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Cross-Coupling Catalysis by an Anionic Palladium Complex

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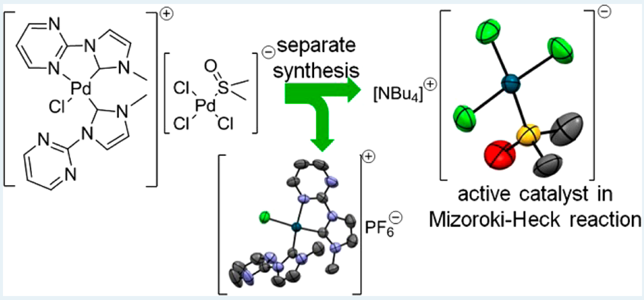
Supporting Information

ABSTRACT: Recent studies have shown that anionic palladium complexes are viable catalysts for a range of catalytic cross-coupling reactions. We present a one-step synthesis of the anionic "ligandless" palladium complex $[NBu_4][Pd(DMSO)Cl_3]$ together with its crystal structure. This compound has been shown to be an active precatalyst in the Mizoroki−Heck reaction. Under Jeffery conditions, activated aryl chlorides can be coupled in yields of up to 94% without the need of an additional ligand. The presence of a small amount of water was necessary for product formation. An Amatore−Jutand-type catalytic cycle is consistent with the results presented herein. For comparison with the known mixed complex $[(pym\text{-}Im\text{-}Me)_2PdCl][Pd(DMSO)Cl_3]$, the cationic complex $[(pym\text{-}Im\text{-}Me)_2PdCl]PF_6$ (pym = pyrimidyl, Im = imidazolin-2-ylidene) has been synthesized and characterized using standard techniques.



KEYWORDS: *palladium, Mizoroki−Heck reaction, C−C coupling, NHC, anionic complex*

1. INTRODUCTION

Of the many palladium-catalyzed reactions developed in the past 50 years, catalytic carbon−carbon cross-couplings are among the most important and thoroughly studied transformations.[1] Consequently, the 2010 Nobel Prize in chemistry was awarded jointly to Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki.[2] Particularly interesting, in terms of cost and atom efficiency, is the concept of "ligandless" catalytic systems,[3] e.g., the absence of stabilizing phosphine or *N*-heterocyclic carbene (NHC) ligands,[4] or the use of nanoparticles in ionic liquids.[5]

Although anionic species are frequently proposed to participate in cross-coupling catalysis,[6] the direct use of anionic palladium complexes remains scarce and is mostly limited to compounds that contain imidazolium cations.[7] However, these cannot be considered as truly ligandless systems, since, under the basic reaction conditions, the formation of NHC complexes is possible.[7a] On the other hand, several neutral coordination compounds of palladium salts and DMSO are known,[8] and these compounds show an interesting catalytic behavior in oxidation and cycloisomerization reactions, as demonstrated by Stahl and others.[9] The trichlorido dimethylsulfoxido palladate(II) ($[Pd(DMSO)Cl_3]$) anion combines these types of catalysts. It has been described in a limited number of complexes[10] and salts,[11] yet only few accounts on its catalytic activity exist.[12]

Originating from the use of (C^C)-chelating biscarbene palladium complexes[13] in the Mizoroki−Heck reaction,[14] we investigated a related series of (C^N)-chelating NHC palladium complexes (Figure 1).[10b] Several other palladium-containing cations of the latter type comprising the pyrimidyl moiety were reported.[15] We found that, for small substituents at the NHC ligands (e.g., those substituted by a methyl group), two ligands are bound at a cationic palladium center, accompanied by a $[Pd(DMSO)Cl_3]$ counterion (**1**, Figure 1). In the Mizoroki−Heck reaction, complex **1** showed superior activity compared to the other neutral complexes. We reasoned that the higher catalytic activity might result from the anionic palladium species. Indeed, recent examples of catalytically active anionic palladium species were reported by Navarro for the Mizoroki−Heck reaction[16] and by Trzeciak for the related oxidative Heck reaction[17] (Figure 1).

