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Microwave-Assisted Synthesis of Cyclopentadienyl–Cobalt Sandwich Complexes from Diaryl Acetylenes

Emily M. Harcourt,[†] Shifra R. Yonis,[†] Daniel E. Lynch,[‡] and Darren G. Hamilton*[,†]

Department of Chemistry, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts 01075, and Faculty of Health and Life Sciences, Coventry University, Priory Street, Coventry CV1 5FB, U.K.

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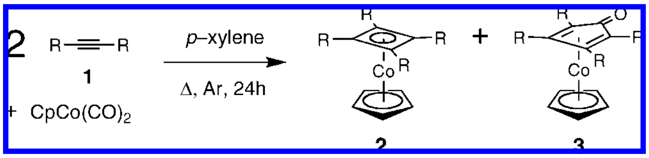
Summary: Sealed tube microwave dielectric heating of diaryl acetylenes with cyclopentadienyl cobalt dicarbonyl at elevated temperature in p-xylene provides access to metallocenes in both the cyclobutadiene (Ar_4C_4CoCp) and cyclopentadienone ($Ar_4C_4(C{=}O)CoCp$) families. When compared with the traditional thermal approach, the current method offers dramatically reduced reaction times and, especially with respect to cyclopentadienone complexes, increased yields. In the case of an especially bulky diarylacetylene the microwave approach allows access to a complex that cannot be readily obtained under traditional thermal conditions. An initial microwave-promoted Sonogashira coupling may be employed for in situ generation of the diarylacetylene, although lower yields of the metallocene complexes are ultimately obtained.

The application of microwave irradiation to chemical transformations has received a great deal of attention in recent years.[1] Numerous important classes of organic reactions have been examined that benefit from this approach, with issues of time and energy economy and waste minimization adding further to the technique's appeal. Among this wealth of investigative effort the preparation of organometallic compounds has received comparatively little attention,[2] while the use of microwaves to promote many important metal-catalyzed or metal-mediated organic transformations has met with great success.[1]

A highly pertinent, yet rare, example of the preparation of an organometallic compound using a microwave protocol was published during prosecution of the work described here. Richards and co-workers have reported a number of *intramolecular* acetylene cycloadditions, mediated by cyclopentadienyl cobalt dicarbonyl ($CpCo(CO)_2$), leading to *exclusive* cyclopentadienone–CoCp complex formation.[3] It is explicitly noted in this work that none of the corresponding cyclobutadienyl complexes were obtained. Contrasting with this outcome we report here that *intermolecular* cobalt-mediated cycloaddition of diarylacetylenes and capture by cyclopentadienyl cobalt proceeds rapidly and efficiently under microwave conditions to yield *both* cyclobutadienyl–CoCp and cyclopentadienone–CoCp complexes. Total conversion efficiencies, based on consumption of the starting diarylacetylene, exceed 90% in the optimal case. The approach is illustrated with the preparation of a number of known and novel metallocenes and with a representative X-ray structure of a new mononuclear complex.

Scheme 1. Traditional Thermal Preparation of 18-Electron Cobalt Sandwich Complexes from Acetylenes



Rausch and co-workers reported the preparation of 18-electron cobalt metallocene complexes from the reaction of diaryl acetylenes with $CpCo(CO)_2$ in 1970.[4] With the exception of the example noted above an essentially unchanged preparative approach, when $CpCo(CO)_2$ has been the source of cyclopentadienyl–cobalt, has been employed ever since: lengthy reflux of a *p*-xylene solution of $CpCo(CO)_2$ with 2 molar equiv of the appropriate diaryl acetylene **1** (Scheme 1). In this manner a number of tetraarylcyclobutadienyl–CoCp complexes **2** have been prepared, alongside typically smaller production of the corresponding tetraarylcyclopentadieneone–CoCp complexes **3** that result from CO insertion during complex formation.[5] Rausch's initial report quotes (for R = phenyl) approximately 50% and 10% yields of **2** and **3**, respectively. A more recent application of this methodology has realized yields of **2** bearing a variety of aryl substituents of up to 75%.[6] It was against this background that we approached the use of microwaves to promote complex assembly.

A 2:1.3 ratio of diphenylacetylene **1a** (3 mmol scale) and $CpCo(CO)_2$ was added to 3 mL of *p*-xylene in a capped microwave reactor tube. The tube was maintained at 175 °C via microwave irradiation for 10 min, after which thin-layer

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* To whom correspondence should be addressed. E-mail: hamilton@mtholyoke.edu.

