

anisotropy may be controlled by their aspect ratio, which gives rise to ferromagnetic nanomaterials at room temperature. The rods grow after the initial formation of spherical nanoparticles; the exact mechanism of this process is not known but we note that the initial formation of nanoparticles, followed by formation of nanorods or nanowires either through coalescence of the initial particles^[21] or upon using the particles as nuclei for an anisotropic growth process, have been very recently reported.^[22] Further work will be necessary to determine the exact mechanism that operates in our case.

In conclusion, we describe in this report a new and simple method for the preparation of cobalt nanoparticles, nanorods, and nanowires of uniform diameter that does not require a special procedure or size selection. The magnetic nanowires have no equivalent, whereas the rods differ from those previously described by their uniformity of diameter, their thermodynamic stability, and the possibility of fine tuning of their aspect ratio. We further demonstrate that, under these conditions, the nanomaterials maintain a magnetization at saturation similar to bulk cobalt. This results from the choice of ligands that do not display π -accepting behavior, which is in agreement with previous research work from our group. All of these aspects emphasize the role of an organometallic approach in the design of precursors and ligands. Finally, these objects may find use in many practical applications such as, for example, in data storage.

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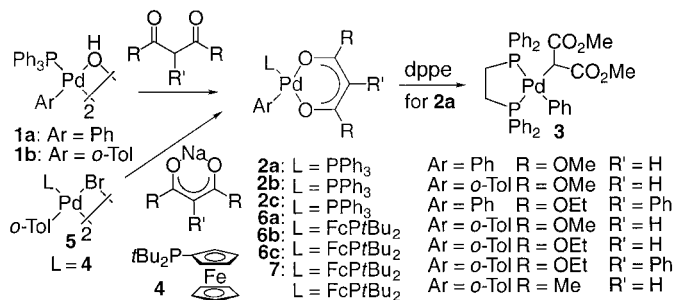
Generation of Reactivity from Typically Stable Ligands: C–C Bond-Forming Reductive Elimination from Aryl Palladium(II) Complexes of Malonate Anions**

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Anions of 1,3-dicarbonyl compounds are some of the most common ligands in transition-metal chemistry.^[1,2] They typically bind in an η^2 -O,O fashion,^[3] have delocalized charge, and donate electron density more weakly to a metal center than alkyls or alkoxides. They are usually supporting ligands that are ancillary to the site of reaction. Anions of 1,3-dicarbonyl compounds are also common nucleophiles in metal-catalyzed allylic substitution,^[4–6] but the facility of this chemistry relies on external attack of the anion without coordination to the metal center. If metal fragments could induce reactivity from coordinated versions of these anions, then complexes of these common ligands could serve as intermediates in catalytic processes.

Complexes of malonate anions are likely intermediates in recently developed palladium-catalyzed arylations of malonates.^[7–11] Although palladium complexes of malonate anions have been isolated previously,^[12–16] their reactivity has been limited.^[17–20] We report here reductive elimination of arylmalonate and acetylarylaceton from isolated aryl palladium complexes of malonate and acetylaceton anions, respectively. Our results suggest that the propensity of these complexes to undergo reductive elimination depends critically on the steric properties of the ancillary phosphane ligand.

Our synthesis of aryl palladium malonates is summarized in Scheme 1. Addition of dimethyl malonate or diethyl phenylmalonate to the basic PPh_3 -ligated palladium hydroxide dimers **1a**^[21,22] and **1b** generated the O,O'-bound palladium dimethyl malonate complexes **2a–c**. Complexes **2a** and **2c** were characterized by X-ray diffraction (Figure 1). No unusual angles at the palladium center were found in **2a** or



Scheme 1. Synthesis of aryl palladium malonates.

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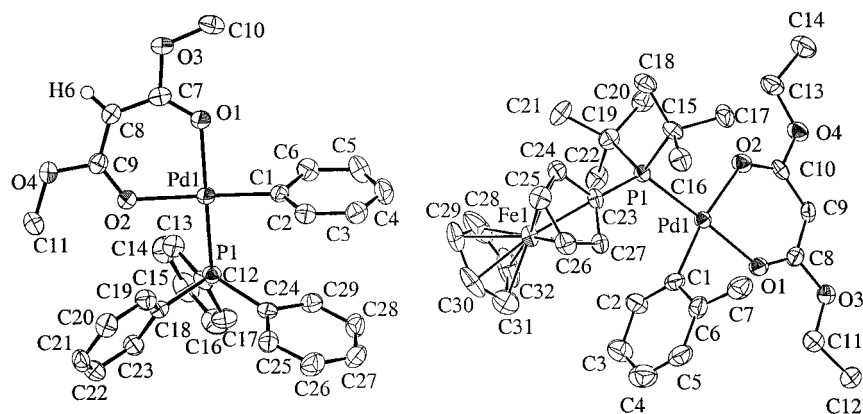
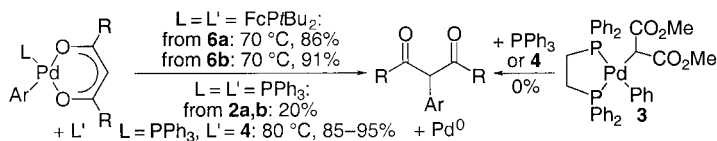


Figure 1. ORTEP plot of **2a** (left) and **6b** (right).

