# Mononuclear Palladium(I) Aryl Complexes Performs Cross-Coupling Reactions with Organic Halides

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*Supporting Information Placeholder*

**ABSTRACT:** Mononuclear Pd(I) species represent the least understood Pd intermediates in Pd-catalyzed reactions and isolable complexes of the type are exceedingly rare. Herein, we report the synthesis and characterization of mononuclear Pd(I) complexes bearing aryl ligands, namely [(IPr)Pd(Ar$^{Trip}$-R-*p*)] (Ar$^{Trip}$-R-*p* = 4-R-2,6-bis(2',4',6'-triisopropylphenyl)phenyl, R = H, $CF_3$), as well as their reactions with organic halides. The Pd(I) aryl complexes were prepared from the reactions of $[(IPr)PdCl_2]_2$ with the corresponding aryl lithium salts and have been characterized by various spectroscopic methods. EPR spectroscopy and calculation studies suggest their Pd(I) nature. Reactivity studies using [(IPr)Pd(Ar$^{Trip}$-$CF_3$-*p*)] as the representative revealed the capability of the Pd(I) aryl complex in activating the carbon-halogen bonds of organic iodide and benzyl halides. In the reactions with *para*-substituted benzyl bromides, C(aryl)-C(benzyl) cross-coupling products are formed in moderate to good yields. Kinetic studies, radical trapping experiments, and theoretical calculations point out that the cross-coupling products are likely formed from the sequential steps of stepwise oxidative addition reaction of Pd(I) aryl complex with benzyl bromide involving Pd(II) intermediate followed by reductive elimination reactions of the resulting Pd(III) intermediates.

## INTRODUCTION

Pd(I) is the least understood oxidation-state for palladium species.[1–8] However, in recent years, Pd(I) species have received increasing attention for their roles in Pd-catalyzed organic transformations.[9,10] A number of dimeric Pd(I) compounds have proved effective catalysts for cross-coupling reactions.[8,11–15] As a notable example, the Pd(I) dimer $[(P^tBu_3)PdBr]_2$ can function as the reservoir of the highly reactive 12-electron Pd(0) species and has been applied as precatalysts for an array of C-C and C-N bond cross-coupling reactions.[8,16] Mononuclear Pd(I) species are invoked as putative intermediates in Pd-catalyzed halogen-atom-transfer reactions,[17–20] carbonylation reactions,[21,22] cross-couplings,[23–28] as well as light-driven Pd-catalyzed reactions.[29–31] In these catalytic reactions, single-electron redox reactions between Pd(0) species and organic halides and light-driven decomposition of Pd(II) species are proposed to yield Pd(I) intermediates. The transient nature of these mononuclear Pd(I) intermediates, however, prevents isolation and detailed characterization.

So far, isolable mononuclear Pd(I) complexes are exceedingly rare. Figure 1 lists the known examples. The $P^tBu_3$-supported two-coordinate Pd(I) complexes $[Pd(P^tBu_3)_2][X]$ (**I**, X = $CB_{11}H_{12}$, $PF_6$)[32,33] reported independently by Chaplin's and Ozerov's groups in 2016 were prepared by single-electron oxidation of the Pd(0) complex $[Pd(P^tBu_3)_2]$ with ferrocenium or triphenylmethyl cation. In similar way, the two-coordinate Pd(I) complexes with $PAd_3$ and *N*-heterocyclic carbene as supporting ligands $[Pd(PAd_3)_2][BAr^F_4]$ (**II,** $Ar^F$ = 3,5-$(CF_3)_2C_6H_3$)[34] and $[Pd(IPr)_2][PF_6]$ (**III**, IPr = 1,3-bis(2',6'-diisopropylphenyl)imidazole-2-ylidene)[35] were prepared by oxidizing the corresponding Pd(0) precursors. The reactivity of the homoleptic Pd(I) complexes **I-III** remains poorly understood. Ozerov's study noted that $[Pd(P^tBu_3)_2]^+$ can coordinate MeCN to form the T-shaped complex $[Pd(P^tBu_3)_2(NCMe)][CB_{11}H_{12}]$ (**IV**).[33] Chaplin found that the cation $[Pd(P^tBu_3)_2]^+$ can react with organic iodides to yield the Pd(I) dimer $[Pd(P^tBu_3)(I)]_2$ and phosphonium salts.[36] The heteroleptic Pd(I) complexes **V** reported by Mirica's group can be prepared by reducing Pd(II) species supported by cyclic tetra- and tri-dentate ligands with $Cp_2Co$ or by ligand-exchange reaction between$[Pd(P^tBu_3)_2]^+$ and the cyclic ligands.[37,38] Among them, the Pd(I) complex featuring a tridentate $NS_2$ ligand proved effective catalyst for the cross-coupling reaction of aryl bromides with alkyl Grignard reagents.[38] A Pd(I)-Pd(III)-Pd(I) catalytic cycle was proposed for this Pd(I)-catalyzed cross-coupling reaction. While, based on the Covalent-Bond-Classification method,[39] the Pd(I) complexes **I-V** are unanimously the ones supported by

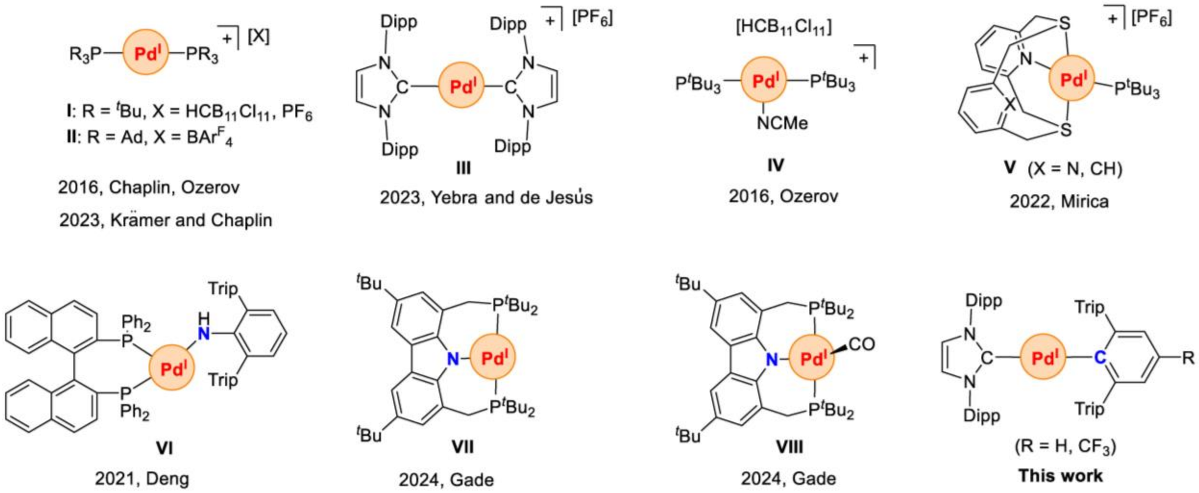

Figure 1. Structurally well-defined mononuclear Pd(I) complexes.

