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Pd PEPPSI-IPr-Mediated Reactions in Metal-Coated Capillaries Under MACOS: The Synthesis of Indoles by Sequential Aryl Amination/ Heck Coupling**

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Abstract: A method has been devised for the microwave-assisted, continuous-flow preparation of indole alkaloids by a two-step aryl amination/cross-coupling sequence of bromoalkenes and 2-bromoanilines. This process requires both the presence of a metal-lined flow tube (a 1180 micron capillary) and the Pd PEPPSI-IPr catalyst; without either, the catalyst or the film, there is zero turnover of this catalytic process. A silver film has been shown to provide some conversion (48–62 %), but optimal results (quantitative) across a variety of bromoalkenes and bromoanilines were achieved by using a highly porous palladium film. Possible roles for the Pd film are considered, as is the interplay of the catalyst and the film.

Keywords: cross-coupling · cycloaddition · flow synthesis · microwaves · palladium · thin films

Introduction

Microwave-assisted organic synthesis (MAOS) has been applied very successfully to both homo- and heterogeneous reactions leading to marked reductions in reaction times.[1] Oftentimes, the crude products of MAOS reactions are cleaner (e.g., fewer byproducts) than those obtained from the corresponding conventionally heated transformations, which has been attributed to the significantly longer times necessary to achieve the same level of conversion by using, for example, an oil bath. However, while reaction times are shorter when using MAOS, the method requires that transformations be conducted in specialized, sealed high-pressure vials; this requires significant handling of each individual transformation (e.g., capping and decapping) that significantly slows the overall synthetic process. To overcome these issues, we have been working on the development of microwave-assisted, continuous-flow organic synthesis (MACOS) that eliminates such flasks and minimizes sample handling.[2,3] Synthesis in a flowed format has the advantage of rapid reaction optimization because all that is required is a single drop of product from the reaction tube to evaluate the progress of the transformation; every subsequent drop will be the same. Further, once an optimized set of conditions has been reached, the process is infinitely scaleable.[4,5]

We have demonstrated that complete reaction mixtures can be flowed through capillary-sized reaction tubes that traverse the microwave cavity leading to excellent conversions (in minutes or less) over a variety of transformations.[2a] We have also illustrated that separated reaction components (e.g., two or more solutions) can be flowed through separate inlets, mixed at the site of reaction in the microwave, and also have excellent chemical conversion.[2b] We have also disclosed the use of thin Pd films in conjunction with MACOS to promote metal-catalyzed cross-coupling reactions (e.g., Heck and Suzuki–Miyaura coupling) in the absence of any homogeneous catalyst.[6,7] In this report, we detail the use of the Pd film to promote a sequential intermolecular amination/intramolecular Heck transformation employing the Pd PEPPSI-IPr (PEPPSI: pyridine, enhanced, precatalyst, preparation, stabilization, and initiation) catalyst[8] to prepare a collection of indoles by using the MACOS methodology.

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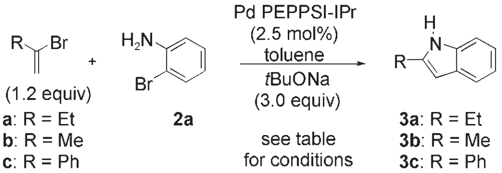
[**] PEPPSI: pyridine, enhanced, precatalyst, preparation, stabilization, and initiation; MACOS: microwave-assisted, continuous-flow organic synthesis.

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author and contains methods for the preparation of all thin films used and all MACOS reaction conditions as well as ^{1}H and/or ^{13}C NMR and LCMS spectra for all compounds prepared in this study.

Table 1. MACOS-mediated conversion of 2-bromoalkenes and 2-bromoanilines to indoles by using the Pd PEPPSI-IPr catalyst, both with and without metal-lined capillaries.