2c. The Pd–O bonds located *trans* to the phenyl ligand in **2a** and **2c** are longer than those *trans* to the phosphane (2.113(2) Å vs. 2.088(2) Å for **2a**; 2.097(2) Å vs. 2.070(2) Å for **2c**). The Pd–O distances in **2c** are shorter than those in **2a**, but addition of diethyl phenylmalonate to **2a** or *vis a versa* indicated an equilibrium constant for the exchange that is close to unity and, therefore, equivalent thermodynamic stabilities for the two malonate complexes.

Coordination of two phosphorus donors generated C-bound isomers. For example, addition of 1,2-bis(diphenylphosphanyl)ethane (dppe) to **2a** generated the C-bound palladium dimethyl malonate **3** (Scheme 1). However, addition of excess PPh₃ to **2a** did not generate a stable diphosphane complex. Instead, exchange of free and coordinated phosphane occurred on the NMR timescale. A single broad ³¹P NMR resonance was observed for the free and coordinated PPh₃, and the same ¹H NMR resonance for the central malonate proton was observed in the presence and absence of added PPh₃.

Heating of **2a** or **2b** for 48 h at 110 °C in THF or C₆D₆ in the presence of added PPh₃ to trap the Pd⁰ product fully converted the starting complex into a PPh₃-ligated Pd⁰ species, but arylmalonate was formed in only 20% yield (Scheme 2) from **2a** and in <5% yield from **2b**. Biaryls from the phosphane and palladium-bound aryl group, along with free malonate (25%), were the major organic products formed. Heating of **3** for 15 h at 70 °C fully converted it to PPh₃- and dppe-ligated Pd⁰ complex, but free dimethyl malonate, toluene, and products from self-condensation of dimethyl malonate were the major organic products. In contrast to the slow and low-yielding reductive elimination from these complexes, aryl palladium methyl complexes undergo facile reductive elimination.^[21,22] Thus, the electron-withdrawing property of the two carbonyl groups dramatically increases the barrier for reductive elimination.



Scheme 2. Reductive elimination of malonates.

To generate complexes that could be induced to undergo reductive elimination because of increased steric hindrance, we prepared complexes ligated by di-*tert*-butylphosphanylferrocene (FcP(t-Bu)₂) (**4**)^[23] (Scheme 1). Metathetical exchange between the anion of dimethyl malonate and the halide of dimeric aryl palladium bromide complexes **5** ligated by **4** occurred readily to form the desired palladium malonate complexes **6a** and **6b** in high yield. Reaction with the sodium anion of diethyl-2-phenylmalonate occurred similarly.

Complexes **6a–c** were isolated and fully characterized by spectroscopic and microanalytical methods, and the diethyl malonate complex **6b** was characterized by X-ray diffraction (Figure 1). Complex **6b** displays the same η²-O,O-coordination mode as **2a** and **2c**, but the geometry is distorted. The Pd–O distances are much longer than those of **2a** and **2c**. For example, the Pd–O bond *trans* to the aryl group (2.189(3) Å) is nearly 0.1 Å longer than that in complex **2c**. Moreover, the P1–Pd1–O2 angle is larger (100.4(1)°), and the O1–Pd1–C1 is smaller (82.6(2)°) than the ideal 90°. These distorted angles and long metal–ligand bond distances presumably arise from the steric demands of the hindered phosphane.

Warming of malonate complexes **6a** and **6b** to 60–105 °C in the presence of **4** to trap the Pd⁰ product formed dimethyl and diethyl *o*-tolylmalonate in 86% and 91% yield, respectively (by ¹H NMR spectroscopy with an internal standard, Scheme 2). Heating of the phenylmalonate complex **6c** formed the diarylmalonate from reductive elimination in less than 10% yield. This difference in reactivity between **6a,b** and **6c** is consistent with the high selectivity for monoarylation observed from the palladium-catalyzed reaction of aryl halides with malonates.^[7]

Heating of the PPh₃-ligated **2a** at 80 °C in the presence of 3–15 equivalents of the bulky ligand **4** also led to reductive elimination of arylmalonate in 75–90% yield. This reaction was nearly complete after 45 min when conducted with 15 equivalents of added **4**. In contrast, it occurred to about 50% conversion after this time when 3 equivalents of **4** were added. The same reaction required roughly 12 h for completion at 110 °C and formed only 65% yield of arylmalonate when conducted in the presence of 3 equivalents of **4** and 1 equivalent of PPh₃. dppe-ligated **3** did not form arylmalonate when heated in the presence of added **4**. Thus, reductive elimination from **2a** most likely occurs after exchange of **4** for PPh₃, and the increased steric hindrance of the FcP(t-Bu)₂ ligand triggers the reductive elimination. Most important, this steric hindrance dominates the electronic and structural properties of the malonate anion that are unfavorable for reductive elimination.