L-type ligands, the Pd(I) amido complex $[(\mathrm{BINAP})\mathrm{Pd}(\mathrm{NHAr}^{\mathrm{Trip}})]$ (**VI**, BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene, $\mathrm{Ar}^{\mathrm{Trip}}$ = 2,6-bis(2',4',6'-triisopropylphenyl)phenyl) is unique for the X-type amido ligand.[40] Complex **VI** was prepared from the reaction of the Pd(II) complex $(\mathrm{BINAP})\mathrm{PdCl_2}$ with two equiv. of $\mathrm{LiNHAr}^{\mathrm{Trip}}$. It is heat- and light-sensitive and can readily fragment into Pd(0) species and aminyl radical at ambient conditions.[40] Very recently, Gade and his coworkers reported the preparation of the mononuclear Pd(I) pincer **VII** by the reduction of the corresponding Pd(II) chloride complex or by thermolysis of the corresponding Pd(II) neopentyl complex.[41] Under high CO pressure (5 atm.), **VII** coordinates reversibly with CO to form the Pd(I) carbonyl complex **VIII** that slowly reacts with di(tert-butyl) disulfide to give palladathioester. [41]

The limited knowledge on mononuclear Pd(I) complexes, particularly those bearing X-type ligands, urges further exploration on them. Herein, we wish to report the isolation and characterization of the first mononuclear Pd(I) aryl complexes [(IPr)Pd(Ar)], as well as their reactions with organic halides, which produce C-C cross-coupling products.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Pd(I) Aryl Complexes.** The Pd(I) aryl complexes $[(\mathrm{IPr})\mathrm{Pd}(\mathrm{Ar}^{\mathrm{Trip}})]$ (**1**) and $[(\mathrm{IPr})\mathrm{Pd}(\mathrm{Ar}^{\mathrm{Trip}}\text{-}\mathrm{CF_3}\text{-}p)]$ (**2**, $\mathrm{Ar}^{\mathrm{Trip}}\text{-}\mathrm{CF_3}\text{-}p$ = 2,6-bis(2',4',6'-triisopropylphenyl)-4-trifluoromethylphenyl) were synthesized from the reactions of $[(\mathrm{IPr})\mathrm{PdCl_2}]_2$ with the corresponding aryl lithium salts $\mathrm{Ar}^{\mathrm{Trip}}\mathrm{Li}(\mathrm{OEt_2})$ and $p\text{-}\mathrm{CF_3}\text{-}\mathrm{Ar}^{\mathrm{Trip}}\mathrm{Li}(\mathrm{OEt_2})$ (four equiv.) in $\mathrm{Et_2O}$ (Figure 2a). These reactions gave red mixtures. Further workup upon column chromatography separation led to the isolation of **1** and **2** as red solids in moderate isolated yields (51% and 59%, respectively) along with the arenes $\mathrm{HAr}^{\mathrm{Trip}}$ (**3-H**) and $\mathrm{HAr}^{\mathrm{Trip}}\text{-}\mathrm{CF_3}\text{-}p$ (**3-CF₃**) (73% and 69% isolated yields, respectively). Complexes **1** and **2** have been characterized by $^1$H and $^{19}$F NMR, UV-vis absorption, EPR spectroscopies, as well as elemental analysis. Their structures have been established by single-crystal X-ray diffraction studies.

As shown in Figures S1 and 2b, **1** and **2** are two-coordinate Pd(I) complexes featuring linear C(carbene)-Pd-C(aryl) core (180.0° for **1** and 179.2(1)° for **2**). Irrespective their different *para*-substituents on aryl ligands, **1** and **2** have the bond distances and angles around the C(carbene)-Pd-C(aryl) cores very close to each other. The Pd-C(aryl) bond distances in **1** and **2** are 2.066(4) and 2.055(7) Å, respectively, which locate on the long end of the Pd-C(aryl) bonds of the reported palladium aryl complexes that are mostly known for Pd(II) complexes.[42,43] The distance of Pd-C(carbene) bonds in **1** and **2** are 2.121(4) and 2.115(7) Å, respectively, which are longer than the Pd-C(carbene) bonds in $[(\mathrm{IPr})_2\mathrm{Pd}]$ (2.013 Å) and $[(\mathrm{IPr})_2\mathrm{Pd}][\mathrm{PF_6}]$ (2.055(7) Å in average).[35] The long Pd-C(carbene) bonds can be attributed to the joint effect of the strong *trans*-influence of aryl ligand and severe steric repulsion between IPr and the bulky aryl ligands in the aryl complexes. Probably due to steric reason, the imidazole planes of the IPr ligands in **1** and **2** are not co-planar with the central arene planes of their aryl ligands, but form dihedral angles around 41 degree. The dihedral angles are close to those in the homoleptic Pd NHC complexes $[(\mathrm{IPr})_2\mathrm{Pd}][\mathrm{PF_6}]$ (46 degree) and $[(\mathrm{IPr})_2\mathrm{Pd}]$ (39 degree).[35]

Complexes **1** and **2** are air-sensitive. Under a dinitrogen atmosphere and at room temperature, their solids and THF solutions, however, can be stored for months without noticeable decomposition. In line with their mononuclear nature, complexes **1** and **2** are paramagnetic. The $^1$H NMR spectra of **1** and **2** measured on their $\mathrm{C_6D_6}$ solutions display broad signals in the range 10 to -1 ppm. A heavily broadened $^{19}$F NMR signal with width-at-half-height reaching 125 Hz appears at -74.7 ppm in the spectrum of **2**. The EPR spectra of **1** and **2** collected at 40K in toluene glasses show anisotropic signals in companion with noticeable sextets arising from hyperfine coupling to $^{105}$Pd nucleus ($I$ = 5/2, 22% abundance) (Figures 2c and S11). Both spectra can be simulated as $S = 1/2$ systems with $g_1 = 1.97$, $g_2 = 2.29$ and $g_3 = 2.36$ and large $^{105}$Pd hyperfine coupling constants ($A_{\mathrm{Pd\_1}}$ = 880 MHz, $A_{\mathrm{Pd\_2}}$ = 820 MHz and $A_{\mathrm{Pd\_3}}$ = 808 MHz for **1**; $A_{\mathrm{Pd\_1}}$ = 875 MHz, $A_{\mathrm{Pd\_2}}$ = 798 MHz, and $A_{\mathrm{Pd\_3}}$ = 818 MHz for **2**). The g-values and $^{105}$Pd hyperfine coupling constants are in line with those of the reported two-coordinate Pd(I) complexes $[\mathrm{Pd}(\mathrm{P}^t\mathrm{Bu_3})_2][\mathrm{X}]$ (X = $\mathrm{PF_6}$, $\mathrm{HCB_{11}H_{11}}$),[32,33]