Entry	Vinyl bromide	Mode	Conditions[a,b]	Product	Conversion [%][c] (Yield [%])[d]
1	**1c**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, 200 W, T = 100 °C, clear 1180 μm ID capillary	**3c**	0 (0)
2	**1a**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, 240 W, T = 105 °C, clear 1180 μm ID capillary	**3a**	0 (0)
3	**1c**	batch	240 W, T = 105 °C, 20 min	**3c**	85 (74)
4	**1b**	batch	240 W, T = 175 °C, 22 min	**3b**	83 (70)
5	**1c**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, 22 W, T = 205 °C, Pd-coated 1180 μm ID capillary[e] (no Pd PEPPSI-IPr catalyst)	**3c**	0 (0)
6	**1a**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, 22 W, T = 205 °C, Ag-mirror coated 1180 μm capillary (i.e., dense Ag film)[e]	**3a**	48 (32)
7	**1a**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, 22 W, T = 205 °C, Ag-coated 1180 μm ID capillary from colloidal Ag (i.e., porous Ag film)[e]	**3a**	62 (47)
8	**1a**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, 22 W, T = 205 °C, Pd-coated 1180 μm, ID capillary[e]	**3a**	95 (81)
9	**1a**	flow	flow rate: 15 L min^{-1}, 75 psi back pressure, oil bath, T = 200 °C, Pd-coated 1180 μm ID capillary[e]	**3a**	57

[a] The temperature reported for these transformations is the temperature observed by the IR sensor in the irradiation chamber of the Biotage Smith Creator Microwave Synthesizer. Because the sensor measures only the surface temperature of the capillary, this may, or may not accurately reflect the temperature of the solution inside of the tube during flow. [b] For the structure of Pd PEPPSI-IPr, see Scheme 1. [c] Percent conversion is determined by evaluating the ratio of starting material to indole product in the ^{1}H NMR spectrum of the crude effluent taken directly from the reaction capillary. [d] Percent yield is determined by following purification on silica-gel chromatography of a fixed volume of reaction mixture containing a known amount of **1** and **2** to begin the transformation. [e] All metal-coated capillaries are prepared to a thickness of 6 microns; of the total length of the capillary (≈12 cm), approximately 3 cm is actually irradiated in the microwave chamber.

Results and Discussion

We have been interested for some time in metal-catalyzed, multistep sequences to rapidly build up significant molecular structures[9] and recently we have applied multicomponent reaction methodology to the MACOS format.[10] Indoles are compounds of considerable biological significance,[11] and as part of our medicinal chemistry program we were interested in developing an effective "one-pot" coupling sequence to prepare them using a flow-synthesis format.

The amination/Heck MACOS sequence,[12] utilizing our active Pd PEPPSI-IPr catalyst,[8,13] employing a simple glass capillary as the flow tube showed no conversion (Table 1, entries 1 and 2; residence time in the irradiation zone of the microwave instrument during flow is approximately 120 s). The catalyst is fully soluble and was premixed with the substrates at 2.5 mol % and the whole solution was flowed down the capillary setup. This negative result left us with a number of questions. We have demonstrated that metal-catalyzed reactions, such as Suzuki–Miyaura coupling and ring-closing metathesis, can be driven to completion by MACOS in the brief time that the sample resides in the irradiation chamber of the microwave;[2a] perhaps it is possible that the Pd PEPPSI-IPr catalyst is simply ineffective for this particular sequence. Alternatively, the catalyst may be active but simply requires longer than 120 s (in continuous flow) to show appreciable catalytic activity in this particular sequence. To probe these queries, we performed batch irradiations with the same substrates and discovered that, in fact, the catalyst was active but the transformation indeed required 20–22 min to reach >80 % conversion (Table 1, entries 3 and 4).