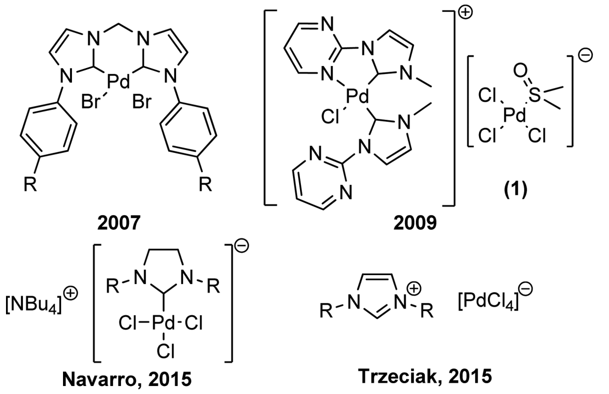


Figure 1. Selected palladium precatalysts for the Mizoroki−Heck and related reactions.

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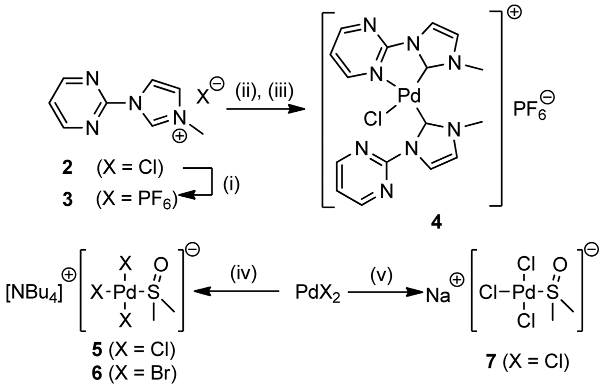
To investigate the origin of the catalytic activity of **1**, we decided to separately synthesize the palladium-containing species in complex **1** to identify the palladium species responsible for the superior catalytic activity. During the course of the investigation, we found that water plays an important role in the Mizoroki−Heck reaction. Finally, the scope of this reaction using different aryl bromides and chlorides has been explored.

2. RESULTS AND DISCUSSION

Synthesis and Analytical Data. The synthesis of complex **1** from the imidazolium salt **2** and dichloro(1,5-cyclooctadiene)palladium(II) (Pd(cod)Cl_2) has been described previously.[10b] Complex **4** was synthesized following a modified literature procedure by Chen (Scheme 1, i−iii).[15c] In the first step, the imidazolium hexafluorophosphate salt **3**,[18] which was generated by salt metathesis from the known compound **2**,[19] is deprotonated by silver oxide, yielding an intermediate silver carbene complex. The crude product is used in the following transmetalation reaction to palladium, yielding compound **4**. The anionic complex **5** was synthesized following a modified literature procedure by Sharutina (Scheme 1, iv).[11c] Equimolar amounts of tetrabutylammonium chloride and palladium chloride are dissolved in dimethylsulfoxide (DMSO). The excess solvent is removed *in vacuo* and the product is precipitated by adding diethyl ether to a concentrated solution of **5** in dichloromethane. This procedure allows for a convenient one-step access to compound **5** with significantly higher yield, compared to a previously described synthesis.[11b] Compound **6** has been synthesized analogously for comparison (Scheme 1, iv). Complexes **5** and **6**, with melting points of 76 and 51 °C, respectively, are ionic liquids.[20] To investigate the influence of the cation, compound **7** was synthesized by refluxing a suspension of 1 equiv each of sodium chloride, palladium chloride, and DMSO (Scheme 1, v).

Scheme 1. Synthesis of Compounds 3−7[a]



[a]Conditions: (i) KPF_6, H_2O/MeOH, rt, 2 d, 94%; (ii) Ag_2O, MeCN, rt, overnight; (iii) Pd(cod)Cl_2, MeCN, rt, overnight, 70% (over two steps); (iv) NBu_4X, DMSO, 60 °C, 15 min, **5**: 95%, **6**: 93%; and (v) NaCl, DMSO, DCM, reflux, 5 d, 94%.