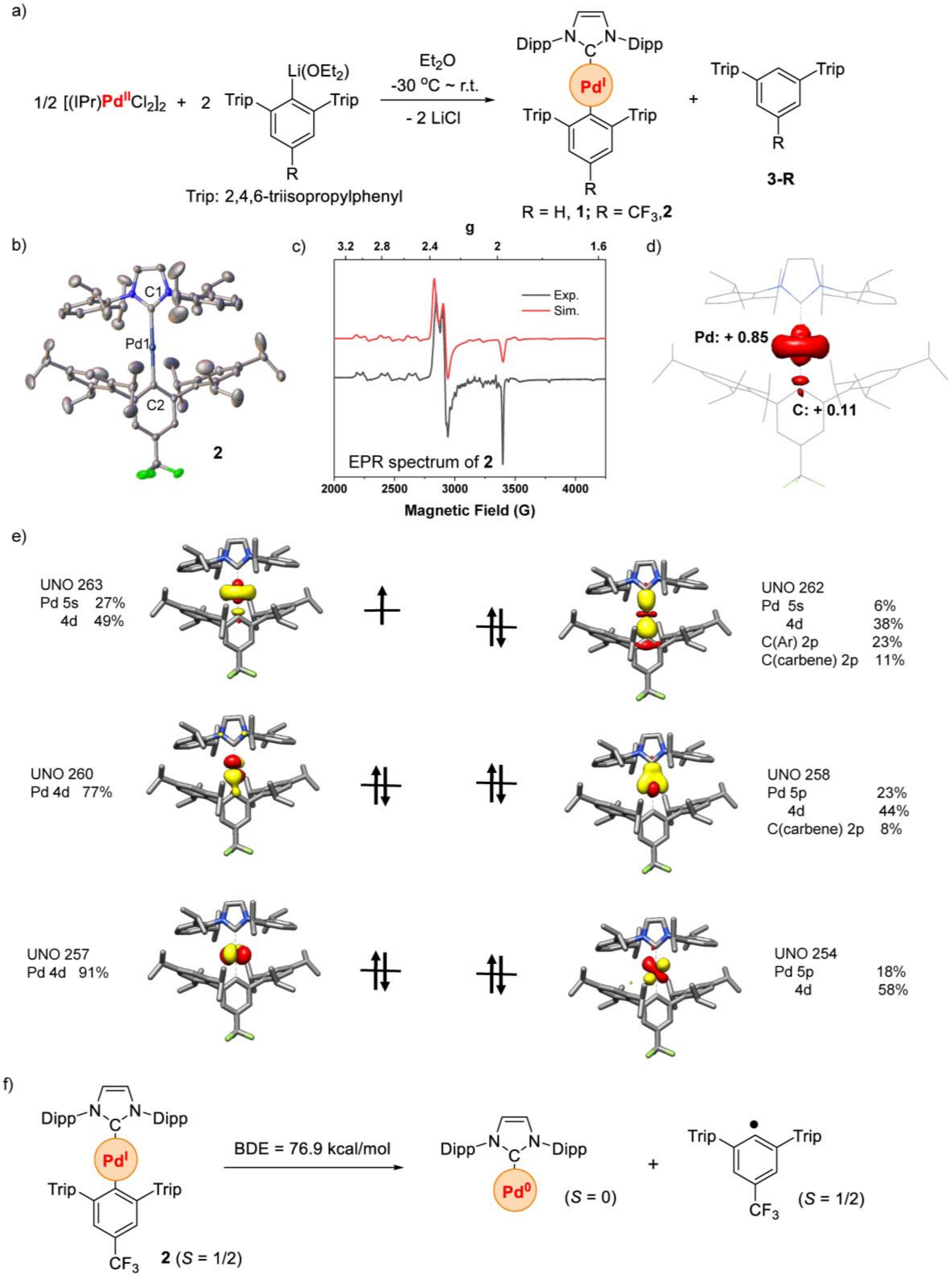

Figure 2. Synthetic route to the Pd(I) aryl complexes and their structure and spectroscopic features. a) The reaction giving the Pd(I) ary complexes $[\mathrm{(IPr)Pd(Ar^{Trip})}]$(**1**) and $[\mathrm{(IPr)Pd(}p\text{-}\mathrm{CF_3\text{-}Ar^{Trip})}]$(**2**). b) Molecular structure of **2** showing 30% displacement ellipsoids and the partial atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Pd1-C1 2.115(7), Pd1-C2 2.055(7), C1-Pd1-C2 179.2(1). c) EPR spectrum of **2** measured on its toluene glass at 40 K (black line) and the simulation (red line) using the following parameters: $g$ = (1.971, 2.292, 2.368) and $A_{\mathrm{Pd}}$ = (875, 798, 818 MHz). d) Spin density distribution of **2** at its $S$ = ½ state. e) Frontier molecular orbitals of **2** at its S = ½ state. f) Calculated bond dissociation energy of the Pd-C(aryl) bond in **2** (B3LYP/def2-TZVP).

$[Pd(PAd_3)_2][BAr^F{}_4]$,[34] and $[Pd(IPr)_2][PF_6]$ [35](Table S1), implying the location of high spin-density on the Pd centers of **1** and **2**. Accordingly, density functional theory (DFT) calculations on **2** at its $S = 1/2$ state indicated that 85% of the unpaired spin resides on the Pd center (Figure 2d). Molecular orbital analysis identified an electronic configuration of $(4d_{xz}+5p)^2(4d_{yz})^2(d_{x2\text{-}y2}+5p)^2(4d_{xy})^2(4d_{z2}+5s)^1$ for its Pd center (Figure 2e), arguing for its Pd(I) nature. It is interesting to note that, despite of the low-valent nature of the Pd(I) complex, the orbital interactions between the Pd center and its aryl and NHC ligands are essentially σ-type in-character (UNO 262). The bond dissociation energy of the Pd-C(aryl) bond in **2** is estimated to be 77 kcal mol$^{-1}$ based on single-point-energy calculations (Figure 2f), which is much higher than that of the Pd-N(amido) bond in (BINAP)Pd(NHAr$^{Trip}$) (**F** in Figure 1, 51 kcal mol$^{-1}$)[40] and accounts for the stability of the Pd(I) aryl complex at ambient temperature.

Complexes **1** and **2** are likely formed *via* salt-elimination reactions between the aryl lithium reagents and *in-situ* generated Pd(I) species, presumably $[(IPr)PdCl]_2$ (Figure 3a). The Pd(I) chloride species could be generated by the single-electron redox reaction between $[(IPr)PdCl_2]_2$ and the bulky aryl lithium salts ArLi. As an indirect supporting evidence for the formation of $[(IPr)PdCl]_2$, which is known to be too unstable to isolate,[44] the reaction of $[(IPr)PdCl_2]_2$ with *p*-$CF_3$-Ar$^{Trip}$Li($OEt_2$) (two equiv.) and LiI (two equiv.) in $Et_2O$ is found to produce the Pd(I) iodide dimer $[(IPr)PdI]_2$ and the arene HAr$^{Trip}$-$CF_3$-*p* in high yields (Figure 3b). Furthermore, treatment of $[(IPr)PdI]_2$ with two equiv. of *p*-$CF_3$-Ar$^{Trip}$Li($OEt_2$) can lead to the formation of $[(IPr)_2Pd]$ and HAr$^{Trip}$-$CF_3$-*p* as the major products along with the Pd(I) complex **2** in trace amount (Figure 3c). The low yield of **2** in the later trial as compared to that of the reaction of $[(IPr)PdCl_2]_2$ with *p*-$CF_3$-Ar$^{Trip}$Li($OEt_2$) (four equiv.) indicates the halogen effect on the salt metathesis reactions.[45]

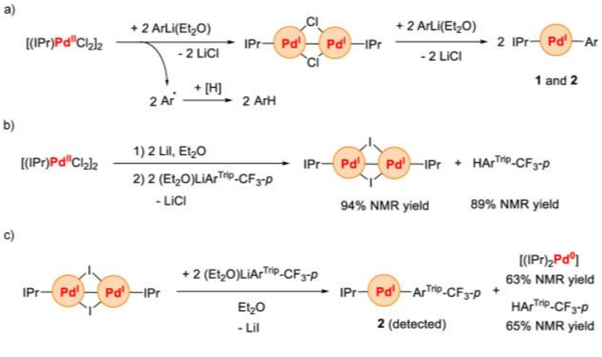

Figure 3. Proposed formation route for **1** and **2** and its supporting mechanistic evidence. a) Proposed formation route to **1** and **2**. b) Reaction of $[(IPr)PdCl]_2$ with LiI and *p*-$CF_3$-Ar$^{Trip}$Li($OEt_2$). c) Reaction of $[(IPr)PdI]_2$ with *p*-$CF_3$-Ar$^{Trip}$Li($OEt_2$).