[†] Mount Holyoke College.

[‡] Coventry University.

(1) (a) For a comprehensive overview see: *Microwaves in Organic Synthesis*; Loupy, A., Ed.; Wiley-VCH: Weinheim, 2002. (b) For a review of recent advances in the field see: Kappe, C. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250–6284.

(2) (a) Ardon, M.; Hogarth, G.; Oscroft, G. T. W. *J. Organomet. Chem.* **2004**, *689*, 2429–2435. (b) Whittaker, A. G.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **2002**, *21*, 3967–3970. (c) VanAtta, S. L.; Duclos, B. A.; Green, D. B. *Organometallics* **2000**, *19*, 2397–2399. (d) Dabirmanesh, Q.; Roberts, R. M. G. *J. Organomet. Chem.* **1997**, *542*, 99–103. (e) Dabirmanesh, Q.; Fernando, S. I. S.; Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 1* **1995**, 743–749. (f) Mingos, D. M. P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991**, *20*, 1–47.

(3) Taylor, C. J.; Motevalli, M.; Richards, C. J. *Organometallics* **2006**, *25*, 2899–2902.

(4) (a) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888–3897. This work dramatically improved access to $CpCoC_4Ph_4$, thus allowing full investigation of its chemistry, especially its aromatic reactivity. (b) Selected cyclobutadienyl–CoCp complexes may also be obtained via a more complex route, but one that avoids acetylene cyclodimerization: Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1978**, *149*, 377–384.

(5) For diverse examples of the preparation and utility of these classes of complex see: (a) Nguyen, H. V.; Butler, D. C. D.; Richards, C. J. *Org. Lett.* **2006**, *8*, 769–772(asymmetric organic synthesis). (b) Waybright, S. M.; Singleton, C. P.; Wachter, K.; Murphy, C. J.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2001**, *123*, 1828–1833(oligonucleotide chemistry). (c) Johannessen, S. C.; Brisbois, R. G.; Fischer, J. P.; Grieco, P. A.; Counterman, A. E.; Clemmer, D. E. *J. Am. Chem. Soc.* **2001**, *123*, 3818–3819(supramolecular chemistry).

(6) Harrison, R. M.; Brotin, T.; Noll, B. C.; Michl, J. *Organometallics* **1997**, *16*, 3401–3412.

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Scheme 2. Microwave-Assisted Assembly of 18-Electron Cobalt Sandwich Complexes from Diarylacetylenes

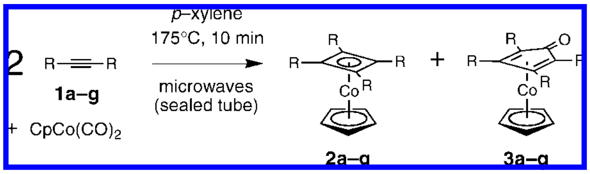

Table 1. Exploration of the Sealed Tube Reaction of Diphenylacetylene with $CpCo(CO)_2$

entry	solvent	method[a]	scale[b]	time	temp (°C)	yield **2a** (%)[c]	yield **3a** (%)[c]
1	*p*-xylene	MW	3 mmol	10 min	175	52[d]	40[d]
2	Decalin[e]	MW	3 mmol	10 min	175	37	25
3	DME	MW	3 mmol	30 min	120[f]	21	17
4	*p*-xylene	MW	3 mmol	60 min[g]	138	45	35
5	*p*-xylene	MW	3 mmol	10 min	200	48	38
6	*p*-xylene	MW	3 mmol	2 min	175	20	14
7	*p*-xylene	MW	3 mmol	120 min	175	<10[h]	<10[h]
8	*p*-xylene	MW	12 mmol	20 min[i]	175	44	35
9	*p*-xylene	oil bath[j]	3 mmol	10 min[j]	175	30	35
10	*p*-xylene	oil bath[j]	3 mmol	24 h	175	42	44

[a] MW = microwave reaction. [b] With respect to diphenylacetylene. [c] Based on consumption of diphenylacetylene. [d] Averaged over three reactions. [e] *cis/trans* isomeric mix. [f] A higher temperature was not explored for safety reasons. [g] Monitored at 10 min intervals by TLC for consumption of diphenylacetylene. [h] Decomposition materials made clean product isolation problematic. [i] Complete consumption of diphenylacetylene required a doubling of the reaction time. [j] 2 min were allowed for equilibration of the reaction to the bath temperature.