To understand the coordination of the DMSO ligand toward the anionic palladium center, infrared (IR) spectroscopy has been employed (see Figure S1 in the Supporting Information (SI)). The coordination modes of DMSO to transition metals have been investigated thoroughly.[21] Generally, S-coordination of the DMSO ligand leads to an increase of the wavenumbers of the characteristic S−O vibration mode while O-coordination leads to a decrease.[21c] The characteristic S−O vibration mode in liquid DMSO has a wavenumber of 1019 cm^{-1}, while this value increases to 1123 cm^{-1} for complexes **1**, **5**, and **7** and 1119 cm^{-1} for complex **6**, respectively. In contrast, no S−O vibration mode with a lower wavenumber, compared to free DMSO, has been observed. These results indicate that, in complexes **1** and **5**−**7**, the DMSO ligand is bound to the palladium center via the S atom.

Solid-state structures of compounds **4** and **5** have been obtained via slow diffusion of diethyl ether into a saturated solution of the corresponding complex in DCM (see Figures 2a and 2b). Selected bond lengths, angles, and torsions are given in the caption of Figure 2. In both cases, palladium adopts a slightly distorted square planar geometry. In compound **4**, the Pd−C1 and the Pd−C9 distances are similar, having values of 1.969(3) Å and 1.976(3) Å, respectively. This shows that the nature of the metal−carbene bond is only slightly affected by the bonding of the ligand in a κ^2 or κ^1 fashion. The κ^1-bound ligand is tilted out of the palladium coordination plane by 73.9(3)°.

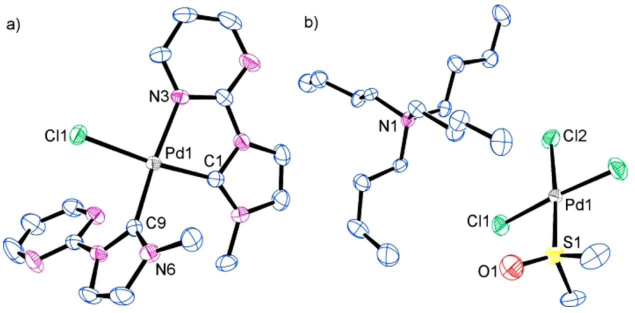


Figure 2. ORTEP representations of the synthesized compounds. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. (a) Compound **4** (excluding one molecule of co-crystallized DCM and the disordered hexafluorophosphate counterion). [Selected bond lengths (Å), angles (deg), and torsions (deg): Pd1−Cl1, 2.3350(8); Pd1−C1, 1.969(3); Pd1−C9, 1.976(3); Pd1−N3, 2.094(2); C1−Pd1−C9, 97.73(11); C1−Pd1−C9−N6, 73.9(3).] (b) Compound **5**. [Selected bond lengths (Å), angles (deg) and torsions (deg): Pd1−Cl1, 2.295(2); Pd1−Cl2, 2.298(2); Pd1−S1, 2.230(2); S1−O1, 1.460(5); Cl1−Pd1−S1−O1, 51.6(2).]

In compound **5**, the Pd−Cl1 and Pd−Cl2 bonds are 2.295(2) and 2.298(2) Å, respectively. Thus, the trans influence of the DMSO ligand is small. The Pd−S distance of 2.230(2) Å is similar to analogous reported complexes.[11c] All bond lengths, angles, and torsions of compounds **4** and **5** are similar to those reported for the mixed compound **1**.[10b]

In the packing diagram of compound **5**, chains of DMSO ligands are visible, with an average intermolecular C−O distance of 3.18 Å, slightly shorter than the sum of the van der Waals radii of 3.22 Å (Figure 3).[22] This indicates that significant dipole−dipole interactions of the highly polar DMSO molecules among themselves are still present in the solid-state structure of complex **5**. The Pd atom and the three Cl atoms are attached perpendicular to these DMSO chains. Between two palladium ligand spheres, the noncoordinating tetrabutylammonium counterion is enclosed. The unusual folding of one butyl group has also been reported in some structurally related palladium complexes.[23]

Catalysis. Following the observation that complex **1** performs exceptionally well in the Mizoroki−Heck reaction,[10b]

