Zürich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland*

b New address: Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany

Email: franziska.schoenebeck@rwth-aachen.de

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General Experimental

Reagents. 9-Bromoanthracene, 9-bromophenanthrene, 1-iodonaphthalene, tris(dibenzylideneacetone)dipalladium(0) and tetrabutylammonium bromide were purchased from Aldrich. Tri-*tert*-butylphosphine was purchased from ABCR. Br-dimer **1**, I-dimer **2** and Pd(P*t*Bu$_3$)$_2$ were prepared according to known procedures. 9-Iodoanthracene and 9-iodophenanthrene were prepared according to a modified method of Zhao.[1] 1-Iodo-2-methoxynaphthalene was prepared by methylation of 1-iodo-2-naphthol, according to the method of Wang.[2] Aryl iodides were prepared for use by stirring over silver nitrate (to remove any iodide salts that may be present), followed by column chromatography, with subsequent drying by azeotroping with toluene, and finally degassing. Tetrabutylammonium bromide was prepared for use by heating under vacuum.

Solvents. THF, toluene and diethyl ether for reactions were purified by a solvent drying system from LC Technology Solutions Inc. SP-105 under a nitrogen atmosphere (H_2O content <10 ppm as determined by Karl-Fischer titration) and degassed prior to use. Acetone and benzene were purchased from Aldrich and degassed prior to use. Extraction solvents and column chromatography eluents, *n*-hexane, diethyl ether and ethyl acetate were technical grade and distilled prior to use.

Experimental Techniques. All reactions involving Pd were carried out in the dark in the glovebox. All other reactions were carried out in oven-dried glassware under an inert atmosphere of N_2. Reaction temperatures other than room temperature were recorded as bath or aluminum heating block temperatures. Column chromatography was performed on Fluka silica gel, particle size 60 μm and analytical thin layer chromatography (tlc) was performed on Merck Kieselgel 60 F_{254} pre-coated plastic-backed plates which were visualized by ultraviolet light.

Characterization. All ^{31}P NMR spectra were recorded on a Varian Gemini 300 spectrometer at 126 MHz and were proton decoupled. ^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer at 400 MHz. All NMR spectra were recorded at ambient temperature. Chemical shifts (δ) are quoted in parts per million (ppm) and were referenced to the residual solvent peak in the case of ^{1}H NMR spectra, and added P(O)(OMe)$_3$ in the case of ^{31}P NMR spectra. Conversion of aryl iodides to aryl

bromides was monitored with the use of an Agilent Technologies 5975 series MSD mass spectrometer coupled with an Agilent Technologies 7820A gas chromatograph (with an Agilent 19091s-433 HP-SMS column (30 m x 0.250 μm x 0.250 μm)). GC-MS conditions: front inlet mode: split; temperature: 250°C; pressure: 1.1066 psi; total flow: 50.474 mL/min; split ratio: 100 : 1; split flow: 50 mL/min; run time: 23.667 min; oven programme: 50°C for 2 min then 15°C/min to 300°C then 300°C for 5 min; flow: 0.5 mL/min. Calibrations to quantify the conversion of aryl iodide to aryl bromide were done *via* a calibration curve using the internal GC-MS software ("ChemStation"), where 1,3,5-trimethylbenzene was used as an internal standard. Supercritical Fluid Chromatography (SFC) conditions: column, silica; eluent, CO_2 : *i*PrOH (5%); oven temperature, 40°C; outlet pressure, 100 bar; flow rate, 3.0 mL/min; detection wavelength, 220 nm.

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General Procedure for Quantifying the Concurrent Formation of I-dimer 2 and Aryl Bromide from Br-dimer 1 and Aryl Iodide (See Scheme 2 and Figure 4, Main Paper)

A solution of aryl iodide (10.0 equiv) in THF (or THF-d8, in the case of 1-iodo-2-methoxynaphthalene) (0.41 M) was added to Br-dimer **1** (1.0 equiv). The solution was stirred vigorously for 3 h (9-iodoanthracene), 36 h (1-iodo-2-methoxynaphthalene) or 60 h (1-iodonaphthalene, 9-iodophenanthrene) at room temperature, after which the conversion to mixed-dimer **3** and I-dimer **2** (as well as various products of side-reaction in some cases) was observed by ^{31}P NMR spectroscopy, using $P(O)(OMe)_3$ as an internal standard, and the conversion to aryl bromide was observed by GC-MS, after first passing a sample of the reaction mixtures through a plug of silica to remove the palladium species. The remaining reaction mixture was purified by column chromatography to remove all traces of the catalyst (100% *n*-hexane for all aryl halides) (with the exception of the reaction involving 1-iodo-2-methoxynaphthalene, where the aryl bromide formation was quantified by ^{1}H NMR spectroscopy). SFC was then used to quantify the yield of aryl bromide.

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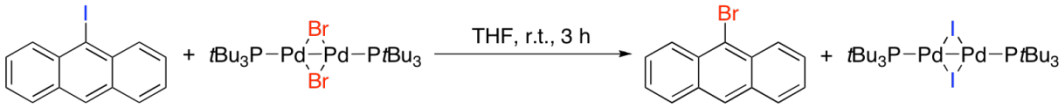
^{31}P NMR Spectrum of the Reaction of 9-Iodoanthracene with Br-dimer 1, GC-MS to Show the Formation of 9-Bromoanthracene and SFC Chromatogram Used for Quantification



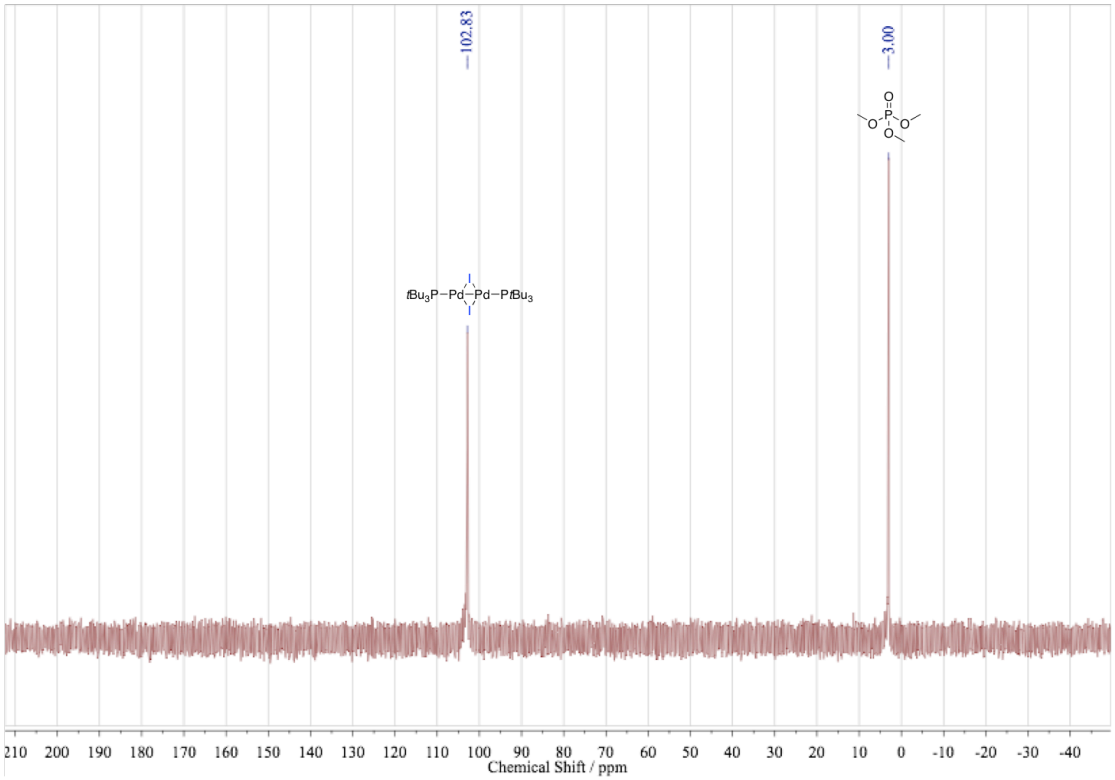


Figure S1. ^{31}P NMR spectrum (126 MHz, THF) showing the conversion of Br-dimer **1** to I-dimer **2**

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GC-MS Chromatogram and Spectra:

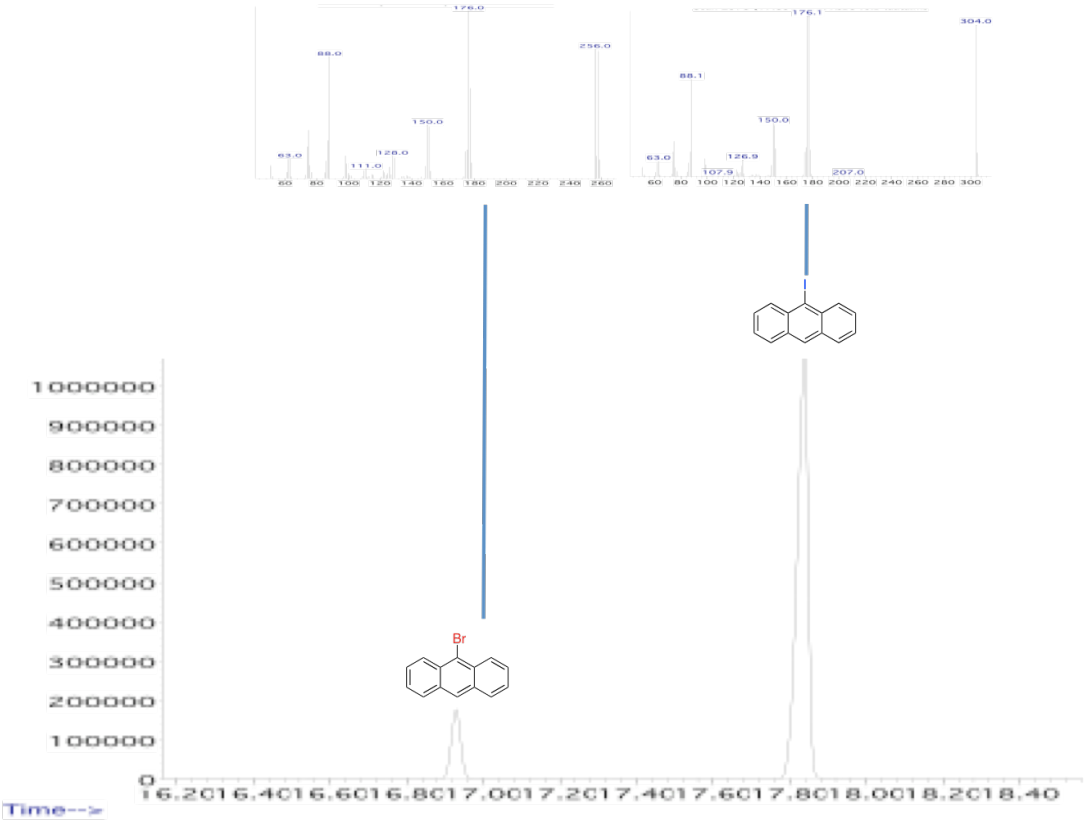

Figure S2.

SFC Chromatogram:

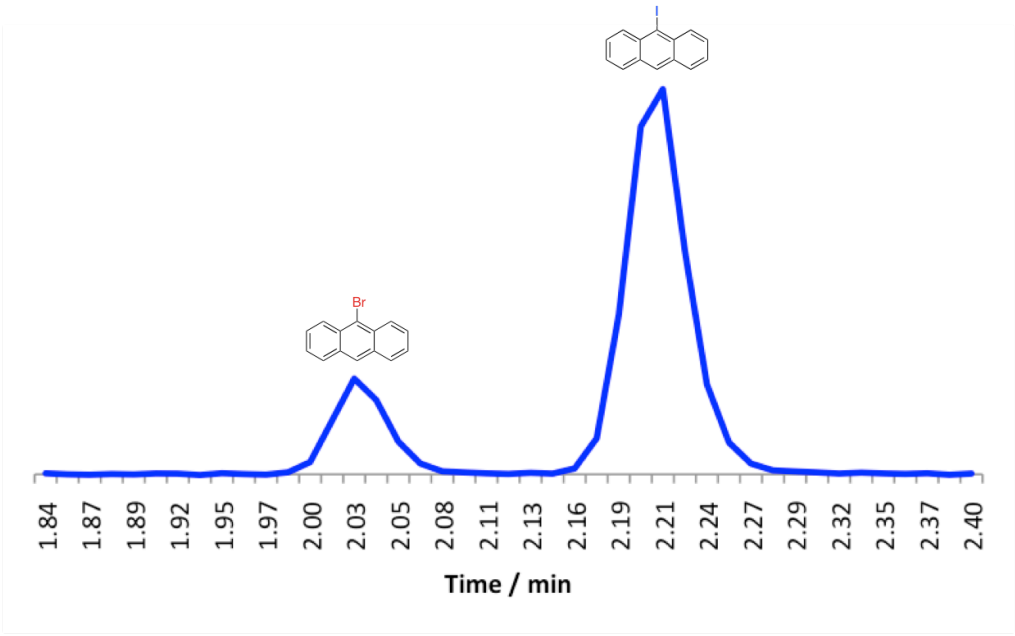

Figure S3.

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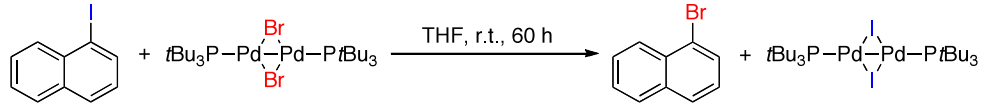
^{31}P NMR Spectrum of the Reaction of 1-Iodonaphthalene with Br-dimer 1, GC-MS to Show the Formation of 1-Bromonaphthalene and SFC Chromatogram Used for Quantification



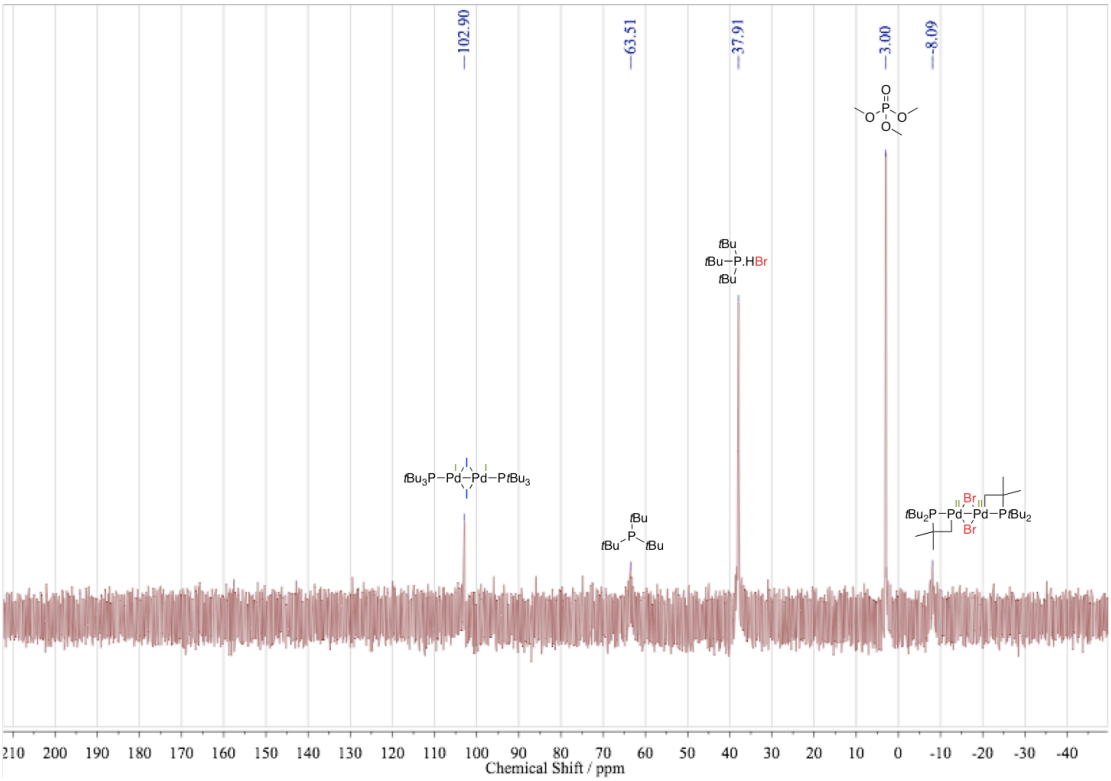


Figure S4. ^{31}P NMR spectrum (126 MHz, THF) showing the conversion of Br-dimer **1** to I-dimer **2** as well as side-products P*t*Bu$_3$, P*t*Bu$_3$.HBr and [Pd(P*t*Bu$_3$)$_2$(C(CH$_3$)$_2$CH$_2$)(μ-Br)]$_2$.

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GC-MS Chromatogram and Spectra:

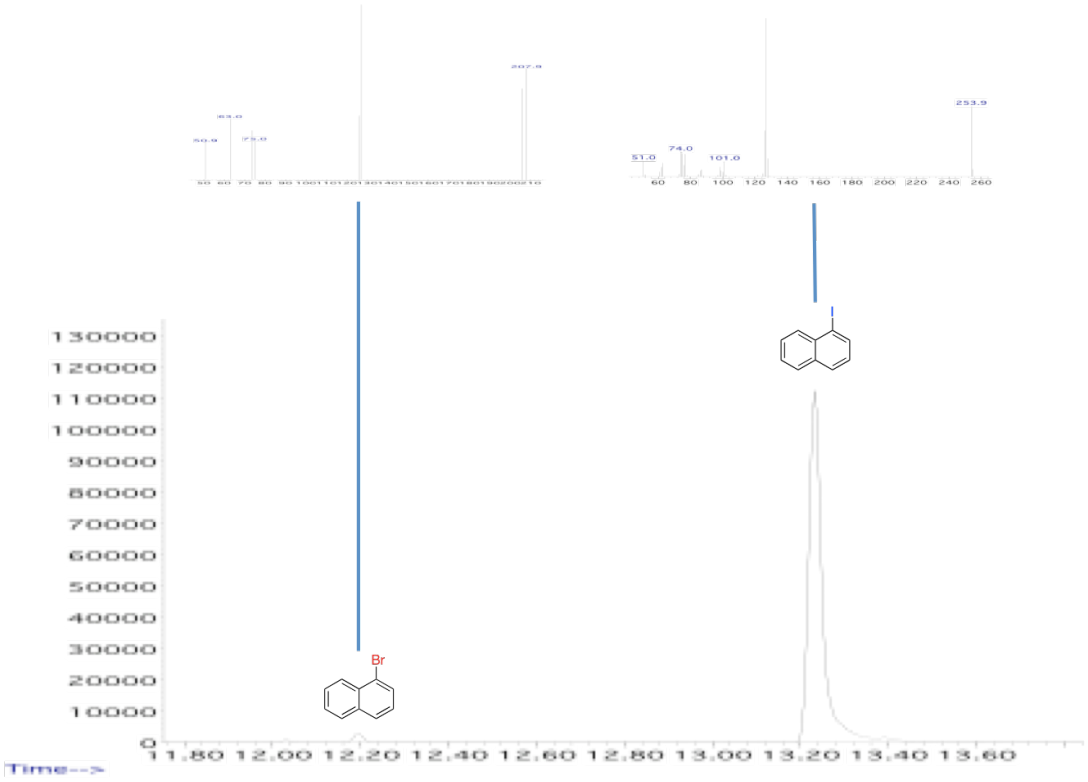

Figure S5.

SFC Chromatogram:

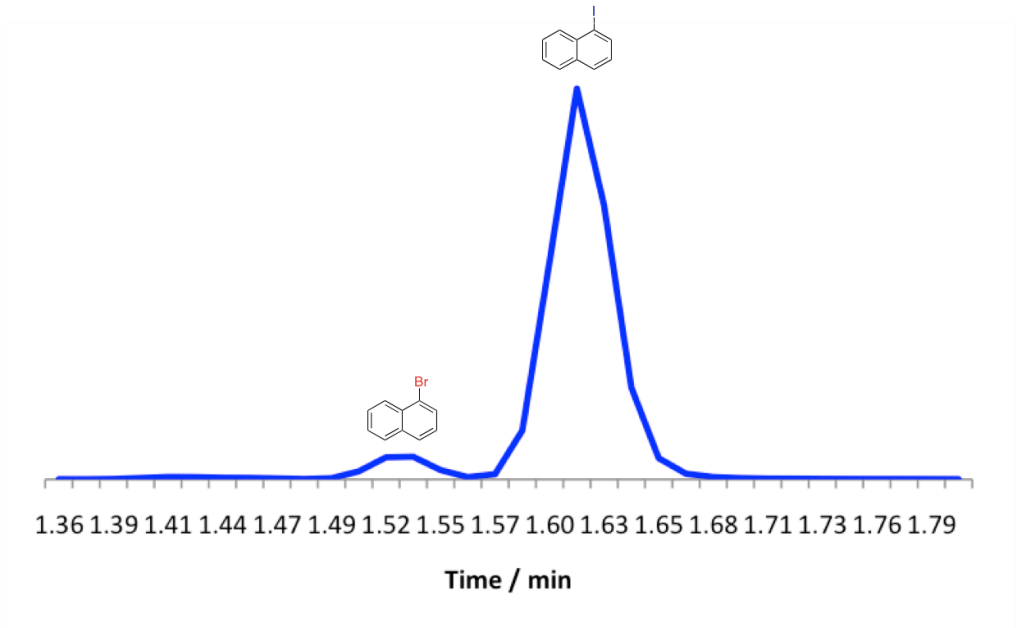

Figure S6.

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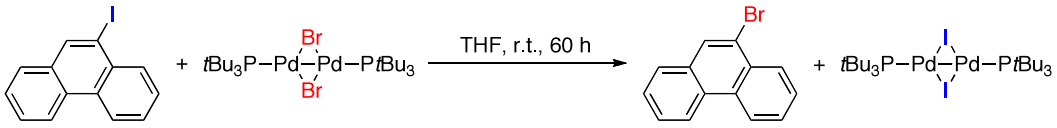
^{31}P NMR Spectrum of the Reaction of 9-Iodophenanthrene with Br-dimer 1, GC-MS to Show the Formation of 9-Bromophenanthrene and SFC Chromatogram Used for Quantification



^{31}P NMR Spectrum (126 MHz, THF):

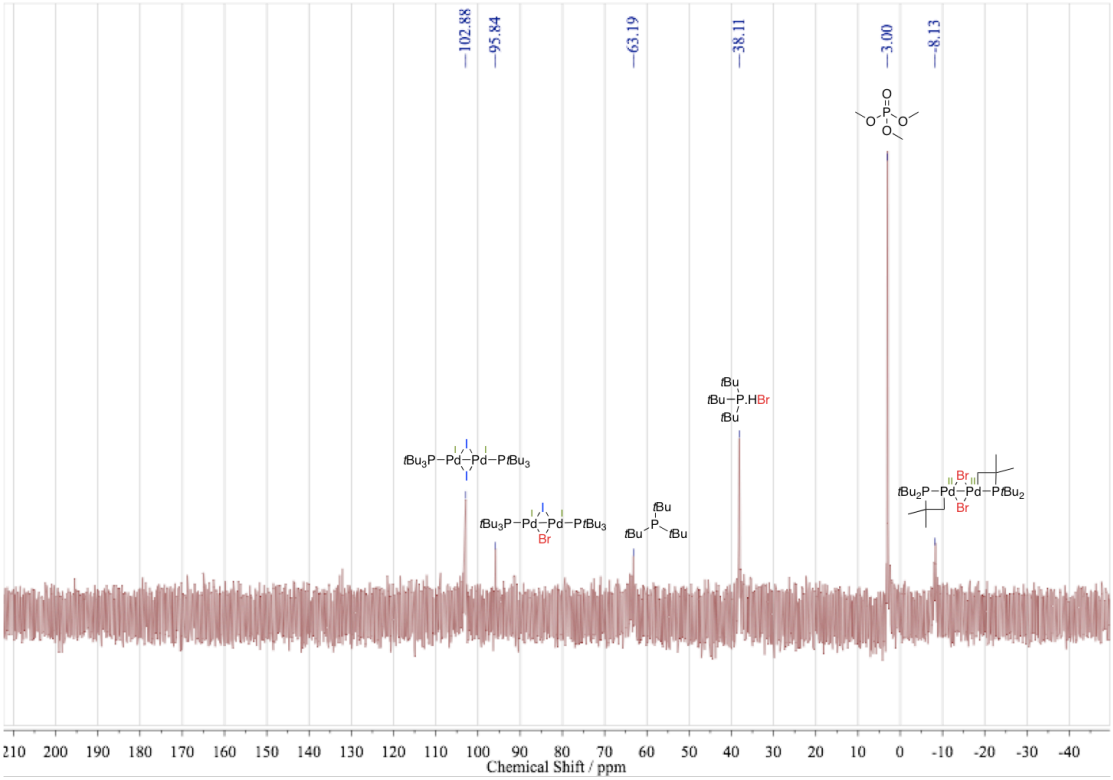


Figure S7. ^{31}P NMR spectrum (126 MHz, THF) showing the conversion of Br-dimer **1** to I-dimer **2** as well as side-products P*t*Bu$_3$, P*t*Bu$_3$.HBr and [Pd(P*t*Bu$_3$)$_2$(C(CH$_3$)$_2$CH$_2$)(μ-Br)]$_2$.

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GC-MS Chromatogram and Spectra:

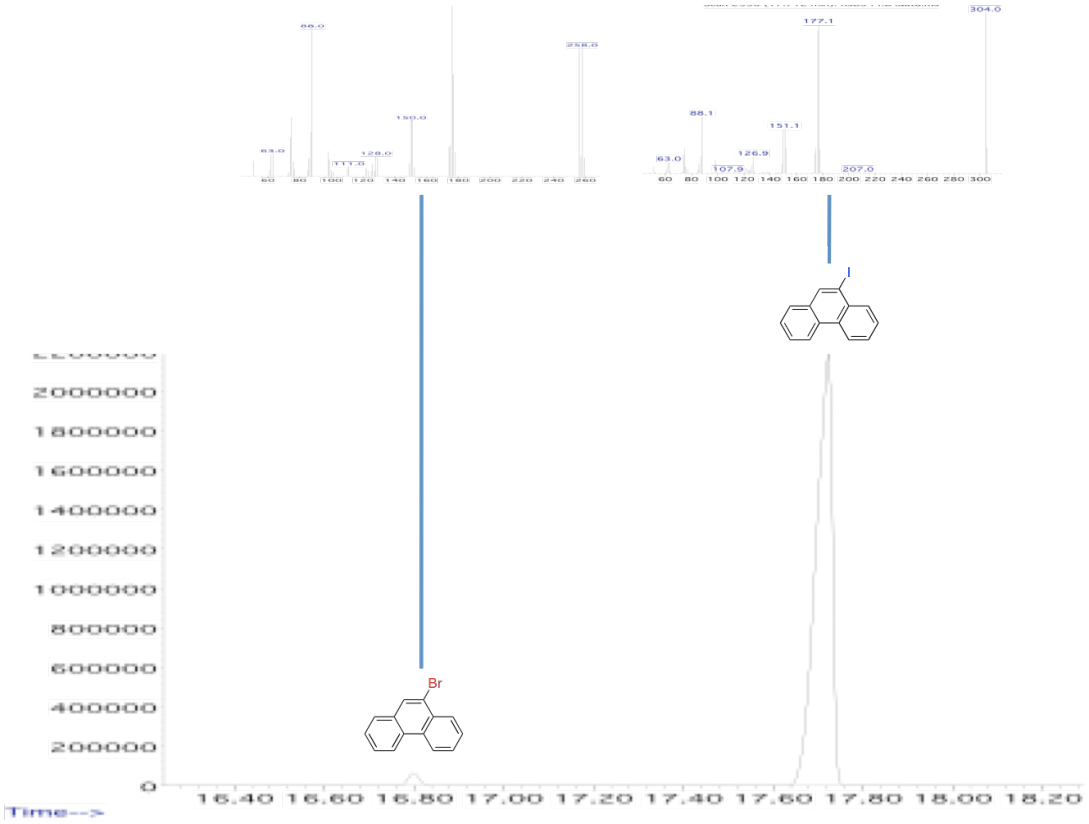

Figure S8.

SFC Chromatogram:

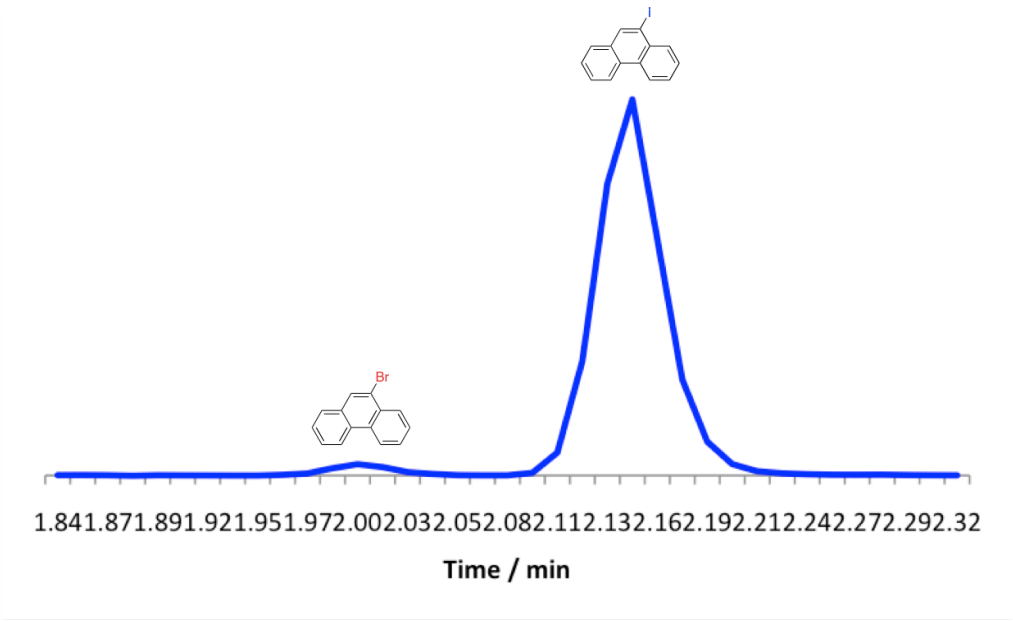

Figure S9.