**Reactions of Pd(I) Aryl Complexes with Organic Halides.** The presence of aryl ligands in the Pd(I) complexes **1** and **2** prompted studies on their reactions with organic halides, which might yield C-C cross-coupling products. Investigating the reactions of **2** with organic halides revealed that cross-coupling products indeed can be formed in the reactions with benzylic halides. The reaction of **2** with methyl 4-(bromomethyl)benzoate takes place quickly at room temperature. In 1 hour, complex **2** was fully consumed and the C-C cross-coupling product **5-$CH_2C_6H_4COOMe$** was produced in 75% NMR yield, along with the *m*-terphenyl derivative bearing an *iso*-propenyl group **4**, the dehalogenation product *p*-$MeC_6H_4COOMe$, and benzyl radical coupling product $MeOOCC_6H_4CH_2CH_2C_6H_4COOMe$ as the byproducts (Figure 4a). The cross-coupling product **5-$CH_2C_6H_4COOMe$** has been characterized by NMR spectroscopies, high-resolution mass spectroscopy, and single-crystal X-ray diffraction study (Figure S21). In addition to these organic products, palladium black and Pd(II) bromide were observed as the resultant Pd-containing products (Figures 4b and S22). Complex **2** is also reactive toward methyl 4-iodo-butanate, wherein the NMR yield of the cross-coupling product **5-$CH_2CH_2CH_2COOMe$** is merely 13% and that of the *m*-terphenyl derivative **4** reaches 76% (Figure 4a). Different from the reaction with the benzyl bromide, significant amount of black solid was produced in the reaction with the alkyl iodide. Further analysis indicated that it contains mainly the imidazolium salt [HPr]I and palladium black (Figures 4b and S26). Intriguingly, complex **2** can even react with the aryl iodide 3,5-dimethylphenyl iodide though with decreased rate. In this reaction, the *m*-terphenyl derivative **4** (94% NMR yield) and 1,3-dimethylbenzene (62% GC yield) were the major products and no cross-coupling product was detected (Figure 4a). Along with these organic products, the Pd(I) iodide dimer $[(IPr)PdI]_2$ and Pd(II) iodide dimer $[(IPr)PdI_2]_2$ were identified as the major palladium-containing products (Figures 4b and S16). On the other hand, complex **2** is found inert toward 1-octyl bromide, cyclohexyl bromide, and phenyl bromide.

The product pattern of the aforementioned reactions implies that single-electron redox reactions between the Pd(I) aryl complex and these organic halides might have occurred. It can be proposed that the single-electron transfer reactions between **2** and the organic halides R-X might form the Pd(II) species (IPr)Pd(Ar$^{Trip}$-$CF_3$-*p*)(X) (**A**) and the organic radical R$^•$ (Figure 4c). The relatively long lifetimes of alkyl and benzylic radicals as compared to aryl radicals might allow them to combine with intermediate **A**, yielding the Pd(III) species (IPr)Pd(Ar$^{Trip}$-$CF_3$-*p*)(X)(R) (**B**). Further reductive elimination reactions from **B** can yield the cross-coupling products R-Ar$^{Trip}$-$CF_3$-*p* (**5-R**) and the Pd(I) species (IPr)PdX. Proposals on radical combination with Pd(II) species to form Pd(III) species and C-X bond-forming reductive elimination from Pd(III) species have been known.[46–50] There is also report on C-X bond-forming reductive elimination from isolable mononuclear Pd(III) species.[51] Alternatively, **B** might undergo Pd-C(aryl) bond homolysis reaction to form the aryl radical [*p*-$CF_3$-Ar$^{Trip}$]$^•$ and the Pd(II) species (IPr)Pd(R)(X).[48,50] The aryl radical can then transform into **3-$CF_3$** and **4** upon hydrogen-atom abstraction reactions. When R is an alkyl group containing $\beta$-hydrogen, (IPr)Pd(R)(I) might undergo $\beta$-hydride elimination to yield

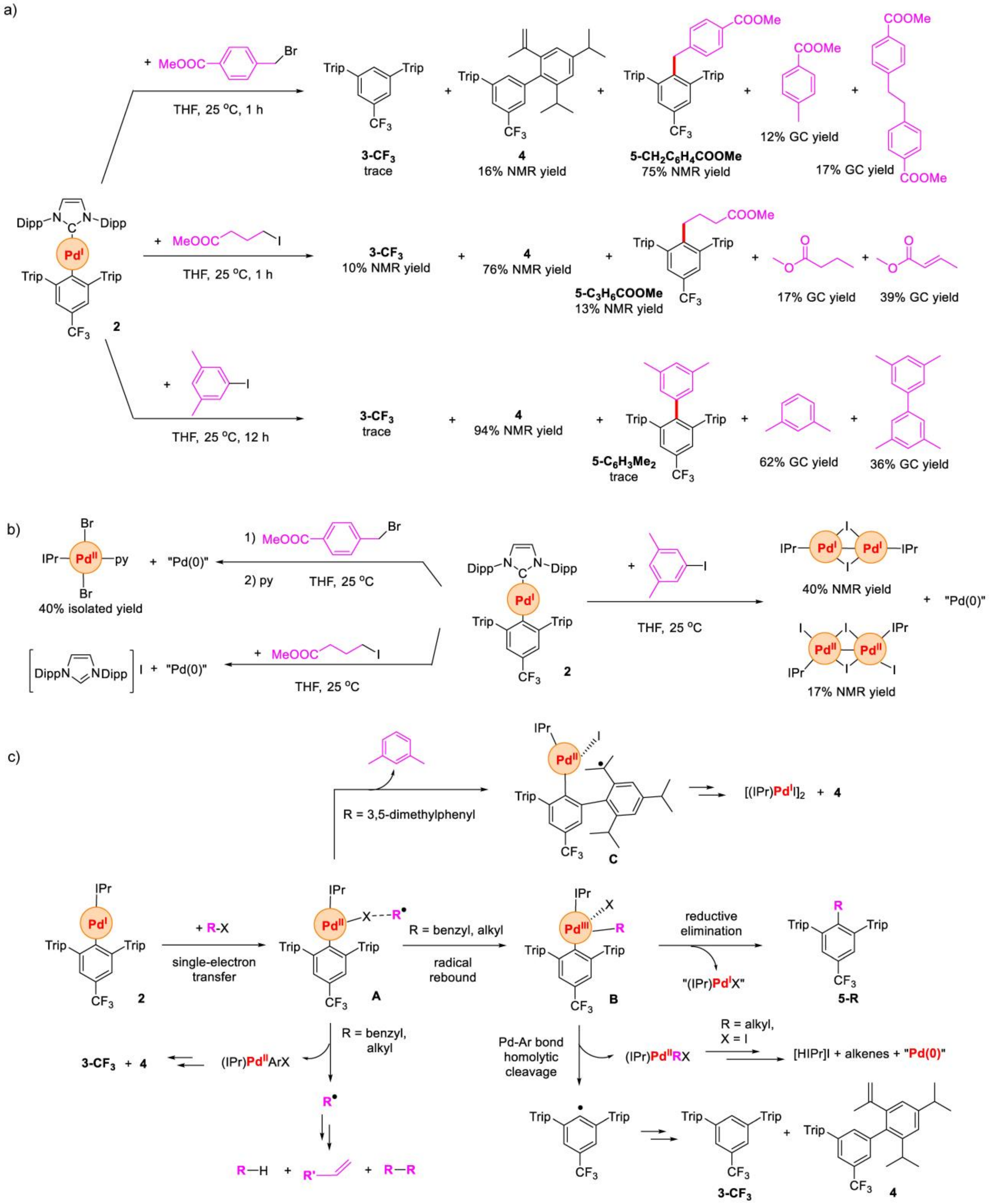

Figure 4. Reactions of the Pd(I) aryl complex **2** with organic halides and their proposed mechanisms. a) Reactions of **2** with organic bromides and iodides. b) Pd-containing complexes formed in the reactions of **2** with the organic halides. c) Proposed reaction pathways for the reactions of **2** with the organic halides.

(IPr)Pd(H)(I) and alkene. The decomposition of (IPr)Pd(H)(I) could form [HPr]I and palladium black (Figure 4c).[52] As to the reaction with 3,5-dimethylphenyl iodide, the resulting aryl radical $[3,5\text{-}Me_2C_6H_3]^•$ is highly reactive and might quickly perform hydrogen-atom-abstraction reaction with the benzylic C-H bonds of the Trip groups on **A**, giving 1,3-dimethylbenzene and the Pd(II) aryl intermediate **C** that could decompose into **3-CF$_3$** and **4**. Indeed, our studies showed that the Pd(II) aryl species [(IPr)Pd(Ar$^{Trip}$-

$CF_3$-*p*)]$^{1+}$, which was generated by single-electron-oxidation of **2** with $AgBF_4$, is unstable at ambient temperature and can convert into a complex mixture containing **3-$CF_3$** and **4** (Figures S39 and S40). The high lability of low-coordinate Pd(II) hydrocarbyl species with NHC ligation has been well documented in literature.[53–55] The aryl homo-coupling product bis(3,5-dimethylphenyl) might come from the interaction of *in-situ* formed Pd(0) species with 3,5-dimethylphenyl iodide.