We were interested in ascertaining the kinetics of this reaction in batch mode to determine if there was necessarily a lag phase, such as would be the case if catalyst activation under these particular conditions was slow. This might account for the prolonged reaction times necessary to drive the reactions to completion under MAOS, which for most cross coupling reactions occurs much more quickly.[1] We determined that this reaction mixture under batch conditions takes approximately 2.5 min to reach the desired temperature (i.e., ≈200 °C); assuming for now that the top end temperature is necessary to initiate the catalytic cycle, we began taking readings at that time (Figure 1). Interestingly, there appears to be no lag phase and conversion followed almost linear kinetics, albeit slowly. This was concerning for it implied that the sequence might not be suitable for MACOS as continuously flowed reactions must proceed as far as possible within ≈120 seconds to avoid the need for stop flow, or passing the sample back through the microwave cavity multiple times,[14] which compromises some of the advantages of working in a flowed format.

The poor MACOS results when using Pd PEPPSI-IPr suggested the use of metal-coated capillaries for this coupling sequence due to success of these capillaries in related coupling reactions.[6] In those cases, no additional (homogene-

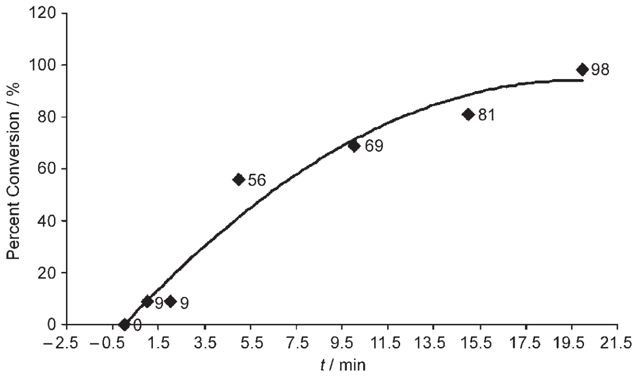
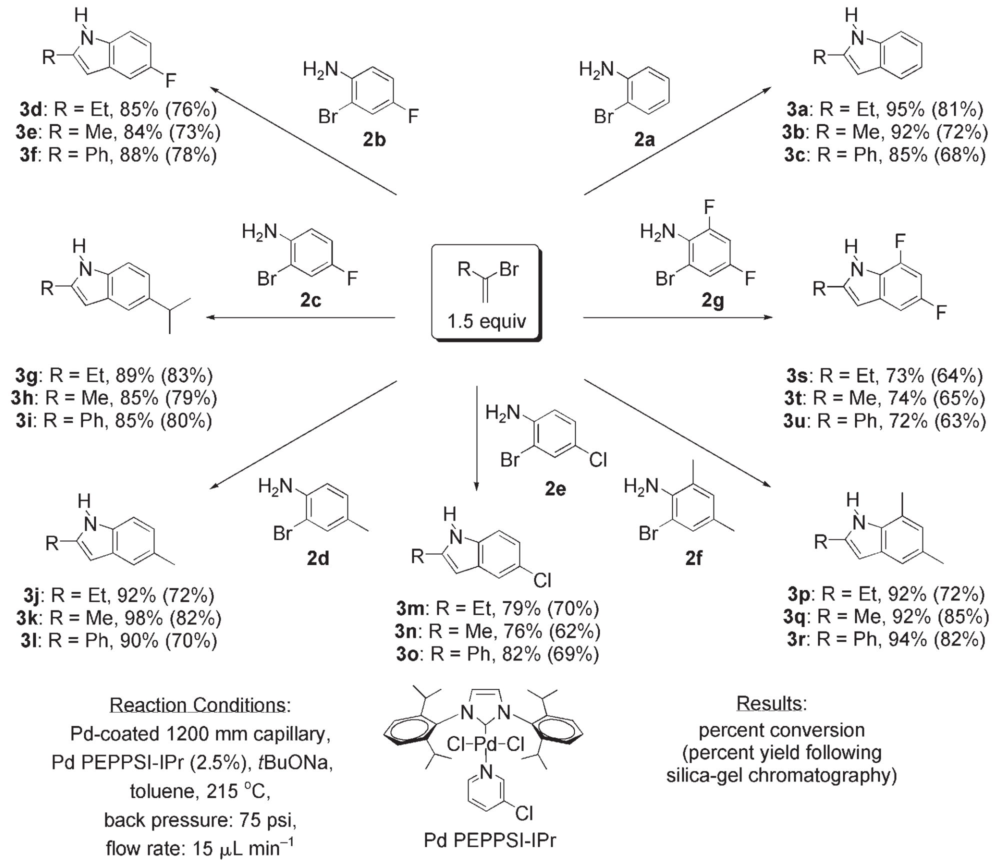