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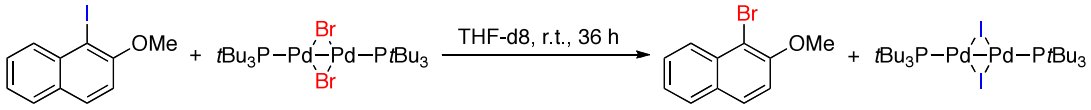
^{31}P NMR Spectrum of the Reaction of 1-Iodo-2-methoxynaphthalene with Br-dimer 1, and ^{1}H NMR Spectrum to Show the Formation of 1-Bromo-2-methoxynaphthalene



^{31}P NMR Spectrum (126 MHz, THF-d8):

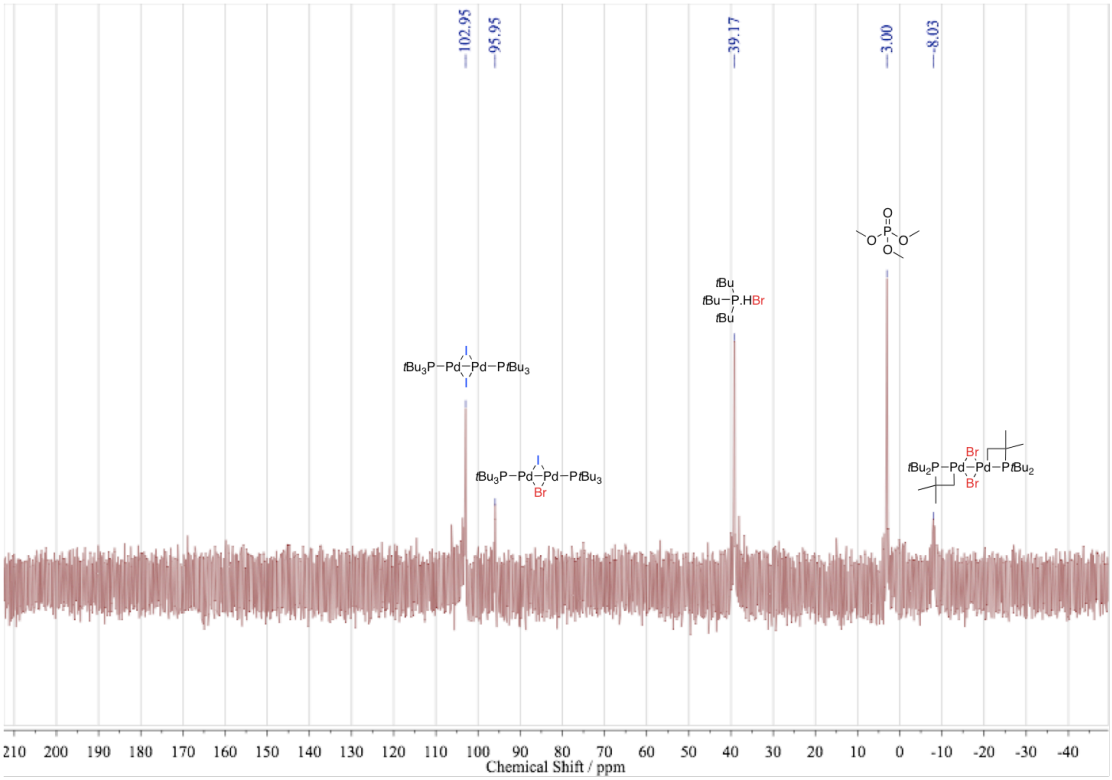


Figure S10. ^{31}P NMR spectrum (126 MHz, THF) showing the conversion of Br-dimer **1** to I-dimer **2** as well as side-products P*t*Bu$_3$, P*t*Bu$_3$.HBr and [Pd(P*t*Bu$_3$)$_2$(C(CH$_3$)$_2$CH$_2$)(μ-Br)]$_2$.

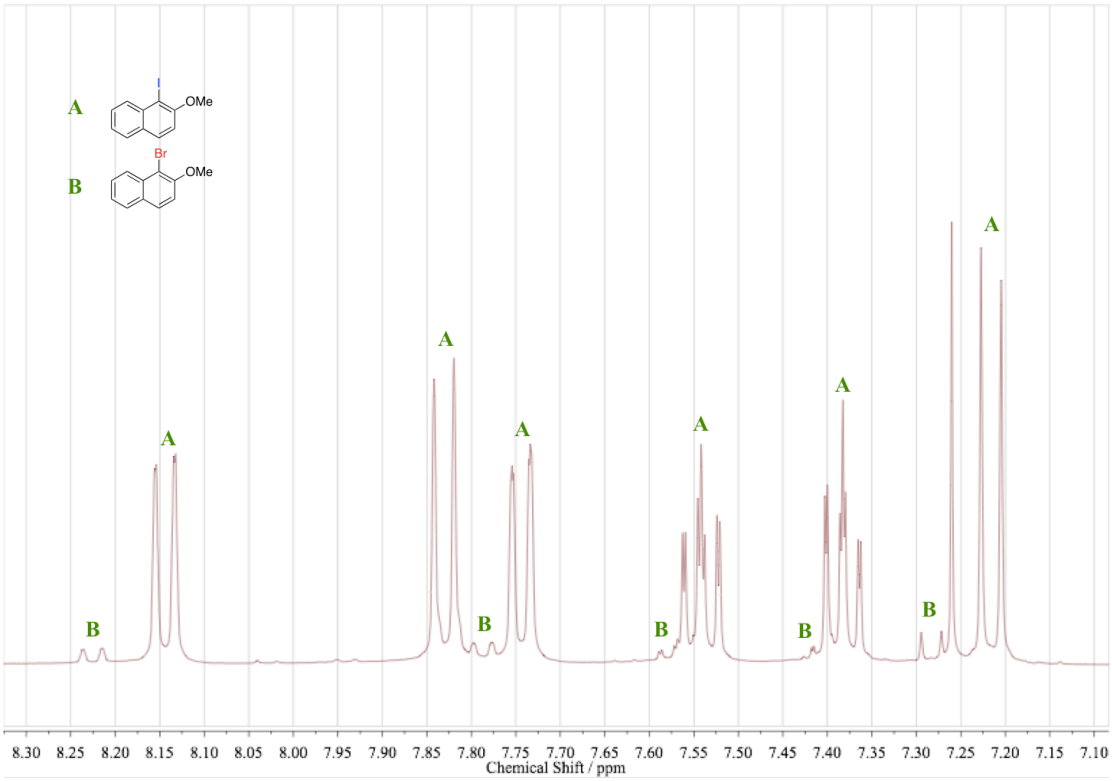


Figure S11. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$).[3]

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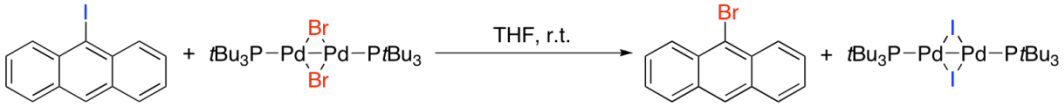
Demonstration of Halide Exchange between Br-Dimer 1 and I-Dimer 2

Initially, 9-iodoanthracene and Br-dimer **1** were mixed together and the conversion to I-dimer **2**, mixed-dimer **3** and 9-bromoanthracene were quantified at various time intervals using ^{31}P NMR spectroscopy and calibrated GC-MS, respectively:



Scheme 1.

Procedure: A solution of 9-iodoanthracene (7.5 equiv) in THF (0.32 M) was added to Br-dimer **1** (1.0 equiv) and stirred vigorously at room temperature. Aliquots were taken after 30, 120 and 180 minutes and were analysed by both ^{31}P NMR spectroscopy (using $P(O)(OMe)_3$ as an internal standard) and also calibrated GC-MS (using mesitylene as an internal standard) to quantify the conversion to I-dimer **2**, mixed-dimer **3** and 9-bromoanthracene.

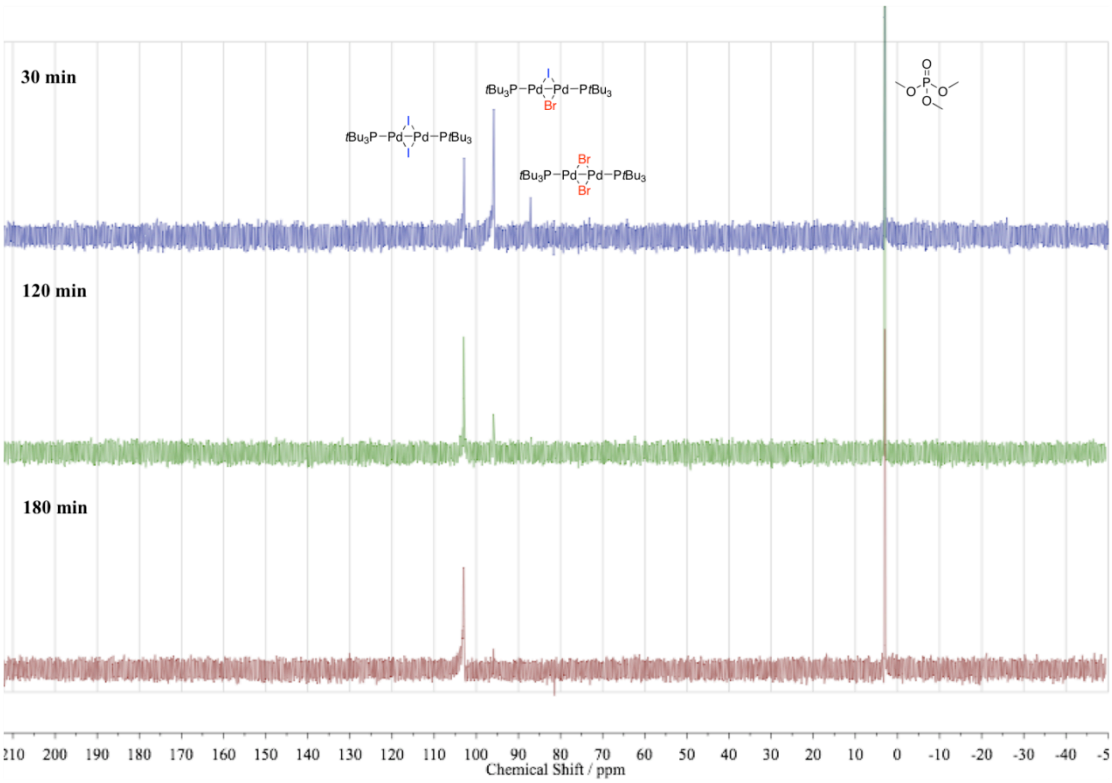


Figure S12. ^{31}P NMR spectra (126 MHz, THF) to show the conversion of Br-dimer **1** to I-dimer **2** in the presence of 9-iodoanthracene after 30, 120 and 180 minutes.

Table S1.

Entry	Time / min	I-Dimer / %[a]	Mixed-Dimer / %[a]	ArBr / %[b,c]
1	30	27	54	120
2	120	84	16	170
3	180	92	8	190

[a] Quantified by integration of the ^{31}P NMR spectrum, where $P(O)(OMe)_3$ was used as an internal standard.

[b] Quantified by calibrated GC-MS, where mesitylene was used as an internal standard.

[c] Based on a possible maximum of 200%, as 1 equivalent of Br-dimer **1** can react with 2 equivalents of aryl iodide to form 1 equivalent of I-dimer **2** and 2 equivalents of aryl bromide.

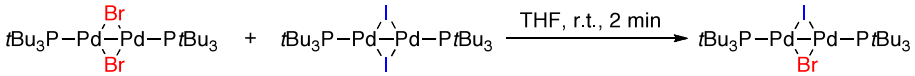
The conversion to aryl bromide at each time interval was then used to calculate the quantity of I-dimer **2** that this would be expected to correspond to. Br-dimer **1** and I-dimer **2** were then mixed together in the corresponding ratios to investigate if the ^{31}P NMR spectra resemble the spectra above from the reaction of Br-dimer **1** with 9-iodoanthracene:

Table S2.

Entry	Time / min	ArBr / %[a,b]	Calculated Conversion to I-Dimer 2 / %	Ratio of 1 : 2 for Mixing
1	30	120	60	40 : 60
2	120	170	85	15 : 85
3	180	190	95	5 : 95

[a] Quantified by calibrated GC-MS, where mesitylene was used as an internal standard.

[b] Based on a possible maximum of 200%, as 1 equivalent of Br-dimer **1** can react with 2 equivalents of aryl iodide to form 1 equivalent of I-dimer **2** and 2 equivalents of aryl bromide.



Scheme S2.

Procedure: A solution of Br-dimer **1** (80 mg, 0.10 mmol 1 equiv) in THF (4 mL) was added to a solution of I-dimer **2** (89 mg, 0.10 mmol, 1 equiv) in THF (4 mL) in the ratios shown in the previous table and the reaction mixture was left for 2 min at room temperature before being analysed by ^{31}P NMR spectroscopy (using P(O)(OMe)$_3$ as an internal standard).

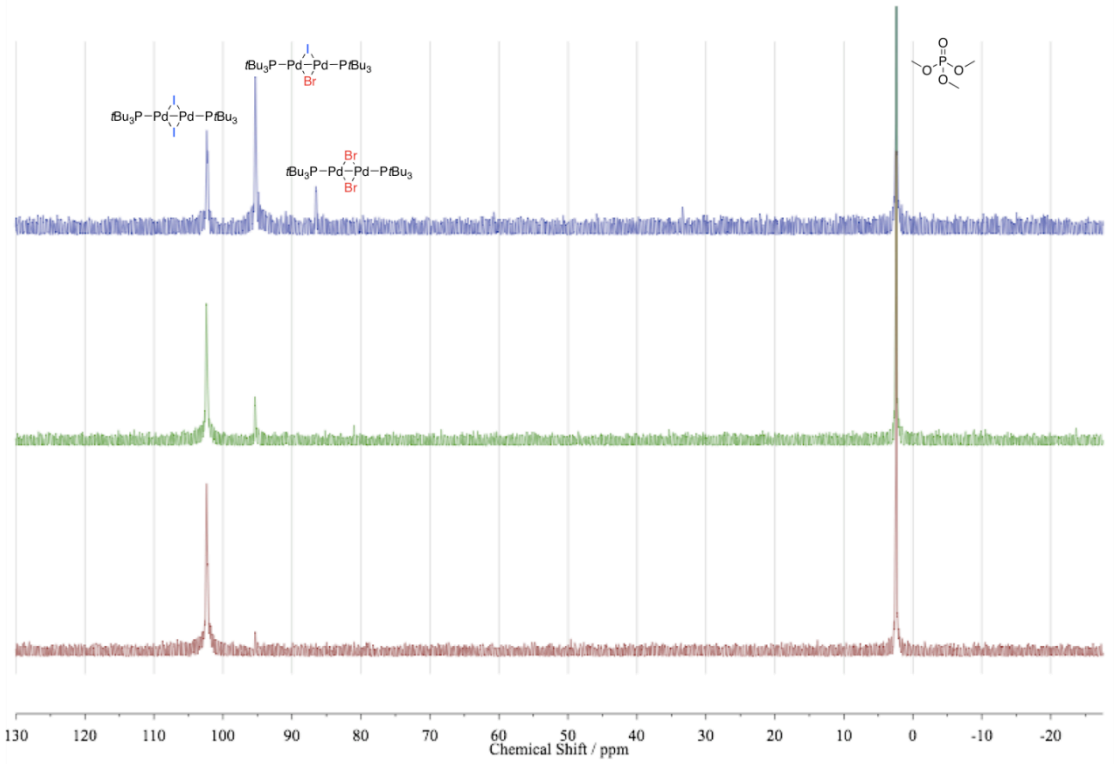


Figure S13. ^{31}P NMR spectra (126 MHz, THF) showing the formation of mixed dimer **3** upon mixing different ratios of Br-dimer **1** and I-dimer **2** (**1** : **2** = 40 : 60 (top), 15 : 85 (middle), 5 : 95 (bottom)).

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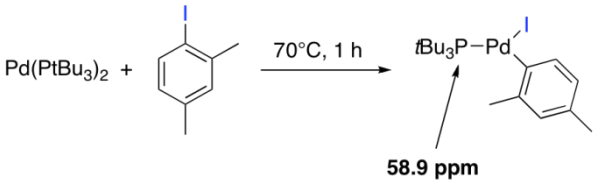
Data to Demonstrate that the Conversion of Br-Dimer 1 to I-Dimer 2 Does Not Proceed *via* a Pd(II) Intermediate

Hartwig has previously reported that mixing $Pd(PtBu_3)_2$ with 4-iodo-*m*-xylene gives rise to the formation of $tBu_3PPd^{II}(Ar)(I)$ after 1 h at 70°C[4]:



Scheme S3.

The structure of this Pd(II) species was unambiguously assigned by single crystal X-ray crystallography, and the ^{31}P NMR chemical shift was found to be 58.9 ppm.

We envisaged that if we were to mix any of the aryl iodides in Scheme 2 or Figure 4 of the main paper with either $Pd(PtBu_3)_2$ or $Pd_2(dba)_3/PtBu_3$ then we should generate analogous Pd(II) species. We chose 1-iodonaphthalene and 9-iodoanthracene as the aryl iodides to use in the reactions, and we observed new resonances at 59.3 and 62.4 ppm respectively:

1-Iodonaphthalene: A solution of 1-iodonaphthalene (390 mg, 1.54 mmol, 7.5 equiv) in THF (2.5 mL) was added to $Pd(PtBu_3)_2$ (105 mg, 0.21 mmol, 1.0 equiv) and after 24 h at room temperature the mixture was analysed by ^{31}P NMR spectroscopy, using $P(O)(OMe)_3$ as an internal standard.

9-Iodoanthracene: A solution of tri-*tert*-butylphosphine (4 mg, 0.02 mmol, 2.0 equiv) in THF (0.25 mL) was added firstly to $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 1.0 equiv) and then to 9-iodoanthracene (45 mg, 0.15 mmol, 15.0 equiv). After 1.5 h at room temperature the reaction mixture was assessed by ^{31}P NMR spectroscopy using $P(O)(OMe)_3$ as an internal standard.

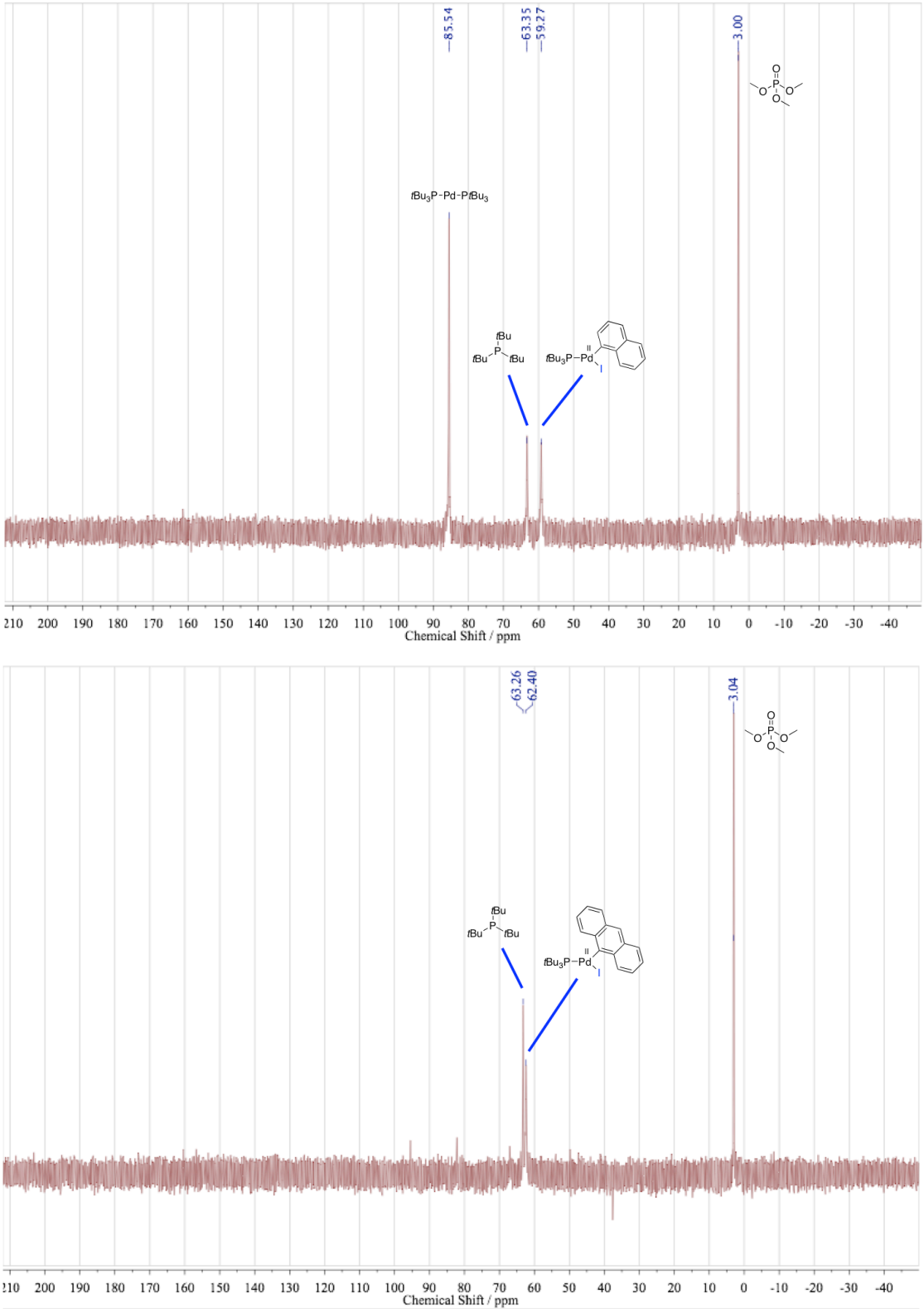
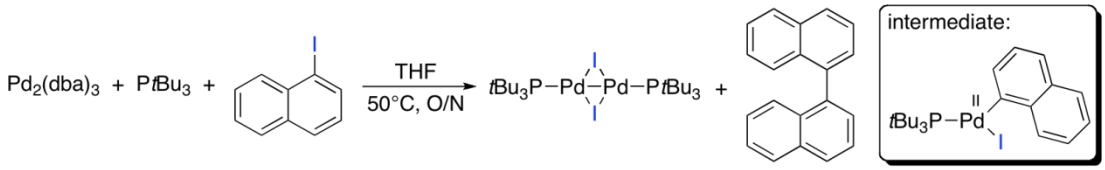


Figure S14. Reaction of 1-iodonaphthalene (top) and 9-Iodoanthracene (bottom) with Pd(0) sources in THF at room temperature.

Neither of these species have been observed by ^{31}P NMR spectroscopy in reactions utilising the Pd(I)-Br-dimer **1**. This gives strong support that the halide exchange reaction does not proceed *via* this intermediate. However, Hartwig has also noted that two molecules of tBu$_3$PPd(Ar)(I) can react to form Pd(I)-I-dimer **2** (if the reaction is heated).[5] Biaryl is also formed in the latter reaction. We chose 1-iodonaphthalene to investigate this reaction with both Pd(0) and the Pd(I)-dimer:



Scheme S4.

Procedure: A solution of PtBu$_3$ (4.3 mg, 0.021 mmol, 2 equiv) in THF (0.25 mL) was added to Pd$_2$(dba)$_3$ (10 mg, 0.011 mmol, 1 equiv), followed by 1-iodonaphthalene (10 mg, 0.039 mmol, 4 equiv). The reaction mixture was heated at 50°C for 20 h after which it was analysed by ^{31}P NMR spectroscopy (using P(O)(OMe)$_3$ as an internal standard). The mixture was subsequently filtered through a plug of silica and was analysed by GC-MS.

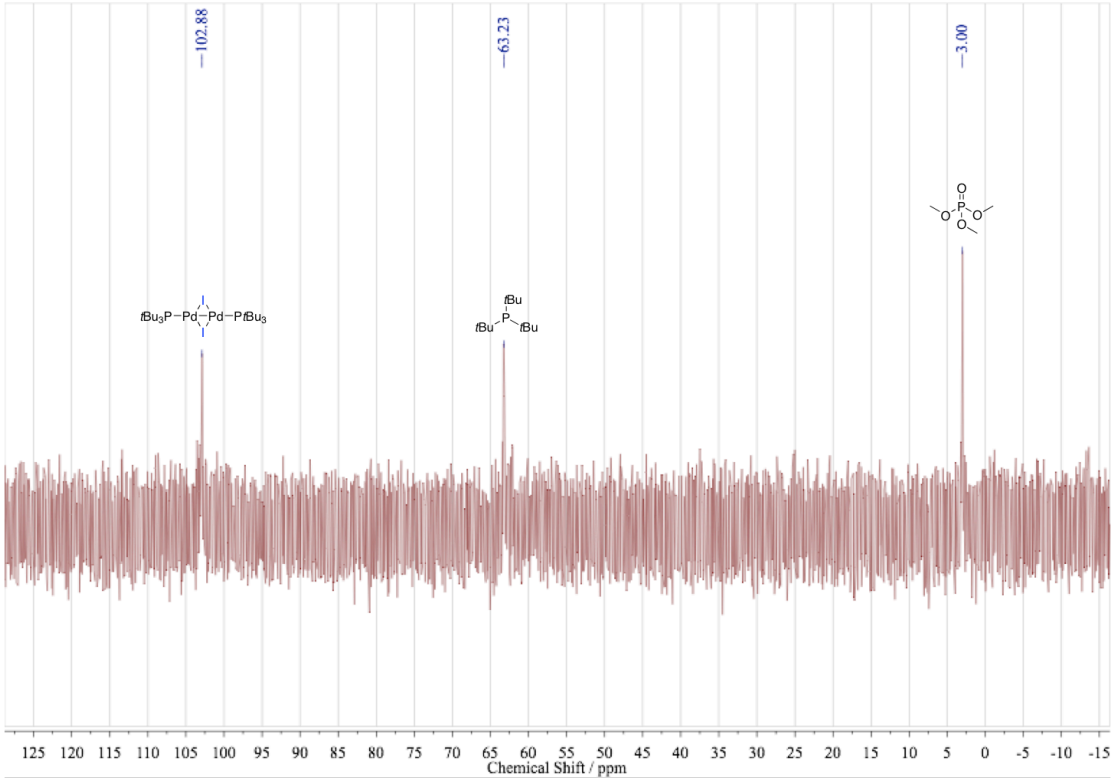


Figure S15.

After heating the reaction mixture at 50°C overnight the ^{31}P NMR spectrum shows exclusively the free phosphine ligand P^{t}Bu$_3$ and I-dimer **2**. As anticipated, GC-MS of this reaction mixture showed the presence of 1,1'-binaphthyl:

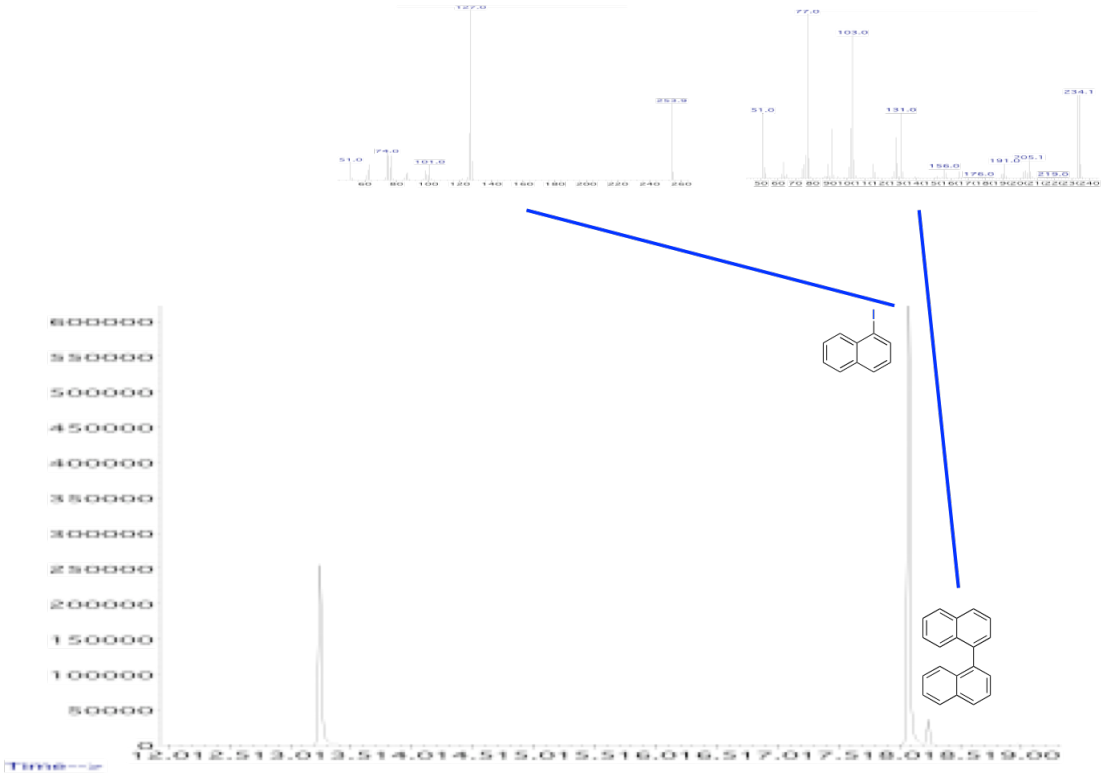


Figure S16.

In the reaction of 1-iodonaphthalene with Br-dimer **1** there was no observation of biaryl by GC-MS (see pS8), thus this provides support for the statement that the halide exchange and formation of I-dimer **2** does not occur *via* the monomeric Pd(II) intermediate.

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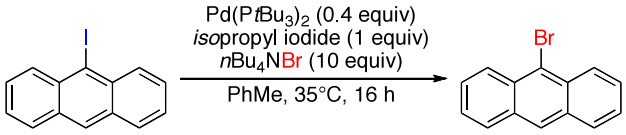
Investigating the Possibility of Free Radical Involvement in the Halide Exchange Reactions

The reaction of Pd-phosphine complexes with alkyl iodides, such as *iso*propyl iodide, has previously been reported to result in the generation of Pd-based radicals (see refs 22 and 30, main paper). We envisaged that we could use this to investigate whether bromination of 1-iodoanthracene can be catalysed by Pd radicals. A negative result would support the conclusion that the halide exchange occurs *via* oxidative addition to the Pd(I)-dimer, rather than the involvement of radicals. We chose $Pd(PtBu_3)_2$ and $Pd(PPh_3)_4$ as representative Pd complexes.

Procedure: A solution of Pd-phosphine complex (0.03 mmol, 0.4 equiv) and *iso*propyl iodide (13 mg, 0.08 mmol, 1.0 equiv) in toluene (0.5 mL) was stirred at room temperature for 15 min prior to the addition of 9-iodoanthracene (24 mg, 0.08 mmol, 1.0 equiv) and tetrabutylammonium bromide (250 mg, 0.80 mmol, 10.0 equiv). This was then stirred overnight at room temperature, and the reaction mixture was subsequently passed through a plug of silica and analysed by GC-MS.



Scheme S6.