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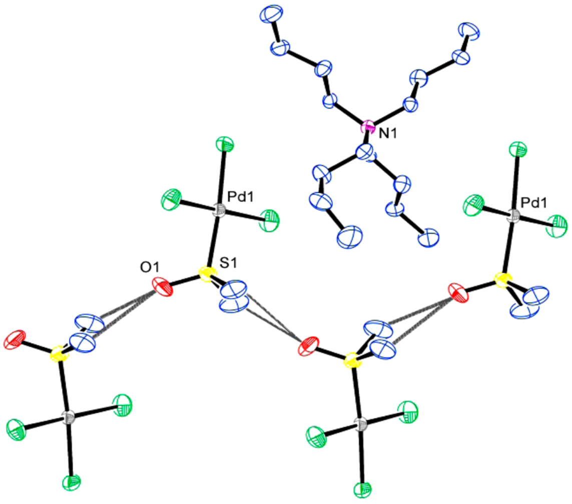
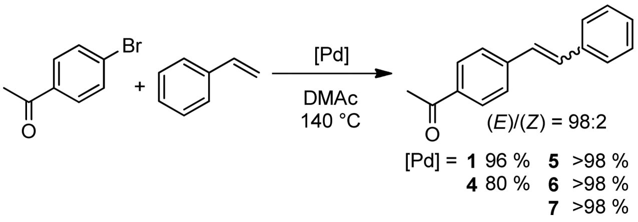


Figure 3. Packing of compound **5** as an ORTEP drawing. Hydrogen atoms are omitted, and only one tetrabutylammonium cation is shown for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 2. The Mizoroki–Heck Reaction Using Aryl Bromides[a]



[a]General reaction conditions: 1 mmol 4-bromoacetophenone, 1.4 mmol styrene, 0.014 mol % [Pd], 1.1 equiv NaOAc, 5 mL DMAc, 140 °C, 24 h. All yields were determined by GC using dodecane as internal standard and are given as an average of two runs. The 1,1-regioisomer was not detected.

we investigated to what extent each of the palladium species in the complex contributes to the catalytic activity. The reaction of bromoacetophenone and styrene in the presence of sodium acetate as a base in dimethylacetamide was chosen as a model system (see Scheme 2). A first direct comparison revealed that the cationic precatalyst **4** itself does not lead to full conversion, even after 24 h. However, with any of the anionic complexes **5**–**7**, full conversion is achieved. In every case, the E/Z selectivity is ≥98:2, while the 1,1-regioisomer was not observed. All yields are given for the major product. If the reaction is performed in air, no product is obtained using complex **4**, while the catalytic activity of complexes **5** and **6** is retained.

We chose complex **5** for further optimization studies, because it showed high catalytic activity, tolerance toward air, and can be synthesized in one step, starting from commercially available reagents.

Coupling of Aryl Chlorides. The Mizoroki–Heck coupling of aryl chlorides requires different reaction conditions, since these are less-reactive substrates than aryl bromides (see Table 1, as well as Table S1 in the SI). The addition of tetrabutylammonium chloride (TBACl) was crucial for product formation to occur. The reduction of the catalyst load led to improved yields (Table 1, entries 1–3).[24] We noted that the yield was identical after reaction times of 6 and 24 h, indicating that catalyst decomposition occurs. Doubling the amount of sodium acetate further increased the yield to 74% (Table 1, entries 3 and 4). An increase of catalyst load to 5 mol % was less efficient, as well as varying the reaction temperature (Table 1, entries 5–7).