Figure 1. Percent conversion of 1-bromo-1-phenylethylene (**1c**) and 2-bromoaniline (**2a**) to 2-phenylindole (**3c**) by Pd PEPPSI-IPr under batch reaction conditions as a function of time by using the conditions listed in Table 1, entry 3.

ous) Pd catalyst was required as a Pd film by itself promoted Suzuki–Miyaura and Heck reactions.[6] While successful in those applications, there was no conversion in the present sequence with just the Pd-coated capillary and no Pd PEPPSI-IPr catalyst (Table 1, entry 5).

Metal films possibly have a dual role in these coupling procedures.[6] Clearly, cross-coupling reactions performed with just a Pd-coated reaction capillary (i.e., no additional homogeneous catalyst) point to a catalytic role, at least with Pd, but metal films are also known to couple very effectively with microwave irradiation to generate a current that generates significant heat.[15] In light of this, we considered flowing the Pd PEPPSI-IPr-containing solution through a metal-coated capillary to see if the superior heating might help promote this transformation. We have found that silver films absorb microwave irradiation suitably, thus we first tried such a capillary (Table 1, entry 6). For the first time with MACOS, we began to see appreciable conversion (48 %) that proceeded straight through to the indole, that is, we saw no intermediate coupling products and starting materials which could account for the balance of the reaction mixture. We tried the same transformation by using a Pd-coated capillary (Table 1, entry 8) and noticed another significant improvement in conversion (essentially quantitative) relative to the Ag-mirror-coated capillary. With this observation in hand, we subjected a variety of coupling partners to the MACOS procedure employing the Pd-coated capillary and it worked very smoothly (Scheme 1); the reactions were very clean with minimal, if any, byproducts.

According to our mechanistic understanding of this particular coupling sequence, it is not likely that the Ag film is capable of serving in any role other than as an effective heat source, that is, it is not actively catalyzing any of the chemistry. Given that the Pd film on its own did not yield any



Scheme 1.

product, it is not immediately clear why the Pd film provided considerably better results than its Ag-mirror film counterpart when the Pd PEPPSI-IPr catalyst was employed. The Pd film[16] is made of nanoparticles and it is highly porous in contrast to the Ag-mirror film; the Ag-mirror film is compact with only small voids between the grains (Figure 2b and d). This latter morphology gives the Ag film its mirror-like appearance, while the porous nature of the Pd film (Figure 2a and c) leads to a dark grey, partially transparent film, despite the fact that both films were prepared such that they contained the same quantity of metal by weight. The more porous Pd film is not likely to heat up any more effectively en masse than the Ag-mirror film at the macroscopic level. This is supported by the IR sensor temperature readings in the microwave cavity (see Table 1, entry 6 and Scheme 1) indicating that the same temperature was reached in both systems.[17] That said, perhaps the Pd film, possessing more irregularities, could potentially have hotter sites at the microscopic level; steps and corners on the surface of metal films have been suggested to enhance microwave absorption that could lead to localized "hot spots" in the film.[6] So, while the bulk temperature recorded by the IR sensor is 200 °C, microscopic regions in the film could be 300 or 400 °C (or higher) and this could lead to a much higher reactivity of the Pd PEPPSI-IPr catalyst in those regions. This might be considered analogous to flash vacuum thermolysis transformations in which gas-phase reactants under high vacuum are flowed through a quartz tube that is generally heated to ≈500 °C; contact with the super-heated walls results in very fast and remarkably clean conversions (e.g., retro-Diels–Alder reactions). With this in mind, we re-examined the morphology of the Ag film and tried to create a microstructure that was more similar to the porous Pd film. This was achieved by depositing Ag_2O colloids from ethylene glycol onto the glass surface; the resulting films were dull gray and semitransparent. SEM (Figure 3) and EDX analysis confirmed that the films have a larger surface area than the corresponding silver-mirror films (see Figure 2b to compare images at the same magnification) and that they contained mostly Ag^0, respectively. However, the surface area is still much lower than for the Pd films (see Figure 2a to compare images obtained at the same magnification). The resultant porous Ag film did result in significantly better conversion when compared to the silver mirror (Table 1, entry 7 versus 6); the film's morphology clearly plays an important role in this chemistry.