The good yield of the cross-coupling product in the reaction with the benzyl bromide promoted further experimental and theoretical studies on its mechanism, which support the involvement of radical process in the reaction. Examining the rates of the reactions of **2** with a series of *para*-substituted benzyl bromides (30 equiv.) in THF revealed that the incorporation of electron-donating or electron-withdrawing substituent on the *para*-position of benzyl bromides can accelerate the consumption of **2** (Table S3). Thus, plotting log($k_X/k_H$) versus $\sigma_p$ [56] gave a nonlinear plot (Figure S36). However, when taking both polar substituent and spin-delocalization constant parameters into consideration, the multiple linear regression for the dual-parameter equation for radical reactions [log($k_X/k_H$) = $\rho_{mb}\sigma_{mb}$ + $\rho_{JJ}^{\bullet}\sigma_{JJ}^{\bullet}$ + C] using Jiang's $\sigma_{mb}$ and $\sigma_{JJ}^{\bullet}$ scales can give good linear correlation (Figure 5a).[57] The value of $|\rho_{mb}/\rho_{JJ}^{\bullet}|$ equals 1.36, emphasizing the significance of both polar and spin-delocalizing effects. [57] Dual parameter correlation analysis has been successfully applied for the kinetic data of a bromo-abstraction reaction by a nucleophilic silyl radical, [58] the aziridation reaction of iron imido species with substituted styrenes,[59] and the cyclopropanation reaction of an iron ylide complex with styrenes.[60] Furthermore, controlled experiment showed that in the presence of the radical quencher 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) the reaction of **2** with methyl 4-(bromomethyl)benzoate does not produce the cross-coupling product **5-$CH_2C_6H_4COOMe$**, but yields the coupling product of the benzylic radical with TEMPO, **6** (Figure 5b). The adduct of benzylic radical with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), **7**, was also detected by EPR in the reaction of **2** with methyl 4-(bromomethyl)benzoate and DMPO (Figure 5c).

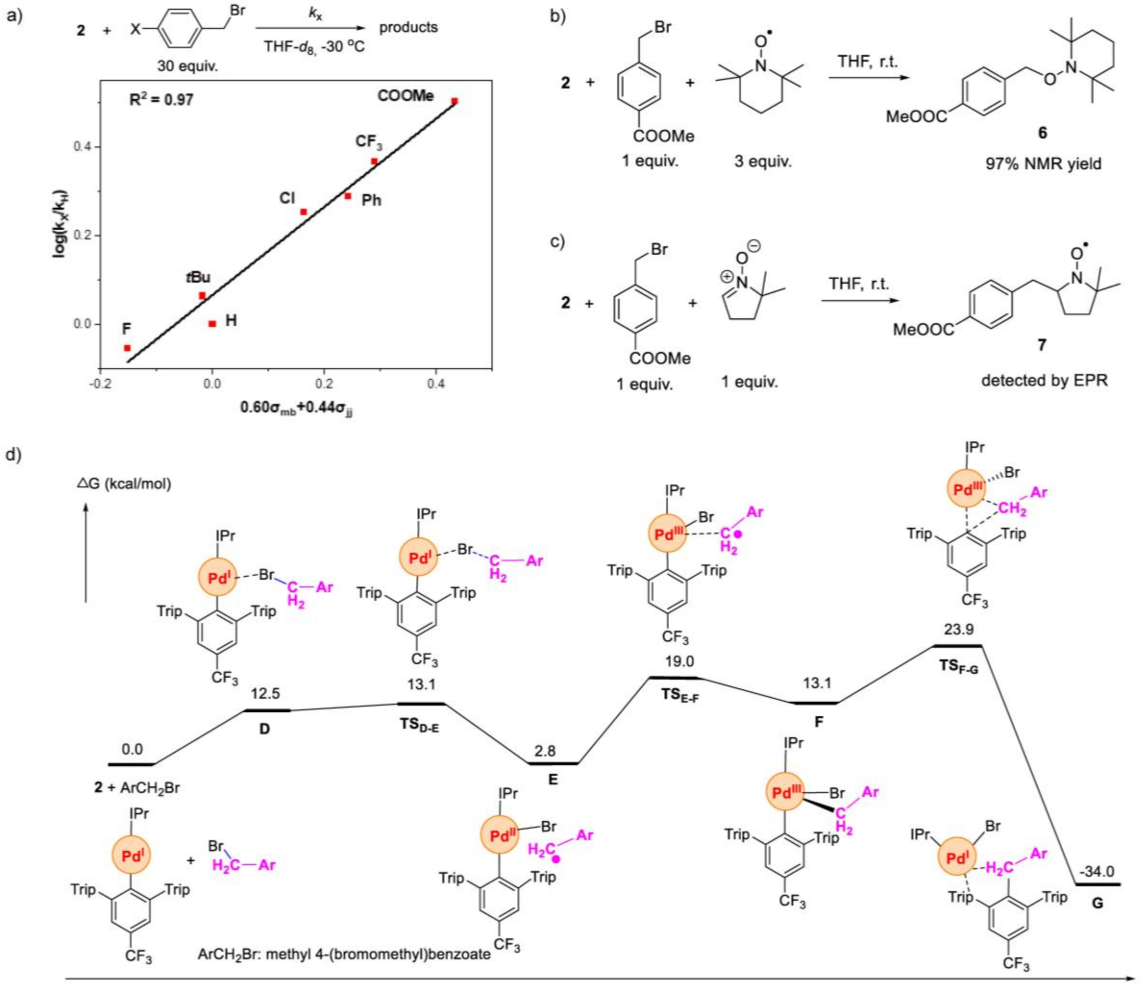

Figure 5. Mechanistic studies on the reactions of **2** with benzylic halides. a) Linear correlation of log($k_X/k_H$) vs 0.60$\sigma_{mb}$ + 0.44$\sigma_{jj}$ for the reactions of **2** and *para*-substituted benzyl bromides in THF-$d_8$ at -30 °C. $\sigma_{mb}$ and $\sigma_{JJ}$ are Jiang's substituent constants. b) Radical trapping experiment of **2** with methyl 4-(bromomethyl)benzoate in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). c) Radical trapping experiment of **2** with methyl 4-(bromomethyl)benzoate in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). d) DFT calculated reaction profile of the C-C cross-coupling reaction of **2** with methyl 4-(bromomethyl)benzoate.

DFT studies on the reaction profile of the cross-coupling reaction of **2** with methyl 4-(bromomethyl)benzoate suggest that the reaction should start in an inner-sphere single-electron transfer process and that reductive elimination reaction from Pd(III) intermediates should be responsible for the C-C bond formation step (Figure 5d). The calculation at the BP86/TZVP level of theory indicates that the single-electron-transfer step that generates a Pd(II) bromide species (IPr)Pd(Br)($Ar^{Trip}$-$CF_3$-*p*) and the benzylic radical $^{\bullet}CH_2C_6H_4COOMe$ is nearly thermal neutral as indicated by the small change of Gibbs free energy of 2.8 kcal/mol (Figure 5d). The coordination of the benzylic radical to the Pd(II) intermediate forms a Pd(III) intermediate (IPr)Pd(Br)($Ar^{Trip}$-$CF_3$-*p*)($CH_2C_6H_4COOMe$) (**F**) that lies above the reactant **E** in energy by about 10.3 kcal/mol. Notably, due to the steric demanding nature of IPr and the *m*-terphenyl ligand, the palladium centers in the intermediates **E** and **F** are found to adapt T-shape and see-saw geometries, respectively, wherein their C(carbene)-Pd-C(aryl) alignments are nearly linear. The C-C bond forming reductive elimination reaction from **F** yields the cross-coupling product and Pd(I) species (IPr)PdBr. This step with a substantial change of Gibbs free energy reaching -47.1 kcal/mol is highly exothermic, resulting in an energy gain of 34 kcal/mol for the full conversion from **2** and methyl 4-(bromomethyl)benzoate to the adduct of the cross-coupling product and (IPr)PdBr (**G**). Among the transition-states throughout the path, the one of the reductive elimination step, $\mathbf{TS_{E\text{-}F}}$, that is 23.9 kcal/mol higher in energy than that of the initial starting materials, is the highest one in energy. The calculated low barrier is consistent with the observation that the cross-coupling reaction can readily take place at room temperature.