Table 1. Results of the Mizoroki–Heck Reaction with Aryl Chlorides and Different Stabilizers[a]

entry	catalyst[b]	stabilizer[b]	base [equiv]	yield[c] [%]
1	**5** (0.5)	TBACl (20)	1.1	50
2	**5** (0.1)	TBACl (20)	1.1	58
3	**5** (0.05)	TBACl (20)	1.1	66
4	**5** (0.05)	TBACl (20)	2.2	74
5	**5** (5)	TBACl (20)	2.2	44
6	**5** (0.05)	TBACl (20)	2.2	11[d]
7	**5** (0.05)	TBACl (20)	2.2	54[e]
8	**5** (0.05)	LiCl (20)	2.2	4
9	**5** (0.05)	$TBAPF_6$[f] (20)	2.2	1
10	**5** (0.05)	TBABr[g] (20)	2.2	21
11	**5** (0.05)	TBACl (15) TBABr (5)	2.2	67
12[h]	**5** (0.05)	TBACl (20)	2.2	0
13[h,i]	**5** (0.05)	TBACl (20)	2.2	55 (48)[j]
14[h,i]	**5** (0.05)	TBACl (20) NaCl (400)	2.2	82
15[h,i]	**5** (0.05)	NaCl (400)	2.2	7
16[h,i]	**5** (0.05)	TBACl (50)	2.2	**94**[k] (88)[l]
17[h,i]	**1** (0.05)	TBACl (50)	2.2	55
18[h,i]	**4** (0.05)	TBACl (50)	2.2	7
19[h,i]	**6** (0.05)	TBACl (50)	2.2	77
20[h,i]	**7** (0.05)	TBACl (50)	2.2	48
21[h,i]	$PdCl_2$ (0.05)	TBACl (50)	2.2	69 (35)[l]
22[h,i]	$PdBr_2$ (0.05)	TBACl (50)	2.2	70

[a]General reaction conditions: 1 mmol 4-chloroacetophenone, 1.4 mmol styrene, 5 mL DMAc, sodium acetate, 140 °C, 6 h. [b]Catalyst and stabilizer amounts (shown in parentheses) are given in units of mol %. [c]Yield given for the major product; the 1,1-regioisomer was not observed. The yield after 24 h was identical in every case. [d]At 120 °C. [e]At 160 °C. [f]Tetrabutylammonium hexafluorophosphate. [g]Tetrabutylammonium bromide. [h]Using rigorously dried reagents. [i]50 μL water added. [j]100 μL water added. [k]Corresponding to a TON of 1880 and a TOF of 313 h^{-1}, [l]After 2 h.

Subsequently, different stabilizers were tested. The use of lithium chloride or tetrabutylammonium hexafluorophosphate led to an almost-complete loss of catalytic activity, indicating that the simultaneous presence of chloride and tetrabutylammonium ions is necessary for the reaction (Table 1, entries 8 and 9). However, if tetrabutylammonium bromide (TBABr) is added instead of TBACl, the yield is decreased to 21%, compared to 74% yield, respectively (Table 1, entry 10). This effect persists, to a lesser extent, if a mixture of TBACl and TBABr is employed (Table 1, entry 11). Other stabilizers also were less efficient (see Table S1 (entries 7–14) in the SI).

In the course of the optimization, we noticed a complete loss of catalytic activity, if rigorously dried reagents are employed (Table 1, entry 12). However, the catalytic activity reappeared after addition of a defined small amount of water, while larger amounts of water led to lower catalytic activity (Table 1, entry 13). We reasoned that the presence of trace amounts of water might be responsible for catalyst activation, as described previously.[3a,25] Since water might play a dual role, i.e., also leading to catalyst deactivation,[26] we chose to increase the amount of stabilizer. Indeed, the addition of a large amount of sodium chloride, in addition to TBACl, led to a yield of 82% (Table 1, entry 14), while adding only sodium chloride led to low yields (Table 1, entry 15). A yield of 94% was achieved if the amount of TBACl was increased to 50 mol % (Table 1, entry 16). Comparing different precatalyst systems under the optimized reaction conditions, we found that catalyst **5** is superior not only to the other complexes presented, but also to commercially available palladium sources (see Table 1, entries 17–22, as well as Table S1 (entries 18 and 19)).

