

Synthesis of Surface Organopalladium Intermediates in Coupling Reactions: The Mechanistic Insight

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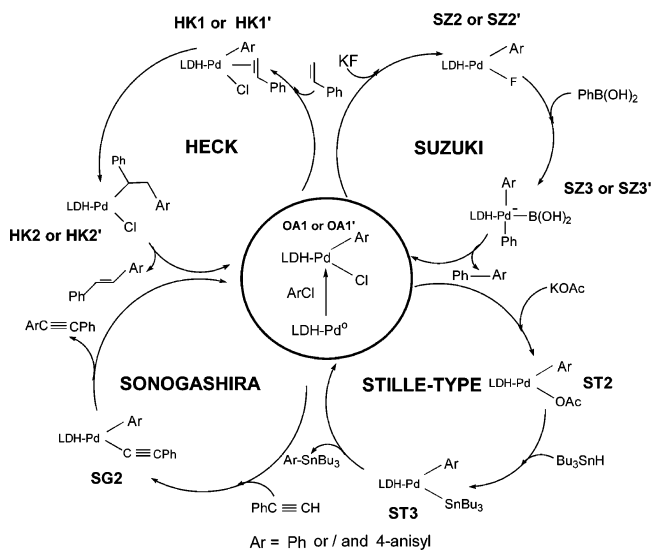
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Palladium-catalyzed coupling of haloarenes by Heck-, Suzuki-, Sonogashira-, and Stille-type reactions is a widely used methodology in modern organic synthesis, because the coupling products find good applications as intermediates in the preparation of materials,¹ natural products,² and bioactive compounds.³ Although kinetic,⁴ electrospray mass spectrometry,^{5–7} NMR and cyclic voltammetry,^{8,9} and IR¹⁰ studies suggest the plausible mechanistic path based on the identification of some of the transient species formed in the homogeneous catalytic reactions, no serious attempt is made to isolate and characterize the intermediates to validate the mechanism. Moreover, it is a very difficult task to isolate or extract molecular organometallic intermediates from the homogeneous reaction, while the surface transient organometallic intermediates formed in the heterogeneous catalysis can be isolated by simple filtration. However, the greatest challenge lies in the conceptual transfer of molecular organometallic chemistry to surface organometallic chemistry to achieve single-site industrially desired heterogeneous catalyst, and to realize high order of activity and selectivity in the chemical reactions.¹¹ In an effort to validate the mechanism of the C–C coupling involving Heck-, Suzuki-, Sonogashira-, and Stille-type reactions, and evolution of single site catalysis, we disclose here the preparation of surface transient organometallic (STO) intermediates sequentially for each of the C–C coupling reactions of chloroarenes on layered double hydroxides (LDH)–Pd⁰ and characterization by XPS and TGA–MS for the first time.

The oxidative addition of haloarenes to Pd⁰ is the first step in these coupling reactions (see the Supporting Information). LDH–MeOC₆H₄PdCl (OA1) and LDH–PhPdCl (OA1') freshly prepared and well characterized by the reaction of 4-chloroanisole and chlorobenzene, respectively, with the defect sites of the nanopalladium particles (4–6 nm) immobilized on layered double hydroxides (LDH)–Pd⁰¹² are used directly in the succeeding C–C coupling reactions to isolate and elucidate the structures of sequentially synthesized STO intermediates unambiguously in the reaction path.¹³

The reaction of STO intermediates (OA1) and (OA1') with excess styrene gives rise to surface transient σ -complex (HK2) and (HK2'), respectively, in quantitative yields, obtained from initially formed π -complex via π - σ transition because of the faster π - σ transition, which is in consonance with earlier observations (Scheme 1). High-resolution XPS spectra of Pd 3d on deconvolution for both the surface transient intermediates (HK2) and (HK2') show a set of two lines each at 336.4 eV (3d_{5/2}), 342.2 eV (3d_{3/2}) and 336.3 eV (3d_{5/2}), and 342.4 eV (3d_{3/2}), respectively, in addition to the lines for Pd⁰ {335.0 eV (3d_{5/2}) and 340.2 eV (3d_{3/2})}, which are observed in all the STO intermediates which we will not be describing