Aryl palladium acetylacetonate complex **7** ligated by phosphane **4** was prepared by addition of the sodium salt of 2,4-pentanedione to aryl palladium halide **5**. Complex **7** was much more stable than the malonate complexes. Complete consumption of **7** in the presence of ligand **4** required 36 h at 140 °C, instead of the similar times at 110 °C for the analogous

malonate complex **6b**. Complex **7** did form the corresponding 2-aryl 1,3-diketone during this thermolysis, but in only 22 % yield.

One would expect that rearrangement of the η^2 -O,O-bound complexes to their C-bound tautomers would precede reductive elimination. Indeed, complexes of 1,3-dicarbonyl anions that we could not observe as a C-bound isomer did not undergo reductive elimination in high yield. For example, arylmalonate anions **2c** and **6c**, and acetylacetonate **7** produced Pd⁰ complexes and free malonate or acetylacetonate upon addition of the chelating ligands dppe, dppbz = 1,2-bis(diphenylphosphanyl)benzene (dppbz), 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl (binap), and 1,1'-bis(diphenylphosphanyl)ferrocene (dppf). No complex of a C-bound anion was detected.

In summary, the greater steric hindrance of FcPtBu₂ (**4**), relative to that of phenylphosphanes, induces reductive elimination from complexes of typically unreactive ligands derived from malonate and acetylacetonate anions. This steric effect overrides the stabilizing effect of the η^2 -O,O-coordination mode and the electron-withdrawing groups on the central carbon atom of the malonate anion. Studies on the mechanism of these new reductive eliminations and the synthesis of complexes with related stabilized anions are in progress.

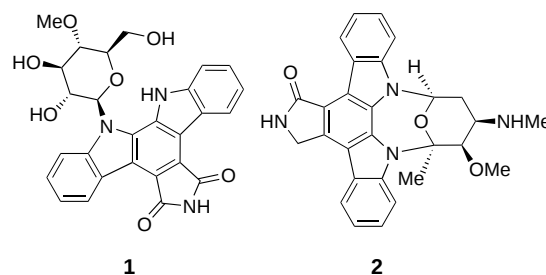
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A Five-Component Synthesis of Hexasubstituted Benzene**

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Bis(indolyl)maleimides and indolo[2,3-*a*]carbazole alkaloids constitute a rapidly growing family of natural products with diverse biological activities.^[1] Thus, rebeccamycin (**1**)^[2] and staurosporine (**2**)^[3] are potent topoisomerase I and



protein kinase C inhibitors, respectively. Structurally, this class of compounds is characterized by an hexasubstituted benzene ring with a fused indolo (forming an indolocarbazole entity) and a fused lactam or an imide ring with a pendant sugar moiety. The novelty of the structures combined with their interesting biological profile have stimulated numerous synthetic efforts from both academic and industrial researchers.^[4]

Transition-metal-mediated cyclization of appropriately functionalized enynes^[5] and Diels–Alder cycloaddition of furan^[6] are two main strategies used for the synthesis of hexasubstituted benzenes.^[7] Although high level of structural complexity can be generated from these two key transformations, the overall efficiency is often counter-balanced by efforts associated with the synthesis of linear precursors. In connection with our continued interest in the development of highly efficient synthesis of druglike polyheterocycles,^[8] we report herein a conceptually new strategy for the synthesis of hexasubstituted benzenes **3** based on a novel one-pot five-component domino process.^[9,10]

The underlying principle of our synthesis is shown in Scheme 1. A recently developed three-component reaction based on Ugi chemistry pioneered by Ugi and co-workers^[9] provides the 5-aminooxazole **7**.^[11] Reaction of the latter with acyl chloride **8** (X = Cl) should give 5,6-dihydrofuro[2,3-*c*]pyrrol-4-one **10** following a sequence of acylation, intramolecular Diels–Alder cycloaddition and retro-Diels–Alder cycloreversion.^[12] Addition of a second dienophile **11** to the reaction mixture should initiate an intermolecular Diels–Alder reaction of furan^[6,7e] to give, after directed fragmenta-

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