Reaction Scope. Various aryl bromides and chlorides were coupled under the optimized reaction conditions. Activated aryl chlorides with varying *meta-* or *para*-substituents were coupled with styrene in very good yields (Figure 4, condition A). For example, 1-chloro-4-nitrobenzene was coupled to styrene in an excellent yield of 91%. Coordinating functional groups are able to poison the catalyst, leading to yields of 36% and 15% for 4-chlorobenzonitrile and 3-chloropyridine, respectively, while deactivated aryl chlorides were unreactive. However, deactivated aryl bromides were coupled efficiently. Activated aryl bromides can be coupled in excellent yields using a smaller amount of stabilizer and base, since these are more reactive substrates (Figure 4, condition B). Generally, both inductively and mesomerically electron-withdrawing substituents in the *meta-* or *para*-position of the aryl halide are tolerated. Substrates with larger *ortho*-substituents were unreactive under the employed conditions. Different alkenes were tolerated in the reaction. The use of electron-rich styrenes still led to high yields and high selectivity for the (E)-product, while only small amounts of the 1,1-regioisomer were observed. The 1,1-regioisomer was not observed if styrene was used as the alkene.

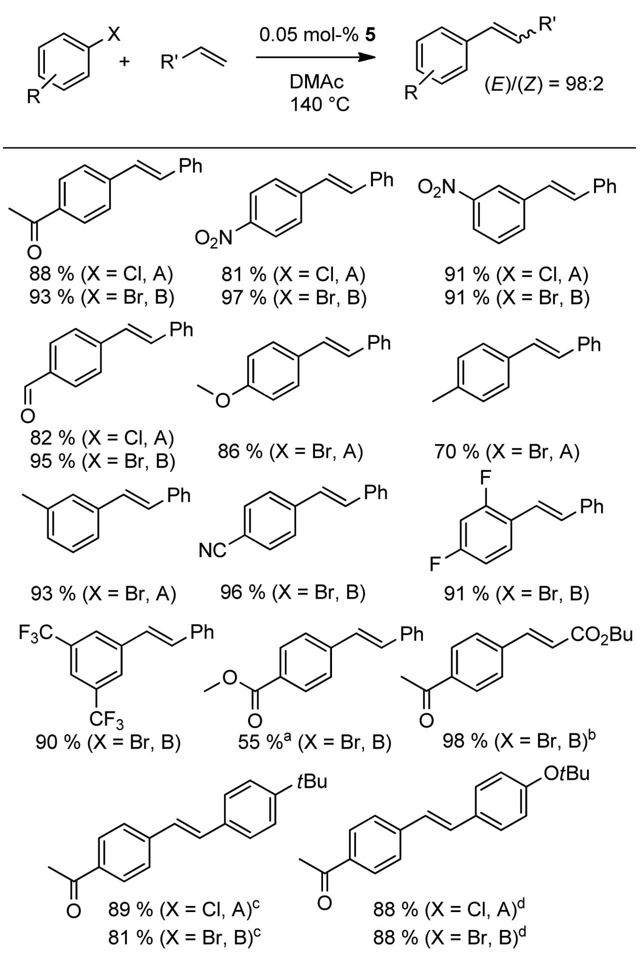
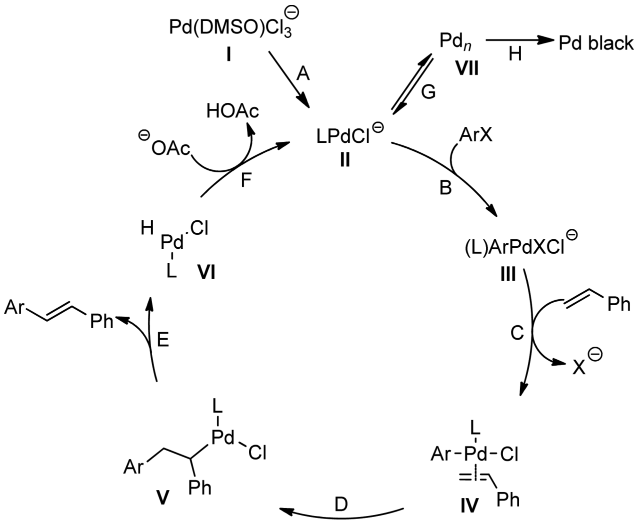


Figure 4. Results in the Mizoroki–Heck reaction using different substrates. Reaction conditions: 1 mmol haloarene, 1.4 mmol styrene, 5 mL DMAc, 140 °C, 6 h ((A) 2.2 mmol NaOAc, 50 mol % TBACl, 50 μL water; (B) 1.1 mmol NaOAc, 20 mol % TBACl); isolated yield, average of two runs. [Footnotes shown in figure: (a) At full conversion. In a side reaction, the methyl ether was cleaved, leading to lowered yields. (b) For X = Cl, hydrolysis of butyl acrylate occurred, instead of product formation. (c) 3% of the 1,1-regioisomer were observed. (d) 1% of the 1,1-regioisomer was observed.]