It is worth mentioning that Mirica and Chaplin had independently studied the reactions of $[Pd(P^tBu_3)_2]^+$ with aryl iodide and proposed the formation of Pd(III) intermediates via concerted oxidative addition reactions in their systems.[36,38] Our calculation studies on a concerted oxidation addition pathway between **2** and the benzyl bromide, however, failed in locating its transition state probably due to high steric congestion. The mechanistic difference can be ascribed to the different steric and redox properties of the Pd(I) species and the organic halides. Cyclic voltammetry study on **2** indicates the redox event of $\mathbf{2}^{1-/0}$ has the half-wave potential $E_{1/2}$ = -1.30 V (versus standard calomel electrode (*SCE*)), which is much lower than that of $[Pd(P^tBu_3)_2]^{0/1+}$ ($E_{1/2}$ = 0.0 V vs *SCE*),[33] and the redox process of $\mathbf{2}^{0/1+}$ with the potential of the oxidation peak $E_p$ = 0.66 V is irreversible (Figure S9). These potentials hint that the Pd(I) aryl species **2** is more reducing than $[Pd(P^tBu_3)_2]^+$. On the other hand, the benzylic bromide is more oxidizing than aryl iodide. These two factors, in addition with sever steric hindrance around the Pd(I) center in **2** caused by its bulky NHC and aryl ligands, could thus lead to the preference of a stepwise oxidative addition mechanism.

## CONCLUSION

The synthesis and characterization of mononuclear Pd(I) aryl complexes as well as their reactions with organic halides have been studied. The reactions of $[(IPr)PdCl_2]_2$ with the *m*-terphenyl lithium salts $LiAr^{Trip}$-R-*p* in $Et_2O$ are found to yield the two-coordinate Pd(I) aryl complexes [(IPr)Pd($Ar^{Trip}$-R-*p*)] (R = H, $CF_3$) in moderate yields. These Pd(I) aryl complexes are the rare examples of isolable mononuclear Pd(I) complexes featuring X-type co-ligands. Reactivity studies on their reactions with organic halides disclosed their ability in mediating C(aryl)-I, C(alkyl)-I, and C(benzyl)-Br bond cleavage, among which the reactions with *para*-substituted benzyl bromides yield cross-coupling products $ArCH_2$-$Ar^{Trip}$-$CF_3$-*p* in moderate yields. Mechanistic studies by kinetic experiments, radical trapping reactions, as well as theoretic studies have collectively revealed a stepwise oxidative addition-concerted reductive elimination pathway for these cross-coupling reactions.

## ASSOCIATED CONTENT

**Supporting Information**. This material is available free of charge via the Internet at http://pubs.acs.org.
Experimental procedures and characterization data (PDF)
Crystal structures (CIF)
Cartesian coordinates of the calculated structures (XYZ)

**Accession Codes**

CCDC 2346228-2346230 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Fujiwara, S.; Nakamura, M. Electron Spin Resonance of Pd(I). I. γ-Irradiated Bis(acetylacetonato)palladium(II). *J. Chem. Phys.* **1970**, *52* (12), 6299–6301. https://doi.org/10.1063/1.1672940.

(2) Goggin, P. L.; Mink, J. Palladium(I) Carbonyl Halide Complexes. *J. Chem. Soc., Dalton Trans.* **1974**, 534–540. https://doi.org/10.1039/dt9740000534.

(3) Taarit, Y. B.; Vedrine, J. C.; Dutel, J. F.; Naccache, C. Epr Investigation of Structure and Reactivity of Pd(I) Species Generated in Synthetic Mordenite-Type Zeolite. *J Magn Reson* **1978**, *31* (2), 251–257. https://doi.org/10.1016/0022-2364(78)90187-7.

(4) Blake, A. J.; Gould, R. O.; Hyde, T. I.; Schröder, M. Stabilisation of Monovalent Palladium by Tetra-Aza Macrocycles. *J. Chem. Soc., Chem. Commun.* **1987**, 431–433. https://doi.org/10.1039/c39870000431.

(5) Lane, G. A.; Geiger, W. E.; Connelly, N. G. Palladium(I) .π-Radicals. Electrochemical Preparation and Study of Their Reaction Pathways. *J. Am. Chem. Soc.* **1987**, *109* (2), 402–407. https://doi.org/10.1021/ja00236a018.

(6) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. Addition of Ammonia, Water, and Dihydrogen Across a Single Pd-Pd Bond. *J. Am. Chem. Soc.* **2007**, *129* (34), 10318–10319. https://doi.org/10.1021/ja0731571.

(7) Hazari, N.; Hruszkewycz, D. P. Dinuclear Pd(I) Complexes with Bridging Allyl and Related Ligands. *Chem. Soc. Rev.* **2016**, *45* (10), 2871–2899. https://doi.org/10.1039/c5cs00537j.

(8) Fricke, C.; Sperger, T.; Mendel, M.; Schoenebeck, F. Catalysis with Palladium(I) Dimers. *Angew. Chem. Int. Ed.* **2021**, *60* (7), 3355–3366. https://doi.org/10.1002/anie.202011825.

(9) Liu, Q.; Dong, X.; Li, J.; Xiao, J.; Dong, Y.; Liu, H. Recent Advances on Palladium Radical Involved Reactions. *ACS Catal.* **2015**, *5* (10), 6111–6137. https://doi.org/10.1021/acscatal.5b01469.

(10) Sun, X.; Dong, X.; Liu, H.; Liu, Y. Recent Progress in Palladium-Catalyzed Radical Reactions. *Adv. Synth. Catal.* **2021**, *363* (6), 1527–1558. https://doi.org/10.1002/adsc.202001315.

(11) Hama, T.; Hartwig, J. F. α-Arylation of Esters Catalyzed by the Pd(I) Dimer {[P(t-Bu)$_3$]PdBr}$_2$. *Org. Lett.* **2008**, *10* (8), 1545–1548. https://doi.org/10.1021/ol8002578.

(12) Hruszkewycz, D. P.; Wu, J.; Hazari, N.; Incarvito, C. D. Palladium(I)-Bridging Allyl Dimers for the Catalytic Functionalization of CO$_2$. *J. Am. Chem. Soc.* **2011**, *133* (10), 3280–3283. https://doi.org/10.1021/ja110708k.

(13) Bonney, K. J.; Proutiere, F.; Schoenebeck, F. Dinuclear Pd(I) Complexes—Solely Precatalysts? Demonstration of Direct Reactivity of a Pd(I) Dimer with an Aryl Iodide. *Chem. Sci.* **2013**, *4* (12) 4434–4439. https://doi.org/10.1039/c3sc52054d.

(14) Bonney, K. J.; Schoenebeck, F. Experiment and Computation: A Combined Approach to Study the Reactivity of Palladium Complexes in Oxidation States 0 to IV. *Chem. Soc. Rev.* **2014**, *43* (18), 6609–6638. https://doi.org/10.1039/c4cs00061g.

(15) Johansson Seechurn, C. C. C.; Sperger, T.; Scrase, T. G.; Schoenebeck, F.; Colacot, T. J. Understanding the Unusual Reduction Mechanism of Pd(II) to Pd(I): Uncovering Hidden Species and Implications in Catalytic Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2017**, *139* (14) 5194–5200. https://doi.org/10.1021/jacs.7b01110.