Table 2. Results of Microwave Reactions of a Variety of Diarylacetylenes with $CpCo(CO)_2$[a]

diarylacetylene	R group	yield **2** (%)[b]	yield **3** (%)[b]
1a	phenyl	52	40
1b	4-pyridyl	3	85
1c	4-methylphenyl	10	14
1d	4-fluorophenyl	20	28
1e	2-thienyl	44	33
1f	1-napthyl	4[c]	26[c]
1g	2,4,6-trimethylphenyl	no reaction	no reaction

[a] 3 mmol of diarylacetylene/*p*-xylene/175 °C/10 min. [b] Isolated yields, averaged over a minimum of three reactions. [c] Isolated yields after 1 h.

chromatographic analysis revealed complete consumption of the starting acetylene and confirmed the presence of complexes **2a** and **3a** (Scheme 2). After flash chromatographic isolation **2a** and **3a** were obtained in analytically pure form in yields of 53% and 45%, respectively (see Experimental Section). The initial choices of solvent, reaction temperature, and reaction duration subsequently proved optimal. The results of multiple iterations of this benchmark reaction (entry 1) are summarized in Table 1 and reveal the following: (1) employment of the high boiling point hydrocarbon solvent Decalin led to small reductions in the yields of both complexes (entry 2),[7] while use of 1,2-dimethoxyethane (DME)[8] led to further yield decreases, even after extending the reaction time to 30 min (entry 3);[9] (2) reducing the reaction temperature to the boiling point of *p*-xylene (138 °C) considerably extended the time required for consumption of the starting acetylene but did not otherwise substantially affect the final yield of complexes, nor their relative ratio (entry 4); (3) further elevation of the reaction temperature (to 200 °C) did not noticeably alter the reaction outcome (entry 5); (4) both far shorter (2 min; entry 6) and far longer (2 h; entry 7) reaction times led to substantial reductions in the yields of both complexes for reasons of incomplete reaction and product degradation, respectively; (5) the reaction scale could be increased by a factor of 4 (the maximum possible due to volume constraints of the reaction vessel) with only a small decrease in product yield, affording approximately 1 g amounts of each complex (entry 8).

The final two entries in Table 1 (9 and 10) detail attempts to draw as direct as possible a comparison between the microwave reactions and a traditional thermal approach. These reactions were prepared in an identical manner to those destined for microwave irradiation, using microwave-dedicated reaction tubes and caps, and were then maintained at 175 °C in an oil bath. The 10 min reaction afforded around 30% yields of each complex. Periodic TLC analysis of the lengthier reaction revealed diphenylacetylene consumption to be complete after 24 h, while isolated yields of each of the product complexes rose by roughly an additional 10%. While the yields after 10 min for the traditionally heated reaction are certainly lower than those for the corresponding microwave reaction, the difference is not such to suggest that any *microwave-specific* effect is in operation. Rather, microwave irradiation appears to provide a moderate enhancement of yields of the desired complexes via simultaneous heating of the whole reaction volume, in contrast to conventional heating methods, where heat is transferred to the reacting species from the surface of the vessel.[10]

Notably, these *sealed tube* syntheses, whether microwave irradiated or thermally heated, realize far higher yields of cyclopentadienone complex **3a** than was observed in the original studies of Rausch (10%).[4] This outcome may be rationalized as a result of the relatively high local concentrations of CO generated during these sealed tube transformations, in contrast to reactions where the CO is allowed to escape under a nitrogen flow. While approaches have been developed to selectively prepare cyclobutadienyl–CoCp complexes from diarylacetylenes,[11] there exists no corresponding preparative approach to cyclopentadienone–CoCp metallocenes. The production of comparable amounts of both complexes (for certain diarylacetylenes) under the current method may therefore be viewed as a reasonable synthetic compromise, especially given the ready separation of the products.

Under the optimal microwave reaction conditions (i.e., Table 1, entry 1) diarylacetylenes **1b–f** are each converted into a mixture of the two product complexes, although none of these reactions approach the overall efficiency of conversion for diphenylacetylene. The results of these experiments are summarized in Scheme 2 and Table 2 (the results for dipheny-

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[7] Decalin was investigated, as this was the solvent employed for the previously reported microwave-assisted preparations of cyclopentadienone cobalt metallocenes (see ref 3).