Mechanistic Considerations. Based on the results in this paper and the available literature,[16] a catalytic cycle involving anionic palladium species is reasonable (Scheme 3). This important mechanistic proposal has been made by Amatore and Jutand, who studied the influence of quaternary ammonium salts on the Mizoroki–Heck reaction in detail.[6a,27] In this mechanism, a palladium(II) precursor (**I**) is transformed to the active anionic, dicoordinate palladium(0) species (**II**) by reduction (Scheme 3, step A).[3a] The presence of TBACl ensures a high chloride ion concentration and thus might enhance the stability of a highly active anionic palladium(0) species **II**, leading to improved catalytic activity of complex **5**. The anionic species **II** undergoes oxidative addition more easily than their neutral counterparts (Scheme 3, step B),[6e] leading to an anionic palladium(II) species (**III**). After coordination of the alkene by displacement of an anionic ligand, migratory insertion occurs, followed by β-hydride elimination and subsequent base-assisted reductive elimination (Scheme 3, steps C–F).[16] The active species **II** could be in equilibrium with palladium nanoparticles (**VII**) as a resting state, serving as a catalyst reservoir (Scheme 3, step G).[24,28] However, it cannot be completely ruled out that these nanoparticles also are catalytically active by themselves. Aggregation of these

Scheme 3. Proposed Mechanism[a]



[a](A) Reduction of the palladium(II) precursor, (B) oxidative addition, (C) coordination of the alkene, (D) migratory insertion, (E) β-hydride elimination and simultaneous decoordination, (F) reductive elimination, (G) reversible formation of stabilized palladium nanoparticles by aggregation, (H) irreversible formation of palladium black. L = DMSO, X = Cl, Br.

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palladium nanoparticles might then irreversibly deactivate the catalyst (Scheme 3, step H).[24b] The stabilization of palladium nanoparticles by TBACl has been discussed,[29] ultimately slowing the formation of inactive palladium black. The fact that reducing the catalyst load increases the yield provides evidence for the presence of palladium nanoparticles.[24b]

3. CONCLUSIONS

In summary, the origin of the catalytic activity of complex **1**, containing two different palladium species, has been investigated. Therefore, the cationic complex **4** has been synthesized and an improved protocol has been developed as a high-yielding, one-step access to complex **5**. The anionic complex **5** showed higher activity in the Mizoroki−Heck coupling of 4-bromoacetophenone and styrene, compared to the cationic complex **4**. Complex **5** was also successfully used in the Mizoroki−Heck reaction of activated aryl chlorides under Jeffery conditions. The scope of the reaction has been explored, revealing that complex **5** is well-suited for the Mizoroki−Heck coupling of aryl bromides and activated aryl chlorides.

It was shown that a high catalytic activity of complex **5** is linked to the simultaneous presence of tetrabutylammonium cations, chloride anions, and trace amounts of water. The fact that a defined small amount of water is necessary for catalytic activity might be important for further work on ligandless catalytic systems. The observations are consistent with an Amatore−Jutand-type catalytic cycle. Detailed investigations on the mechanism of the Mizoroki−Heck reaction catalyzed by complex **5**, especially on the activation step and the role of water, and further cross-couplings will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b03655.

Additional figures and tables, experimental procedures, analytical data and NMR data, and spectra (PDF)

Crystallographic data (CCDC 1540014) for compound **4** (CIF)

Crystallographic data (CCDC 1540013) for compound **5** (CIF)

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Notes

The authors declare no competing financial interest.

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