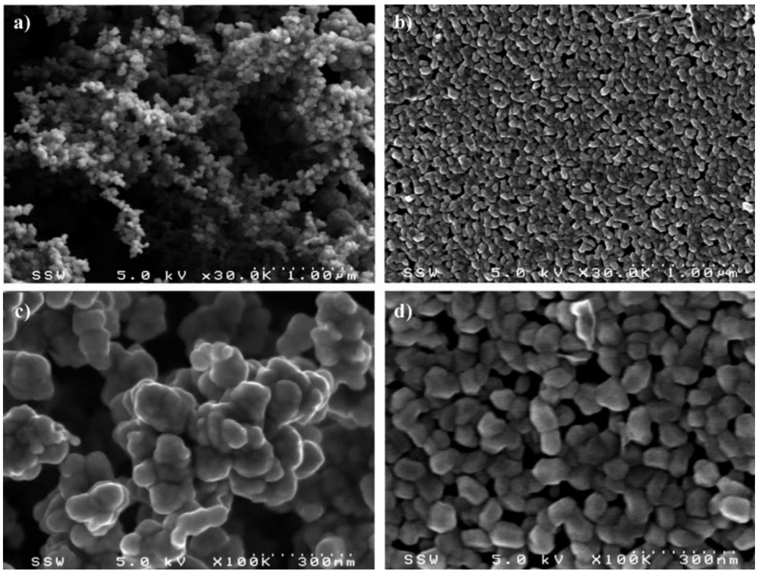


Figure 2. SEM images depicting the morphology of the Pd and Ag films lining the capillaries that are used in the MACOS process to generate indoles by an amination/Heck coupling sequence. Panels a) and b) show a section of the Pd- and Ag-thin film removed from the capillary at ×30 000 magnification, respectively. Panels c) and d) show images obtained for the same region of Pd- and Ag-thin films at ×100 000 magnification, respectively.