[8] DME was investigated, as this solvent has proven particularly effective in reactions involving cobalt-mediated acetylene cycloadditions: Boñaga, L. V. R.; Zhang, H.-C.; Gauthier, D. A.; Reddy, I.; Maryanoff, B. E *Org. Lett.* **2003**, *24*, 4537–4540.

[9] Reactions in DME were maintained at temperatures of no more than 120 °C for reasons of safety. Inevitably rates of production of the desired metallocenes would be reduced at this temperature when compared with reactions in either *p*-xylene or Decalin. However, lengthier reaction times did not produce comparable yields to reactions conducted in either of these hydrocarbon solvents.

[10] For a critical overview of the origin of differences in reaction outcome between microwave and traditional heating approaches, see: De la Hoz, A.; Díaz-Ortiz, Á.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164–178.

[11] (a) Stevens, A. M.; Richards, C. J. *Organometallics* **1999**, *18*, 1346–1348. (b) Uno, M.; Ando, K.; Komatsuzaki, N.; Tsuda, T.; Tanaka, T.; Sawada, M.; Takahashi, S. *J. Organomet. Chem.* **1994**, *473*, 303–311.

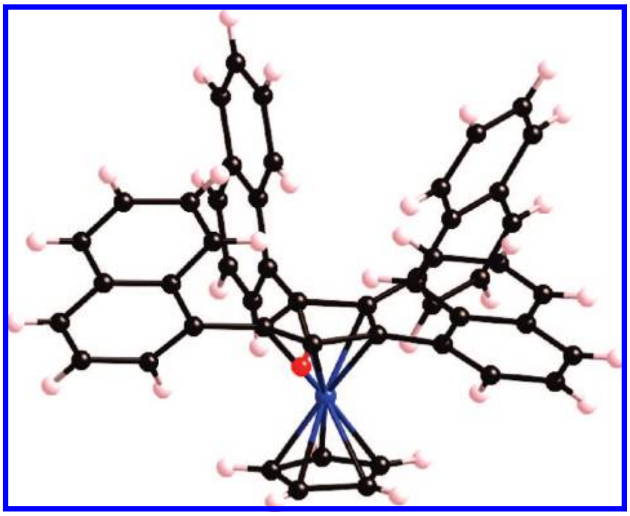

Figure 1. Ball-and-stick representation of the X-ray structure of metallocene **3f**.

lacetylene are included for comparative purposes).[12] No attempt was made to optimize yields in each individual case in the manner performed for diphenylacetylene, although periodic TLC of reactions involving di(1-naphthyl)acetylene (**1f**) revealed comparatively slow consumption of starting material and prompted an increase in reaction time to 1 h. All materials, whether previously prepared (**2a**, **3a**, **2b**, **3b**, and **2d**) or novel, gave spectroscopic data in accordance with their proposed structures (see Supporting Information).[13]

For R = 4-fluorophenyl, 2-thienyl, or 1-naphthyl complexes in both series are obtained in reasonable yield (with the exception of **2f**, vide infra). For R = 4-pyridyl the outcome of the microwave experiment (**2b**, 3%; **3b**, 85%) is even more extreme than that obtained under a standard thermal protocol (**2b**, 15%; **3b**, 45%),[6] indicative of a favorable pathway for CO inclusion in this specific case. The total failure of dimesitylacetylene (mesityl = 2,4,6-trimethylphenyl) to produce either complex **2g** or **3g** indicates that this degree of steric crowding of the carbon–carbon triple bond entirely shuts down the metallocene formation pathways. Complex formation from this particular acetylene is also known to fail under a standard thermal protocol.[14]