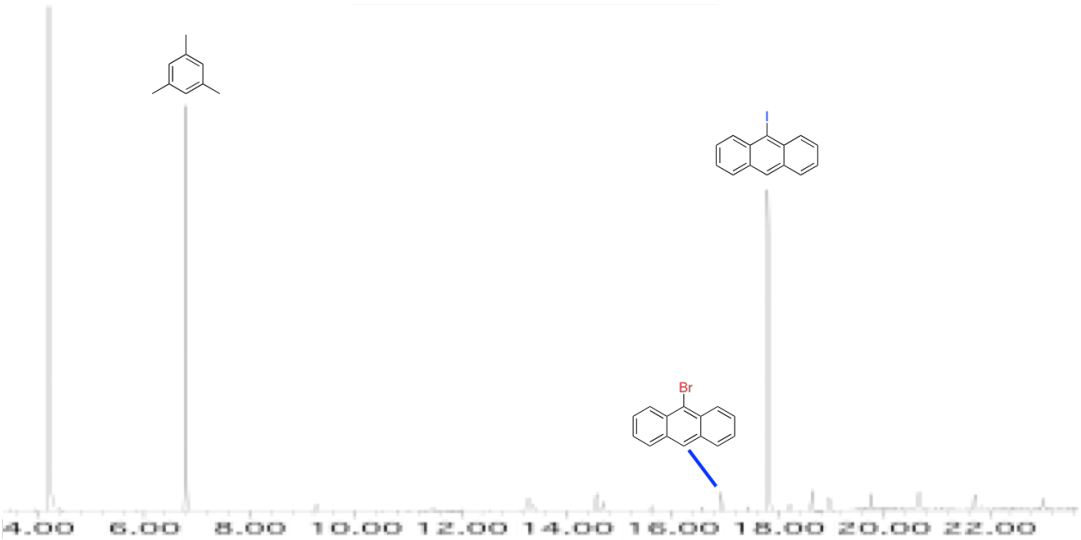
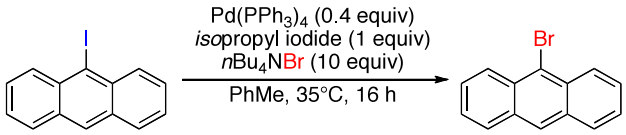


Figure S17.

In the reaction with $Pd(PtBu_3)_2$ there was a small quantity of 9-bromoanthracene formed, however this is in line with that observed in toluene when the analogous reaction was carried out without *iso*propyl iodide (*vide infra*). No anthracene formation was observed in the reaction (as judged by GC-MS) and no biaryl was formed (as judged by ^{1}H NMR spectroscopy).



Scheme S7.

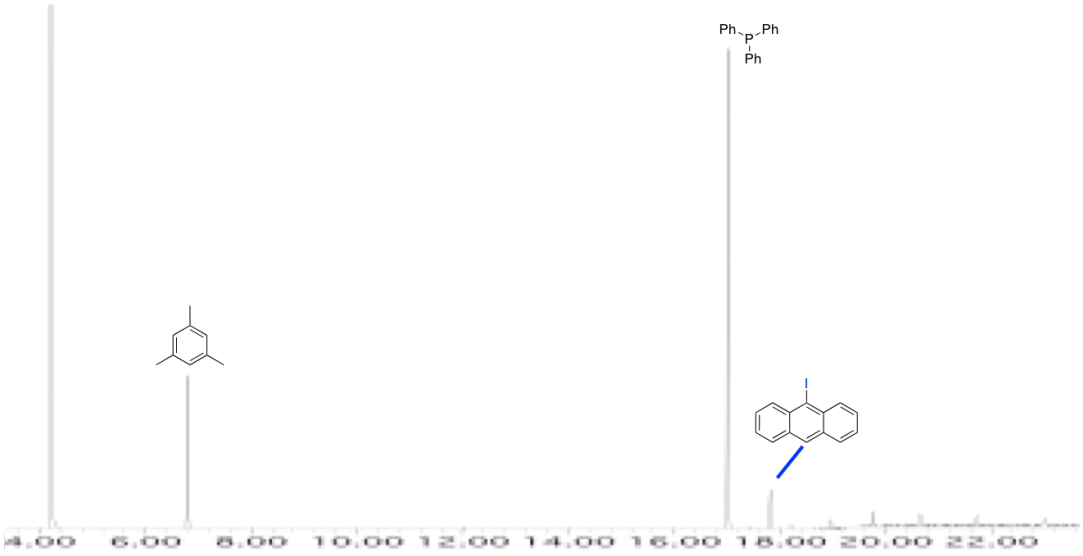
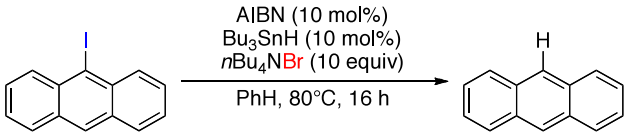


Figure S18.

In the reaction with $Pd(PPh_3)_4$ there was no reaction, with no 9-bromoanthracene, anthracene or biaryl formation observed, as judged by SFC, ^{1}H-NMR and GC-MS analysis.

We also wanted to conduct reactions under conditions where anthracene radicals would be generated in order to investigate whether bromination can occur. We chose to use AIBN as a radical initiator and tributyltin hydride as a chain carrier. We conducted two reactions, one with a catalytic amount of tributyltin hydride and the other with a stoichiometric quantity, where both reactions also contained a large excess of tetrabutylammonium bromide.



Scheme S8.

Benzene (0.5 mL) was added to 9-iodoanthracene (24 mg, 0.08 mmol, 1.0 equiv), AIBN (1 mg, 0.008 mmol, 10 mol%), tributyltin hydride (2 mg, 0.008 mmol, 10 mol%) and tetrabutylammonium bromide (250 mg, 0.80 mmol, 10.0 equiv) and the solution was stirred at 80°C overnight. After this time the reaction mixture was passed through a plug of silica and analysed by GC-MS:

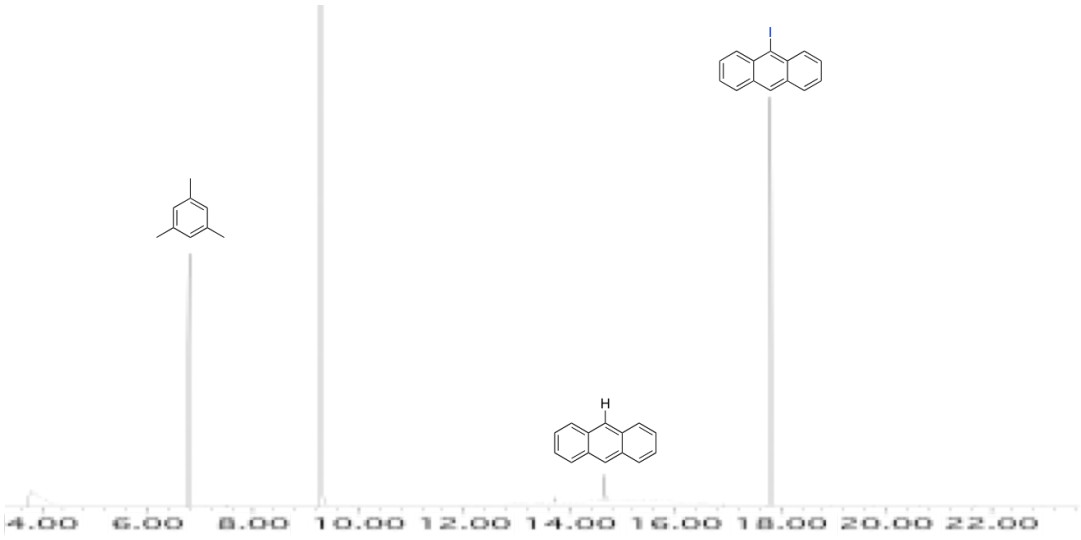
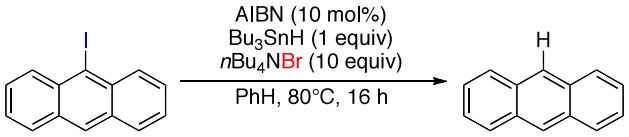


Figure S19.



Scheme S9.

Benzene (0.5 mL) was added to 9-iodoanthracene (24 mg, 0.08 mmol, 1.0 equiv), AIBN (1 mg, 0.008 mmol, 10 mol%), tributyltin hydride (23 mg, 0.08 mmol, 1.0 equiv) and tetrabutylammonium bromide (250 mg, 0.80 mmol, 10.0 equiv) and the

solution was stirred at 80°C overnight. After this time the reaction mixture was passed through a plug of silica and analysed by GC-MS:

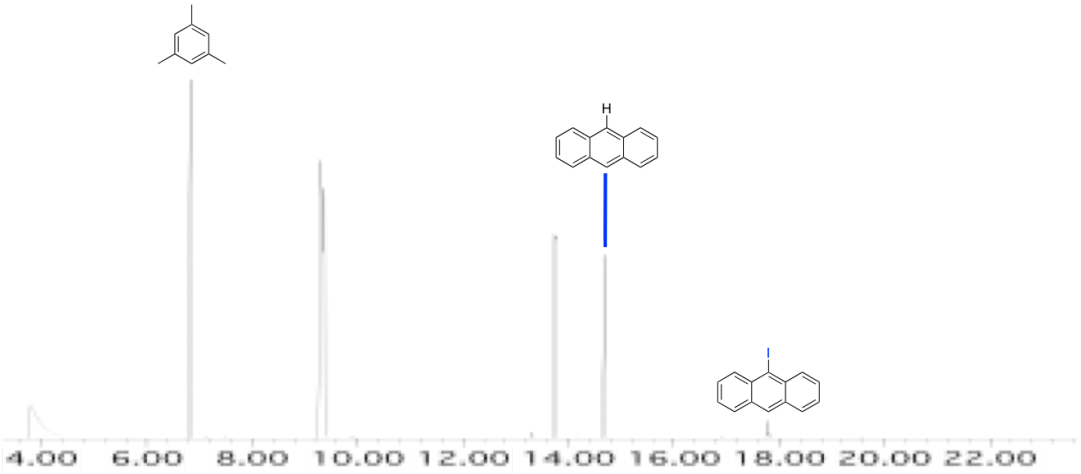


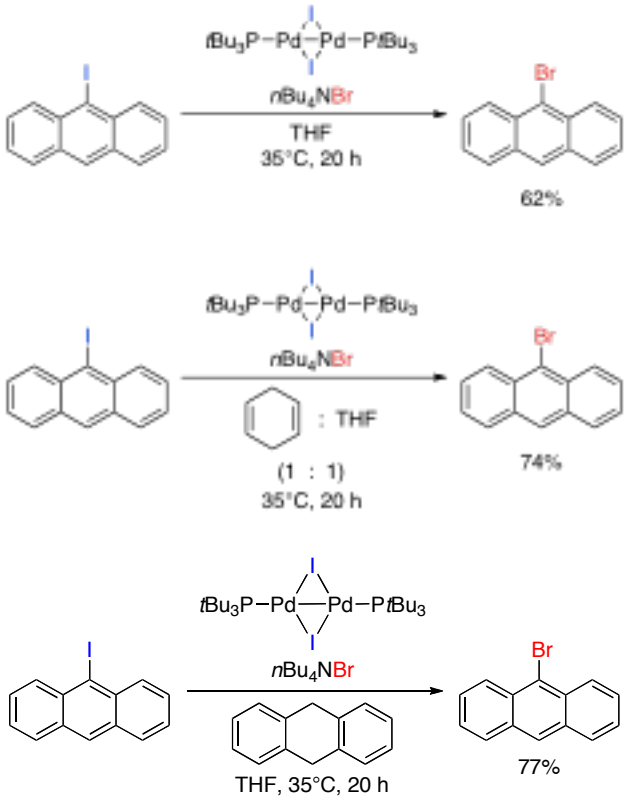
Figure S20.

9-Bromoanthracene and biaryl formation was not observed in either of these reactions (as judged by GC-MS and ^{1}H NMR spectroscopy, respectively). The formation of anthracene in each case is consistent with the quantity of tributyltin hydride used in the reaction.

Finally, we treated 9-iodoanthracene and either the Br-dimer **1** or I-dimer **2** with tetrabutylammonium bromide in the presence of either a large excess of 1,4-cyclohexadiene (=co-solvent, Procedure 1) or the presence of an excess of 9,10-dihydroanthracene (Procedure 2). These are both efficient hydrogen atom donors, therefore if radicals are generated in the reaction with Br-dimer **1** it would be anticipated that anthracene would be formed instead of 9-bromoanthracene.

Procedure 1: A mixture of 1,4-cyclohexadiene and THF (0.6 mL, 2 : 1 v/v) was added to 9-iodoanthracene (24 mg, 0.08 mmol, 1.0 equiv), Br-dimer **1** (12 mg, 0.02 mmol, 25 mol%) and tetrabutylammonium bromide (250 mg, 0.80 mmol, 10.0 equiv). The reaction mixture was stirred at 35°C for 20 h, after which it was passed through a plug of silica and analysed by GC-MS.

Procedure 2: THF (0.50 mL) was added to a mixture of 9-iodoanthracene (56 mg, 0.18 mmol, 1.0 equiv), I-dimer **2** (40 mg, 0.046 mmol, 25 mol%), tetrabutylammonium bromide (660 mg, 2.05 mmol, 11.4 equiv) and 9,10-dihydroanthracene (284 mg, 1.58 mmol, 8.8 equiv). The reaction mixture was heated at 35°C for 20 h, after which it was passed through a plug of silica and analysed by GC-MS.



Scheme S10.

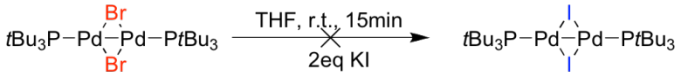
The reactions with the excess of cyclohexadiene and 9,10-dihydroanthracene provided almost the same conversion to 9-bromoanthracene as the reaction without these additives. As the previous reactions have shown that bromination of 9-iodoanthracene does not occur *via* a radical mechanism, this then indicates that the anticipated oxidative addition mechanism was in operation.

Overall these results support the conclusion that the halide exchange reactions and the catalytic bromination of 9-iodoanthracene does not occur *via* radical reactions.

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

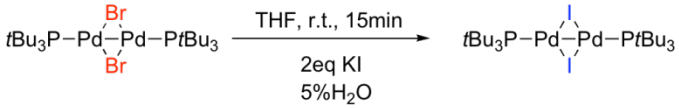
Halide Salt-Mediated Interconversion of Pd(I)-Dimers 1 and 2

Due to the evidently higher thermodynamic stability of I-dimer **2** over Br-dimer **1**, we reasoned that we should be able to readily convert **1** into **2** through the addition of an iodide salt.



Scheme S11.

Initially we stirred Br-dimer **1** with 2 equivalents of potassium iodide in THF for 15 min at room temperature. After this time there was no observation of conversion to either I-dimer **2** or mixed-dimer species **3**. However, the addition of 2.5% v/v water to the reaction mixture resulted in complete conversion to I-dimer **2** within 15 min at room temperature:



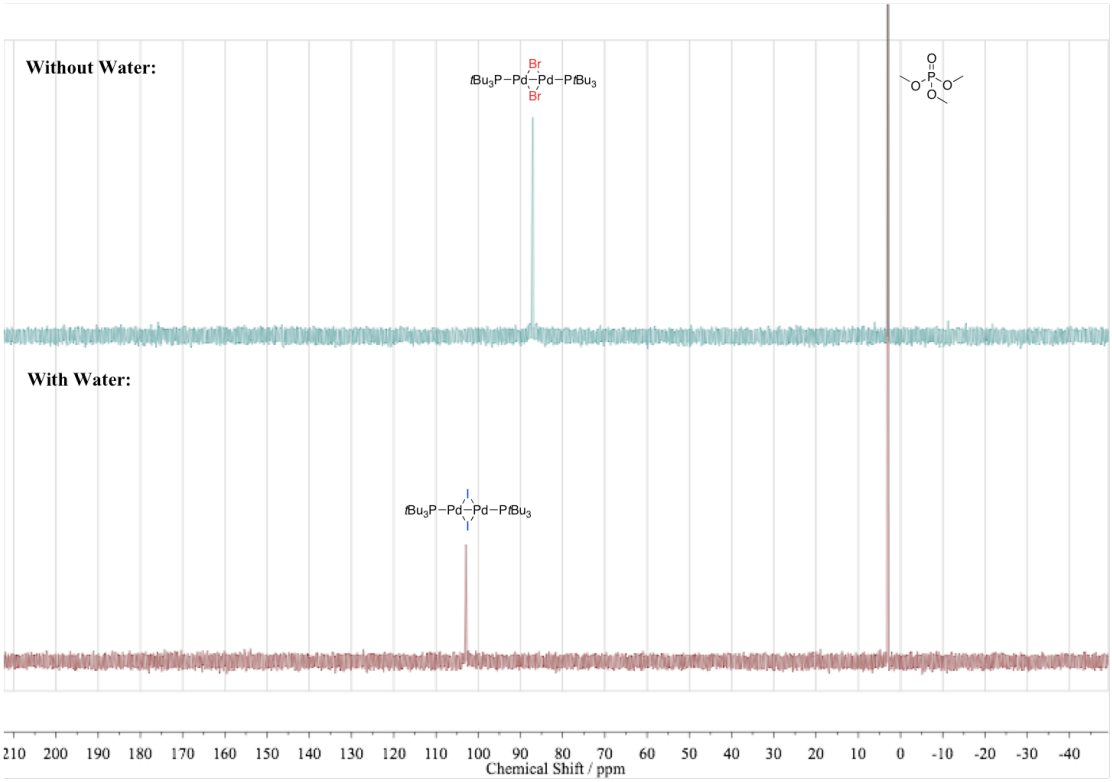
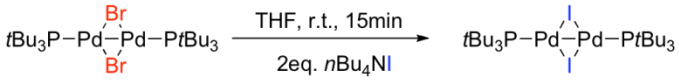


Figure S21.

We reasoned that this difference in halide exchange in the presence of water was due to increased solubility of the iodide salt. Therefore we decided to use

tetrabutylammonium iodide in place of potassium iodide, as this salt is much more soluble in organic solvents.



Scheme S12.

When stirring Br-dimer **1** in the presence of 2 equivalents of tetrabutylammonium iodide in THF (i.e. with no added water) there was complete conversion to I-dimer **2** within 15 minutes at room temperature:

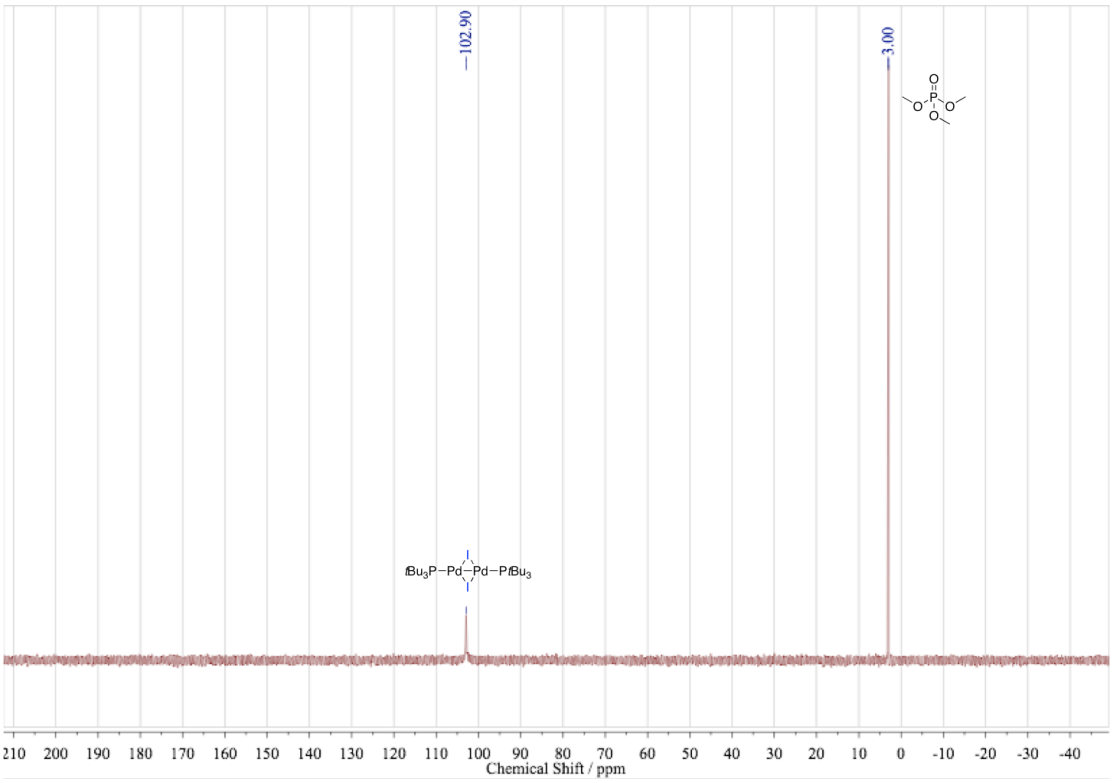
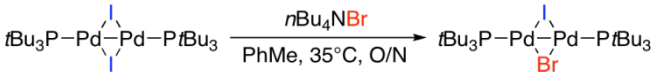


Figure S22.

We subsequently investigated whether the use of a large excess of tetrabutylammonium bromide salt would allow conversion of the thermodynamically-stable I-dimer **2** into Br-dimer **1**, or mixed-dimer species **3**:



Scheme S13.

Procedure: A solution of I-dimer **2** (14 mg, 0.016 mM, 1 equiv) in PhMe (0.25 mL) was added to tetrabutylammonium bromide (254 mg, 0.79 mmol, 50 equiv) and the

reaction mixture was stirred at 35°C overnight, before being analysed by ^{31}P NMR spectroscopy (using $P(O)(OMe)_3$ as an internal standard).

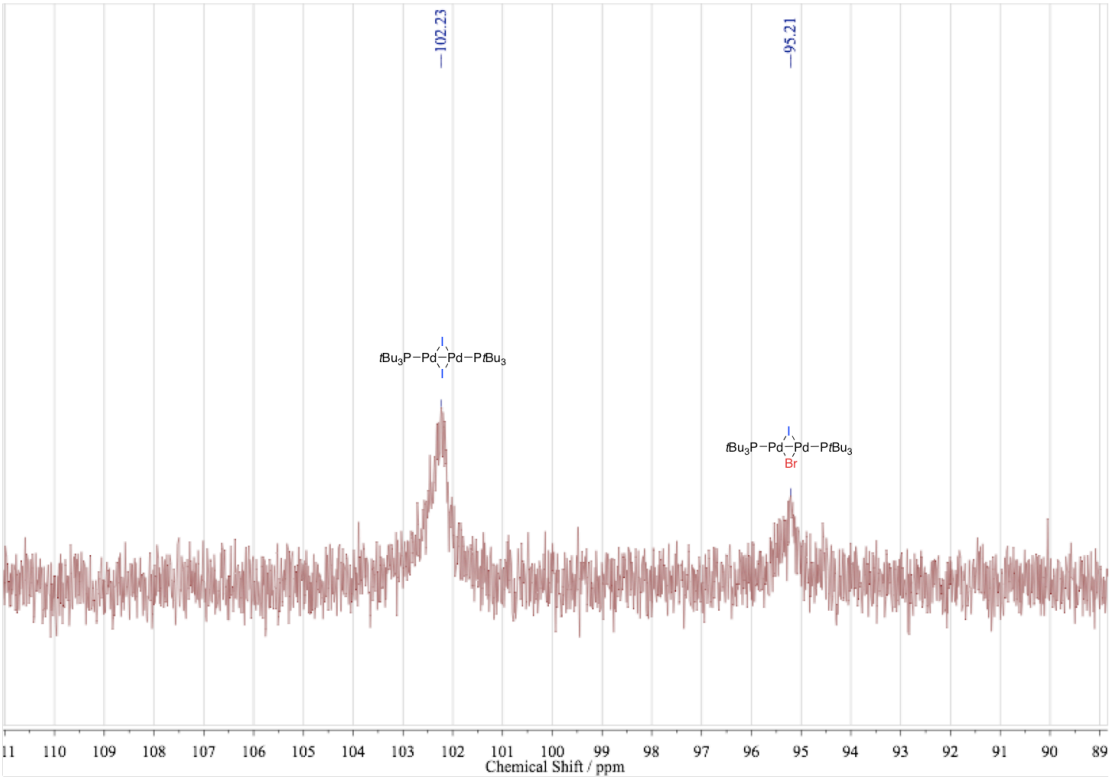
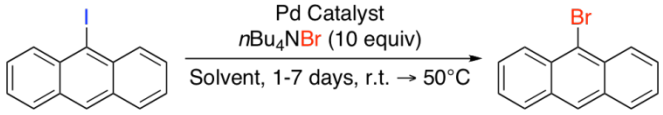


Figure S23. ^{31}P NMR spectrum (126 MHz, THF) showing the conversion of I-dimer **2** to mixed species **3** upon addition of tetrabutylammonium bromide.

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

Catalytic Conversion of 9-Iodoanthracene to 9-Bromoanthracene



Scheme S14.

General procedure for reactions using I-dimer **2**:

A solution of 9-iodoanthracene (24 mg, 0.079 mmol, 1 equiv) and I-dimer **2** (14 mg, 0.016 mmol, 20 mol%) in THF or PhMe (0.25 mL) was added to tetrabutylammonium bromide (254 mg, 0.789 mmol 10 equiv) and the reaction mixture was stirred vigorously (for temperature and reaction time see the following table). The reaction mixture was subsequently filtered through a plug of silica and the conversion was quantified by calibrated GC-MS (where mesitylene was used as an internal standard).

General procedure for reactions using $Pd(PtBu_3)_2$:

A solution of 9-iodoanthracene (24 mg, 0.079 mmol, 1 equiv) and $Pd(PtBu_3)_2$ (16 mg, 0.031 mmol, 40 mol%) in THF or PhMe (0.25 mL) was added to tetrabutylammonium bromide (254 mg, 0.789 mmol, 10 equiv) and the reaction mixture was stirred vigorously (for temperature and reaction time see the following table). The reaction mixture was subsequently filtered through a plug of silica and the conversion was quantified by calibrated GC-MS (where mesitylene was used as an internal standard).

General procedure for reactions using $Pd_2(dba)_3$ and $PtBu_3$:

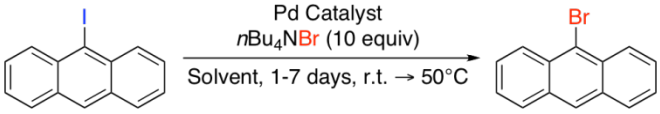
A solution of $Pd_2(dba)_3$ (14 mg, 0.015 mmol, 20 mol%) and $PtBu_3$ (6 mg, 0.030 mmol, 40 mol%) in THF or PhMe (0.25 mL) was added to 9-iodoanthracene (24 mg, 0.079 mmol, 1 equiv), followed by tetrabutylammonium bromide (254 mg, 0.789 mmol, 10 equiv) and the reaction mixture was stirred vigorously (for temperature and reaction time see the following table). The reaction mixture was subsequently filtered through a plug of silica and the conversion was quantified by calibrated GC-MS (where mesitylene was used as an internal standard).

General procedure for reactions without a Pd catalyst:

A solution of 9-iodoanthracene (24 mg, 0.079 mmol, 1 equiv) in THF, PhMe or PhH

(0.25 mL) was added to tetrabutylammonium bromide (254 mg, 0.789 mmol, 10 equiv) and the reaction mixture was stirred vigorously (for temperature and reaction time see the following table). The reaction mixture was subsequently filtered through a plug of silica and the conversion was quantified by calibrated GC-MS (where mesitylene was used as an internal standard).

Table S3. Catalytic halide exchange with different Pd-catalysts.



Scheme S15.

Entry	Catalyst	Solvent	Temperature	Reaction Time / h	Conversion / %[a]
1	I-dimer **2**	THF	25°C	48	67
2	I-dimer **2**	THF	25°C	96	81
3	I-dimer **2**	THF	35°C	20	62
4	I-dimer **2**	THF	35°C	48	65[b]
5	I-dimer **2**	THF	50°C	20	56[b]
6	I-dimer **2**	PhMe	a.t.	42	24
7	I-dimer **2**	PhMe	35°C	18	32
8	I-dimer **2**	PhMe	35°C	42	67
9	$Pd_2(dba)_3$ / P*t*Bu_3	THF	a.t.	19	1
10	$Pd_2(dba)_3$ / P*t*Bu_3	THF	35°C	48	5
11	$Pd_2(dba)_3$ / P*t*Bu_3	PhMe	a.t.	42	0
12	$Pd_2(dba)_3$ / P*t*Bu_3	PhMe	35°C	42	8
13	Pd(P*t*$Bu_3)_2$	THF	a.t.	19	3
14	Pd(P*t*$Bu_3)_2$	PhMe	a.t.	42	0
15	Pd(P*t*$Bu_3)_2$	PhMe	35°C	42	7
16	None	THF	35°C	42	0
17	None	PhMe	35°C	42	0
18	None	PhH	80°C	42	0

[a] Conversion quantified by calibrated GC-MS, where mesitylene was used as an internal standard.
[b] Presumably in these reactions the catalyst has undergone decomposition due to the heat applied to the reaction, explaining the lower than anticipated conversion.

Computational Details

Geometry optimizations in the gas-phase were performed at B3LYP/6-31G(d)[6,7] (with LANL2DZ as ECP for Pd and I) using the Gaussian09 suite of programs. Frequency calculations were performed (at 298.15 K) on all optimized geometries to verify the nature of all the stationary points as either minima or transition states (for gas-phase and continuum calculations). Energy calculations were carried out at M06L[9]/6-311++G(d,p) (with SDD for Pd, I) and employing a solvation model for THF (CPCM). B3LYP thermal and free energy corrections were subsequently applied. Thermal corrections are by default computed at 1 atm (gas-phase standard state). For solution phase, they were converted to the standard state of 1 M (1.89 kcal/mol were added to every species for this conversion). Images were created with *CYLview* (© C. Legault).

Full reference 20 for Gaussian09

Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

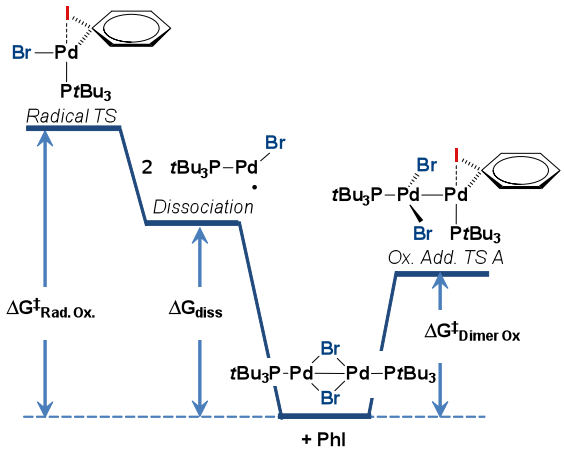


Figure S24. Radical pathway versus direct oxidative addition. See Table S2 for variety of methods.