(16) Firsan, S. J.; Sivakumar, V.; Colacot, T. J. Emerging Trends in Cross-Coupling: Twelve-Electron-Based L$_1$Pd(0) Catalysts, Their Mechanism of Action, and Selected Applications. *Chem. Rev.* **2022**, *122* (23), 16983–17027. https://doi.org/10.1021/acs.chemrev.2c00204.

(17) Tsuji, J.; Sato, K.; Nagashima, H. Palladium-Catalyzed Addition Reaction of Polyhaloalkanes to Olefins. *Tetrahedron* **1985**, *41* (2), 393–397. https://doi.org/10.1016/S0040-4020(01)96431-2.

(18) Chen, Q.-Y.; Yang, Z.-Y.; Zhao, C.-X.; Qiu, Z.-M. Studies on Fluoroalkylation and Fluoroalkoxylation. Part 28. Palladium(0)-Induced Addition of Fluoroalkyl Iodides to Alkenes: An Electron Transfer Process. *J. Chem. Soc., Perkin Trans. 1* **1988**, 563-567. https://doi.org/10.1039/p19880000563.

(19) Liu, H.; Li, C.; Qiu, D.; Tong, X. Palladium-Catalyzed Cycloisomerizations of (*Z*)-1-Iodo-1,6-Dienes: Iodine Atom Transfer and Mechanistic Insight to Alkyl Iodide Reductive Elimination. *J. Am. Chem. Soc.* **2011**, *133* (16), 6187–6193. https://doi.org/10.1021/ja201204g.

(20) Chen, C.; Tong, X. Synthesis of Organic Halides via Palladium(0) Catalysis. *Org. Chem. Front.* **2014**, *1* (4), 439–446. https://doi.org/10.1039/C4QO00004H.

(21) Ishiyama, T.; Miyaura, N.; Suzuki*, A. Palladium-Catalyzed Carbonylative Cross-Coupling Reaction of Iodoalkanes with 9-Alkyl-9-BBN Derivatives. A Direct and Selective Synthesis of Ketones. *Tetrahedron Lett.* **1991**, *32* (47), 6923–6926. https://doi.org/10.1016/0040-4039(91)80445-C.

(22) Ryu, I. Radical Carboxylations of Iodoalkanes and Saturated Alcohols Using Carbon Monoxide. *Chem. Soc. Rev.* **2001**, *30* (1), 16–25. https://doi.org/10.1039/a904591k.

(23) Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. Unparalleled Rates for the Activation of Aryl Chlorides and Bromides: Coupling with Amines and Boronic Acids in Minutes at Room Temperature. *Angew. Chem. Int. Ed.* **2002**, *41* (24), 4746–4748. https://doi.org/10.1002/anie.200290036.

(24) Proutiere, F.; Aufiero, M.; Schoenebeck, F. Reactivity and Stability of Dinuclear Pd(I) Complexes: Studies on the Active Catalytic Species, Insights into Precatalyst Activation and Deactivation, and Application in Highly Selective Cross-Coupling Reactions. *J. Am. Chem. Soc.* **2012**, *134* (1), 606–612. https://doi.org/10.1021/ja209424z.

(25) Wu, X.; See, J. W. T.; Xu, K.; Hirao, H.; Roger, J.; Hierso, J.; Zhou, J. (Steve). A General Palladium-Catalyzed Method for Alkylation of Heteroarenes Using Secondary and Tertiary Alkyl Halides. *Angew. Chem. Int. Ed.* **2014**, *53* (49), 13573–13577. https://doi.org/10.1002/anie.201408355.

(26) Parasram, M.; Iaroshenko, V. O.; Gevorgyan, V. Endo-Selective Pd-Catalyzed Silyl Methyl Heck Reaction. *J. Am. Chem. Soc.* **2014**, *136* (52), 17926–17929. https://doi.org/10.1021/ja5104525.

(27) Feng, Z.; Min, Q.; Xiao, Y.; Zhang, B.; Zhang, X. Palladium-Catalyzed Difluoroalkylation of Aryl Boronic Acids: A New Method for the Synthesis of Aryldifluoromethylated Phosphonates and Carboxylic Acid Derivatives. *Angew. Chem. Int. Ed*. **2014**, *53* (6), 1669–1673. https://doi.org/10.1002/anie.201309535.

(28) Venning, A. R. O.; Bohan, P. T.; Alexanian, E. J. Palladium-Catalyzed, Ring-Forming Aromatic C–H Alkylations with Unactivated Alkyl Halides. *J. Am. Chem. Soc.* **2015**, *137* (11), 3731–3734. https://doi.org/10.1021/jacs.5b01365.

(29) Parasram, M.; Gevorgyan, V. Visible Light-Induced Transition Metal-Catalyzed Transformations: Beyond Conventional Photosensitizers. *Chem. Soc. Rev.* **2017**, *46* (20), 6227–6240. https://doi.org/10.1039/c7cs00226b.

(30) Zhao, B.; Shang, R.; Wang, G.-Z.; Wang, S.; Chen, H.; Fu, Y. Palladium-Catalyzed Dual Ligand-Enabled Alkylation of Silyl Enol Ether and Enamide under Irradiation: Scope, Mechanism, and Theoretical Elucidation of Hybrid Alkyl Pd(I)-Radical Species. *ACS Catal.* **2019**, *10* (2), 1334–1343. https://doi.org/10.1021/acscatal.9b04699.

(31) Torres, G. M.; Liu, Y.; Arndtsen, B. A. A Dual Light-Driven Palladium Catalyst: Breaking the Barriers in Carbonylation Reactions. *Science* **2020**, *368* (6488), 318–323. https://doi.org/10.1126/science.aba5901.

(32) Troadec, T.; Tan, S.-y.; Wedge, C. J.; Rourke, J. P.; Unwin, P. R.; Chaplin, A. B. One-Electron Oxidation of [M(P$^t$Bu$_3$)$_2$] (M=Pd, Pt): Isolation of Monomeric [M(P$^t$Bu$_3$)$_2$]$^+$ and Redox-Promoted C-H Bond Cyclometalation. *Angew. Chem. Int. Ed*. **2016**, *55* (11), 3754–3757. https://doi.org/10.1002/anie.201511467.

(33) MacInnis, M. C.; DeMott, J. C.; Zolnhofer, E. M.; Zhou, J.; Meyer, K.; Hughes, R. P.; Ozerov, O. V. Cationic Two-Coordinate Complexes of Pd(I) and Pt(I) Have Longer Metal-Ligand Bonds Than Their Neutral Counterparts. *Chem* **2016**, *1* (6), 902–920. https://doi.org/10.1016/j.chempr.2016.11.007.

(34) Krämer, T.; Gyton, M. R.; Bustos, I.; Sinclair, M. J. G.; Tan, S.-y.; Wedge, C. J.; Macgregor, S. A.; Chaplin, A. B. Stability and C–H

Bond Activation Reactions of Palladium(I) and Platinum(I) Metalloradicals: Carbon-to-Metal H-Atom Transfer and an Organometallic Radical Rebound Mechanism. *J. Am. Chem. Soc.* **2023**, *145* (25), 14087–14100. https://doi.org/10.1021/jacs.3c04167.

(35) Maties, G.; Gómez-Sal, P.; Yebra, C. G.; Andrés, R.; De Jesús, E. Reversible Single-Electron-Transfer to Oxygen in a Stable N-Heterocyclic Carbene Palladium(I) Metalloradical. *Inorg. Chem.* **2023**, *62* (49), 19838–19842. https://doi.org/10.1021/acs.inorgchem.3c02878.

(36) Sinclair, M. J. G.; Chaplin, A. B. Heterolytic Carbon–Iodine Bond Cleavage by a Palladium(I) Metalloradical. *Dalton Trans.* **2022**, *51* (31), 11617–11619. https://doi.org/10.1039/D2DT02152H.