The yield of cyclopentadienone complex **3f**, derived from di(1-napthyl)acetylene, appears impressive for such a crowded metallocene. This material crystallized readily, and the structure reveals the expected cobalt sandwich complex of cyclopentadienyl and cyclopentadienone ligands buried at the center of a propellor-like array of 1-naphthyl substituents (Figure 1).[15] The aromatic substituents of the cyclopentadienone ligand occupy constrained environments in this complex. They cannot readily rotate into downward (i.e., Cp facing) positions because of unfavorable interactions with the Cp ring, nor can they adopt orientations that would bring them into coplanarity with the cyclopentadienone ligand. The result is that all four naphthyl units are directed away from the vertical axis of the complex, and the strikingly well-resolved proton NMR spectrum presented by this material argues against the presence of significant barriers to rotation about the 1-naphthylcyclopentadienone bonds. In stark contrast, the corresponding cyclobutadiene complex offers evidence of severe structural constraints. In fact, the very low yield of **2f** reported in the table appears to represent a mixture of atropisomers resulting from hindered rotation of the naphthyl substituents about their 1-naphthylcyclobutadiene bonds. Proton NMR analysis reveals the cyclobutadienyl complex containing fractions obtained from an initial chromatographic purification to be composed of a minimum of five materials of very similar polarity. However, these individual components could not be satisfactorily separated by additional chromatography (see Supporting Information).[16]

The reaction of di(1-naphthyl)acetylene with $CpCo(CO)_2$ appeared a sensible choice to further compare the microwave and traditional thermal approaches: a preparative advantage conferred by the unique heating mode offered by microwave irradiation would likely be highlighted in a case where the product complexes are sterically constrained (implying significant energetic barriers to formation).[17] From a sealed tube reaction maintained at 175 °C for 10 min in an oil bath only traces of complexes **2f** and **3f** could be detected by TLC. Production of the desired complexes did not increase with prolonged reaction time.[18] The whole volume heating conferred by microwave irradiation therefore offers, in this specific case, a viable preparative route to a metallocene product that cannot be conveniently prepared by a traditional thermal route.

As a possible extension of the utility of microwave-assisted chemistry in the preparation of these complexes, it was intriguing to explore whether the diarylacetylene component could be prepared as an immediate prelude to metallocene formation. The Sonogashira reaction, coupling of an aryl halide to a terminal acetylene, has itself previously been adapted for the application of microwaves: an approach using catalytic copper iodide with cesium carbonate in a high-boiling solvent appeared potentially compatible with the conditions described

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[12] All quoted yields are the average of a minimum of three independent runs and are based on conversion of the respective starting acetylene to complexes **2** and **3**. These reactions also typically produced very small amounts of hexasubstituted benzene derivatives, the products of metal-catalyzed cyclotrimerization of the parent acetylene, and non-cobalt-complexed tetraarylcyclopentadieneones. The presence of these materials was confirmed by TLC comparison with, where available, authentic samples, but the amounts were generally too small for practical isolation.

[13] Complexes **2a** and **3a** have long been known (see ref 4a), while **2b** and **3b** have also been previously prepared (see ref 6). All other materials reported are new, with the exception of cyclobutadiene complex **2c**, which has previously been prepared by an alternative route: Wang, H.; Tsai, F.–Y.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2002**, *6*, 578–579.

[14] Rausch, M. D.; Westover, G. F.; Mintz, E.; Reisner, G. M.; Bernal, I.; Clearfield, A.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2605–2615.

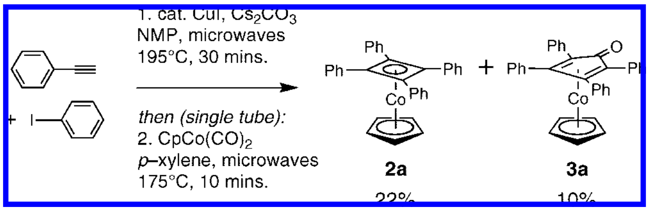
[15] Crystal data for **3f**: $a = 12.4176(4)$ Å, $b = 21.1018(6)$ Å, $c = 14.7313(4)$ Å, $\beta = 114.4950(10)°$, $V = 3512.68(18)$ Å^3, $M = 708.69$, $R_1 = 0.0614$. CCDC entry 643536.

[16] Hindered rotation about the 1-naphthylcyclobutadiene bonds would result in *up* (away from the Cp ring) or *down* (toward the Cp ring) orientations. Accordingly, a total of six atropisomers are possible for **2f**: all *up*, three *up*/one *down*, two *up*/two *down* (two possibilities), one *up*/three *down*, and all *down*. Proton NMR analysis of the cyclobutadienyl complex containing fractions revealed five resonances of varying intensity attributable to Cp ring protons in the range 5.28–4.91 ppm, and an extremely complex aromatic region. Integration of the entire Cp proton versus aromatic region gave an excellent fit to the required ratio (5:28). Potential simplification of this putative mixture of atropisomers was not observed on heating at high temperature (d_6-DMSO, 140 °C). Preparative TLC did not allow for separation of any individual isomer, but did allow two components to be isolated from the remainder (see Supporting Information).