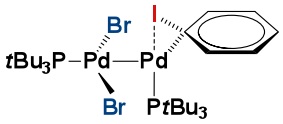
Table S4. Radical pathway versus direct oxidative addition by the Pd(I) dimer for various computational methods. Compare with Figure S12.

Method*	$\Delta G^{‡}$ Dimer Ox	ΔG diss	$\Delta G^{‡}$ Rad. Ox.
[a,b] B3LYP/ 6-311++G(d,p)	35.2	19.7	37.9
[a,b] B3LYP-D3/ 6-311++G(d,p)	10.0	29.2	35.8
[a,b] M06L/ 6-311++G(d,p)	14.8	22.6	32.7
[a,b] PBE0-D3/ 6-311++G(d,p)	15.9	12.4	25.0
[a,b] B3LYP/6-31G(d) gCP-D3	27.1	23.3	38.2

[*]ECP for Pd is SDD; [a] Energy in THF (CPCM); [b] Structure optimized with B3LYP/6-31G(d) and LNL2DZ for Pd

XYZ coordinates and thermal data

TSA



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C	5.00933200	-3.10858000	1.41346100
C	3.78262100	-2.51623300	-0.59429000
C	2.62548900	-2.34958800	0.18330700
C	2.63501700	-2.61714200	1.56099500
H	1.71953000	-2.52787800	2.13638600
H	3.74754900	-2.38058000	-1.66942300
C	3.83880800	-2.97347800	2.16879800
C	4.97670900	-2.87901900	0.03680700
H	3.85584700	-3.15964200	3.23966300
H	5.87739200	-2.99767600	-0.56037900
Pd	1.55547500	-0.47097900	-0.31009900
Br	-0.86476900	0.27958200	-2.52130500
Pd	-1.20237900	-0.08202800	-0.05241200

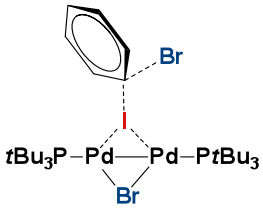
Br	-0.53726100	-0.66455100	2.29662000
I	0.63508600	-2.96746200	-0.96704600
H	5.93557600	-3.41143200	1.89356800
H	2.47951500	2.83195300	-3.65899000
C	2.13083100	2.79421100	-2.61869500
C	3.28924400	2.27567100	-1.73491800
H	1.26222900	2.12900600	-2.58004900
H	1.81384700	3.80541600	-2.35091200
P	2.60126500	1.79110100	0.02434900
C	4.42463900	3.31943100	-1.75247900
C	3.78781500	0.97912200	-2.41583500
C	1.47537700	3.25493000	0.66083700
C	4.10239600	1.64203900	1.26366600
H	5.33269900	2.96723800	-1.25747000
H	4.68968100	3.53014400	-2.79774200
H	4.13304600	4.26787000	-1.29520200
H	4.62071300	0.50546600	-1.89442100
H	2.97619300	0.24883800	-2.50100400
H	4.12952600	1.22544000	-3.43040400
C	2.05151900	4.66938200	0.43190500
C	0.10357000	3.17515400	-0.03855300
C	1.18446200	3.07163300	2.16730300
C	3.61607200	0.86435900	2.50857000
C	5.22012500	0.78438100	0.63228100
C	4.73061100	2.97365300	1.72484900
H	3.03145200	4.81757900	0.88924100
H	2.12824400	4.92122100	-0.62856900
H	1.36655200	5.39907600	0.88489700
H	-0.39579900	2.22737200	0.18327000
H	-0.52523300	3.99051900	0.34573000
H	0.14834200	3.27308900	-1.12155600
H	0.40531600	3.79124400	2.45279600
H	0.80627100	2.06983600	2.39396800
H	2.05041000	3.27756800	2.79950800
H	2.86941900	1.40056100	3.09318500
H	3.19438100	-0.10327700	2.23191400
H	4.47881800	0.68267000	3.16401200
H	5.74301100	1.29053000	-0.18267900
H	5.96722700	0.57089800	1.40803700
H	4.84808700	-0.17568900	0.26977000
H	5.58721000	2.74488600	2.37373700
H	5.10612600	3.57963100	0.89653300
H	4.04147900	3.58320800	2.31260300
P	-3.62924400	0.27104500	0.21981900
C	-4.53091300	0.88389000	-1.41354600
C	-4.32204100	-1.50130100	0.67526600
C	-4.12056500	1.52538800	1.64448000
C	-6.01718700	1.26553800	-1.21764800
C	-3.81265500	2.12432700	-1.99756700
C	-4.45584300	-0.22588900	-2.48644400
C	-3.55467500	-2.53735800	-0.17926600
C	-4.02024400	-1.84190600	2.15083000
C	-5.83800200	-1.68951500	0.44999800
C	-3.93447300	2.98046400	1.16009400
C	-5.57675300	1.35658600	2.13857000
C	-3.18880300	1.36713300	2.86276100
H	-6.62387400	0.47071000	-0.78136900
H	-6.14215200	2.16825800	-0.61502900
H	-6.43547100	1.48619100	-2.20856900
H	-2.76335200	1.92497500	-2.21170500
H	-4.30310700	2.37236200	-2.94842100
H	-3.88593900	3.00427800	-1.36025400
H	-4.82524800	0.19375300	-3.43111900
H	-3.43062100	-0.55871600	-2.65944000
H	-5.08449600	-1.08769500	-2.25243000
H	-3.67633900	-2.39101800	-1.25342600
H	-2.48509700	-2.52089200	0.04756400
H	-3.93631000	-3.53754000	0.06685700
H	-4.63008000	-1.26842100	2.85286600
H	-4.26431300	-2.90112700	2.30553200
H	-2.96575500	-1.70530200	2.39942800

H	-6.10672000	-2.69692800	0.79428600
H	-6.44463200	-0.98203800	1.02034900
H	-6.12733700	-1.62572400	-0.60083900
H	-2.94912200	3.14516500	0.71455000
H	-4.70015400	3.29857000	0.45043200
H	-4.01413100	3.63941400	2.03434300
H	-5.72142900	0.42591700	2.69150200
H	-5.79522900	2.17781900	2.83428400
H	-6.31937000	1.40083800	1.34150000
H	-3.18808700	0.36484600	3.28658600
H	-2.15605000	1.61800200	2.61912500
H	-3.53637300	2.06105800	3.64056100

Zero-point correction= 0.840234
Thermal correction to Energy= 0.893352
Thermal correction to Enthalpy= 0.894296
Thermal correction to Gibbs Free Energy= 0.752173
Sum of electronic and thermal Energies= -7268.325965
Sum of electronic and thermal Enthalpies= -7268.325021
Sum of electronic and thermal Free Energies= -7268.467144

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7277.17366612

TSB



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

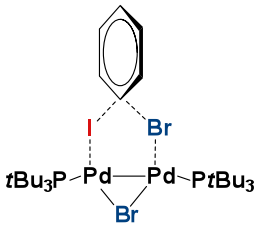
Pd 1.300575 -0.766320 -0.101073
P 3.681336 -1.038304 0.038325
C 4.261230 -0.028542 1.595335
C 4.146158 -2.914952 0.278672
C 4.589835 -0.368405 -1.544675
Pd -1.419654 -0.724657 -0.161472
P -3.803947 -0.826277 -0.148297
C -4.414495 -2.392603 -1.133517
C -4.297004 -1.014497 1.727959
C -4.687708 0.750254 -0.877149
C 3.325280 -3.769712 -0.717457
H 3.547508 -4.827876 -0.524677
H 2.251094 -3.624345 -0.580056
H 3.567980 -3.572799 -1.761415
C 5.645052 -3.233862 0.089799
H 6.290176 -2.657926 0.757123
H 5.806983 -4.296643 0.314753
H 5.983147 -3.070041 -0.936122
C 3.722161 -3.382874 1.688781
H 4.337649 -2.957291 2.484445
H 2.670928 -3.161391 1.894295
H 3.842905 -4.472821 1.737840
C 3.215857 -0.248349 2.716202
H 3.181189 -1.272970 3.087570
H 3.471504 0.403279 3.562280
H 2.209126 0.017509 2.375215
C 5.661029 -0.388429 2.133725
H 5.889020 0.273946 2.979620
H 5.722503 -1.414072 2.505835
H 6.448781 -0.244436 1.389853
C 4.233811 1.481232 1.273610
H 3.278342 1.823332 0.866747
H 4.401426 2.031635 2.208559
H 5.021047 1.787220 0.581842
C 4.428603 -1.369099 -2.711120
H 4.782621 -0.880690 -3.627986

H 5.016104 -2.281052 -2.585179
H 3.380872 -1.643621 -2.871869
C 3.884454 0.926445 -2.007448
H 3.853885 1.726338 -1.269181
H 4.417377 1.312316 -2.886808
H 2.854099 0.721579 -2.310788
C 6.094546 -0.085041 -1.346892
H 6.520425 0.221969 -2.311475
H 6.276612 0.731926 -0.645209
H 6.653776 -0.960818 -1.008123
C -4.341719 -2.111316 -2.650686
H -3.361714 -1.724994 -2.948920
H -4.497331 -3.058050 -3.183593
H -5.113857 -1.420083 -2.994938
C -5.844669 -2.860862 -0.790866
H -6.098165 -3.712967 -1.435926
H -5.936839 -3.205378 0.241816
H -6.598264 -2.088674 -0.962378
C -3.430149 -3.557618 -0.876346
H -2.410355 -3.292232 -1.167242
H -3.403832 -3.885704 0.162479
H -3.746754 -4.415290 -1.484922
C -4.017371 1.136235 -2.217139
H -4.181288 0.408632 -3.011397
H -4.446623 2.088651 -2.555088
H -2.940861 1.277375 -2.103185
C -4.458074 1.945553 0.074108
H -3.399343 2.092762 0.306780
H -4.810614 2.856583 -0.425933
H -5.013759 1.859913 1.010340
C -6.204306 0.593962 -1.119996
H -6.605834 1.559590 -1.455477
H -6.427137 -0.133152 -1.904998
H -6.755375 0.307207 -0.221709
C -5.779936 -0.742672 2.052559
H -5.944634 -0.934733 3.121233
H -6.069075 0.294585 1.868013
H -6.461429 -1.392483 1.497179
C -3.407841 -0.046467 2.546706
H -3.576222 1.005210 2.314763
H -3.627391 -0.190161 3.613280
H -2.345588 -0.261036 2.388936
C -3.944246 -2.434061 2.225118
H -4.065704 -2.452147 3.315926
H -4.601183 -3.205876 1.817706
H -2.905613 -2.699358 2.007670
I -0.085528 1.485293 -1.082807
Br -0.088667 -2.700502 0.819910
C -0.323444 3.368959 0.469550
C -0.133872 3.031885 1.800346
C -1.211051 4.342586 0.035108
Br 2.047094 4.116982 -0.590781
C -0.848462 3.764384 2.756295
H 0.560657 2.255295 2.096634
C -1.911168 5.055090 1.015098
H -1.320131 4.581087 -1.015916
C -1.735084 4.772311 2.371882
H -0.698714 3.534618 3.808374
H -2.589719 5.844603 0.701416
H -2.284030 5.333068 3.122542
Zero-point correction= 0.838814
Thermal correction to Energy= 0.892302
Thermal correction to Enthalpy= 0.893247
Thermal correction to Gibbs Free Energy= 0.750393
Sum of electronic and thermal Energies= -7268.276643
Sum of electronic and thermal Enthalpies= -7268.275699
Sum of electronic and thermal Free Energies= -7268.418552

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7277.12483726

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

TSC



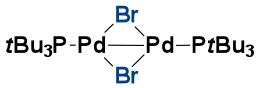
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

Pd 1.583621 -0.356492 -0.093440
P 3.857491 -1.186790 -0.015215
C 4.513993 -0.761708 1.775463
C 3.897174 -3.137008 -0.230841
C 5.094022 -0.439351 -1.335166
Pd -1.588096 -0.307722 0.076641
P -3.889748 -1.032465 0.026457
C -4.556132 -0.613592 -1.762401
C -3.995035 -2.977536 0.270654
C -5.091337 -0.229899 1.345267
C 3.066185 -3.547288 -1.470870
H 3.025369 -4.644359 -1.502459
H 2.040758 -3.180115 -1.417682
H 3.502070 -3.214710 -2.412262
C 5.308424 -3.745614 -0.390461
H 5.982320 -3.496176 0.430912
H 5.209226 -4.839214 -0.410820
H 5.785186 -3.453949 -1.328994
C 3.220914 -3.804560 0.987722
H 3.806375 -3.711186 1.904477
H 2.216349 -3.413763 1.166112
H 3.122001 -4.877584 0.777768
C 3.335058 -0.943398 2.762462
H 2.959747 -1.966263 2.808949
H 3.679590 -0.669512 3.768955
H 2.497161 -0.290112 2.499949
C 5.714532 -1.600304 2.263968
H 6.020071 -1.223551 3.249373
H 5.473899 -2.658089 2.389963
H 6.582623 -1.521117 1.604758
C 4.915192 0.727401 1.856040
H 4.119003 1.388587 1.506049
H 5.106688 0.970149 2.909556
H 5.830850 0.952240 1.304632
C 4.807391 -1.056966 -2.721671
H 5.350063 -0.471812 -3.475274
H 5.150214 -2.089657 -2.812225
H 3.743419 -1.012785 -2.975982
C 4.839218 1.074415 -1.498161
H 4.970621 1.644599 -0.579469
H 5.557141 1.461330 -2.234303
H 3.832860 1.273746 -1.870048
C 6.589361 -0.641792 -1.001517
H 7.184884 -0.268133 -1.845481
H 6.898691 -0.075197 -0.119855
H 6.863365 -1.686636 -0.848053
C -4.911728 0.885657 -1.864486
H -4.088124 1.530762 -1.548738
H -5.119199 1.114611 -2.917957
H -5.806179 1.152080 -1.297142
C -5.789412 -1.418951 -2.225512
H -6.087509 -1.054572 -3.217890
H -5.587472 -2.487140 -2.328143
H -6.650444 -1.293956 -1.564096
C -3.395622 -0.850213 -2.759310
H -2.525658 -0.236298 -2.505470
H -3.068428 -1.889535 -2.804318
H -3.735316 -0.564589 -3.764213

C -4.784861 1.276628 1.485412
H -4.883650 1.835483 0.555270
H -5.496457 1.705032 2.204364
H -3.777994 1.444319 1.872492
C -4.811813 -0.835540 2.738611
H -3.744162 -0.824071 2.980791
H -5.325989 -0.221025 3.488916
H -5.187943 -1.854677 2.848544
C -6.595928 -0.385643 1.028901
H -7.170479 0.015575 1.874738
H -6.895925 0.182001 0.144597
H -6.905448 -1.422258 0.889013
C -5.422534 -3.535803 0.465338
H -5.361116 -4.632077 0.493756
H -5.871015 -3.221117 1.410614
H -6.104057 -3.270310 -0.344718
C -3.153431 -3.393955 1.501585
H -3.556677 -3.026466 2.444700
H -3.151207 -4.490995 1.555391
H -2.116972 -3.064372 1.418874
C -3.364240 -3.688308 -0.947703
H -3.294434 -4.759818 -0.719190
H -3.963930 -3.594071 -1.855174
H -2.351694 -3.332939 -1.152978
I -1.643549 2.389173 -0.010156
Br -0.026106 -2.285293 -0.044021
C 0.422345 4.000734 -0.002210
C 0.504635 4.669707 1.216577
C 0.532320 4.657583 -1.225559
Br 1.947714 2.118078 0.019612
C 0.687751 6.055949 1.199375
H 0.425706 4.128913 2.153139
C 0.713056 6.043996 -1.218185
H 0.477848 4.106832 -2.158035
C 0.790315 6.745338 -0.011792
H 0.749883 6.592902 2.142901
H 0.794670 6.571729 -2.165427
H 0.931440 7.822423 -0.015641
Zero-point correction= 0.839874
Thermal correction to Energy= 0.893006
Thermal correction to Enthalpy= 0.893950
Thermal correction to Gibbs Free Energy= 0.751680
Sum of electronic and thermal Energies= -7268.302319
Sum of electronic and thermal Enthalpies= -7268.301375
Sum of electronic and thermal Free Energies= -7268.443645

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7277.12842431

Pd(I)-Br-dimer 1



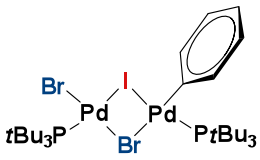
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
Pd -1.327752 0.058989 -0.046462
Br -0.000067 2.276995 -0.000116
P -3.695663 -0.004878 -0.009691
C -4.194582 -0.850072 1.672676
C -4.473686 1.780033 -0.076287
C -4.405033 -1.052999 -1.489147
Br -0.000040 -2.161423 0.000032
Pd 1.327758 0.059013 0.046389
P 3.695676 -0.004898 0.009649
C 4.473768 1.779998 0.075755
C 4.404945 -1.052481 1.489526
C 4.194667 -0.850657 -1.672420
C -3.753861 2.602080 -1.173216
H -4.138179 3.630392 -1.137753

H -2.675230 2.640105 -1.002720
H -3.926782 2.227428 -2.182038
C -5.992553 1.818344 -0.343666
H -6.568144 1.241029 0.383416
H -6.334769 2.860139 -0.280574
H -6.247720 1.459524 -1.344167
C -4.183329 2.514441 1.252123
H -4.749948 2.116339 2.096954
H -3.117256 2.499409 1.499392
H -4.477940 3.565214 1.134123
C -3.256553 -0.300143 2.776056
H -3.383352 0.766113 2.963386
H -3.475533 -0.828761 3.713744
H -2.205465 -0.477338 2.525345
C -5.660586 -0.651823 2.109817
H -5.828996 -1.212924 3.039034
H -5.899302 0.393491 2.321412
H -6.377063 -1.023211 1.372190
C -3.907083 -2.366119 1.597625
H -2.884536 -2.571339 1.266819
H -4.017204 -2.785570 2.606226
H -4.604798 -2.903429 0.950940
C -4.300853 -0.232199 -2.793614
H -4.523834 -0.897116 -3.638079
H -5.014372 0.593359 -2.838790
H -3.291734 0.164697 -2.944521
C -3.499523 -2.289404 -1.701044
H -3.515050 -2.989778 -0.866388
H -3.856733 -2.828563 -2.588836
H -2.459296 -2.001078 -1.872891
C -5.863872 -1.525223 -1.318363
H -6.167972 -2.063733 -2.226260
H -5.982523 -2.218087 -0.481917
H -6.566496 -0.699864 -1.179733
C 4.183189 2.514205 -1.252720
H 3.117078 2.499116 -1.499830
H 4.477795 3.565000 -1.134914
H 4.749689 2.115998 -2.097579
C 5.992684 1.818291 0.342852
H 6.334929 2.860064 0.279552
H 6.248010 1.459600 1.343360
H 6.568119 1.240848 -0.384252
C 3.754204 2.602245 1.172705
H 2.675540 2.640292 1.002427
H 3.927312 2.227729 2.181549
H 4.138563 3.630534 1.137015
C 3.256559 -0.301232 -2.775981
H 3.383302 0.764949 -2.963768
H 3.475505 -0.830235 -3.713459
H 2.205494 -0.478362 -2.525128
C 3.907341 -2.366713 -1.596838
H 2.884837 -2.571945 -1.265908
H 4.017458 -2.786497 -2.605302
H 4.605156 -2.903720 -0.950010
C 5.660644 -0.652406 -2.109647
H 5.829130 -1.213893 -3.038617
H 5.899220 0.392846 -2.321697
H 6.377167 -1.023369 -1.371852
C 5.863659 -1.525128 1.318850
H 6.167721 -2.063231 2.227002
H 5.982076 -2.218459 0.482759
H 6.566457 -0.700001 1.179723
C 3.499149 -2.288554 1.702149
H 3.514524 -2.989425 0.867910
H 3.856234 -2.827268 2.590262
H 2.458985 -1.999893 1.873819
C 4.301090 -0.230961 2.793566
H 4.524022 -0.895466 3.638369
H 5.014791 0.594472 2.838212
H 3.292074 0.166236 2.944367
Zero-point correction= 0.749697

Thermal correction to Energy= 0.795356
Thermal correction to Enthalpy= 0.796300
Thermal correction to Gibbs Free Energy= 0.672410
Sum of electronic and thermal Energies= -7025.439651
Sum of electronic and thermal Enthalpies= -7025.438707
Sum of electronic and thermal Free Energies= -7025.562597

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7034.10415519

Intermediate 1

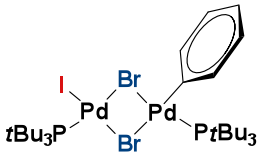


Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
C 4.816536 4.332379 0.302243
C 3.661116 2.498678 1.392774
C 3.279545 1.985783 0.146992
C 3.641925 2.671285 -1.019387
H 3.319052 2.310712 -1.992122
H 3.359221 1.999978 2.309749
C 4.412999 3.837070 -0.939422
C 4.431141 3.664536 1.466877
H 4.689934 4.359327 -1.852394
H 4.724302 4.051705 2.440066
H 4.045433 -4.323100 1.053687
C 4.600900 -3.600041 1.654263
C 3.948177 -2.200389 1.659634
H 5.634146 -3.588641 1.303012
H 4.611339 -3.980254 2.684752
P 3.869083 -1.305098 -0.068467
C 4.716263 -1.314094 2.664933
C 2.509592 -2.322543 2.211401
C 3.312677 -2.601532 -1.437420
C 5.694660 -0.748217 -0.542725
H 4.350485 -0.282588 2.667561
H 4.560670 -1.721824 3.672119
H 5.793453 -1.304996 2.485002
H 2.558958 -2.798142 3.200250
H 2.042959 -1.340439 2.332722
H 1.851749 -2.927073 1.587479
C 2.176533 -3.514478 -0.926544
C 2.729952 -1.788000 -2.618513
C 4.416919 -3.543720 -1.964795
C 6.166447 0.484062 0.266221
C 6.758561 -1.849851 -0.324986
C 5.715080 -0.298487 -2.021811
H 2.504498 -4.216149 -0.156857
H 1.321637 -2.953761 -0.553124
H 1.822501 -4.113171 -1.776095
H 3.460132 -1.127227 -3.089166
H 2.376364 -2.488618 -3.386792
H 1.876784 -1.181426 -2.300542
H 3.959691 -4.219086 -2.699936
H 5.230489 -3.025804 -2.473606
H 4.843438 -4.170521 -1.176442
H 5.639162 1.387788 -0.024882
H 6.077494 0.369431 1.344681
H 7.231178 0.633273 0.040904
H 6.512127 -2.810838 -0.774418
H 7.699045 -1.508439 -0.777417
H 6.960657 -2.009906 0.737552
H 5.595137 -1.117390 -2.732374
H 4.951057 0.457322 -2.222782
H 6.690217 0.163220 -2.224513
Pd 2.052707 0.402729 0.053723
Br -3.336873 2.794500 -0.436516

Pd -2.126336 0.663293 0.025442
Br -0.247330 -1.125391 0.074543
I 0.075212 2.333255 0.096347
H 5.414379 5.237887 0.362571
P -4.139972 -0.836425 0.086951
C -4.095373 -2.063945 1.614185
C -5.891087 0.064576 0.145869
C -4.053041 -1.865167 -1.572069
C -4.993339 -3.310249 1.443159
C -2.659041 -2.553471 1.884684
C -4.522553 -1.312151 2.894688
C -5.909136 1.148982 1.251164
C -6.154627 0.775479 -1.202069
C -7.084700 -0.879971 0.420509
C -2.967782 -2.959849 -1.486024
C -5.367106 -2.560763 -1.990716
C -3.613709 -0.891150 -2.692367
H -6.035739 -3.072277 1.232814
H -4.630165 -3.981114 0.660945
H -4.971302 -3.876486 2.384127
H -1.998814 -1.731080 2.163231
H -2.699623 -3.256159 2.728080
H -2.205970 -3.074556 1.042676
H -4.268550 -1.939782 3.758445
H -3.989556 -0.363025 3.011383
H -5.595763 -1.121918 2.943451
H -5.898969 0.732314 2.257651
H -5.088862 1.858039 1.150576
H -6.846372 1.711520 1.146124
H -6.324112 0.077502 -2.023904
H -7.070958 1.369946 -1.092985
H -5.350089 1.461373 -1.468504
H -8.002893 -0.286158 0.321050
H -7.162046 -1.712359 -0.280935
H -7.079286 -1.280459 1.436556
H -1.997809 -2.563008 -1.184994
H -3.240810 -3.776991 -0.814044
H -2.850270 -3.394507 -2.487608
H -6.171576 -1.862421 -2.225823
H -5.167853 -3.136987 -2.904075
H -5.730239 -3.265714 -1.238654
H -4.303922 -0.059647 -2.840245
H -2.624107 -0.470991 -2.488712
H -3.556106 -1.450400 -3.635943
Zero-point correction= 0.842399
Thermal correction to Energy= 0.895489
Thermal correction to Enthalpy= 0.896434
Thermal correction to Gibbs Free Energy= 0.754907
Sum of electronic and thermal Energies= -7268.364049
Sum of electronic and thermal Enthalpies= -7268.363105
Sum of electronic and thermal Free Energies= -7268.504632

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7277.19347163

Intermediate 2



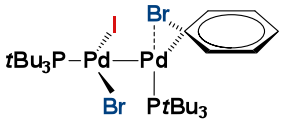
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
C 4.182102 4.538609 1.231447
C 3.119017 2.442998 1.833876
C 3.050562 2.081360 0.483380
C 3.520954 2.966387 -0.493519

H 3.435737 2.718921 -1.548063
H 2.727131 1.781869 2.601945
C 4.090457 4.188824 -0.116998
C 3.687235 3.666424 2.203979
H 4.453913 4.868928 -0.883965
H 3.736534 3.937808 3.256044
H 4.319426 -4.216481 0.516884
C 4.676773 -3.581341 1.330012
C 3.885471 -2.261323 1.452022
H 5.748087 -3.424630 1.194360
H 4.545852 -4.149533 2.260769
P 4.027822 -1.058572 -0.075104
C 4.355148 -1.533026 2.731113
C 2.393009 -2.593185 1.674305
C 3.883039 -2.101951 -1.733351
C 5.833496 -0.282679 -0.060247
H 3.885332 -0.550778 2.843687
H 4.062065 -2.139334 3.597919
H 5.439501 -1.410991 2.777879
H 2.311495 -3.237066 2.560549
H 1.806215 -1.688368 1.858014
H 1.932900 -3.119912 0.838763
C 2.770399 -3.167931 -1.634497
C 3.454358 -1.119308 -2.851270
C 5.159606 -2.850177 -2.177631
C 6.006136 0.804271 1.028721
C 6.953733 -1.322407 0.177263
C 6.085045 0.438094 -1.404322
H 3.023026 -3.989121 -0.960331
H 1.810737 -2.748742 -1.336804
H 2.635705 -3.603757 -2.633171
H 4.173421 -0.315974 -3.020765
H 3.357980 -1.679574 -3.790854
H 2.482906 -0.666099 -2.632319
H 4.918567 -3.412641 -3.089301
H 5.994031 -2.192088 -2.424620
H 5.498635 -3.576592 -1.433899
H 5.438679 1.702686 0.804357
H 5.740792 0.474770 2.031701
H 7.069542 1.078745 1.047723
H 6.904533 -2.192273 -0.475823
H 7.918178 -0.830131 -0.004891
H 6.968796 -1.670933 1.213334
H 6.178957 -0.240421 -2.252959
H 5.303226 1.170355 -1.621587
H 7.031803 0.987740 -1.323818
Pd 2.054710 0.428988 -0.051257
Pd -1.956801 0.480893 -0.131792
Br -0.054675 -1.221676 -0.721481
H 4.622401 5.488846 1.521635
P -3.834668 -1.068785 0.311383
C -3.350151 -2.244523 1.803550
C -5.554048 -0.236197 0.795161
C -4.113376 -2.142016 -1.292154
C -4.204390 -3.530159 1.889462
C -1.872693 -2.676950 1.714075
C -3.473162 -1.468524 3.134231
C -5.326510 0.894323 1.828460
C -6.207073 0.400770 -0.454048
C -6.588071 -1.210486 1.407903
C -2.994138 -3.193307 -1.461423
C -5.456507 -2.902036 -1.349916
C -4.011347 -1.181824 -2.501035
H -5.277385 -3.345436 1.929973
H -4.005511 -4.213298 1.060458
H -3.929897 -4.059733 2.811732
H -1.194722 -1.827567 1.808393
H -1.676258 -3.362026 2.550105
H -1.622556 -3.198269 0.791735
H -2.991693 -2.063309 3.920973
H -2.960826 -0.501720 3.095037

H -4.506467 -1.306788 3.444355
H -5.054847 0.519352 2.814881
H -4.572236 1.611431 1.507412
H -6.271537 1.441637 1.940163
H -6.564769 -0.339929 -1.171579
H -7.083212 0.970223 -0.118221
H -5.544439 1.100658 -0.962968
H -7.520933 -0.649954 1.551958
H -6.820646 -2.063313 0.767725
H -6.290668 -1.582653 2.390518
H -1.998037 -2.752193 -1.426098
H -3.052651 -3.997401 -0.723776
H -3.116029 -3.654812 -2.450057
H -6.326110 -2.244987 -1.384187
H -5.468961 -3.496824 -2.272702
H -5.581016 -3.597495 -0.516252
H -4.769895 -0.398243 -2.493814
H -3.031048 -0.697972 -2.542320
H -4.141672 -1.765886 -3.421872
Br 0.060769 2.060386 -0.105917
I -3.310319 2.794075 -0.673401
Zero-point correction= 0.842634
Thermal correction to Energy= 0.895696
Thermal correction to Enthalpy= 0.896640
Thermal correction to Gibbs Free Energy= 0.755550
Sum of electronic and thermal Energies= -7268.363713
Sum of electronic and thermal Enthalpies= -7268.362769
Sum of electronic and thermal Free Energies= -7268.503859

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7277.19575415

Reductive Elimination TS



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C	5.12946100	-3.49350900	0.07718900
C	3.68105500	-2.34536100	-1.49562700
C	2.68232800	-2.30848500	-0.51184500
C	2.85635500	-2.93691100	0.72904500
H	2.03793500	-2.96802100	1.44087500
H	3.49628700	-1.93968500	-2.48352900
C	4.09726700	-3.50115700	1.02341300
C	4.91633600	-2.91892500	-1.17776300
H	4.25053900	-3.96574200	1.99418600
H	5.70341300	-2.93175400	-1.92756300
Pd	1.56919100	-0.44620500	-0.51570700
Br	-0.66989000	0.71193800	-2.45651000
Pd	-1.20723200	-0.14776300	-0.13960100
H	6.08435600	-3.95648200	0.30935000
H	2.81637400	3.44035300	-3.11532800
C	2.39392000	3.16700200	-2.13904600
C	3.48710400	2.42220800	-1.33918900
H	1.51630100	2.54152700	-2.32413400
H	2.07353200	4.09523500	-1.66088500
P	2.71711800	1.62437500	0.27100800
C	4.66167800	3.39507500	-1.10798400
C	3.96220100	1.26950300	-2.25550400
C	1.61492200	2.97480300	1.14901300
C	4.16615500	1.16673400	1.49364300
H	5.54281100	2.90635700	-0.68574100
H	4.96223100	3.81350100	-2.07816800
H	4.39442400	4.23489000	-0.46265300
H	4.73397800	0.64450800	-1.80470000