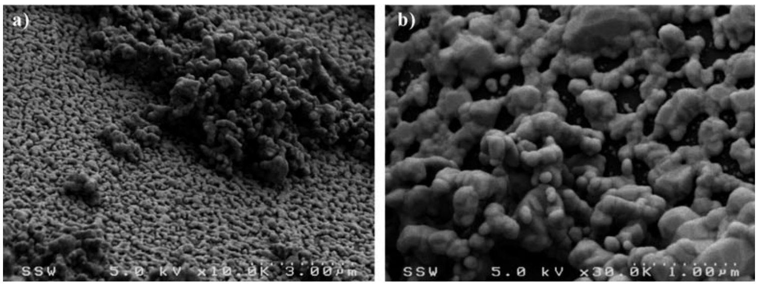


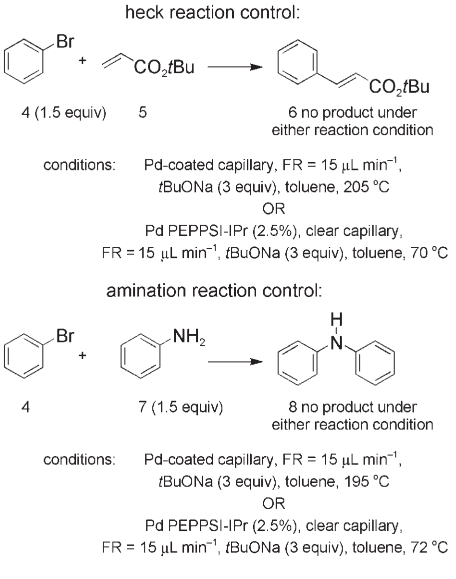
Figure 3. SEM images depicting the morphology of the Ag film prepared by using Ag_2O colloids. Panels a) and b) are taken at ×10 000 and ×30 000 magnifications, respectively.

While an improvement in conversion was observed when the Ag film's surface area was enhanced, it still fell noticeably short of the quantitative conversion obtained when the structurally-analogous Pd film was used. It is possible that the Pd film is doing more than just providing heat. Perhaps Pd PEPPSI-IPr catalyzes one of the steps quite efficiently when a metal film is present, but it catalyzes the other step less effectively. The Ag film can provide high temperatures, but no catalytic role, whereas the Pd film is capable of providing both heat and catalytic activity and this leads to the high conversion in the Pd case that is absent with Ag. This might be supported by the fact that Pd PEPPSI-IPr has been demonstrated to be highly efficient in sp^3–sp^3 couplings with little or no competing β-hydride elimination, which, of course, is a requisite for the Heck reaction in this sequence.[13] Perhaps it is the Heck component of the sequence that is responsible for the prolonged reaction times in batch mode employing Pd PEPPSI-IPr in which full conversion to product requires >20 min., whereas the flowed reactions through Pd-coated capillaries are complete in <120 s!

There is perhaps some concern over the thermal stability of the Pd PEPPSI-IPr catalyst during prolonged irradiation, and this might account for the sluggish reactivity in the batch runs; that is, some of the catalyst may be decomposing. To probe this possibility, we performed two control experiments; both involved stressing the catalyst. In one case, we flowed Pd PEPPSI-IPr through a Pd-coated capillary while irradiating at 205 °C and in another case we simply heated Pd–PEPPSI-IPr at 205 °C in a batch setting for 20 min. Both stressed catalysts were used (separately) for the batch reaction shown in Table 1, entry 3; both yielded complete conversion to the indole product, thus catalyst stability does not appear to be an issue in this chemistry.

To further probe the reliance of Pd PEPPSI-IPr on the Pd-coated capillary for this process (and vice versa), we ran several additional control experiments. We have already published that MACOS with Pd films smoothly performs the Heck reaction of **4** with **5** in 99 % conversion by using DMA (DMA = dimethylacetamide) solvent (Scheme 2).[6] Under the optimized conditions developed for the two-step coupling sequence in this manuscript with toluene as the solvent, but otherwise identical conditions to our previous Heck results, there was no conversion at all to **6**. Not surprisingly, based on our alkyl–alkyl coupling results when using Pd PEPPSI-IPr,[13] we also saw no Heck coupling when it was used in the MACOS reactor with no Pd film. Similarly, we tried independent amination reactions of **4** with **7** (Scheme 2), which we know to work with Pd PEPPSI-IPr from other studies in our laboratories which use DME (DME = dimethoxyethane) solvent in batch. Once again, there is a high solvent dependence as the reaction completely failed when using MACOS, as it did with just the Pd-coated capillary. Thus, under the optimized reaction conditions for the two-step process to generate indoles in this report, none of the independent reactions proceeded under MACOS in the absence of either the homogeneous catalyst or the Pd film. We believe that the codependence of a homogeneous catalyst with a metal surface demonstrated in this study is without precedent.