[17] An additional bulky diarylacetylene, di(9-phenanthrenyl)acetylene, was also prepared. This material failed to provide any evidence of metallocene complex production from reactions with $CpCo(CO)_2$ under microwave conditions, lending credence to the view that 1-naphthyl substituents are at the upper limit of those aryl groups that may be successfully incorporated.

[18] The small amount of complex **2f** produced in this reaction could be isolated by column chromatography and corresponded to a yield of 1–2%. While TLC analysis also indicated the presence of complex **3f**, this material could not be separated from a number of additional products of similar polarity.

Scheme 3. Microwave-Promoted Assembly of Complexes 2a and 3a via in Situ Generation of Diphenylacetylene



here for cobalt complex formation.[19] Accordingly, a single tube sequential reaction was performed where diphenylacetylene, formed from an initial microwave-promoted Sonogashira coupling, was used without isolation or purification as the acetylene source for metallocene formation. Scheme 3 summarizes this sequential approach. While yields of the eventual product complexes **2a** and **3a** are considerably lower than those obtained from direct inclusion of diphenylacetylene, this one-tube approach is clearly effective and augers well for development of other metallocene syntheses from simple aromatic starting materials.[20]

Detailed examinations of parallel microwave and conventional heating approaches are complicated by the fact that direct comparisons are frequently difficult to establish.[10] For the reactions described here reactant concentrations are typically higher than the corresponding conventional reactions, while simultaneously both temperature and pressure are significantly enhanced. The result of the combination of these effects is to provide a very convenient route to a variety of cobalt metallocenes, at least one of which cannot be effectively prepared by traditional means. The reaction outcomes do not point to the operation of a specific microwave effect, but product yields are enhanced over traditional thermal reactions as a result of the whole volume heating conferred by microwave irradiation.

Experimental Section

Example Preparative Procedure. To a mixture of anhydrous *p*-xylene (3 mL) and diphenylacetylene (0.48 g, 2.8mmol) in a capped, thick-walled, microwave reactor tube was added $CpCo(CO)_2$ (0.34 g, 0.25 mL, 1.9 mmol) via syringe. The tube was then heated at 175 °C for 10 min with stirring in a microwave reactor (ramp time to the target temperature varied from 1 to 2 min at full power, with 0–50 W power required to maintain the target temperature throughout the reaction period). After cooling to room temperature the reaction mixture was dissolved in chloroform (10 mL) and purified by flash chromatography on silica gel to yield **2a** (0.36 g, 53%) and **3a** (0.32 g, 45%). See Supporting Information for full spectroscopic data. Cautionary note: the high temperatures and pressures involved in these reactions demand that only dedicated microwave reactors with accurate temperature feedback controls, and their matching thick-walled reaction tubes, be used.

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Supporting Information Available: General experimental details, preparative and isolation procedures, and selected spectroscopic data for **1b**–**g**, **2a**–**f**, and **3a**–**f**. CIF file for **3f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] He, H.; Wu, Y.-J. *Tetrahedron Lett.* **2004**, *45*, 3237–3239.

[20] Procedure: Cesium carbonate (650 mg, 2 mmol), copper(I) iodide (20 mg, 0.1 mmol), NMP (1.35 mL), iodobenzene (204 mg, 110 μL, 1 mmol), and phenylacetylene (106 mg, 120 μL, 1.06 mmol) were added, in that order, to a microwave reactor tube. The mixture was held, with stirring, at 195 °C for 30 min (ramp time to target temperature $\approx$ 10 min). The tube was cooled to room temperature, and through the tube cap septum were then added anhydrous *p*-xylene (1.6 mL) and $CpCo(CO)_2$ (162 mg, 120 μL, 0.9 mmol); the mixture was heated, with stirring, at 175 °C for an additional 10 min. After final cooling the reaction mixture was worked up and purified according to the example preparative procedure to afford complex **2a** (50 mg, 21%) and complex **3a** (30 mg, 12%). Yields quoted in Scheme 3 are the average of three independent runs at this scale. No attempt was made to fully optimize solvent or temperature conditions, nor reaction times.