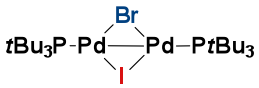
H	3.12169000	0.62641800	-2.53775900
H	4.37838300	1.70275100	-3.17537200
C	2.24374400	4.38456900	1.20499100
C	0.25883000	3.07239000	0.41735600
C	1.28054700	2.53368000	2.59189900
C	3.60918000	0.19514100	2.56069100
C	5.25826900	0.38916200	0.72885800
C	4.83895200	2.35528500	2.21277000
H	3.21500100	4.40204600	1.70327200
H	2.35832100	4.83381500	0.21614200
H	1.57224400	5.03916100	1.77710300
H	-0.28625400	2.12368600	0.46187300
H	-0.34908700	3.83450600	0.92500300
H	0.33653500	3.35512100	-0.63135500
H	0.51267900	3.21413500	2.98350800
H	0.86972500	1.52054800	2.63075400
H	2.13482900	2.59797300	3.26923900
H	2.87607200	0.65346800	3.22305800
H	3.14703100	-0.68123500	2.10296800
H	4.44562500	-0.15022800	3.18358500
H	5.81561100	1.01513000	0.02887400
H	5.98024600	0.00194200	1.45943900
H	4.85219500	-0.46747100	0.18762000
H	5.66817400	1.96657800	2.81944100
H	5.25909800	3.09140500	1.52336700
H	4.16184700	2.87254700	2.89622100
P	-3.64206900	0.24580600	0.02482800
C	-4.36377100	1.26207500	-1.49710500
C	-4.42387200	-1.54808800	-0.01503500
C	-4.24299900	1.16730300	1.64661400
C	-5.84907200	1.66827800	-1.34870600
C	-3.55631200	2.56464100	-1.71421100
C	-4.22827400	0.42265300	-2.78783200
C	-3.59516700	-2.39282800	-1.01216600
C	-4.29377800	-2.23857200	1.35951600
C	-5.91302800	-1.60318300	-0.42093700
C	-3.95094100	2.68004000	1.53231500
C	-5.74731100	0.97534100	1.95098600
C	-3.45335100	0.68250400	2.87773300
H	-6.51995800	0.82804900	-1.16547900
H	-6.00502800	2.41475100	-0.56700700
H	-6.15972600	2.13142200	-2.29448700
H	-2.49118300	2.37390800	-1.83720600
H	-3.91686500	3.02479300	-2.64377300
H	-3.69992700	3.29541600	-0.91948800
H	-4.50507400	1.06271900	-3.63558800
H	-3.20310400	0.08912500	-2.95444500
H	-4.89785300	-0.43950100	-2.80764200
H	-3.61118100	-2.00287900	-2.03076900
H	-2.55032900	-2.46755400	-0.69629800
H	-4.01395900	-3.40788200	-1.03628800
H	-4.94476000	-1.80242400	2.12086000
H	-4.60096700	-3.28546000	1.23692200
H	-3.26672400	-2.24216400	1.72919200
H	-6.24115100	-2.64864500	-0.35135800
H	-6.55605900	-1.01929400	0.24205800
H	-6.09235600	-1.28317600	-1.44880000
H	-2.92081200	2.87809500	1.22050800
H	-4.63037600	3.20015300	0.85490100
H	-4.08459300	3.12724000	2.52577600
H	-5.98559800	-0.05304800	2.23115000
H	-5.99975100	1.60696700	2.81321400
H	-6.40392000	1.26855900	1.13189900
H	-3.51909800	-0.39082500	3.04703500
H	-2.39618200	0.94063600	2.80715100
H	-3.86676100	1.18639100	3.76197200
Br	0.62641600	-2.60180700	-1.39913400
I	-0.58444700	-1.34349700	2.23911300

Zero-point correction= 0.840423
Thermal correction to Energy= 0.893375
Thermal correction to Enthalpy= 0.894320

Thermal correction to Gibbs Free Energy= 0.754120
Sum of electronic and thermal Energies= -7268.323168
Sum of electronic and thermal Enthalpies= -7268.322224
Sum of electronic and thermal Free Energies= -7268.462423

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -7277.17200337

Pd(I)-Br-I-dimer 3

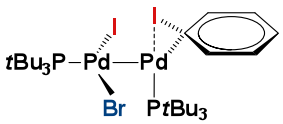


Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
Pd -1.343840 0.019984 -0.055871
P -3.714922 -0.162181 -0.011668
C -4.146485 -1.015895 1.686859
C -4.608552 1.569113 -0.089792
C -4.383663 -1.268685 -1.469320
Br -0.000003 -2.180445 -0.000205
Pd 1.343840 0.019982 0.055477
P 3.714928 -0.162223 0.011781
C 4.608513 1.569075 0.090191
C 4.383340 -1.268763 1.469557
C 4.146891 -1.015795 -1.686719
C -3.972010 2.418712 -1.216360
H -4.398481 3.429499 -1.166539
H -2.890044 2.505003 -1.094018
H -4.171377 2.033712 -2.216268
C -6.133376 1.511969 -0.322613
H -6.660448 0.921977 0.430611
H -6.533169 2.534026 -0.276075
H -6.390747 1.115875 -1.308453
C -4.337582 2.337916 1.222784
H -4.864862 1.917338 2.081860
H -3.268667 2.387763 1.451979
H -4.695357 3.368181 1.099174
C -3.234149 -0.399232 2.776661
H -3.428996 0.657325 2.961425
H -3.408415 -0.936070 3.719064
H -2.176048 -0.508443 2.516542
C -5.617089 -0.900304 2.136457
H -5.742027 -1.458179 3.074380
H -5.914992 0.131586 2.337663
H -6.317749 -1.323476 1.411956
C -3.768404 -2.512256 1.623227
H -2.735916 -2.657148 1.291671
H -3.851029 -2.929619 2.635277
H -4.433199 -3.095572 0.981988
C -4.361865 -0.456608 -2.782972
H -4.552338 -1.144753 -3.616711
H -5.134216 0.314453 -2.821359
H -3.387025 0.010017 -2.957816
C -3.406089 -2.446887 -1.690149
H -3.341422 -3.125889 -0.840301
H -3.759988 -3.029989 -2.551340
H -2.395525 -2.093962 -1.910343
C -5.804976 -1.832774 -1.262305
H -6.096787 -2.390008 -2.162907
H -5.857553 -2.531561 -0.423922
H -6.554812 -1.053900 -1.104755
C 4.337798 2.337936 -1.222407
H 3.268924 2.387824 -1.451786
H 4.695584 3.368186 -1.098697
H 4.865211 1.917371 -2.081409
C 6.133285 1.511953 0.323345
H 6.533070 2.534019 0.276923
H 6.390440 1.115839 1.309233

H 6.660535 0.921990 -0.429776
C 3.971702 2.418590 1.216669
H 2.889768 2.504906 1.094062
H 4.170810 2.033499 2.216595
H 4.398200 3.429376 1.167043
C 3.235304 -0.398501 -2.776788
H 3.430665 0.658024 -2.961201
H 3.409782 -0.935179 -3.719243
H 2.177040 -0.507345 -2.517177
C 3.768170 -2.512014 -1.623610
H 2.735491 -2.656565 -1.292501
H 3.851022 -2.929153 -2.635733
H 4.432476 -3.095768 -0.982262
C 5.617742 -0.900709 -2.135641
H 5.742864 -1.458426 -3.073633
H 5.916161 0.131102 -2.336483
H 6.317904 -1.324334 -1.410924
C 5.804289 -1.833719 1.262394
H 6.095956 -2.390913 2.163067
H 5.856298 -2.532728 0.424161
H 6.554545 -1.055316 1.104516
C 3.405131 -2.446338 1.690933
H 3.339951 -3.125606 0.841341
H 3.758826 -3.029336 2.552278
H 2.394799 -2.092763 1.911154
C 4.362289 -0.456319 2.782995
H 4.552467 -1.144360 3.616887
H 5.135140 0.314258 2.821037
H 3.387780 0.010983 2.957880
I -0.000034 2.437408 -0.000093
Zero-point correction= 0.748820
Thermal correction to Energy= 0.794835
Thermal correction to Enthalpy= 0.795779
Thermal correction to Gibbs Free Energy= 0.670891
Sum of electronic and thermal Energies= -4465.421422
Sum of electronic and thermal Enthalpies= -4465.420478
Sum of electronic and thermal Free Energies= -4465.545366

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -4471.50376554

2nd Oxidative Addition TS



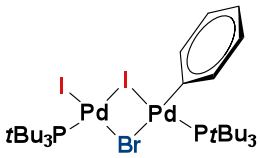
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
C 5.129001 -3.072520 1.390354
C 3.816078 -2.494996 -0.566376
C 2.696570 -2.310461 0.261202
C 2.767228 -2.565403 1.639782
H 1.877207 -2.471425 2.253291
H 3.733329 -2.372963 -1.640241
C 3.994963 -2.922564 2.196860
C 5.035773 -2.856932 0.013952
H 4.059174 -3.099949 3.267414
H 5.907796 -2.987867 -0.621853
Pd 1.588446 -0.485025 -0.238947
Pd -1.197995 -0.078851 0.002999
Br -0.432322 -0.625682 2.345675
I 0.644276 -2.992318 -0.791561
H 6.074303 -3.376144 1.831284
H 2.937475 2.804305 -3.592864
C 2.460072 2.745635 -2.605606
C 3.509773 2.229472 -1.596026
H 1.604106 2.071137 -2.695504
H 2.096835 3.747971 -2.368313

P 2.645369 1.781805 0.096866
C 4.650056 3.265715 -1.514804
C 4.063333 0.918483 -2.203723
C 1.480221 3.266111 0.593551
C 4.026388 1.649479 1.474880
H 5.508415 2.907887 -0.941846
H 5.008266 3.469956 -2.533092
H 4.328183 4.218495 -1.088109
H 4.827089 0.441266 -1.588287
H 3.256029 0.197241 -2.369900
H 4.516377 1.148060 -3.177823
C 2.085730 4.671118 0.381661
C 0.172686 3.176212 -0.221115
C 1.062860 3.127463 2.075420
C 3.423322 0.916748 2.695337
C 5.180854 0.763733 0.959545
C 4.630009 2.986526 1.953538
H 3.032734 4.817162 0.904139
H 2.237913 4.906026 -0.674277
H 1.378537 5.414063 0.774872
H -0.360564 2.241394 -0.016962
H -0.478201 4.008543 0.081294
H 0.312249 3.242221 -1.299130
H 0.253431 3.844305 2.268212
H 0.681503 2.128058 2.305723
H 1.870062 3.369160 2.770127
H 2.684708 1.511236 3.231649
H 2.951779 -0.024315 2.408117
H 4.235348 0.688689 3.399181
H 5.766141 1.241659 0.170869
H 5.865665 0.570627 1.795610
H 4.829502 -0.204102 0.597716
H 5.421841 2.766317 2.682520
H 5.084801 3.564438 1.145540
H 3.898886 3.620207 2.459895
P -3.622685 0.267201 0.406786
C -4.650542 0.811369 -1.181050
C -4.284760 -1.484175 0.984053
C -4.013898 1.585339 1.804478
C -6.122727 1.197565 -0.901393
C -3.992094 2.035098 -1.863193
C -4.651877 -0.348129 -2.202960
C -3.560839 -2.555001 0.135022
C -3.904002 -1.758013 2.454705
C -5.811063 -1.680869 0.856203
C -3.847276 3.011541 1.235799
C -5.435288 1.455668 2.399113
C -3.008637 1.473777 2.968317
H -6.695719 0.421381 -0.392977
H -6.211673 2.125478 -0.331781
H -6.606263 1.376033 -1.871016
H -2.926103 1.898907 -2.037629
H -4.466236 2.168228 -2.844322
H -4.142630 2.960508 -1.307857
H -5.096901 0.021375 -3.135619
H -3.645586 -0.695624 -2.441989
H -5.254679 -1.197821 -1.876435
H -3.743739 -2.458696 -0.936074
H -2.480272 -2.521449 0.298517
H -3.919164 -3.545127 0.447605
H -4.473884 -1.150608 3.161750
H -4.141843 -2.808007 2.670318
H -2.838007 -1.615741 2.639432
H -6.054469 -2.679020 1.243626
H -6.381836 -0.958935 1.445730
H -6.165072 -1.644147 -0.175151
H -2.902178 3.135005 0.698565
H -4.667036 3.307283 0.579062
H -3.841693 3.715078 2.078192
H -5.559943 0.538539 2.978555
H -5.590161 2.294197 3.091297

H -6.229039 1.500652 1.653382
H -2.994512 0.494189 3.442747
H -1.990426 1.697586 2.649147
H -3.298799 2.211430 3.729246
I -0.883224 0.174956 -2.712223
Zero-point correction= 0.840282
Thermal correction to Energy= 0.893424
Thermal correction to Enthalpy= 0.894369
Thermal correction to Gibbs Free Energy= 0.753868
Sum of electronic and thermal Energies= -4708.301319
Sum of electronic and thermal Enthalpies= -4708.300375
Sum of electronic and thermal Free Energies= -4708.440875

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -4714.57115173

Intermediate 3

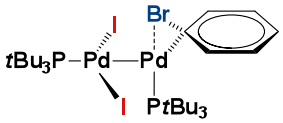


Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
C 4.651622 4.371239 0.972714
C 3.423837 2.407155 1.693794
C 3.261309 2.007429 0.361644
C 3.770586 2.812877 -0.664914
H 3.619925 2.538572 -1.705467
H 3.003984 1.814590 2.501910
C 4.467183 3.987838 -0.357289
C 4.121158 3.581781 1.995576
H 4.859070 4.604429 -1.162996
H 4.242524 3.880709 3.034252
H 4.103823 -4.309503 0.875260
C 4.511406 -3.618128 1.615326
C 3.816167 -2.239278 1.596818
H 5.590140 -3.554235 1.463928
H 4.348935 -4.073544 2.601626
P 4.010447 -1.221928 -0.053127
C 4.363262 -1.412477 2.781347
C 2.308102 -2.439782 1.869878
C 3.750617 -2.426622 -1.583658
C 5.867641 -0.586250 -0.158276
H 3.967967 -0.392301 2.792498
H 4.048989 -1.897852 3.714410
H 5.454411 -1.366159 2.796042
H 2.198189 -2.963593 2.829007
H 1.783552 -1.482319 1.943742
H 1.803647 -3.034005 1.108450
C 2.581877 -3.407552 -1.342939
C 3.348539 -1.541135 -2.788555
C 4.964048 -3.298716 -1.976729
C 6.152016 0.591118 0.806876
C 6.916250 -1.676473 0.164742
C 6.130062 -0.025029 -1.575176
H 2.814195 -4.168422 -0.595169
H 1.658146 -2.905614 -1.061208
H 2.388398 -3.933810 -2.286867
H 4.110887 -0.808410 -3.058557
H 3.188659 -2.187963 -3.661528
H 2.414555 -1.005756 -2.594585
H 4.661919 -3.931799 -2.821421
H 5.830811 -2.724979 -2.306281
H 5.276165 -3.969027 -1.170664
H 5.663757 1.508581 0.490369
H 5.873272 0.396465 1.840491

H 7.235763 0.769593 0.789902
H 6.784431 -2.605596 -0.387062
H 7.907926 -1.280888 -0.091932
H 6.937979 -1.911345 1.232486
H 6.159672 -0.788662 -2.353939
H 5.391264 0.731995 -1.852754
H 7.111529 0.466697 -1.569855
Pd 2.133146 0.414230 -0.094872
Pd -2.027987 0.470246 -0.118509
Br -0.056309 -1.125762 -0.772778
H 5.191648 5.284082 1.209519
P -3.845835 -1.204501 0.271385
C -3.304098 -2.455630 1.681118
C -5.593465 -0.484414 0.821973
C -4.098045 -2.179798 -1.399447
C -4.093427 -3.784965 1.679356
C -1.807472 -2.806835 1.561465
C -3.458469 -1.781070 3.062970
C -5.404052 0.582386 1.927980
C -6.288528 0.201587 -0.377449
C -6.578493 -1.542908 1.373293
C -2.923468 -3.149342 -1.651207
C -5.398960 -3.005985 -1.497569
C -4.065318 -1.135980 -2.541719
H -5.174547 -3.656664 1.729099
H -3.861645 -4.401852 0.807737
H -3.792365 -4.359844 2.565599
H -1.173212 -1.933168 1.718609
H -1.573792 -3.540564 2.345083
H -1.534113 -3.245377 0.603273
H -2.943804 -2.404829 3.805099
H -2.994952 -0.789618 3.089877
H -4.496644 -1.692730 3.386061
H -5.121426 0.150457 2.887581
H -4.671640 1.342143 1.658275
H -6.365723 1.091209 2.073583
H -6.621698 -0.510177 -1.134764
H -7.184790 0.709303 0.001320
H -5.664565 0.960138 -0.849359
H -7.533469 -1.035558 1.563751
H -6.781387 -2.358272 0.676419
H -6.255561 -1.969852 2.324735
H -1.954791 -2.652163 -1.597719
H -2.921974 -4.000890 -0.966665
H -3.032368 -3.552849 -2.666376
H -6.303189 -2.396447 -1.471973
H -5.394420 -3.529545 -2.462780
H -5.473868 -3.768120 -0.717808
H -4.871729 -0.403852 -2.483139
H -3.118433 -0.587945 -2.553154
H -4.163452 -1.664897 -3.499157
I -3.515570 2.738794 -0.473267
I 0.075314 2.267697 -0.056914
Zero-point correction= 0.842520
Thermal correction to Energy= 0.895723
Thermal correction to Enthalpy= 0.896667
Thermal correction to Gibbs Free Energy= 0.755051
Sum of electronic and thermal Energies= -4708.341168
Sum of electronic and thermal Enthalpies= -4708.340224
Sum of electronic and thermal Free Energies= -4708.481839

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -4714.59050163

2nd Reductive Elimination TS



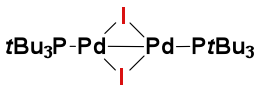
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C 5.133260 -3.546498 -0.232787
C 3.638396 -2.268004 -1.653960
C 2.684481 -2.288533 -0.626555
C 2.900678 -3.007879 0.557024
H 2.111766 -3.081555 1.298006
H 3.416912 -1.790921 -2.601515
C 4.142888 -3.610363 0.754897
C 4.876829 -2.878383 -1.432448
H 4.329321 -4.148501 1.680798
H 5.631237 -2.846848 -2.214476
Pd 1.601512 -0.424548 -0.451587
Pd -1.234268 -0.158121 -0.112902
H 6.089416 -4.038051 -0.077037
H 3.145530 3.583711 -2.748896
C 2.674963 3.257038 -1.812054
C 3.707061 2.417365 -1.026893
H 1.787121 2.676963 -2.076969
H 2.362631 4.158551 -1.281226
P 2.838148 1.530605 0.483495
C 4.903517 3.327074 -0.675525
C 4.182860 1.320868 -2.008309
C 1.740084 2.853076 1.407007
C 4.217715 0.936095 1.727859
H 5.749522 2.773365 -0.261753
H 5.256628 3.806375 -1.598795
H 4.642262 4.125273 0.023351
H 4.913074 0.634980 -1.577626
H 3.334717 0.732499 -2.371814
H 4.651840 1.806780 -2.874920
C 2.400812 4.238457 1.580700
C 0.418309 3.028912 0.628126
C 1.337481 2.332309 2.804720
C 3.587592 -0.081547 2.707305
C 5.314893 0.173983 0.954048
C 4.895090 2.053753 2.548470
H 3.351429 4.196582 2.116789
H 2.567733 4.749130 0.630046
H 1.722962 4.872446 2.168226
H -0.138708 2.087145 0.571202
H -0.204369 3.756636 1.167010
H 0.546818 3.394877 -0.389676
H 0.575036 3.010209 3.211055
H 0.897952 1.331939 2.763691
H 2.167259 2.328030 3.514576
H 2.848985 0.360346 3.374513
H 3.109252 -0.907287 2.178237
H 4.388230 -0.498826 3.333142
H 5.923725 0.826979 0.325128
H 5.990450 -0.289865 1.684325
H 4.905559 -0.627377 0.335879
H 5.691568 1.603256 3.156286
H 5.358502 2.821954 1.925434
H 4.205799 2.542733 3.240335
P -3.675355 0.200385 0.227943
C -4.528513 1.227464 -1.216708
C -4.440059 -1.604046 0.220782
C -4.169265 1.092567 1.901512
C -6.012419 1.594613 -0.976444
C -3.776036 2.563055 -1.443584
C -4.459080 0.409230 -2.526812
C -3.666366 -2.430875 -0.833380
C -4.226806 -2.306548 1.579043
C -5.950591 -1.670943 -0.094637

C -3.907931 2.610277 1.779614
C -5.644881 0.875407 2.311300
C -3.285349 0.605716 3.065183
H -6.658497 0.734095 -0.799811
H -6.143052 2.302485 -0.155510
H -6.377369 2.093811 -1.883942
H -2.693149 2.450356 -1.444655
H -4.060101 2.950093 -2.430089
H -4.050081 3.322639 -0.711526
H -4.797060 1.053743 -3.348107
H -3.445612 0.086002 -2.767472
H -5.116899 -0.462039 -2.513468
H -3.767936 -2.042332 -1.847960
H -2.599699 -2.480821 -0.594938
H -4.061633 -3.455569 -0.828180
H -4.837049 -1.881577 2.379328
H -4.534826 -3.353920 1.463453
H -3.181650 -2.307524 1.892325
H -6.263920 -2.720288 -0.015929
H -6.556166 -1.099975 0.613283
H -6.195129 -1.342133 -1.105902
H -2.916602 2.828033 1.370220
H -4.657833 3.126688 1.178169
H -3.950564 3.045128 2.786450
H -5.845159 -0.156598 2.607364
H -5.847303 1.503761 3.189047
H -6.362323 1.154819 1.539754
H -3.331341 -0.469397 3.230194
H -2.238548 0.872605 2.915327
H -3.634203 1.100000 3.982129
Br 0.577636 -2.495763 -1.426705
I -0.501567 -1.459645 2.197680
I -0.704027 0.894441 -2.610855
Zero-point correction= 0.840339
Thermal correction to Energy= 0.893516
Thermal correction to Enthalpy= 0.894461
Thermal correction to Gibbs Free Energy= 0.753496
Sum of electronic and thermal Energies= -4708.297711
Sum of electronic and thermal Enthalpies= -4708.296767
Sum of electronic and thermal Free Energies= -4708.437732

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -4714.56835414

Pd(I)-I-dimer 2



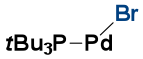
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
Pd -1.362754 0.057195 -0.058698
P -3.753235 -0.012235 -0.013927
C -4.236958 -0.828832 1.690867
C -4.555894 1.765852 -0.096339
C -4.497883 -1.082692 -1.462082
Pd 1.362753 0.057231 0.058850
P 3.753243 -0.012175 0.014237
C 4.555873 1.765943 0.096411
C 4.497809 -1.082529 1.462515
C 4.237068 -0.828989 -1.690415
C -3.889783 2.573819 -1.236107
H -4.263528 3.605396 -1.188859
H -2.803773 2.605917 -1.128050
H -4.121600 2.192484 -2.230255
C -6.083203 1.787803 -0.317872
H -6.635709 1.224474 0.436763
H -6.428028 2.829416 -0.266747
H -6.365384 1.407984 -1.303195

C -4.232410 2.528728 1.208094
H -4.771422 2.143154 2.076272
H -3.160221 2.524524 1.426557
H -4.537521 3.575193 1.079569
C -3.276437 -0.270901 2.770421
H -3.384856 0.801157 2.935997
H -3.491304 -0.776026 3.721955
H -2.231170 -0.469081 2.511107
C -5.693395 -0.607197 2.149319
H -5.850413 -1.153009 3.089524
H -5.918109 0.442913 2.350535
H -6.426293 -0.983033 1.430424
C -3.975371 -2.350266 1.642100
H -2.956759 -2.579824 1.317665
H -4.093061 -2.749024 2.658186
H -4.680919 -2.887670 1.004452
C -4.431899 -0.282633 -2.781953
H -4.657234 -0.966265 -3.610728
H -5.163013 0.527323 -2.827542
H -3.434015 0.131517 -2.958887
C -3.599003 -2.321331 -1.682301
H -3.552103 -2.987561 -0.821170
H -4.008085 -2.897680 -2.523079
H -2.576292 -2.031567 -1.935489
C -5.951658 -1.554771 -1.246941
H -6.279657 -2.098541 -2.143300
H -6.047874 -2.243085 -0.404020
H -6.650769 -0.729383 -1.094492
C 4.232788 2.528422 -1.208354
H 3.160663 2.524168 -1.427132
H 4.537879 3.574921 -1.080066
H 4.772049 2.142566 -2.076254
C 6.083117 1.787970 0.318385
H 6.427959 2.829565 0.267000
H 6.365009 1.408494 1.303922
H 6.635844 1.224379 -0.435891
C 3.889414 2.574287 1.235712
H 2.803432 2.606303 1.127350
H 4.120975 2.193331 2.230062
H 4.263128 3.605863 1.188191
C 3.276477 -0.271340 -2.770050
H 3.384765 0.800706 -2.935785
H 3.491398 -0.776581 -3.721510
H 2.231236 -0.469608 -2.510698
C 3.975648 -2.350444 -1.641373
H 2.957057 -2.580060 -1.316918
H 4.093409 -2.749381 -2.657381
H 4.681240 -2.887651 -1.003604
C 5.693481 -0.607273 -2.148907
H 5.850555 -1.153223 -3.089022
H 5.918083 0.442830 -2.350296
H 6.426422 -0.982911 -1.429951
C 5.951852 -1.553980 1.247828
H 6.279739 -2.097777 2.144211
H 6.048658 -2.242102 0.404820
H 6.650684 -0.728283 1.095783
C 3.599371 -2.321590 1.682157
H 3.553067 -2.987658 0.820866
H 4.008389 -2.897943 2.522963
H 2.576445 -2.032314 1.935029
C 4.430990 -0.282762 2.782518
H 4.656268 -0.966478 3.611241
H 5.161767 0.527469 2.828567
H 3.432871 0.130951 2.959145
I -0.000043 2.453558 -0.000334
I 0.000044 -2.342398 -0.000445
Zero-point correction= 0.749230
Thermal correction to Energy= 0.795202
Thermal correction to Enthalpy= 0.796146
Thermal correction to Gibbs Free Energy= 0.671095
Sum of electronic and thermal Energies= -1905.401166

Sum of electronic and thermal Enthalpies= -1905.400221
Sum of electronic and thermal Free Energies= -1905.525273

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E =-1908.90237234

Pd(I)-Br-radical

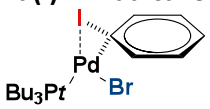


Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd
Pd 1.163390 -1.002780 0.019257
C -2.240476 2.133572 -1.589730
C -0.851441 1.596193 -1.186933
H -2.846469 2.429065 -0.729495
H -2.102782 3.025221 -2.215318
H -2.813794 1.414362 -2.180218
P -0.909182 0.062291 -0.002379
C -0.046681 2.733704 -0.519460
C -0.057214 1.211122 -2.459555
C -2.220335 -1.224918 -0.634753
C -1.354733 0.629587 1.799249
H 0.941460 2.396145 -0.191695
H 0.105993 3.523014 -1.266386
H -0.570908 3.188700 0.323673
H 0.039719 2.108730 -3.084349
H 0.949904 0.864782 -2.208983
H -0.545946 0.447149 -3.064195
C -2.064175 -1.416518 -2.159497
C -1.871170 -2.594508 -0.001290
C -3.691448 -0.876040 -0.331914
C -0.089763 1.248111 2.443610
C -2.519633 1.636508 1.889911
C -1.701681 -0.607928 2.656427
H -2.401789 -0.552571 -2.735190
H -1.030075 -1.641758 -2.439134
H -2.683010 -2.270258 -2.464354
H -1.984990 -2.617477 1.082060
H -2.538607 -3.358828 -0.420855
H -0.841289 -2.892630 -0.240792
H -4.336890 -1.649536 -0.769446
H -3.906882 -0.847346 0.738958
H -3.990992 0.081434 -0.766604
H 0.754822 0.553195 2.416207
H -0.315498 1.475101 3.493991
H -3.443337 1.260629 1.441474
H -2.728558 1.838350 2.948907
H -2.278302 2.595260 1.424612
H -2.652994 -1.068914 2.382115
H -0.913210 -1.366753 2.613847
H -1.789091 -0.287517 3.702212
H 0.229052 2.175241 1.969163
Br 3.316250 0.215927 -0.001335
Zero-point correction= 0.373679
Thermal correction to Energy= 0.395824
Thermal correction to Enthalpy= 0.396768
Thermal correction to Gibbs Free Energy= 0.322415
Sum of electronic and thermal Energies= -3512.693714
Sum of electronic and thermal Enthalpies= -3512.692769
Sum of electronic and thermal Free Energies= -3512.767122