(37) Luo, J.; Tran, G. N.; Rath, N. P.; Mirica, L. M. Detection and Characterization of Mononuclear Pd(I) Complexes Supported by N2S2 and N4 Tetradentate Ligands. *Inorg Chem* **2020**, *59* (21), 15659–15669. https://doi.org/10.1021/acs.inorgchem.0c01938.

(38) Tran, G. N.; Bouley, B. S.; Mirica, L. M. Isolation and Characterization of Heteroleptic Mononuclear Palladium(I) Complexes. *J. Am. Chem. Soc.* **2022**, *144* (43), 20008–20015. https://doi.org/10.1021/jacs.2c08765.

(39) Green, M. L. H. A New Approach to the Formal Classification of Covalent Compounds of the Elements. *J. Organomet. Chem.* **1995**, *500* (1–2), 127–148. https://doi.org/10.1016/0022-328X(95)00508-N.

(40) Liu, J.; Bollmeyer, M. M.; Kim, Y.; Xiao, D.; MacMillan, S. N.; Chen, Q.; Leng, X.; Kim, S. H.; Zhao, L.; Lancaster, K. M.; Deng, L. An Isolable Mononuclear Palladium(I) Amido Complex. *J. Am. Chem. Soc.* **2021**, *143* (28), 10751–10759. https://doi.org/10.1021/jacs.1c04965.

(41) Bruckhoff, T.; Ballmann, J.; Gade, L. H. Radicalizing CO by Mononuclear Palladium(I). *Angew. Chem. Int. Ed*. **2024**, e202320064. https://doi.org/10.1002/anie.202320064.

(42) Yamashita, M.; Hartwig, J. F. Synthesis, Structure, and Reductive Elimination Chemistry of Three-Coordinate Arylpalladium Amido Complexes. *J. Am. Chem. Soc.* **2004**, *126* (17), 5344–5345. https://doi.org/10.1021/ja0315107.

(43) Su, M.; Buchwald, S. L. A Bulky Biaryl Phosphine Ligand Allows for Palladium-Catalyzed Amidation of Five-Membered Heterocycles as Electrophiles. *Angew. Chem. Int. Ed*. **2012**, *51* (19), 4710–4713. https://doi.org/10.1002/anie.201201244.

(44) Pirkl, N.; Del Grosso, A.; Mallick, B.; Doppiu, A.; Gooßen, L. J. Dihalogen-Bridged NHC–Palladium(I) Dimers: Synthesis, Characterisation and Applications in Cross-Coupling Reactions. *Chem. Commun.* **2019**, *55* (36), 5275–5278. https://doi.org/10.1039/C9CC02239B.

(45) Ivančič, A.; Košmrlj, J.; Gazvoda, M. Elucidating the Reaction Mechanism of a Palladium-Palladium Dual Catalytic Process through Kinetic Studies of Proposed Elementary Steps. *Commun. Chem.* **2023**, *6*, 51. https://doi.org/10.1038/s42004-023-00849-x.

(46) Manolikakes, G.; Knochel, P. Radical Catalysis of Kumada Cross-Coupling Reactions Using Functionalized Grignard Reagents. *Angew. Chem. Int. Ed*. **2009**, *48* (1), 205–209. https://doi.org/10.1002/anie.200803730.

(47) Lanci, M. P.; Remy, M. S.; Kaminsky, W.; Mayer, J. M.; Sanford, M. S. Oxidatively Induced Reductive Elimination from $(^t\mathrm{Bu}_2\mathrm{bpy})\mathrm{Pd}(\mathrm{Me})_2$ : Palladium(IV) Intermediates in a One-Electron Oxidation Reaction. *J. Am. Chem. Soc.* **2009**, *131* (43), 15618–15620. https://doi.org/10.1021/ja905816q.

(48) Hickman, A. J.; Sanford, M. S. High-Valent Organometallic Copper and Palladium in Catalysis. *Nature* **2012**, *484*, 177–185. https://doi.org/10.1038/nature11008.

(49) Maestri, G.; Malacria, M.; Derat, E. Radical Pd(III)/Pd(I) Reductive Elimination in Palladium Sequences. *Chem. Commun.* **2013**, *49* (88), 10424–10426. https://doi.org/10.1039/C3CC46355A.

(50) Powers, D. C.; Ritter, T. Palladium(III) in Synthesis and Catalysis. *Top. Organomet. Chem.* 2011, *35*, 129–156. https://doi.org/10.1007/978-3-642-17429-2_6.

(51) Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. Stable Mononuclear Organometallic Pd(III) Complexes and Their C-C Bond Formation Reactivity. *J. Am. Chem. Soc.* **2010**, *132* (21), 7303–7305. https://doi.org/10.1021/ja103001g.

(52) Cavell, K. N-Heterocyclic Carbenes/Imidazolium Salts as Substrates in Catalysis: The Catalytic 2-Substitution and Annulation of Heterocyclic Compounds. *Dalton Trans.* **2008**, 6676-6685. https://doi.org/10.1039/b811449h.

(53) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. Zerovalent Palladium and Nickel Complexes of Heterocyclic Carbenes: Oxidative Addition of Organic Halides, Carbon−Carbon Coupling Processes, and the Heck Reaction. *Organometallics* **1999**, *18* (9), 1596–1605. https://doi.org/10.1021/om9809771.

(54) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. Kinetic and Density Functional Studies on Alkyl-Carbene Elimination from Pd(II) Heterocylic Carbene Complexes: A New Type of Reductive Elimination with Clear Implications for Catalysis. *J. Am. Chem. Soc.* **2001**, *123* (17), 4029–4040. https://doi.org/10.1021/ja003861g.

(55) Marshall, W. J.; Grushin, V. V. Synthesis, Structure, and Reductive Elimination Reactions of the First (σ-Aryl)Palladium Complex Stabilized by IPr *N*-Heterocyclic Carbene. *Organometallics* **2003**, *22* (8), 1591–1593. https://doi.org/10.1021/om030099t.

(56) Hansch, C.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **1991**, *91* (2), 165–195. https://doi.org/10.1021/cr00002a004.

(57) Jiang, X.-K. Establishment and Successful Application of the $\sigma_{JJ}^{\bullet}$ Scale of Spin-Delocalization Substituent Constants. *Acc. Chem. Res.* **1997**, *30* (7), 283–289. https://doi.org/10.1021/ar950121h.

(58) Jiang, X.-K.; Ding, W. F.-X.; Zhang, Y.-H. The Nucleophilic Silyl Radical: Dual-Parameter Correlation Analysis of the Relative Rates of Bromine-Atom Abstraction Reactions as Measured by a Rigorous Methodology. *Tetrahedron* **1997**, *53* (25), 8479–8490. https://doi.org/10.1016/S0040-4020(97)00527-9.

(59) Hennessy, E. T.; Liu, R. Y.; Iovan, D. A.; Duncan, R. A.; Betley, T. A. Iron-Mediated Intermolecular N-Group Transfer Chemistry with Olefinic Substrates. *Chem. Sci.* **2014**, *5* (4), 1526–1532. https://doi.org/10.1039/C3SC52533C.

(60) Liu, J.; Hu, L.; Wang, L.; Chen, H.; Deng, L. An Iron(II) Ylide Complex as a Masked Open-Shell Iron Alkylidene Species in Its Alkylidene-Transfer Reactions with Alkenes. *J. Am. Chem. Soc.* **2017**, *139* (10), 3876–3888. https://doi.org/10.1021/jacs.7b00484.

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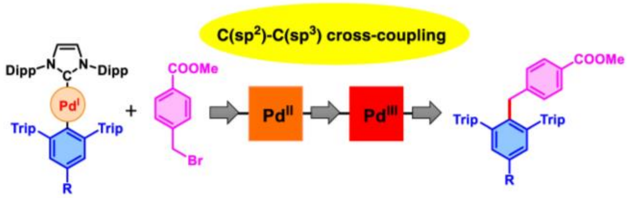
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