A question often asked with MAOS-related methodology relates to the existence of a "microwave effect" that promotes reactions beyond simple effective heating. It is common to run the analogous MAOS reaction by using conventional heating methods and see if there is a significant difference in the results. The reaction outlined in Table 1, entry 8 was repeated in every aspect with the exception that the transformation was conducted in an oil bath set to deliver the identical temperature recorded by the IR sensor in the Biotage Smith Creator Synthesizer (entry 9). A significant reduction in conversion was observed when using conventional heating (57 versus 95 % with microwave irradiation). This result also is suggestive that heating of the film, at least in microscopic regions, may be generating temperatures significantly in excess of the value recorded outside of the metal-coated capillary.[17] This does not necessarily point to a special microwave effect per se, but may none-the-less point to a special relationship between metal films and microwave irradiation that leads to vastly superior heating.



Scheme 2.

Conclusions

A highly effective process has been developed for a two-step amination/Heck coupling sequence to make indoles by flowed synthesis catalyzed by both Pd PEPPSI-IPr and a thin Pd metal film on the surface of the flow tube while being heated by microwave irradiation. The flowed process yields zero product when either the Pd PEPPSI-IPr or the Pd-metal film is omitted. Substitution of the Pd film for an Ag-mirror, which presumably generates that same bulk heating, leads to a significant reduction in conversion, suggesting that both the Pd PEPPSI-IPr and the Pd film are involved in the catalysis. Conversely, irregularities in the structure of the Pd film, which are absent in the Ag-mirror film, could lead to localized "hot spots" of intense temperature in the presence of microwave irradiation[6] that drives the Pd PEPPSI-IPr catalyst more effectively to conduct not only the amination reaction, but the high-energy β-hydride elimination step that is required for the Heck step in this process. The Ag film possesses much lower electrical resistance

($1.617\times10^{-8}\,\Omega$) relative to Pd ($10.73\times10^{-8}\,\Omega$) (values for 298 K) and, therefore, should generate more heat while being irradiated, and yet conversion with Ag is consistently lower than with Pd.[18] Temperatures of microscopic regions in the films cannot be assessed, but it seems to support the morphology argument. This notion might be supported by the observed increase in conversion when the dense Ag-mirror morphology is substituted with a rougher Ag film. Indeed in attempted Heck reactions conducted in our laboratories utilizing Pd PEPPSI-IPr, the Heck product was only observed after prolonged batch heating at 120 °C in an oil bath. Product formation always happened concomitantly with significant darkening of the solution that may well have been the result of the catalyst blacking-out; there is a strong possibility that the conversions in these Heck reactions were catalyzed by Pd black, and not by Pd PEPPSI-IPr. In an analogous manner then, it is also possible that the deposited Pd colloids in the film are promoting the second step. In this case, the Pd film would be incapable of performing the amination (vide supra), hence the need for both the catalyst and the Pd film.

We have discovered a variety of other transformations, both metal-catalyzed and non-metal-catalyzed, that similarly only proceed in the presence of a metal film. This will allow the exploration of a wealth of new chemistries that can be run under the highly efficient MACOS methodology. We will be reporting on these observations in due course.

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[16] Questions have been raised about the actual surface of the Pd film, that is, is it Pd^0 or $Pd^{II}O$. EDX analysis indicates very little oxygen is present (0.3 %) and when we flowed hydrogen gas down the inside of the capillary, significant sparking ensued confirming that a significant portion of the film's surface is metallic Pd.

[17] We recognize that the IR sensor measurement is not likely to deliver an accurate measure of the temperature inside of the capillary. However, we have not yet been successful in getting more accurate measurements, for example, employing a miniature thermocouple as such devices also couple with microwave irradiation leading to current and heating itself; this would lead to erroneous results. What we can say is that the temperature is likely higher than 200 °C, as read by the IR sensor, but less than 600 °C, which is the melting temperature of borosilicate glass.

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