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E =- -3517.02180080

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

Pd(I)-Br-radical oxidative addition TS



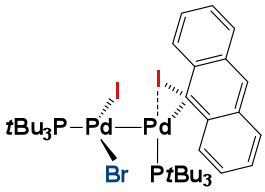
Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C -4.843416 -1.668172 -0.317837
C -3.185586 -0.253036 -1.369187
C -2.677842 0.062678 -0.090951
C -3.326862 -0.396366 1.074893
H -2.970279 -0.091624 2.052608
Pd -0.527298 -0.131868 -0.069228
H -2.733758 0.173586 -2.258429
C -4.387465 -1.285376 0.950313
C -4.243216 -1.151488 -1.472042
H -4.860733 -1.684534 1.843170
H -4.606855 -1.442690 -2.453729
C 4.032776 2.119418 -0.406108
C 2.522128 1.875150 -0.196870
H 4.381683 1.759090 -1.376663
H 4.212341 3.202917 -0.386169
H 4.655265 1.672226 0.370439
P 1.975675 0.000433 -0.054118
C 1.776298 2.541551 -1.378260
C 2.083524 2.626152 1.081463
C 2.591532 -0.683889 1.667364
C 2.868386 -0.981011 -1.483332
H 0.698740 2.378702 -1.333220
H 1.949868 3.624645 -1.328629
H 2.130923 2.204013 -2.351216
H 2.240768 3.700899 0.922147
H 1.023228 2.480510 1.304342
H 2.665643 2.345072 1.961136
C 1.541896 -0.274515 2.728715
C 2.613333 -2.229280 1.663625
C 3.985481 -0.193722 2.113471
C 2.685704 -0.235380 -2.824462
C 4.379681 -1.205320 -1.255553
C 2.190444 -2.355724 -1.671764
H 1.435656 0.805375 2.843559
H 0.560833 -0.693528 2.485859
H 1.851324 -0.681400 3.700805
H 3.411740 -2.643556 1.043616
H 2.802430 -2.562929 2.692683
H 1.656779 -2.651727 1.348167
H 4.238791 -0.693565 3.057833
H 4.770242 -0.443729 1.394673
H 4.022591 0.881130 2.303323
H 1.640717 0.034422 -3.008877
H 2.997348 -0.907946 -3.633682
H 4.580395 -1.862910 -0.407017
H 4.794074 -1.697300 -2.145938
H 4.935647 -0.277510 -1.107865
H 2.244901 -2.993673 -0.791359
H 1.134908 -2.256101 -1.930438
H 2.701999 -2.874397 -2.494167
H 3.301582 0.663129 -2.902055
Br -0.763917 -2.655576 0.183645
H -5.680305 -2.355122 -0.405912
I -1.857955 2.340059 0.107147
Zero-point correction= 0.464359
Thermal correction to Energy= 0.493644
Thermal correction to Enthalpy= 0.494588
Thermal correction to Gibbs Free Energy= 0.403573
Sum of electronic and thermal Energies= -3755.608028
Sum of electronic and thermal Enthalpies= -3755.607084
Sum of electronic and thermal Free Energies= -3755.698098

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E= -3760.10007984

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

Mixed Pd(I)-I-Br-Dimer oxidative addition to iodoanthracene



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

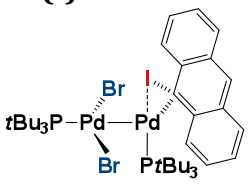
C -5.596391 -1.794883 0.274128
C -3.461826 -1.538887 1.475291
C -2.795610 -1.555816 0.217861
C -3.489390 -1.803870 -0.999910
C -4.933188 -1.893143 -0.954099
C -4.906918 -1.631622 1.480355
Pd -1.250397 -0.011568 0.055071
Br 0.966363 0.136680 2.473413
Pd 1.637938 -0.154204 0.056826
I -0.644720 -2.663045 0.309373
H -6.681059 -1.875561 0.294684
H -1.228676 3.741925 3.386773
C -0.973833 3.506939 2.344544
C -2.286541 3.166750 1.602033
H -0.279538 2.662316 2.362627
H -0.464177 4.383432 1.938483
P -1.897037 2.434339 -0.165593
C -3.191267 4.416698 1.621479
C -2.954742 2.050692 2.432906
C -0.573676 3.596689 -1.004808
C -3.523993 2.533417 -1.238877
H -4.202666 4.211634 1.262467
H -3.284999 4.759249 2.660931
H -2.785203 5.248552 1.041177
H -3.917147 1.725371 2.036030
H -2.303059 1.177440 2.504371
H -3.128301 2.426395 3.450530
C -0.816860 5.110263 -0.814298
C 0.819583 3.249943 -0.436541
C -0.499688 3.310038 -2.521076
C -3.327838 1.642577 -2.487658
C -4.693557 1.915761 -0.441267
C -3.949457 3.940608 -1.707652
H -1.795174 5.435486 -1.173730
H -0.712223 5.428400 0.225265
H -0.059369 5.656177 -1.393205
H 1.082299 2.206165 -0.637846
H 1.563638 3.884813 -0.937636
H 0.910195 3.415636 0.636237
H 0.381294 3.827544 -2.923249
H -0.375436 2.245617 -2.737599
H -1.366834 3.689870 -3.065789
H -2.623561 2.061320 -3.206011
H -2.980284 0.643249 -2.221494
H -4.293977 1.536698 -2.998998
H -5.026809 2.545229 0.386936
H -5.548545 1.795845 -1.119149
H -4.448136 0.926223 -0.049291
H -4.900256 3.851032 -2.250894
H -4.110747 4.638193 -0.883069
H -3.230824 4.386324 -2.398944
P 4.143747 -0.099555 0.219276
C 4.796981 0.347323 2.021708
C 4.696770 -1.934157 -0.179138
C 5.062180 1.115151 -1.018659
C 6.326970 0.553071 2.122169
C 4.129565 1.649692 2.525718
C 4.402262 -0.775236 3.008224
C 3.657065 -2.881485 0.463900
C 4.652852 -2.202185 -1.698642

C 6.105735 -2.319678 0.321032
C 4.958383 2.569390 -0.507884
C 6.554506 0.773589 -1.235324
C 4.376504 1.111065 -2.399096
H 6.911650 -0.300650 1.776436
H 6.666391 1.445106 1.591085
H 6.570549 0.704403 3.182182
H 3.042949 1.578466 2.524888
H 4.448831 1.805671 3.564921
H 4.430349 2.532300 1.962824
H 4.636788 -0.429708 4.023436
H 3.332810 -0.989169 2.978511
H 4.962765 -1.698832 2.848891
H 3.577438 -2.772127 1.546241
H 2.664256 -2.720339 0.034499
H 3.953105 -3.917713 0.251577
H 5.449896 -1.692654 -2.244882
H 4.796274 -3.279682 -1.853499
H 3.691921 -1.933413 -2.141386
H 6.310872 -3.346289 -0.009967
H 6.892143 -1.684751 -0.093424
H 6.192414 -2.313312 1.408889
H 3.930627 2.842867 -0.250289
H 5.603207 2.772343 0.348701
H 5.281913 3.235877 -1.317803
H 6.689593 -0.165998 -1.775009
H 6.995593 1.564307 -1.857002
H 7.132956 0.726466 -0.312792
H 4.321406 0.126685 -2.860316
H 3.361943 1.507741 -2.348288
H 4.960230 1.760405 -3.066010
C -5.603008 -1.582083 2.728924
C -2.797465 -1.442850 2.736012
C -5.656541 -2.101718 -2.169862
C -2.853055 -1.968099 -2.267788
H -6.688880 -1.637508 2.711607
H -1.715557 -1.370983 2.754180
C -3.503744 -1.422853 3.913121
C -4.924879 -1.484174 3.914251
H -5.465909 -1.458718 4.856150
H -2.968761 -1.352611 4.856011
H -1.771993 -1.907134 -2.324894
H -6.741530 -2.152464 -2.117192
C -5.005172 -2.246628 -3.365757
C -3.585060 -2.185997 -3.409010
H -3.070354 -2.309294 -4.357671
H -5.566973 -2.413328 -4.280683
I 1.207484 -0.550849 -2.626342
Zero-point correction= 0.935139
Thermal correction to Energy= 0.993206
Thermal correction to Enthalpy= 0.994150
Thermal correction to Gibbs Free Energy= 0.844106
Sum of electronic and thermal Energies= -5015.472688
Sum of electronic and thermal Enthalpies= -5015.471744
Sum of electronic and thermal Free Energies= -5015.621788

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E = -5021.89100340

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

Pd(I)-Br-Dimer oxidative addition to iodoanthracene



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

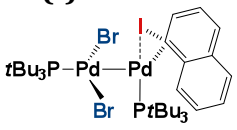
C	-5.56318700	-1.76688400	-0.03216300
C	-3.48588500	-1.59238300	1.27898900
C	-2.76183700	-1.57079900	0.05532000
C	-3.39726000	-1.75640800	-1.20339900
C	-4.84262800	-1.82611900	-1.23042800
C	-4.93097700	-1.66139700	1.21128000
Pd	-1.22148700	-0.03170100	0.03948500
Br	1.10938500	-0.00307400	2.46676800
Pd	1.63619700	-0.15708100	0.01345900
Br	1.18519300	-0.37888200	-2.44945600
I	-0.62335400	-2.70028400	0.19963600
H	-6.64851700	-1.83205000	-0.06693600
H	-1.22532100	3.57413000	3.52323000
C	-0.93515300	3.38959600	2.48010400
C	-2.22245200	3.09834700	1.67461600
H	-0.24367000	2.54193000	2.48011600
H	-0.40905500	4.28272800	2.13539400
P	-1.77397500	2.43650700	-0.10835400
C	-3.11177200	4.35880100	1.71364200
C	-2.93649200	1.95769200	2.43136600
C	-0.40947700	3.62044200	-0.84792100
C	-3.36101500	2.59873100	-1.23650700
H	-4.11117000	4.18249900	1.30910400
H	-3.24067500	4.65961000	2.76221900
H	-2.67435000	5.20842800	1.18427300
H	-3.88222300	1.65709300	1.97931800
H	-2.29634500	1.07535100	2.49803400
H	-3.15253700	2.29582000	3.45404200
C	-0.66159500	5.12750200	-0.62245700
C	0.95739000	3.26260500	-0.22712900
C	-0.26390400	3.36995600	-2.36536800
C	-3.13736800	1.75052500	-2.50918800
C	-4.57011600	1.97398900	-0.50494900
C	-3.74746700	4.02891900	-1.66776400
H	-1.62015200	5.46835800	-1.01797900
H	-0.60677300	5.40892500	0.43154800
H	0.12449800	5.68990400	-1.14471600
H	1.23273300	2.22518800	-0.44264900
H	1.71924600	3.91243300	-0.67985900
H	1.00160900	3.40168800	0.85188400
H	0.62957200	3.90505000	-2.71402000
H	-0.11796800	2.31060200	-2.59631800
H	-1.10784800	3.75528700	-2.94170200
H	-2.36284600	2.14938600	-3.16342400
H	-2.87184900	0.72094100	-2.26687400
H	-4.07346500	1.72913200	-3.08337900
H	-4.92182100	2.57911900	0.33371800
H	-5.40153300	1.89633500	-1.21763300
H	-4.35800000	0.96563800	-0.14169600
H	-4.68508900	3.97684700	-2.23798700
H	-3.91769100	4.70112800	-0.82396100
H	-3.00187300	4.48328400	-2.32441000
P	4.12827500	-0.16976000	0.01036800
C	4.91894200	0.15954600	1.77950300
C	4.59373200	-1.98717900	-0.54021100
C	4.96857600	1.09922900	-1.22789300
C	6.45646700	0.32670800	1.77175300
C	4.31947800	1.43986500	2.40935000
C	4.57400300	-1.01436500	2.72396700
C	3.58840600	-2.95133800	0.13158600
C	4.40837800	-2.15454100	-2.06453000
C	6.02947100	-2.43657100	-0.18982100
C	4.94135700	2.51849000	-0.61940800

C	6.43043300	0.74425800	-1.58477200
C	4.17407200	1.19362100	-2.54603600
H	6.98678900	-0.51115200	1.31744500
H	6.77790900	1.24815300	1.28102000
H	6.78751100	0.39313900	2.81662100
H	3.23309700	1.39307400	2.47636000
H	4.71050700	1.52031400	3.43258700
H	4.60582400	2.35100600	1.88545700
H	4.90498400	-0.74155200	3.73454400
H	3.49975700	-1.19980300	2.77421800
H	5.09099800	-1.93838600	2.45739000
H	3.60569700	-2.91224800	1.22131800
H	2.56722600	-2.74132800	-0.19699300
H	3.83683800	-3.97734700	-0.17154500
H	5.17185800	-1.63068700	-2.64472600
H	4.50555300	-3.22300600	-2.29831500
H	3.42129100	-1.82974000	-2.40038200
H	6.17586500	-3.44546900	-0.59803800
H	6.79595900	-1.79642200	-0.63267700
H	6.20931400	-2.50007600	0.88488200
H	3.94509500	2.79302200	-0.26067300
H	5.65750500	2.65198700	0.19301900
H	5.21430100	3.23134000	-1.40815900
H	6.50216900	-0.16914900	-2.17922800
H	6.83498600	1.55853000	-2.20088100
H	7.08247600	0.64105800	-0.71707300
H	4.08470700	0.24579600	-3.07394300
H	3.16491600	1.57378200	-2.38648300
H	4.70518800	1.89529100	-3.20409000
C	-5.68489000	-1.64818500	2.42689200
C	-2.88101600	-1.55476600	2.57295300
C	-5.50716700	-1.97422800	-2.48788200
C	-2.70006800	-1.87208500	-2.44459900
H	-6.76937100	-1.68598900	2.35637800
H	-1.79991800	-1.50651900	2.64469100
C	-3.64244500	-1.56625500	3.71495900
C	-5.06297200	-1.60486800	3.64578500
H	-5.64822100	-1.60614200	4.56121600
H	-3.15282300	-1.54084200	4.68437600
H	-1.61733500	-1.81337100	-2.44514900
H	-6.59392400	-2.01316600	-2.49084500
C	-4.79910200	-2.07661600	-3.65562200
C	-3.37786900	-2.03042700	-3.62815000
H	-2.81953600	-2.11590100	-4.55608600
H	-5.31721200	-2.19717500	-4.60304300

Zero-point correction= 0.934671 (Hartree/Particle)
Thermal correction to Energy= 0.992821
Thermal correction to Enthalpy= 0.993765
Thermal correction to Gibbs Free Energy= 0.842781
Sum of electronic and zero-point Energies= -7575.555946
Sum of electronic and thermal Energies= -7575.497796
Sum of electronic and thermal Enthalpies= -7575.496852
Sum of electronic and thermal Free Energies= -7575.647837

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E = -7584.49543693

Pd(I)-Br-Dimer oxidative addition to iodonaphthalene



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C	-5.30914500	-2.18176400	-2.00268100
C	-3.57194800	-2.33095900	-0.24791800
C	-2.70252200	-1.63745300	-1.15000400
C	-3.07753000	-1.35212500	-2.45451600
C	-4.40783700	-1.59333400	-2.86421200
C	-4.91808000	-2.57374700	-0.69365500
Pd	-1.41314000	-0.09040000	-0.37676400
Pd	1.47497500	-0.20398600	-0.09873500
Br	1.01893500	0.68489900	-2.42149400

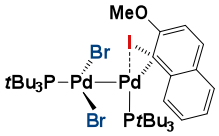
H	-6.32761200	-2.38306100	-2.32517200
H	-2.72203400	1.52102600	4.12725100
C	-2.22027500	1.81756000	3.19667500
C	-3.28435500	1.87790900	2.07754500
H	-1.44876100	1.06995800	2.98931000
H	-1.74017000	2.77984400	3.38715000
P	-2.40893200	2.06321200	0.34513900
C	-4.30681600	2.97801600	2.43217000
C	-3.99297000	0.50616500	2.11174600
C	-1.09060400	3.49328600	0.48900700
C	-3.74412500	2.61215000	-0.96430500
H	-5.17781000	2.97363100	1.77228300
H	-4.67776100	2.79136300	3.44922800
H	-3.87765600	3.98261700	2.42419600
H	-4.77245200	0.39263400	1.35827400
H	-3.27644400	-0.30676000	1.97942600
H	-4.46454900	0.38185800	3.09593200
C	-1.56168000	4.74126900	1.26618400
C	0.17031400	2.92728300	1.18017600
C	-0.63356600	3.93931100	-0.91796400
C	-3.16358100	2.37906200	-2.37950800
C	-4.98627800	1.69991200	-0.85122300
C	-4.21378700	4.07920400	-0.86459400
H	-2.45405800	5.20214300	0.83654700
H	-1.75868900	4.53212200	2.31977100
H	-0.76021900	5.49184800	1.23314200
H	0.59853400	2.09763600	0.60722100
H	0.92476300	3.72495200	1.22780900
H	-0.00058500	2.57366200	2.19594400
H	0.22780600	4.60968800	-0.79609100
H	-0.30468700	3.09464400	-1.53010200
H	-1.39814100	4.50241200	-1.45816700
H	-2.31083600	3.01714200	-2.60859000
H	-2.85206400	1.34174200	-2.51731600
H	-3.94833600	2.59915000	-3.11625700
H	-5.57126100	1.88585800	0.05224500
H	-5.64243800	1.90657800	-1.70689900
H	-4.72642200	0.63916600	-0.88955500
H	-5.00130100	4.24443700	-1.61256200
H	-4.63611300	4.32849100	0.11135400
H	-3.41385500	4.79037700	-1.08283800
P	3.95317300	-0.02452700	-0.06550000
C	4.77564300	-0.50342700	1.65441200
C	4.51709300	-1.34216700	-1.40047000
C	4.67212900	1.72998600	-0.55879500
C	6.30530300	-0.28350700	1.73138100
C	4.14942500	0.32726600	2.80218400
C	4.50303100	-1.99737800	1.94270900
C	3.58604100	-2.57151300	-1.27347300
C	4.32726100	-0.79286900	-2.83122900
C	5.98335200	-1.81256800	-1.27449600
C	4.56587400	2.69318300	0.64463400
C	6.14541200	1.68635600	-1.02721900
C	3.84121400	2.37411000	-1.68685900
H	6.86694000	-0.80798600	0.95749300
H	6.57981300	0.77342700	1.70461100
H	6.64534200	-0.67246700	2.70041600
H	3.06297300	0.37943400	2.74954800
H	4.40255600	-0.16135600	3.75155300
H	4.54866400	1.34044800	2.84852300
H	4.83342500	-2.21158100	2.96695900
H	3.44260300	-2.24777700	1.88698500
H	5.06326700	-2.66126600	1.28115000
H	3.62698100	-3.04897100	-0.29358100
H	2.54538300	-2.30413800	-1.47754500
H	3.89448900	-3.31544200	-2.02028000
H	5.04450700	-0.00845200	-3.08393600
H	4.49854600	-1.62124200	-3.53121000
H	3.31599900	-0.41956700	-3.00159000
H	6.19083200	-2.49164700	-2.11193200
H	6.70162300	-0.99172600	-1.33987100
H	6.17761900	-2.37191900	-0.35749500
H	3.56983300	2.68145700	1.09775600
H	5.30724200	2.49314600	1.42004500

H	4.75050700	3.71190000	0.28040800
H	6.26143400	1.17250500	-1.98377900
H	6.48279700	2.72071300	-1.17746800
H	6.82240800	1.22674000	-0.30690200
H	3.79488300	1.77574200	-2.59495100
H	2.81548300	2.57193100	-1.37443300
H	4.31358800	3.33338300	-1.93959400
C	-5.82034900	-3.23148500	0.18666000
C	-3.18272500	-2.78912600	1.03724000
H	-6.83961300	-3.40370500	-0.15131500
H	-2.16057000	-2.62536700	1.36289500
C	-4.08238500	-3.43875900	1.85500200
C	-5.41566400	-3.65447800	1.43219800
H	-6.11554900	-4.16290600	2.08977600
H	-3.76360100	-3.78880500	2.83281300
H	-4.70654400	-1.32311900	-3.87347100
Br	-0.55107900	-2.34262700	-1.05315200
I	0.79950600	-1.17082200	2.37782300
H	-2.35276000	-0.94323100	-3.14958200

Zero-point correction= 0.887627 (Hartree/Particle)
Thermal correction to Energy= 0.943172
Thermal correction to Enthalpy= 0.944116
Thermal correction to Gibbs Free Energy= 0.797533
Sum of electronic and zero-point Energies= -7421.967759
Sum of electronic and thermal Energies= -7421.912214
Sum of electronic and thermal Enthalpies= -7421.911270
Sum of electronic and thermal Free Energies= -7422.057853

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E = -7430.83311992

Pd(I)-Br-Dimer oxidative addition to 2-methoxy iodonaphthalene



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C	5.41059600	-2.35611700	1.28382900
C	3.47354100	-2.29433600	-0.23117000
C	2.74209700	-1.62858900	0.80495300
C	3.29773800	-1.46598800	2.08249600
C	4.65811100	-1.79778200	2.29445300
C	4.84918400	-2.63197000	0.01283000
Pd	1.36067800	-0.03817700	0.21957300
Pd	-1.54857400	-0.16906900	0.05619900
Br	-1.09754000	0.66057500	2.39020100
H	6.45104400	-2.61287800	1.46601700
H	2.58017900	1.79678900	-4.23340800
C	2.07708800	2.02882200	-3.28534500
C	3.14923300	2.07471000	-2.17299900
H	1.33605300	1.24355200	-3.10787900
H	1.55824800	2.97978400	-3.42466900
P	2.28174200	2.15696600	-0.42887500
C	4.13542200	3.21931100	-2.48607200
C	3.90179600	0.72958800	-2.27295700
C	0.92816400	3.55964800	-0.50022800
C	3.60742500	2.68045200	0.89863000
H	5.01184200	3.20944700	-1.83316500
H	4.50286000	3.08949600	-3.51317400
H	3.67791900	4.20943800	-2.42860900
H	4.70222900	0.61646800	-1.54143500
H	3.21806800	-0.11317300	-2.15622800
H	4.35561900	0.65824500	-3.27070100
C	1.36196200	4.84845200	-1.23197100
C	-0.32803000	2.99207200	-1.19899600
C	0.47534400	3.94510100	0.92637500
C	3.02833900	2.37242300	2.30037900
C	4.86723900	1.80043100	0.74195200
C	4.04943900	4.15872800	0.86409100
H	2.25432200	5.30616800	-0.79852900
H	1.54292900	4.68907100	-2.29714500

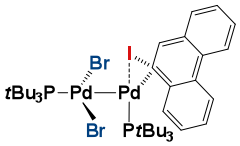
H	0.54800800	5.58177700	-1.15172700
H	-0.74099700	2.14273600	-0.64368100
H	-1.09425200	3.77956800	-1.22359500
H	-0.15867200	2.66408000	-2.22361300
H	-0.40583100	4.59442100	0.83500000
H	0.17685800	3.07357700	1.51558800
H	1.22959800	4.51338900	1.47588700
H	2.19771600	3.02324400	2.57190500
H	2.67794200	1.34070100	2.37858000
H	3.82238500	2.52809700	3.04441700
H	5.44563900	2.04000600	-0.15315000
H	5.52260700	1.98082700	1.60449900
H	4.62826900	0.73421300	0.72955000
H	4.82624200	4.30803100	1.62667900
H	4.47729000	4.45474700	-0.09637900
H	3.23440700	4.84592100	1.10189100
P	-4.03781500	-0.07675900	0.07873200
C	-4.88077100	-0.55293200	-1.63336000
C	-4.53176900	-1.43837500	1.40031100
C	-4.80822100	1.64223400	0.61883100
C	-6.41936000	-0.39306200	-1.67384600
C	-4.31492600	0.32574800	-2.77716600
C	-4.55410700	-2.02843800	-1.95927800
C	-3.55379900	-2.62543400	1.23348200
C	-4.34153300	-0.90977800	2.83864400
C	-5.98002300	-1.96396200	1.28809100
C	-4.76661900	2.62999700	-0.56827000
C	-6.26750100	1.53692800	1.11943600
C	-3.97302400	2.29517600	1.73803100
H	-6.94347000	-0.95754200	-0.90201700
H	-6.73534000	0.65101900	-1.61590400
H	-6.76438300	-0.77239400	-2.64505400
H	-3.23200100	0.43348800	-2.74037500
H	-4.55721100	-0.16041100	-3.73060200
H	-4.76601900	1.31770500	-2.80152300
H	-4.90173000	-2.23633300	-2.97915900
H	-3.48285200	-2.23469300	-1.93512600
H	-5.06855200	-2.72861700	-1.29788300
H	-3.59151600	-3.08336700	0.24412700
H	-2.52189200	-2.31819900	1.42601900
H	-3.81831300	-3.39744300	1.96875900
H	-5.08059600	-0.15423600	3.11511500
H	-4.47695400	-1.75650400	3.52465800
H	-3.34093800	-0.50675800	3.00322000
H	-6.14774100	-2.66531200	2.11601800
H	-6.72845800	-1.17297800	1.37970200
H	-6.16724800	-2.51408800	0.36408600
H	-3.78096500	2.66826300	-1.04241400
H	-5.51607300	2.41396400	-1.33144400
H	-4.98441900	3.63358100	-0.18098600
H	-6.34395000	1.00291300	2.06912400
H	-6.63945700	2.55536400	1.29538700
H	-6.94303100	1.06456300	0.40594300
H	-3.88847300	1.68435300	2.63479000
H	-2.96046500	2.52688000	1.40625500
H	-4.46819400	3.23591800	2.01589400
C	5.60349600	-3.26035800	-1.01504800
C	2.90811000	-2.64312800	-1.48682900
H	6.64709400	-3.49670200	-0.81945000
H	1.86607800	-2.40777100	-1.67436400
C	3.66472500	-3.27188700	-2.45252900
C	5.02793200	-3.57666500	-2.22377200
H	5.61263300	-4.06432500	-2.99888100
H	3.20642600	-3.53263800	-3.40259500
H	5.11016700	-1.61398900	3.26248300
O	2.49921300	-0.96909600	3.05935400
C	2.97742400	-0.92009700	4.39626900
H	3.80327800	-0.20518000	4.50389700
H	2.12893200	-0.58370800	4.99312500
H	3.30114000	-1.90948600	4.74288300
Br	0.59665200	-2.29809600	0.93004900
I	-0.90057800	-1.02797000	-2.46760600

Zero-point correction= 0.920610 (Hartree/Particle)
Thermal correction to Energy= 0.978712

Thermal correction to Enthalpy= 0.979656
Thermal correction to Gibbs Free Energy= 0.829106
Sum of electronic and zero-point Energies= -7536.451286
Sum of electronic and thermal Energies= -7536.393184
Sum of electronic and thermal Enthalpies= -7536.392240
Sum of electronic and thermal Free Energies= -7536.542790

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E = -7545.37455939

Pd(I)-Br-Dimer oxidative addition to iodophenanthrene



Optimized with B3LYP/6-31G(d) with LANL2DZ for Pd

C	-5.42124200	-1.86433000	-0.74099600
C	-3.33934000	-1.99645000	0.64612100
C	-2.62265000	-1.44497200	-0.48221600
C	-3.22230600	-1.26239500	-1.70162200
C	-4.63800300	-1.41884000	-1.84772300
C	-4.75214900	-2.18448600	0.51644000
Pd	-1.12765200	0.07899200	-0.20131800
Pd	1.75905100	-0.25380500	-0.10220500
Br	1.12436300	0.51268800	-2.43024900
H	-1.92411900	2.14090700	4.26681900
C	-1.47534100	2.32071800	3.28098600
C	-2.61602500	2.40449800	2.24197600
H	-0.79507300	1.48876700	3.07437700
H	-0.89509100	3.24269000	3.35939300
P	-1.86219200	2.36759500	0.44482700
C	-3.49703800	3.62824200	2.57054800
C	-3.45177400	1.12261800	2.44799500
C	-0.41349400	3.67383200	0.37729400
C	-3.23868700	2.94042800	-0.81191100
H	-4.41239200	3.65870000	1.97422300
H	-3.80373600	3.56227300	3.62327100
H	-2.97575500	4.57936700	2.44381900
H	-4.29762000	1.02968800	1.76659600
H	-2.83368200	0.22967100	2.34271000
H	-3.85342500	1.13215300	3.47027700
C	-0.71064400	5.01712500	1.07790800
C	0.84326900	3.04863200	1.02429800
C	-0.03067200	3.96755000	-1.09045800
C	-2.79256800	2.53249000	-2.23625100
C	-4.54765500	2.17142800	-0.52768700
C	-3.56271800	4.44974400	-0.81146100
H	-1.59446000	5.52089200	0.68014000
H	-0.83351000	4.91114400	2.15798700
H	0.14551400	5.68646700	0.91759700
H	1.14651700	2.13313500	0.50468300
H	1.66839400	3.76965700	0.94048200
H	0.72516900	2.80467000	2.07929100
H	0.89403900	4.56014500	-1.08668500
H	0.17254300	3.05279100	-1.65394100
H	-0.78188300	4.55901100	-1.61878000
H	-1.89832500	3.05504600	-2.57459000
H	-2.59570000	1.45961300	-2.30155900
H	-3.60362900	2.77329400	-2.93701900
H	-5.03551700	2.49239200	0.39510300
H	-5.24925200	2.36672500	-1.34913000
H	-4.39085900	1.09137400	-0.48525300
H	-4.39199300	4.62702600	-1.50994100
H	-3.87939000	4.81798300	0.16699100
H	-2.72447100	5.06163800	-1.15228800
P	4.23383500	-0.28023300	-0.34272100
C	5.21078100	-0.77574500	1.29334000
C	4.55611200	-1.67200400	-1.68792100
C	5.00826300	1.40423500	-0.97033100
C	6.75232200	-0.68952400	1.18928400
C	4.80171000	0.14327600	2.47190400

C	4.84116000	-2.22847800	1.67251400
C	3.54683900	-2.81474900	-1.42486100
C	4.27038800	-1.15115800	-3.11312200
C	5.98549300	-2.25565300	-1.68957100
C	5.10568600	2.40181300	0.20490500
C	6.41299300	1.24364100	-1.59525900
C	4.09614200	2.07069400	-2.01850100
H	7.18092700	-1.29011400	0.38665600
H	7.10583000	0.33835100	1.08285800
H	7.16642200	-1.06696100	2.13390100
H	3.72928800	0.32135300	2.52673600
H	5.09210400	-0.35381700	3.40597700
H	5.31795700	1.10322100	2.44837100
H	5.28430300	-2.44704200	2.65230600
H	3.76333300	-2.37382700	1.76619100
H	5.24142100	-2.96258300	0.97017700
H	3.63937500	-3.25530000	-0.43119500
H	2.51641100	-2.46984100	-1.54728700
H	3.72502300	-3.61017900	-2.16095500
H	5.01571900	-0.43304900	-3.46301600
H	4.31090600	-2.01114900	-3.79473000
H	3.27773400	-0.70782200	-3.20183900
H	6.05088500	-2.97835600	-2.51351700
H	6.75286500	-1.49749000	-1.86448300
H	6.23135500	-2.79597200	-0.77392500
H	4.17244100	2.46927400	0.77252500
H	5.92024500	2.16882200	0.89224100
H	5.31145400	3.39686800	-0.20997300
H	6.38845400	0.68958500	-2.53553000
H	6.79806700	2.24619200	-1.82511300
H	7.13464300	0.76348400	-0.93358500
H	3.91310100	1.45280200	-2.89539200
H	3.12545600	2.33743600	-1.59925400
H	4.59123800	2.99258100	-2.35339300
C	-5.45080600	-2.70291300	1.63254900
C	-2.69436400	-2.34795400	1.85292200
H	-6.52206900	-2.85918600	1.56947800
H	-1.62146400	-2.20892600	1.93013900
C	-3.41008100	-2.86366700	2.91676500
C	-4.80082800	-3.03596000	2.80671300
H	-5.36857400	-3.43907100	3.64099200
H	-2.89475000	-3.13373800	3.83408800
H	-2.63118500	-0.98981700	-2.56953700
C	-5.26329000	-1.13919000	-3.08765000
C	-6.81563500	-1.99346300	-0.93172200
H	-4.64561300	-0.80787300	-3.91878800
H	-7.44695400	-2.32094800	-0.11302600
C	-6.62842500	-1.27965400	-3.24050500
C	-7.40905000	-1.70641600	-2.14964200
H	-8.48435700	-1.81440800	-2.26195400
H	-7.09816700	-1.06095600	-4.19544100
Br	-0.53123800	-2.29814000	-0.72605800
I	1.29881600	-0.98593900	2.49369200

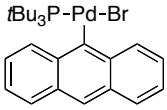
Zero-point correction= 0.934275 (Hartree/Particle)
Thermal correction to Energy= 0.992733
Thermal correction to Enthalpy= 0.993678
Thermal correction to Gibbs Free Energy= 0.841529
Sum of electronic and zero-point Energies= -7575.563624
Sum of electronic and thermal Energies= -7575.505165
Sum of electronic and thermal Enthalpies= -7575.504221
Sum of electronic and thermal Free Energies= -7575.656369

CPCM (THF) M06L/6-311++G(d,p) with SDD (for Pd) E = -7584.49744377

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

Procedures and Data for the Preparation of Pd(II) Complexes

(9-Anthracenyl)(bromo)(tri-tert-butylphosphine)palladium(II)



Bis(tri-*tert*-butylphosphine)palladium(0) (166 mg, 0.65 mmol, 1.1 equiv) and 9-bromoanthracene (300 mg, 0.58 mmol, 1.0 equiv) were dissolved in THF (1 mL) and heated at reflux for 72 h. The reaction mixture was then cooled to 5°C for 48 h to precipitate the product (190 mg, 52%) as an orange powder, which was subsequently filtered: ^{1}H NMR (THF-d8, 400 MHz) δ 9.59 (br app s, 2H, Ar*H*), 7.97-7.15 (br m, 7H, Ar*H*), 1.30-1.04 (br m, 27H, C(C*H*$_3$)$_3$); ^{13}C NMR (THF-d8, 100 MHz) δ 138.9, 136.2, 132.9, 128.5, 125.3, 123.4, 123.3, 41.3, 33.4; ^{31}P NMR (THF-d8, 126 MHz, internal standard = 4,4'-difluorobiphenyl (3.0 ppm)) δ 71.4.