Scheme 1. Validated Mechanistic Cycle for the Coupling Reactions



hereafter for the sake of clarity.¹⁴ The XPS spectra of Cl 2p exhibits three lines on deconvolution at 197.6, 198.4, and 199.6 eV, which are assigned to the interlayer LDH–Cl, PdCl, and chloride present as impurity, respectively. Deconvoluted C 1s XPS spectrum of the (HK2) displays four lines at 284.2, 285.3, 288.8, and 292.0 eV (methoxy carbon), while (HK2') displays three lines at 285.3, 287.1, and 289.0 eV. As the specific assignment is difficult, these samples were subjected to TGA–MS to detect the evolved gas fragments as a function of temperature.¹⁵ The observed m/z values for (HK2) are 15, 30, 36, 51, 90, 91, 103, 104, and 107 amu corresponding to Me, CH₂O, Cl, C₄H₃, C₇H₆, C₇H₇, C₈H₇, C₈H₈, and MeOC₆H₄, respectively.¹⁶ The tropilium radical cation with one unit less is confirmed, which corresponds to phenyl flanked to methoxy group. On the other hand, the observed m/z values 51, 77, 91, and 104 amu for (HK2'), are attributed to C₄H₃ (from phenyl), phenyl, C₇H₇ (tropilium), and C₈H₈, respectively.¹⁶ On heating, both the surface transient species (HK2) and (HK2') at 100 °C in *N*-methyl pyrrolidinone (NMP) solvent give *trans*-4-methoxystilbene and *trans*-stilbene, respectively (see the Supporting Information), which reinforces the structure of STO intermediates as described.

Extended X-ray absorption fine structure (EXAFS) indicates (see the Supporting Information) that the average coordination numbers of LDH–Pd⁰ fresh (CN = 7.6) and used (CN = 8.7) are much lower than that of palladium foil (CN = 12), and we may assume that palladium is in nanoparticle form, which is reconfirmed by TEM.¹² Pd–Pd bond distances obtained from the EXAFS analysis (2.739 Å for LDH–Pd⁰ fresh; 2.76 Å for used) are slightly shorter

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than or similar to the usual value for palladium foil (2.76 Å). This bond feature is also compatible with the formation of nanoparticles.^{17,18}

Next, the palladium(0)-catalyzed cross-coupling reaction of aryl halides and arylboronic acids (Suzuki coupling), an important synthetic method, is studied. The reaction of STO species (OA1) and (OA1') with potassium fluoride in more than equivalent amounts (see the Supporting Information) to the STO intermediate gives only the surface transient species MeOC₆H₄PdF (SZ2) and PhPdF (SZ2'), respectively (Scheme 1). When potassium fluoride is used in 0.5 M equivalent, the unreacted STO intermediates (OA1) and (OA1') are also detected.

The XPS narrow scans of Pd in (SZ2) and (SZ2') show a shift in the binding energy of ~3 eV, which is attributed to the highly electronegative fluoride (F 1s line at 685.3 eV) and clearly indicates the presence of a Pd–F bond.¹⁹ The *m/z* values for (SZ2) and (SZ2') in the TGA–MS are 15, 19, 31, 76, 107 amu and 19, 51, 77 amu, which correspond to Me, F, OMe, C₆H₄, MeOC₆H₄ and F, C₄H₃, C₆H₅, respectively.¹⁶ Further, the reaction of STO intermediate (SZ2) and (SZ2') with phenylboronic acid affords tricoordinated surface transient organometallic species MeOC₆H₄PhPdB(OH)₂ (SZ3) and PhPhPdB(OH)₂ (SZ3'), respectively, which are isolated and characterized by XPS and TGA–MS. Along with the characteristic XPS binding energy peaks for Pd (II) (337.5 and 342.3 eV), both the STO intermediates (SZ3) and (SZ3') exhibit B 1s peak at 192.6 eV, which is assigned to Pd–B.²⁰ The deconvoluted O 1s XPS spectrum of (SZ3) and (SZ3') displays one extra line at 532.6 eV, which is attributed to B(OH)₂.²¹ There is no remnant of the earlier STO intermediates detected, which indicates complete conversion. The observed evolved gas fragments for (SZ3) and (SZ3'), when subjected to TGA–MS, are 15, 17, 19, 26, 31, 45, 51 and 45, 51, 77 amu, respectively, and correspond to Me, OH, F, C₂H₂, OMe, B(OH)₂, C₄H₃ and B(OH)₂, C₄H₃, C₆H₅, respectively.¹⁶ On heating, both the transient species (SZ3) and (SZ3') at 100 °C in 1,4-dioxane/water solvent system give 4-methoxybiphenyl and biphenyl, respectively (see the Supporting Information), which reinforces the structure of transient intermediate species as indicated above.