^{1}H NMR Spectrum (THF-d8, 400 MHz, 20°C) with Expansion of the Aromatic Region Between 6.6 and 10.3 ppm (THF-d8, 300 MHz, –60°C):

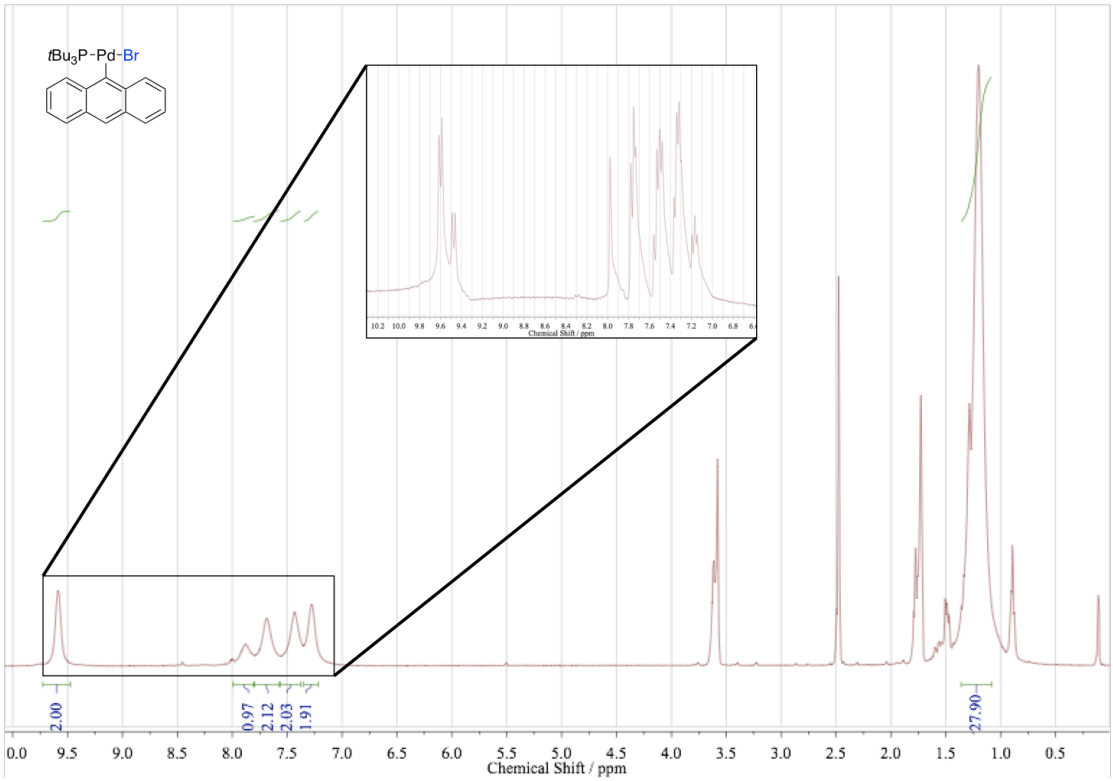


Figure S25.

^{13}C NMR Spectrum (THF-d8, 100 MHz):

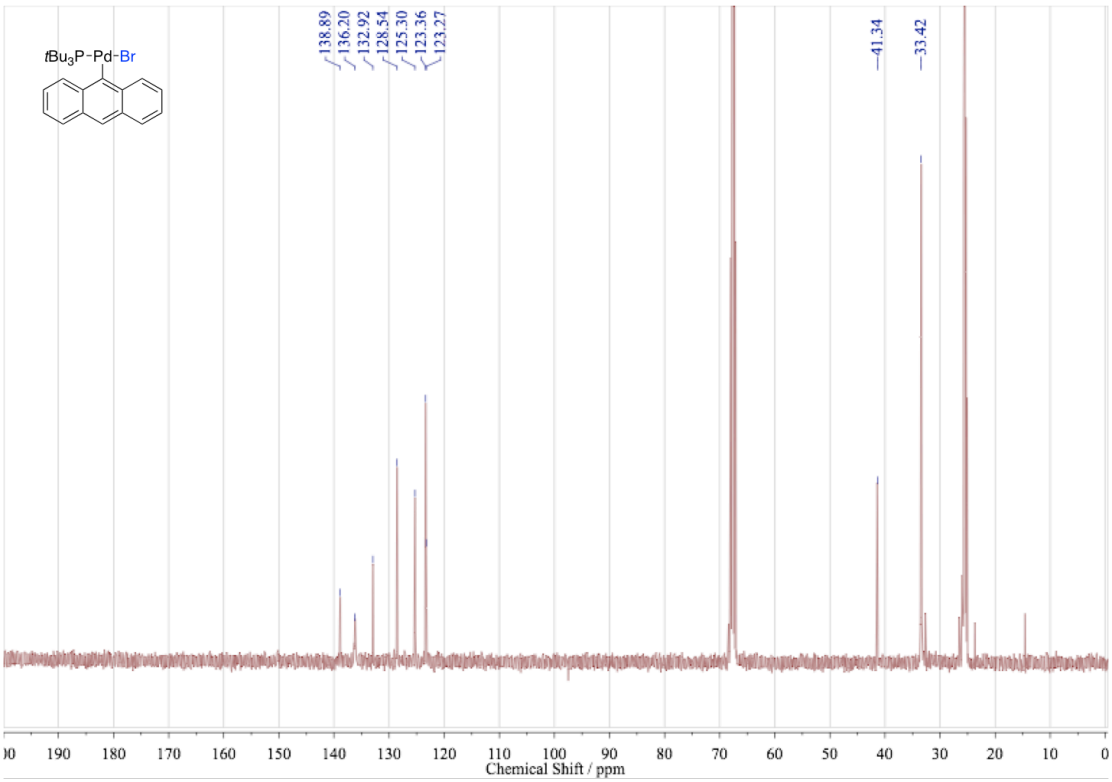


Figure S26.

^{31}P NMR Spectrum (THF-d8, 126 MHz):

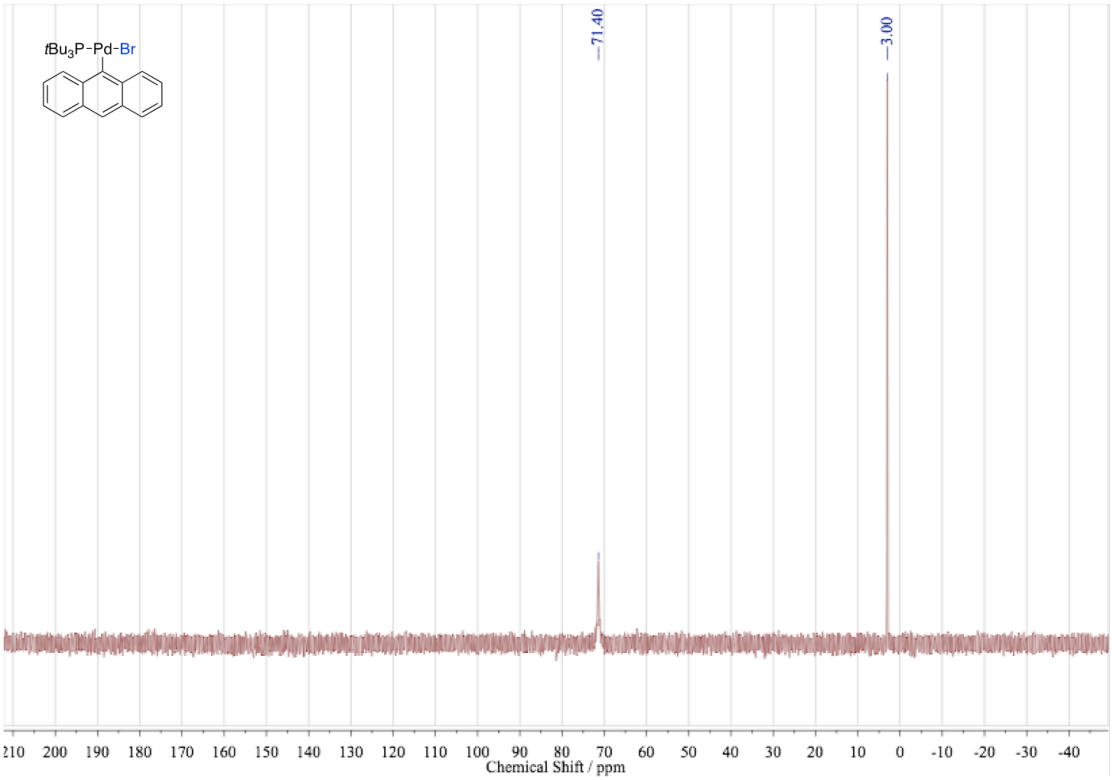


Figure S27.

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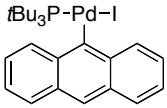
(9-Anthracenyl)(iodo)(tri-tert-butylphosphine)palladium(II)



Bis(tri-*tert*-butylphosphine)palladium(0) (200 mg, 0.66 mmol, 1.0 equiv) and 9-iodoanthracene (336 mg, 0.66 mmol, 1.0 equiv) were dissolved in THF (3 mL) and heated at reflux for 1.5 h. *n*-Hexane (40 mL) was subsequently added and the solution was cooled to -25°C for 18 h to precipitate the product (95 mg, 24%) as an orange powder, which was subsequently filtered: ^{1}H NMR (THF-d8, 400 MHz) δ 9.28 (br, app d, 2H, Ar*H*), 7.95 (br, app s, 1H, Ar*H*), 7.72 (br, app d, 2H, Ar*H*), 7.43 (br, app t, 2H, Ar*H*), 7.32 (br, app t, 2H, Ar*H*), 1.24 (d, *J* = 12.4, 27H, C(CH_3)$_3$); ^{13}C NMR (THF-d8, 100 MHz) δ 136.6, 132.6, 129.1, 128.3, 126.2, 125.8, 124.0, 123.9, 40.9, 32.9; ^{31}P NMR (THF-d8, 126 MHz, internal standard = 4,4'-difluorobiphenyl (3.0 ppm)) δ 61.7.

^{1}H NMR Spectrum (THF-d8, 400 MHz):

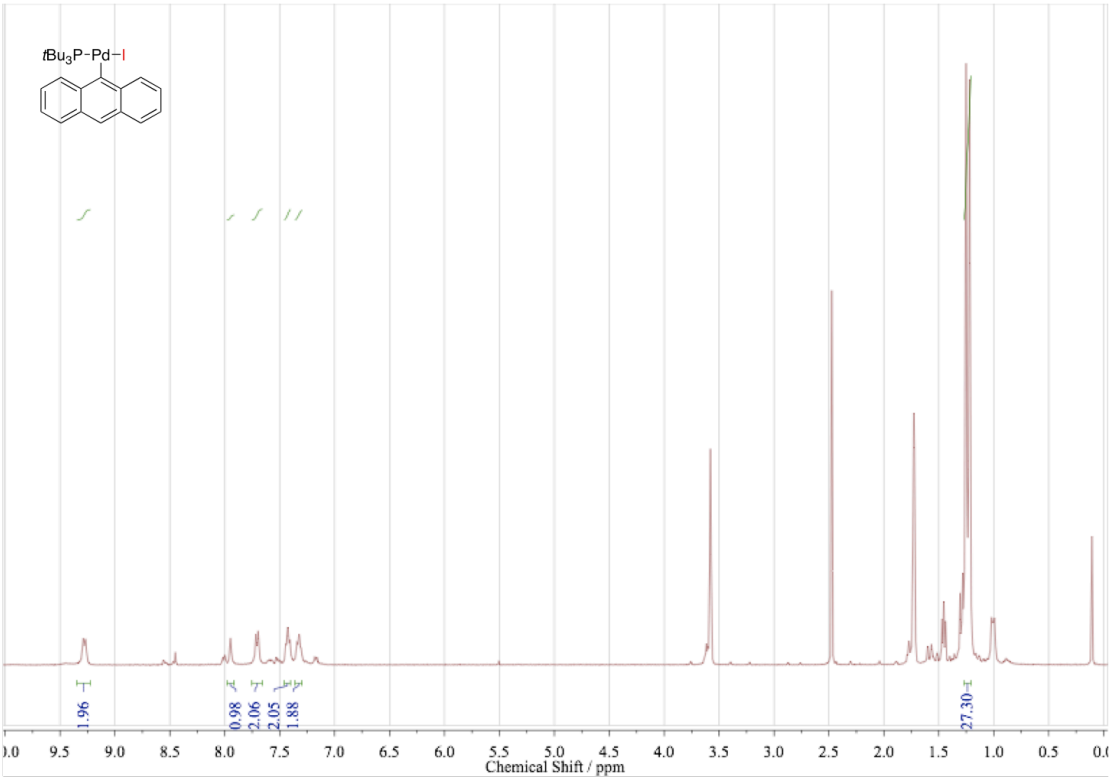


Figure S28.

^{13}C NMR Spectrum (THF-d8, 100 MHz):

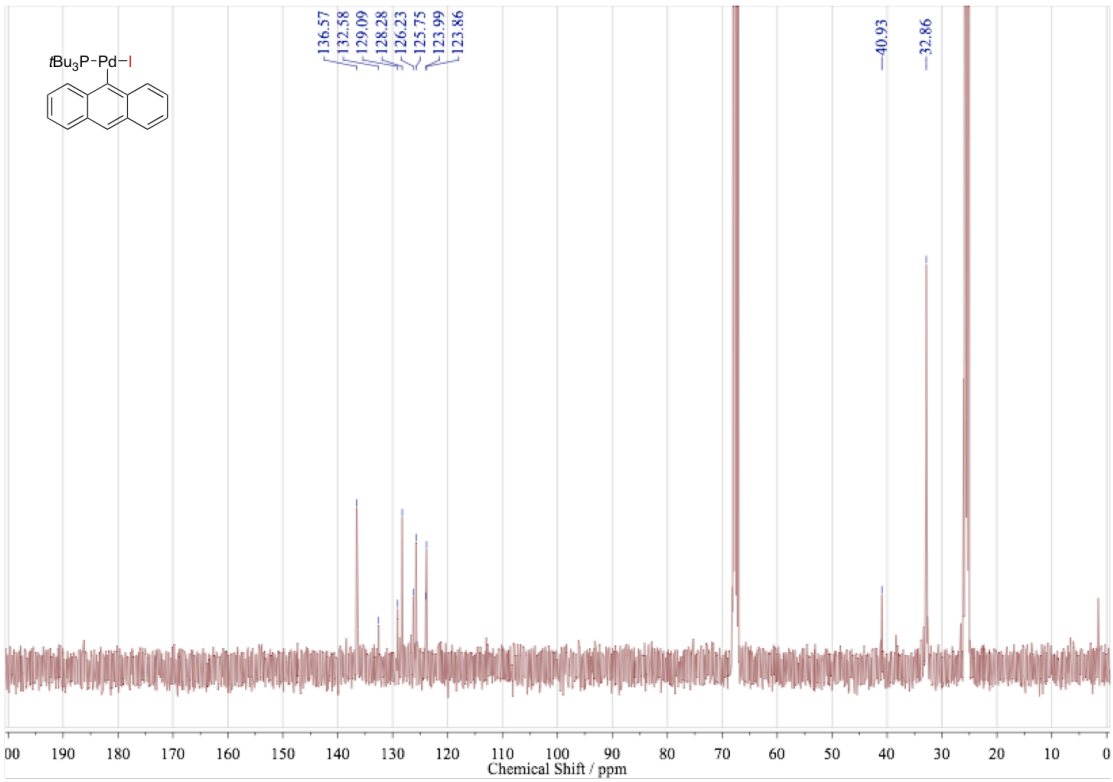


Figure S29.

^{31}P NMR Spectrum (THF-d8, 126 MHz):

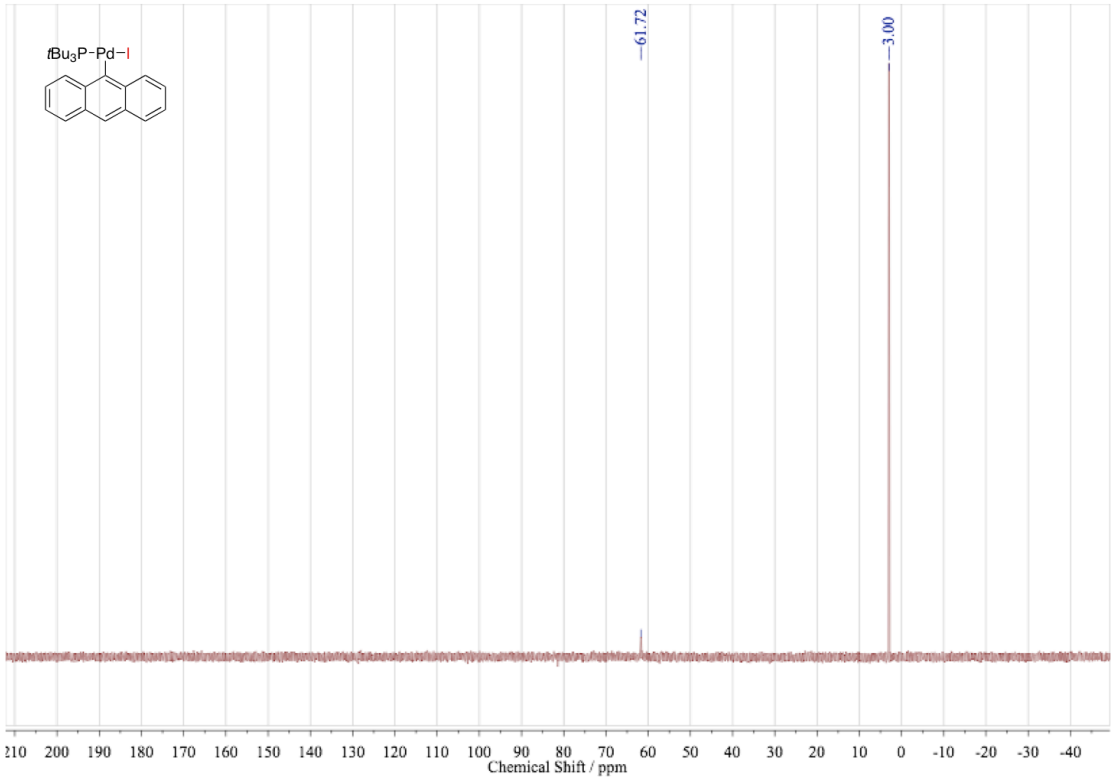
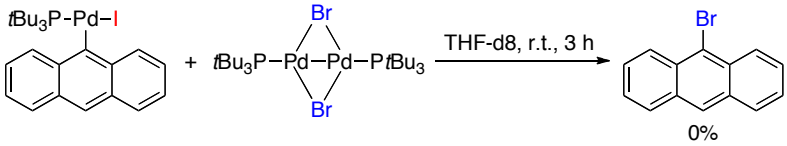


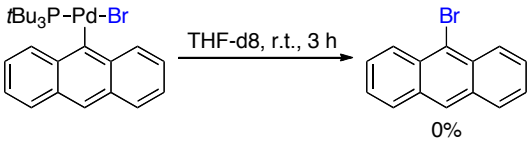
Figure S30.

Procedures for the Reactions of Pd(II) Complexes



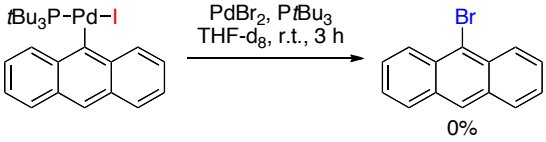
Scheme S16.

(9-Anthracenyl)(iodo)(tri-*tert*-butylphosphine)palladium(II) (10.0 mg, 0.020 mmol, 1.0 equiv) and Pd(I)-Br-dimer **1** (12.7 mg, 0.020 mmol, 1.0 equiv) were mixed in THF-d8 (0.75 mL) in an NMR tube at room temperature. After 3 h there was no formation of aryl iodide or aryl bromide, as judged by ^{1}H NMR spectroscopy.



Scheme S17.

(9-Anthracenyl)(bromo)(tri-*tert*-butylphosphine)palladium(II) (11 mg) was dissolved in THF-d8 (0.50 mL) and stirred at room temperature for 3 h. After this time ^{1}H and ^{31}P NMR spectroscopy revealed that there had been no reaction, with only the starting material being present.



Scheme S18.

(9-Anthracenyl)(iodo)(tri-*tert*-butylphosphine)palladium(II) (12.0 mg, 0.020 mmol, 1.0 equiv), palladium(II) bromide (5.2 mg, 0.020 mmol, 1.0 equiv) and tri-*tert*-butylphosphine (4.0 mg, 0.020 mmol, 1.0 equiv) were stirred in THF-d8 (1.00 mL). After 3 h there was no formation of aryl iodide or aryl bromide, as judged by ^{1}H NMR spectroscopy.

See page S79 for further experiments.

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X-Ray Crystallographic Data for $[Pd(PtBu_3)(Br)(9\text{-anthracenyl})]_2$[9]

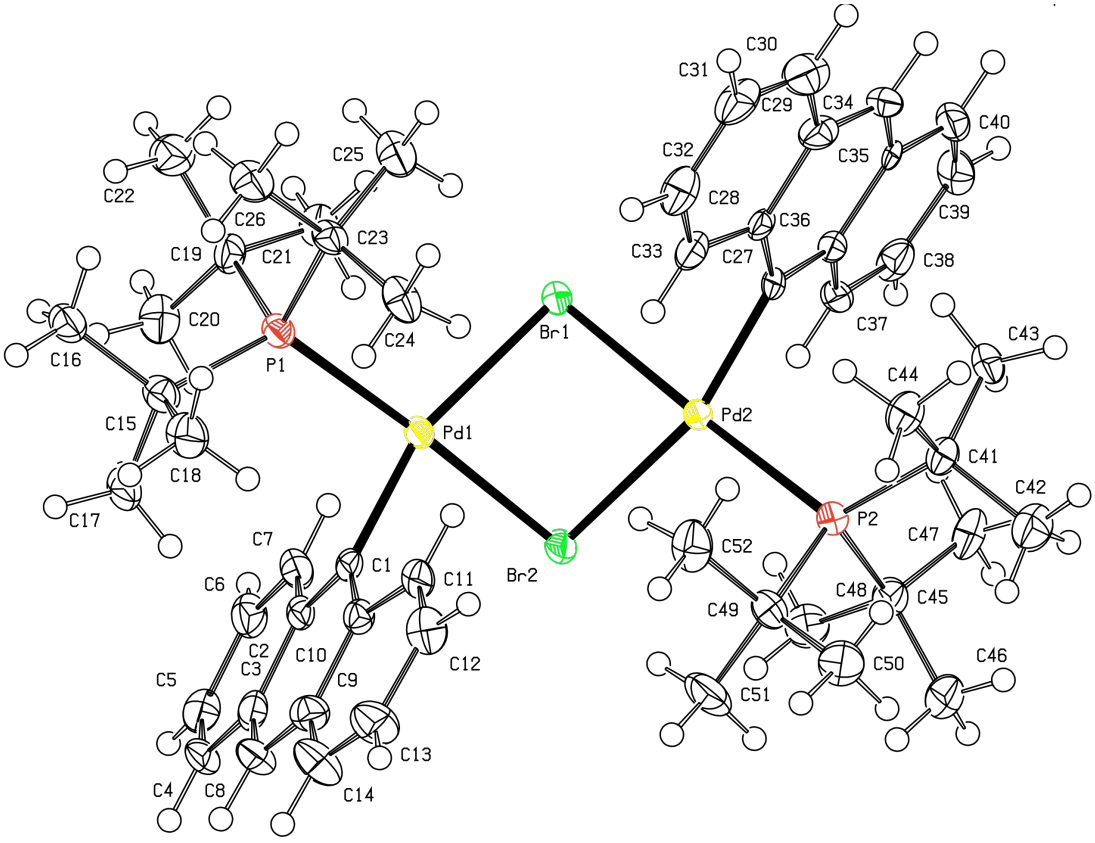


Figure S31.

Experimental

Single crystals of $C_{52}H_{72}P_2Br_2Pd_2$ were prepared by crystallisation from a THF/*n*-hexane mixture at −35°C over a period of 12 h. A suitable crystal was selected and measured on an ApexIID8-Cu diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2[10], the structure was solved with the Superflip[11] structure solution program using Charge Flipping and refined with the XL[11] refinement package using Least Squares minimisation.

Crystal structure determination

Crystal Data for $C_{52}H_{72}P_2Br_2Pd_2$ (M =1131.66): monoclinic, space group $P2_1/c$ (no. 14), a = 12.9358(12) Å, b = 24.285(2) Å, c = 17.862(2) Å, β = 106.401(7)°, V = 5383.1(9) Å^3, Z = 4, T = 100.0 K, μ(CuKα) = 7.912 mm^{-1}, *Dcalc* = 1.396 g/mm^3, 19244 reflections measured ($15.9 \leq 2\Theta \leq 101.04$), 5510 unique ($R_{int}$ = 0.0569) which were used in all calculations. The final R_1 was 0.0367 (>2sigma(I)) and $wR_2$was 0.0880 (all data).

Table S5. Crystal data and structure refinement

Empirical formula	$C_{52}H_{72}P_2Br_2Pd_2$
Formula weight	1131.66
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.9358(12)
b/Å	24.285(2)
c/Å	17.862(2)
α/°	90.00
β/°	106.401(7)
γ/°	90.00
Volume/Å^3	5383.1(9)
Z	4
ρ_{calc}mg/mm^3	1.396
m/mm^{-1}	7.912
F(000)	2304.0
Crystal size/mm^3	0.04 × 0.006 × 0.002
2Θ range for data collection	15.9 to 101.04°
Index ranges	$-12 \leq h \leq 11$, $-24 \leq k \leq 24$, $-17 \leq l \leq 13$
Reflections collected	19244
Independent reflections	5510[R(int) = 0.0569]
Data/restraints/parameters	5510/0/541
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0830
Final R indexes [all data]	R_1 = 0.0540, wR_2 = 0.0880
Largest diff. peak/hole / e Å^{-3}	0.56/-0.81

Table S6. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Pd1	8431.3(3)	1091.80(18)	2350.7(3)	17.67(16)
Pd2	6092.3(3)	1710.04(18)	936.3(3)	17.11(16)
Br1	6834.3(5)	1743.8(3)	2388.6(4)	22.9(2)
Br2	6976.1(5)	736.0(3)	1212.8(4)	24.2(2)
P1	9871.0(13)	1389.3(7)	3434.9(10)	20.9(4)
P2	5458.4(13)	1744.5(7)	-450.7(10)	22.1(4)
C1	9279(5)	495(2)	2035(4)	20.6(17)
C2	9189(5)	-45(2)	2303(4)	19.3(17)
C3	9763(5)	-488(3)	2058(4)	26.0(18)
C4	9667(5)	-1031(3)	2351(4)	28.8(19)
C5	9041(6)	-1130(3)	2828(4)	31.0(19)

C6	8470(5)	-697(3)	3061(4)	30.9(19)
C7	8544(5)	-179(3)	2807(4)	26.8(18)
C8	10386(5)	-380(3)	1559(4)	30.8(19)
C9	10425(5)	146(3)	1248(4)	26.4(18)
C10	9835(5)	585(3)	1481(4)	19.8(17)
C11	9845(5)	1104(3)	1111(4)	25.2(18)
C12	10394(5)	1185(3)	569(4)	30.7(19)
C13	10992(6)	753(3)	377(5)	38(2)
C14	11007(6)	252(3)	710(5)	40(2)
C15	11292(5)	1091(3)	3595(4)	26.1(18)
C16	12074(5)	1221(3)	4407(4)	29.7(18)
C17	11289(5)	453(3)	3518(4)	34.9(19)
C18	11802(5)	1301(3)	2961(4)	36(2)
C19	9479(5)	1261(3)	4374(4)	24.6(17)
C20	9693(5)	659(3)	4630(4)	35.5(19)
C21	8274(5)	1341(3)	4222(4)	32.5(19)
C22	10057(6)	1629(3)	5072(4)	37(2)
C23	10012(5)	2172(2)	3316(4)	23.0(17)
C24	9916(5)	2274(3)	2442(4)	28.5(18)
C25	9084(5)	2494(3)	3484(4)	34(2)
C26	11039(5)	2443(3)	3817(4)	31.1(19)
C27	5471(5)	2440(2)	1096(3)	17.1(16)
C28	6100(5)	2924(2)	1192(4)	20.6(17)
C29	5620(6)	3441(3)	1285(4)	27.2(18)
C30	6263(7)	3926(3)	1373(4)	38(2)
C31	7322(6)	3902(3)	1409(4)	37(2)
C32	7798(6)	3393(3)	1334(4)	32.2(19)
C33	7211(5)	2923(3)	1220(4)	25.6(18)
C34	4538(6)	3456(3)	1289(4)	27.8(18)
C35	3939(5)	2983(3)	1252(3)	17.6(16)
C36	4421(5)	2455(3)	1182(4)	18.5(16)
C37	3804(5)	1973(3)	1193(4)	21.7(17)
C38	2795(5)	2002(3)	1264(4)	30.1(18)
C39	2305(5)	2517(3)	1313(4)	32.2(19)
C40	2864(6)	2983(3)	1316(4)	30.5(18)
C41	4955(5)	2429(3)	-950(4)	23.2(17)
C42	4405(6)	2383(3)	-1830(4)	39(2)
C43	4134(5)	2720(3)	-602(4)	28.6(18)
C44	5895(5)	2837(3)	-834(4)	29.6(18)
C45	4349(5)	1215(3)	-829(4)	29.4(18)
C46	4190(6)	1020(3)	-1683(4)	40(2)
C47	3249(5)	1440(3)	-790(4)	33.5(19)
C48	4574(6)	704(3)	-307(4)	37(2)
C49	6679(5)	1545(3)	-808(4)	27.9(18)
C50	6610(6)	1697(3)	-1657(4)	41(2)

C51	6920(6)	923(3)	-730(5)	43(2)
C52	7663(5)	1835(3)	-263(4)	36(2)

Table S7. Anisotropic Displacement Parameters ($Å^2 \times 10^3$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Pd1	16.0(3)	14.6(3)	21.0(3)	0.3(2)	2.9(2)	1.0(2)
Pd2	16.1(3)	15.9(3)	17.9(3)	-0.6(2)	2.4(2)	1.6(2)
Br1	22.8(4)	25.3(4)	18.6(4)	-0.5(3)	2.5(3)	7.8(3)
Br2	22.2(4)	16.9(4)	27.9(5)	-2.8(3)	-1.9(3)	1.8(3)
P1	19.0(9)	17.6(9)	24.9(11)	0.0(8)	4.2(8)	0.8(8)
P2	21(1)	21.6(10)	21.5(11)	-1.6(8)	2.5(9)	3.3(8)
C1	16(4)	18(4)	22(4)	-4(3)	-5(3)	0(3)
C2	13(4)	17(4)	24(4)	-2(3)	-2(3)	-1(3)
C3	25(4)	25(4)	22(4)	2(4)	-4(4)	1(3)
C4	31(4)	15(4)	35(5)	-1(4)	1(4)	7(3)
C5	37(4)	15(4)	32(5)	3(4)	-5(4)	-8(4)
C6	31(4)	25(5)	32(5)	5(4)	1(4)	1(4)
C7	21(4)	22(4)	34(5)	2(4)	2(4)	3(3)
C8	29(4)	26(5)	38(5)	-4(4)	9(4)	10(3)
C9	23(4)	28(5)	29(5)	-5(4)	8(4)	-1(3)
C10	21(4)	22(4)	17(4)	3(3)	5(3)	2(3)
C11	9(4)	29(4)	35(5)	-6(4)	0(4)	-1(3)
C12	22(4)	34(5)	37(5)	5(4)	10(4)	-4(4)
C13	35(5)	42(5)	44(5)	-2(4)	21(4)	7(4)
C14	35(5)	35(5)	56(6)	4(4)	23(5)	12(4)
C15	20(4)	21(4)	36(5)	-3(4)	5(4)	0(3)
C16	22(4)	25(4)	39(5)	-4(4)	4(4)	3(3)
C17	19(4)	30(4)	46(5)	-6(4)	-5(4)	4(3)
C18	18(4)	41(5)	48(5)	-7(4)	6(4)	0(3)
C19	26(4)	25(4)	19(4)	5(3)	2(3)	2(3)
C20	31(4)	36(4)	37(5)	5(4)	5(4)	-1(3)
C21	33(4)	33(4)	29(5)	1(4)	5(4)	3(3)
C22	31(4)	37(5)	42(5)	-9(4)	7(4)	0(4)
C23	22(4)	13(4)	32(5)	-1(3)	5(3)	-1(3)
C24	23(4)	17(4)	45(5)	9(4)	9(4)	-2(3)
C25	24(4)	22(4)	51(5)	0(4)	2(4)	-2(3)
C26	27(4)	19(4)	46(5)	-3(4)	7(4)	-6(3)
C27	23(4)	18(4)	8(4)	6(3)	2(3)	6(3)
C28	30(4)	14(4)	12(4)	1(3)	-4(3)	1(3)
C29	43(5)	15(4)	21(5)	0(3)	4(4)	-2(4)
C30	60(6)	23(4)	29(5)	4(4)	10(4)	0(4)
C31	46(5)	26(5)	30(5)	-2(4)	-3(4)	-17(4)
C32	28(4)	39(5)	26(5)	4(4)	2(4)	-10(4)

C33	30(5)	23(4)	18(4)	1(3)	-2(3)	-4(4)
C34	36(5)	25(4)	21(5)	-4(3)	6(4)	11(4)
C35	20(4)	23(4)	6(4)	0(3)	-3(3)	7(3)
C36	17(4)	23(4)	15(4)	-1(3)	3(3)	3(3)
C37	14(4)	26(4)	25(4)	-5(3)	5(3)	4(3)
C38	21(4)	45(5)	23(5)	-5(4)	3(3)	-3(4)
C39	22(4)	52(6)	26(5)	5(4)	14(4)	12(4)
C40	35(5)	34(5)	22(5)	4(4)	7(4)	16(4)
C41	25(4)	26(4)	17(4)	3(3)	4(3)	0(3)
C42	40(4)	47(5)	28(5)	2(4)	4(4)	4(4)
C43	30(4)	25(4)	28(5)	5(4)	4(4)	10(3)
C44	34(4)	34(4)	20(4)	7(4)	7(4)	-2(3)
C45	27(4)	24(4)	32(5)	-3(4)	-1(4)	1(3)
C46	36(5)	38(5)	36(5)	-7(4)	-6(4)	2(4)
C47	25(4)	44(5)	25(5)	4(4)	-4(4)	-7(4)
C48	36(4)	22(4)	46(5)	-5(4)	0(4)	-7(3)
C49	21(4)	31(4)	32(5)	-1(4)	8(4)	7(3)
C50	37(5)	60(5)	31(5)	-3(4)	16(4)	12(4)
C51	48(5)	40(5)	45(5)	4(4)	22(4)	24(4)
C52	25(4)	51(5)	34(5)	8(4)	11(4)	2(4)

Table S8. Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	Br1	2.6188(8)	C15	C18	1.550(10)
Pd1	Br2	2.5022(8)	C19	C20	1.533(9)
Pd1	P1	2.3882(17)	C19	C21	1.517(9)
Pd1	C1	1.994(6)	C19	C22	1.545(9)
Pd2	Br1	2.5003(9)	C23	C24	1.550(9)
Pd2	Br2	2.6129(8)	C23	C25	1.532(9)
Pd2	P2	2.3812(19)	C23	C26	1.526(8)
Pd2	C27	1.999(6)	C27	C28	1.414(8)
P1	C15	1.921(6)	C27	C36	1.410(8)
P1	C19	1.910(7)	C28	C29	1.431(9)
P1	C23	1.927(6)	C28	C33	1.424(9)
P2	C41	1.912(6)	C29	C30	1.424(9)
P2	C45	1.902(6)	C29	C34	1.403(9)
P2	C49	1.925(7)	C30	C31	1.355(9)
C1	C2	1.412(8)	C31	C32	1.406(9)
C1	C10	1.395(9)	C32	C33	1.354(9)
C2	C3	1.443(9)	C34	C35	1.377(9)
C2	C7	1.427(9)	C35	C36	1.445(8)
C3	C4	1.437(9)	C35	C40	1.427(9)
C3	C8	1.384(9)	C36	C37	1.421(9)
C4	C5	1.353(9)	C37	C38	1.347(8)

C5	C6	1.415(9)	C38	C39	1.417(9)
C6	C7	1.349(9)	C39	C40	1.343(9)
C8	C9	1.399(9)	C41	C42	1.535(9)
C9	C10	1.440(9)	C41	C43	1.545(9)
C9	C14	1.401(10)	C41	C44	1.536(8)
C10	C11	1.425(9)	C45	C46	1.556(10)
C11	C12	1.367(9)	C45	C47	1.544(9)
C12	C13	1.402(9)	C45	C48	1.531(9)
C13	C14	1.352(10)	C49	C50	1.539(10)
C15	C16	1.548(9)	C49	C51	1.542(9)
C15	C17	1.556(9)	C49	C52	1.538(9)

Table S9. Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br2	Pd1	Br1	79.15(2)	C18	C15	C17	104.7(6)
P1	Pd1	Br1	103.67(5)	C20	C19	P1	110.3(5)
P1	Pd1	Br2	177.07(5)	C20	C19	C22	107.8(5)
C1	Pd1	Br1	161.48(17)	C21	C19	P1	109.6(4)
C1	Pd1	Br2	82.34(17)	C21	C19	C20	105.3(5)
C1	Pd1	P1	94.83(17)	C21	C19	C22	108.0(5)
Br1	Pd2	Br2	79.30(2)	C22	C19	P1	115.3(5)
P2	Pd2	Br1	175.47(5)	C24	C23	P1	106.6(4)
P2	Pd2	Br2	103.43(4)	C25	C23	P1	112.3(4)
C27	Pd2	Br1	82.81(17)	C25	C23	C24	105.7(5)
C27	Pd2	Br2	161.35(17)	C26	C23	P1	117.0(4)
C27	Pd2	P2	94.77(17)	C26	C23	C24	109.3(5)
Pd2	Br1	Pd1	91.60(3)	C26	C23	C25	105.4(5)
Pd1	Br2	Pd2	91.70(3)	C28	C27	Pd2	121.0(4)
C15	P1	Pd1	120.1(2)	C36	C27	Pd2	118.6(4)
C15	P1	C23	105.8(3)	C36	C27	C28	120.2(6)
C19	P1	Pd1	108.9(2)	C27	C28	C29	119.4(6)
C19	P1	C15	106.7(3)	C27	C28	C33	122.9(6)
C19	P1	C23	108.3(3)	C33	C28	C29	117.8(6)
C23	P1	Pd1	106.6(2)	C30	C29	C28	118.6(6)
C41	P2	Pd2	119.2(2)	C34	C29	C28	119.3(6)
C41	P2	C49	105.5(3)	C34	C29	C30	122.0(6)
C45	P2	Pd2	110.4(2)	C31	C30	C29	121.4(7)
C45	P2	C41	107.4(3)	C30	C31	C32	119.9(7)
C45	P2	C49	108.6(3)	C33	C32	C31	120.9(7)
C49	P2	Pd2	105.2(2)	C32	C33	C28	121.4(6)
C2	C1	Pd1	118.3(5)	C35	C34	C29	121.8(6)
C10	C1	Pd1	121.4(5)	C34	C35	C36	119.6(6)
C10	C1	C2	119.8(6)	C34	C35	C40	122.9(6)
C1	C2	C3	119.3(6)	C40	C35	C36	117.5(6)

C1	C2	C7	123.1(6)	C27	C36	C35	119.1(6)
C7	C2	C3	117.7(6)	C27	C36	C37	122.8(6)
C4	C3	C2	117.9(7)	C37	C36	C35	118.1(5)
C8	C3	C2	119.8(6)	C38	C37	C36	121.5(6)
C8	C3	C4	122.2(7)	C37	C38	C39	120.9(7)
C5	C4	C3	121.4(7)	C40	C39	C38	119.7(6)
C4	C5	C6	120.5(6)	C39	C40	C35	122.4(6)
C7	C6	C5	120.1(7)	C42	C41	P2	114.4(5)
C6	C7	C2	122.3(7)	C42	C41	C43	105.9(5)
C3	C8	C9	121.4(6)	C42	C41	C44	107.8(5)
C8	C9	C10	118.7(6)	C43	C41	P2	113.0(4)
C8	C9	C14	121.8(6)	C44	C41	P2	110.2(4)
C14	C9	C10	119.5(6)	C44	C41	C43	105.0(5)
C1	C10	C9	120.6(6)	C46	C45	P2	115.6(5)
C1	C10	C11	122.9(6)	C47	C45	P2	111.0(4)
C11	C10	C9	116.5(6)	C47	C45	C46	106.5(5)
C12	C11	C10	122.0(6)	C48	C45	P2	109.7(4)
C11	C12	C13	119.9(7)	C48	C45	C46	107.4(5)
C14	C13	C12	120.4(7)	C48	C45	C47	106.1(6)
C13	C14	C9	121.6(7)	C50	C49	P2	116.3(4)
C16	C15	P1	114.0(4)	C50	C49	C51	106.1(6)
C16	C15	C17	105.8(5)	C51	C49	P2	112.4(5)
C16	C15	C18	108.4(5)	C52	C49	P2	106.5(5)
C17	C15	P1	112.6(4)	C52	C49	C50	108.7(6)
C18	C15	P1	110.7(4)	C52	C49	C51	106.4(5)

Table S10. Torsion Angles

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Pd1	P1	C15	C16	-167.3(4)	C8	C9	C10	C11	-176.3(6)
Pd1	P1	C15	C17	-46.7(6)	C8	C9	C14	C13	176.1(7)
Pd1	P1	C15	C18	70.2(5)	C9	C10	C11	C12	-0.6(9)
Pd1	P1	C19	C20	81.9(4)	C10	C1	C2	C3	6.0(8)
Pd1	P1	C19	C21	-33.7(5)	C10	C1	C2	C7	-173.4(6)
Pd1	P1	C19	C22	-155.7(4)	C10	C9	C14	C13	-2.9(10)
Pd1	P1	C23	C24	-43.0(4)	C10	C11	C12	C13	-1.7(9)
Pd1	P1	C23	C25	72.3(5)	C11	C12	C13	C14	1.7(10)
Pd1	P1	C23	C26	-165.6(4)	C12	C13	C14	C9	0.6(11)
Pd1	C1	C2	C3	177.6(4)	C14	C9	C10	C1	-177.8(6)
Pd1	C1	C2	C7	-1.8(8)	C14	C9	C10	C11	2.8(9)
Pd1	C1	C10	C9	-178.7(4)	C15	P1	C19	C20	-49.1(5)
Pd1	C1	C10	C11	0.6(8)	C15	P1	C19	C21	-164.6(4)
Pd2	P2	C41	C42	-170.9(4)	C15	P1	C19	C22	73.3(5)
Pd2	P2	C41	C43	-49.6(5)	C15	P1	C23	C24	85.9(4)

Pd2	P2	C41	C44	67.5(5)	C15	P1	C23	C25	-158.8(5)
Pd2	P2	C45	C46	-155.7(4)	C15	P1	C23	C26	-36.7(6)
Pd2	P2	C45	C47	82.9(5)	C19	P1	C15	C16	-42.9(5)
Pd2	P2	C45	C48	-34.1(5)	C19	P1	C15	C17	77.6(5)
Pd2	P2	C49	C50	-162.4(5)	C19	P1	C15	C18	-165.5(4)
Pd2	P2	C49	C51	75.1(5)	C19	P1	C23	C24	-160.0(4)
Pd2	P2	C49	C52	-41.1(5)	C19	P1	C23	C25	-44.7(5)
Pd2	C27	C28	C29	178.4(5)	C19	P1	C23	C26	77.4(5)
Pd2	C27	C28	C33	-3.2(9)	C23	P1	C15	C16	72.3(5)
Pd2	C27	C36	C35	-176.4(4)	C23	P1	C15	C17	-167.1(5)
Pd2	C27	C36	C37	2.7(8)	C23	P1	C15	C18	-50.3(5)
Br1	Pd1	Br2	Pd2	30.81(2)	C23	P1	C19	C20	-162.6(4)
Br1	Pd1	P1	C15	-173.0(2)	C23	P1	C19	C21	81.8(5)
Br1	Pd1	P1	C19	63.7(2)	C23	P1	C19	C22	-40.2(5)
Br1	Pd1	P1	C23	-52.9(2)	C27	Pd2	Br1	Pd1	-154.47(18)
Br1	Pd1	C1	C2	-82.1(8)	C27	Pd2	Br2	Pd1	-49.1(6)
Br1	Pd1	C1	C10	89.4(7)	C27	Pd2	P2	C41	14.5(3)
Br1	Pd2	Br2	Pd1	-32.43(3)	C27	Pd2	P2	C45	-110.5(3)
Br1	Pd2	P2	C41	-43.1(7)	C27	Pd2	P2	C49	132.5(3)
Br1	Pd2	P2	C45	-168.1(6)	C27	C28	C29	C30	-179.4(6)
Br1	Pd2	P2	C49	74.9(6)	C27	C28	C29	C34	0.8(9)
Br1	Pd2	C27	C28	81.4(5)	C27	C28	C33	C32	-178.2(6)
Br1	Pd2	C27	C36	-93.0(5)	C27	C36	C37	C38	-178.9(6)
Br2	Pd1	Br1	Pd2	-32.36(3)	C28	C27	C36	C35	9.2(9)
Br2	Pd1	P1	C15	22.6(11)	C28	C27	C36	C37	-171.7(6)
Br2	Pd1	P1	C19	-100.7(10)	C28	C29	C30	C31	-3.3(10)
Br2	Pd1	P1	C23	142.7(10)	C28	C29	C34	C35	3.8(10)
Br2	Pd1	C1	C2	-83.6(4)	C29	C28	C33	C32	0.2(10)
Br2	Pd1	C1	C10	87.8(5)	C29	C30	C31	C32	2.0(11)
Br2	Pd2	Br1	Pd1	30.82(2)	C29	C34	C35	C36	-1.9(9)
Br2	Pd2	P2	C41	-169.7(2)	C29	C34	C35	C40	175.0(6)
Br2	Pd2	P2	C45	65.4(2)	C30	C29	C34	C35	-175.9(6)
Br2	Pd2	P2	C49	-51.7(2)	C30	C31	C32	C33	0.4(11)
Br2	Pd2	C27	C28	97.8(7)	C31	C32	C33	C28	-1.5(10)
Br2	Pd2	C27	C36	-76.5(8)	C33	C28	C29	C30	2.1(9)
P1	Pd1	Br1	Pd2	148.44(5)	C33	C28	C29	C34	-177.6(6)
P1	Pd1	Br2	Pd2	-164.7(10)	C34	C29	C30	C31	176.5(7)
P1	Pd1	C1	C2	95.6(4)	C34	C35	C36	C27	-4.6(9)
P1	Pd1	C1	C10	-92.9(5)	C34	C35	C36	C37	176.2(6)
P2	Pd2	Br1	Pd1	-96.5(6)	C34	C35	C40	C39	-177.0(6)
P2	Pd2	Br2	Pd1	143.87(5)	C35	C36	C37	C38	0.2(9)
P2	Pd2	C27	C28	-94.8(5)	C36	C27	C28	C29	-7.4(9)
P2	Pd2	C27	C36	90.9(5)	C36	C27	C28	C33	171.0(6)
C1	Pd1	Br1	Pd2	-34.0(6)	C36	C35	C40	C39	0.0(10)
C1	Pd1	Br2	Pd2	-149.7(2)	C36	C37	C38	C39	1.3(10)

C1	Pd1	P1	C15	7.8(3)	C37	C38	C39	C40	-2.2(10)
C1	Pd1	P1	C19	-115.5(3)	C38	C39	C40	C35	1.5(10)
C1	Pd1	P1	C23	127.8(3)	C40	C35	C36	C27	178.3(6)
C1	C2	C3	C4	179.1(5)	C40	C35	C36	C37	-0.9(9)
C1	C2	C3	C8	-0.5(9)	C41	P2	C45	C46	72.8(5)
C1	C2	C7	C6	-179.7(6)	C41	P2	C45	C47	-48.6(5)
C1	C10	C11	C12	-179.9(6)	C41	P2	C45	C48	-165.5(5)
C2	C1	C10	C9	-7.4(9)	C41	P2	C49	C50	-35.5(6)
C2	C1	C10	C11	172.0(6)	C41	P2	C49	C51	-158.1(5)
C2	C3	C4	C5	1.5(9)	C41	P2	C49	C52	85.8(5)
C2	C3	C8	C9	-3.9(9)	C45	P2	C41	C42	-44.4(5)
C3	C2	C7	C6	0.9(9)	C45	P2	C41	C43	76.8(5)
C3	C4	C5	C6	-0.8(9)	C45	P2	C41	C44	-166.1(5)
C3	C8	C9	C10	2.6(10)	C45	P2	C49	C50	79.3(6)
C3	C8	C9	C14	-176.5(6)	C45	P2	C49	C51	-43.2(6)
C4	C3	C8	C9	176.6(6)	C45	P2	C49	C52	-159.3(4)
C4	C5	C6	C7	0.1(10)	C49	P2	C41	C42	71.3(5)
C5	C6	C7	C2	-0.2(10)	C49	P2	C41	C43	-167.5(4)
C7	C2	C3	C4	-1.5(8)	C49	P2	C41	C44	-50.4(5)
C7	C2	C3	C8	179.0(6)	C49	P2	C45	C46	-40.8(5)
C8	C3	C4	C5	-179.0(6)	C49	P2	C45	C47	-162.2(5)
C8	C9	C10	C1	3.1(9)	C49	P2	C45	C48	80.8(5)

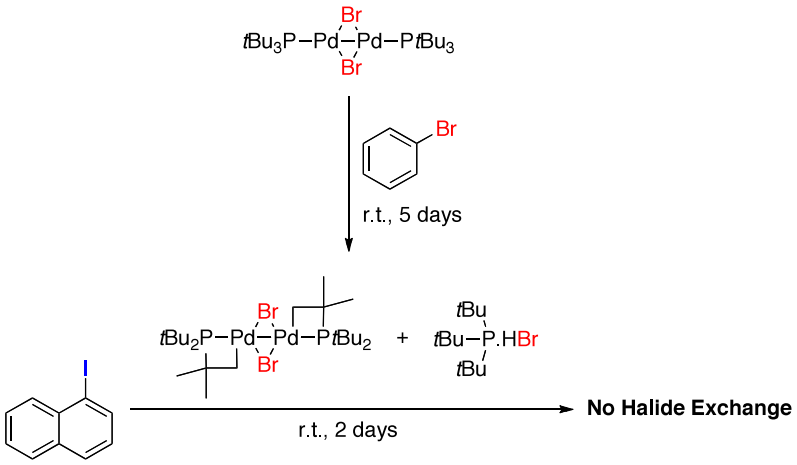
Table S11. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U(eq)
H4	10052	-1327	2206	35
H5	8985	-1494	3008	37
H6	8033	-770	3397	37
H7	8153	106	2969	32
H8	10796	-669	1426	37
H11	9460	1404	1246	30
H12	10369	1534	323	37
H13	11389	813	10	46
H14	11422	-34	577	48
H16A	12041	1615	4517	45
H16B	12811	1124	4410	45
H16C	11867	1008	4807	45
H17A	10808	293	3797	52
H17B	12021	312	3742	52
H17C	11036	351	2965	52
H18A	11307	1231	2443	55
H18B	12484	1109	3011	55
H18C	11937	1698	3027	55

H20A	9337	416	4195	53
H20B	9407	587	5073	53
H20C	10470	589	4784	53
H21A	8084	1722	4062	49
H21B	8072	1261	4700	49
H21C	7889	1090	3806	49
H22A	10838	1592	5172	56
H22B	9850	1515	5536	56
H22C	9848	2014	4950	56
H24A	10475	2064	2294	43
H24B	10009	2667	2357	43
H24C	9204	2155	2123	43
H25A	8395	2350	3159	51
H25B	9147	2885	3363	51
H25C	9116	2455	4036	51
H26A	11112	2370	4369	47
H26B	11002	2841	3724	47
H26C	11663	2291	3679	47
H30	5942	4274	1408	46
H31	7742	4229	1485	44
H32	8543	3378	1363	39
H33	7548	2585	1158	31
H34	4209	3802	1318	33
H37	4108	1623	1150	26
H38	2407	1672	1280	36
H39	1584	2533	1345	39
H40	2532	3325	1362	37
H42A	4859	2165	-2075	59
H42B	4302	2752	-2062	59
H42C	3704	2202	-1916	59
H43A	3618	2449	-516	43
H43B	3749	3003	-965	43
H43C	4515	2891	-104	43
H44A	6288	2856	-278	44
H44B	5613	3202	-1018	44
H44C	6382	2712	-1131	44
H46A	3963	1332	-2040	60
H46B	3635	732	-1812	60
H46C	4870	871	-1737	60
H47A	3304	1559	-256	50
H47B	2704	1149	-943	50
H47C	3041	1753	-1147	50
H48A	5256	537	-325	56
H48B	3988	438	-492	56
H48C	4621	810	231	56

H50A	6023	1490	-2012	62
H50B	7293	1605	-1764	62
H50C	6472	2092	-1736	62
H51A	7005	807	-190	64
H51B	7587	846	-869	64
H51C	6323	719	-1080	64
H52A	7538	2234	-279	54
H52B	8304	1755	-434	54
H52C	7775	1702	272	54

Decomposition Experiment with the Pd(I)-Br-Dimer 1



Scheme S19. Conversion of Pd(I)-Br-dimer **1** into side-products and subsequent attempted bromination.

Procedure: Br-dimer **1** (36 mg, 0.05 mmol) was dissolved in bromobenzene (1 mL) and stirred at room temperature for 5 days until all of the dimer had been consumed (as judged by ^{31}P NMR spectroscopy). The bromobenzene was then removed under reduced pressure and 1-iodonaphthalene (1 mL) was added to the residue. After a further 2 days at room temperature the mixture was passed through a plug of silica and GC-MS showed that there had been no conversion to 1-bromonaphthalene.

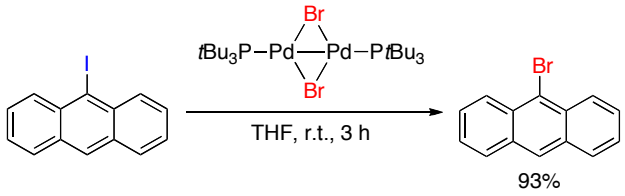
This reaction demonstrates that neither the cyclopalladated species nor the phosphonium salt are involved in the halide exchange reaction on the aromatic.[12]

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

Reductive Elimination from Pd(II)-Monomer, *versus* Equivalent Reaction with Pd(I)-Dimer

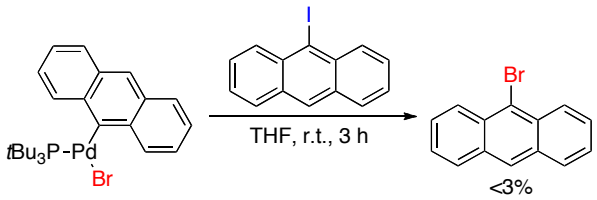
This study was to investigate whether reductive elimination of ArBr from a Pd(II) complex in the presence of ArI can occur at a similar rate to reaction of the Pd(I)-dimer with the same quantity of ArI.

Procedure for the Pd(I)-dimer reaction: THF (0.5 mL) was added to a mixture of 9-iodoanthracene (6 mg, 0.02 mmol, 1 equiv) and Pd(I)-Br-dimer **1** (16 mg, 0.02 mmol, 1 equiv) and this was stirred at room temperature for 3 hours. After this time the mixture was filtered through a plug of silica and analysed by GC-MS:



Scheme S20.

Procedure for the Pd(II) reaction: THF (0.5 mL) was added to a mixture of 9-iodoanthracene (6 mg, 0.02 mmol, 1 equiv) and (*t*Bu$_3$P)Pd(9-anthracenyl)(Br) complex (11 mg, 0.02 mmol, 1 equiv) and this was stirred at room temperature for 3 hours. After this time the mixture was analysed by both ^{31}P NMR spectroscopy and GC-MS:

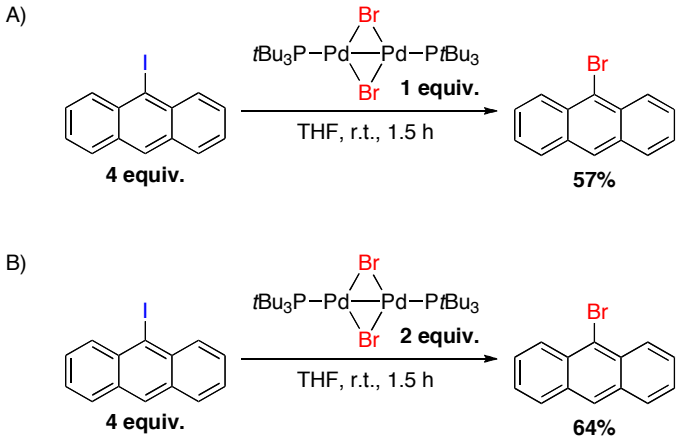


Scheme S21.

*Karl J. Bonney, Fabien Proutiere and Franziska Schoenebeck**

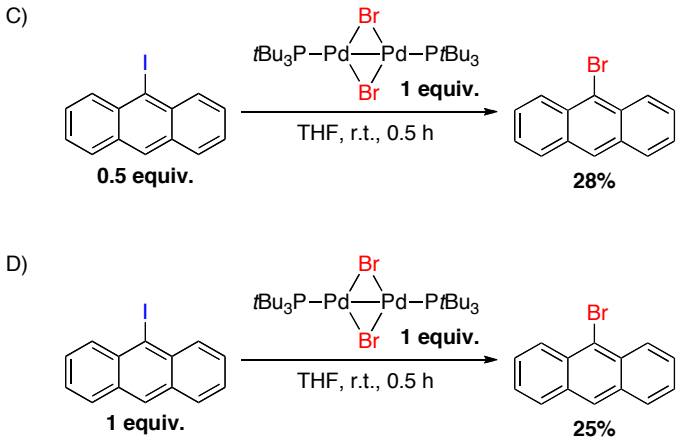
Preliminary Kinetic Studies

The concentrations of Pd(I)-Br-dimer **1** and 9-iodoanthracene were altered in separate experiments to get an indication of the reaction order for the first bromination (*i.e.* Pd(I)-Br-dimer **1** to the mixed Pd(I)-Br-I-dimer **3**)



Scheme S22. Varying the concentration of Pd(I)-Br-dimer **1**

Procedure: THF (0.5 mL) was added to a mixture of 9-iodoanthracene (24 mg, 0.08 mmol, 4 equiv) and Pd(I)-Br-dimer **1** (A: 16 mg, 0.02 mmol, 1 equiv; B: 32 mg, 0.04 mmol, 2 equiv). The reactions were stirred at room temperature for 1.5 hours, after which the conversion was assessed by GC-MS.



Scheme S23. Varying the concentration of 9-iodoanthracene

Procedure: THF (0.5 mL) was added to a mixture of 9-iodoanthracene (C: 3 mg, 0.01 mmol, 0.5 equiv; D: 6 mg, 0.02 mmol, 1 equiv) and Pd(I)-Br-dimer **1** (16 mg, 0.02 mmol, 1 equiv). The reactions were stirred at room temperature for 0.5 hours, after which the conversion was assessed by ^{1}H NMR spectroscopy.

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