The Sonogashira coupling of aryl halides with terminal acetylenes is also a useful coupling reaction. The reaction of surface transient species (OA1') with phenylacetylene gives STO intermediate PhPdC≡CPh (SG2), which was isolated and well characterized by XPS and TGA–MS (Scheme 1). The XPS narrow scan of STO intermediate (SG2) for Pd (II) 3d shows a 3d_{5/2} line at 337.5 eV and 3d_{3/2} line at 341.8 eV. The high-resolution XPS scan of STO intermediate (SG2) for C 1s exhibits five lines on deconvolution at 284.4, 285.3, 286.5, 288.1, and 289.1 eV, in contrast to the two lines present in the LDH–PhPdCl, which clearly indicates the presence of Pd–C≡CPh bond.²² The *m/z* values obtained from TGA–MS are 51 and 77 amu correspond to C₄H₃ and C₆H₅, respectively.¹⁶ The transient species (SG2) on heating at 80 °C with THF/water solvent system gives diphenylacetylene (see the Supporting Information), which strengthens the assigned structure of STO intermediate as described above.

Another widely used coupling reaction is the Stille-type coupling of aryl halides with trialkyltin reagents (see the Supporting Information). The reaction of surface transient species (OA1') with potassium acetate gives surface transient species PhPdOAc (ST2) (Scheme 1). The XPS narrow scans for the STO intermediate (ST2) exhibits Pd (II) 3d_{5/2} line at 337.2 eV and 3d_{3/2} line at 341.3 eV and O 1s at 531.1 and 532.0 eV; the former is attributed to impurity and the latter to Pd–O bond.²³ The deconvoluted C 1s XPS spectrum of the (ST2) displays two lines at 285.0 and 288.9 eV, in

addition to the 284.6 eV as in LDH–Cl. The *m/z* values of (ST2) are observed at 43 and 44 amu, which correspond to OAc and CO₂, respectively. The reaction of STO intermediate (ST2) with tributyltin hydride provides STO intermediate PhPdSnBu₃ (ST3), which is isolated and well characterized by XPS and TGA–MS. The high-resolution narrow scans of STO species (ST3) for Sn and Pd (II) show 3d_{5/2} lines at 485.7 and 336.9 eV and 3d_{3/2} lines at 494.1 and 339.4 eV, respectively, which indicate the presence of a Pd–Sn bond. No residuum of the earlier STO intermediate (ST2) is observed, which clearly indicates the complete conversion. The deconvoluted C 1s XPS spectrum of (ST3) displays four lines at 284.2, 285.0, 286.3, and 288.7 eV. The *m/z* values observed in the TGA–MS are 15, 26, 29, 43, 51, 54, 56, 57, and 77 amu, which correspond to Me, C₂H₂, C₂H₅, C₃H₇, C₄H₃, C₄H₆, C₄H₈, C₄H₉, and C₆H₅, respectively.¹⁶ On heating the STO species (ST3) at 50 °C in NMP solvent gives tributylarylstannane (Supporting Information), which reinforces the structure of STO intermediate as described.

The formation of only one STO intermediate in all the coupling reactions during their reaction sequences and the excellent isolated yields of each of the coupling product (isolated yields 85–95% of the theoretical yield, see the Supporting Information) from the corresponding supported complexes, HK2, SZ3, SG2, and ST3 establish that these supported complexes are the key intermediates of the coupling reactions. This demonstrates the evolution of the single-site heterogeneous catalyst by transfer of molecular organometallic chemistry to surface organometallic chemistry that is responsible for high order of activity.¹²

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Supporting Information Available: Full characterization of all surface transition organometallic intermediates with detailed experimental procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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