A Versatile Route to 2-Substituted Cyclic 1,3-Dienes via a Copper(I)-Catalyzed Cross-Coupling Reaction of Dienyl Triflates with Grignard Reagents

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A general synthesis of 2-substituted cyclic 1,3-dienes in two steps from α,β-unsaturated ketones has been developed. Formation of a dien-2-yl triflate followed by a copper(I)-catalyzed cross-coupling reaction with a Grignard reagent gives 2-substituted dienes in fair to excellent yields. Alkyl, aryl, and allyl Grignard reagents can be used.
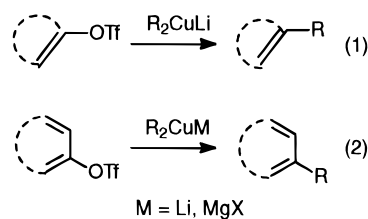
Introduction

Conjugated dienes are versatile starting materials in organic synthesis[1] and selective methods for their preparation are of continuous interest.[2] The most common use of conjugated dienes has been in Diels−Alder reactions[3] and related cycloadditions,[4] together with some limited use in electrophilic addition reactions.[5] More recently, however, there has been an increasing interest in the use of conjugated dienes in metal-mediated reactions.[6,7]

In our laboratory, we have developed synthetic methodology based on palladium catalysis for the 1,4-functionalization of conjugated dienes.[8] Application of this methodology requires access to cyclic 1,3-dienes substituted at the double bonds. For this reason, we previously developed a general and practical procedure for the synthesis of 1-substituted cyclic 1,3-dienes.[9] The synthesis of 2-substituted cyclic 1,3-dienes, however, often

requires lengthy procedures,[2,10,11] and more efficient and general methods for their preparation are highly desirable.

Coupling reactions of vinyl triflates with organometallic reagents are useful for the synthesis of substituted alkenes from ketones.[12] In particular, the vinyl triflate coupling with diorganocuprates was developed into a viable procedure for the stereoselective synthesis of trisubstituted alkenes (eq 1).[13] This method has been extensively used in, for example, natural product syntheses.[12b]

The corresponding reaction of a dienyl triflate would be a potential route for a general synthesis of 2-substituted dienes from α,β-unsaturated ketones (eq 2). To our knowledge, only a few isolated examples of this reaction are present in the literature. In their investigation of couplings between vinyl triflates and allylic cyanocuprates, Lipshutz and Elworthy[14] reported one example of a coupling with a dien-2-yl triflate. In a related study, Dieter et al.[15a] reported one example of coupling between a dien-2-yl triflate and an α-aminoalkyl cyanocuprate. Rúveda et al. coupled a dienyl triflate of a β-keto lactone with lithium dimethylcuprate.[15b] It is noteworthy that these examples, and other cross-couplings between vinyl

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Table 1. Copper(I)-Promoted Cross-Coupling of 1 with Stoichiometric Amounts of Cuprates

entry	RM[a]	CuI:RM[a]	T^b (°C)	product	yield[c] (%)
1	n-BuLi	1:1	0	2	15 (40)[a]
2	n-BuLi	1:2	−20	2	53
3	PhLi	1:2	0	3	92
4	MeLi	1:2	0	4	87
5	n-BuMgBr	1:1	−20	2	23[e]
6	n-BuMgBr	1:2	−20	2	55
7	n-BuMgI	1:2	−20	2	40
8	n-BuMgBr	1:2	0	2	63

[a] M = Li or MgX. [b] The cuprate was preformed at −20 °C. [c] GLC yield, decane as internal standard. Reactions complete within 15 min unless stated otherwise. [d] 15% yield after 20 min, 40% after 5 h. [e] Unreacted **1** recovered, reaction not complete even after several hours.

triflates and copper reagents, employ a stoichiometric amount of a lithium cuprate.

The aim of the present study was to develop a general synthesis of 2-substituted dienes via the organocopper approach and, more importantly, to develop a catalytic version[16] of the reaction.

In this paper, we report on a synthetically useful procedure for the transformation of an α,β-unsaturated ketone into a 2-substituted 1,3-diene in two simple steps via a copper(I)-catalyzed cross-coupling of dienyl triflates with Grignard reagents. We have also studied the corresponding reaction with stoichiometric amounts of alkyl- and arylcuprates.

Results and Discussion

Stoichiometric Reaction. Cyclic dienyl triflates were prepared according to the method of Scott and McMurry.[17] These triflates were then subjected to reactions with cuprates. In the reaction of dienyl triflate **1** with an excess (2 equiv) of preformed lithium organocuprate, n-Bu$_2$CuLi, the desired coupling product **2** was indeed obtained (eq 3).
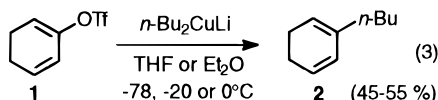
The influence of the copper salt, solvent, and temperature was examined. n-Bu$_2$CuLi, derived from CuI, CuBr, or CuCN and 2 equiv of n-BuLi, in reaction with **1** at −78 °C in THF or Et$_2$O gave **2** in 45−55% yield. Variation of the copper salt or solvent did not result in any significant change of the yield. Increasing the temperature up to 0 °C had no negative effect on the yield as long as the dibutyl cuprate was preformed at a lower temperature (−20 °C). The use of equal amounts of CuX and n-BuLi (n-BuCu(X)Li) gave a much slower reaction and a lower yield of **2** (Table 1, entry 1) compared to the use of CuX and n-BuLi in a 1:2 ratio. Different 2-substituted 1,3-cyclohexadienes were obtained in fair to high yields in THF from **1** and lithium organocuprates (Table 1, entries 2−4).

Table 2. Copper-Catalyzed Cross-Coupling of 1 with n-BuMgBr

entry	CuX	CuX (%)	solvent	T (°C)	yield of **2**[a] (%)
1			THF	−20	<3[b]
2	CuBr	10	THF	−20	31[b]
3	CuCN	10	THF	−20	34[b]
4	CuBr·SMe$_2$	10	THF	−20	58[b]
5	CuCl	10	THF	−20	61
6	CuCl·2LiCl[c]	10	THF	−20	66
7	CuI	10	THF	−20	67−73
8	CuI	5	THF	−20	72
9	CuI	2	THF	−20	69
10	CuCl·2LiCl[c]	1	THF	−20	69
11	CuI	10	THF	−60	<2[b]
12[d]	CuI	10	THF	0	65[b]
13	CuCl·2LiCl[b]	10	Et$_2$O	−20	41[b,e]
14	CuI	10	Et$_2$O	−20	<5[b]

[a] GLC yield, decane as internal standard. [b] Unreacted **1** recovered after reaction. [c] CuCl·2LiCl was prepared as a solution in THF according to the literature.[9] [d] Reaction mixture becomes black within a few min. [e] After 2.5 h.

The reaction could also be performed with stoichiometric amounts of a Grignard-derived copper reagent (1.2 equiv) with equal or better results. Here also, the influence of the copper salt on the yield of **2** was negligible. Furthermore, the stoichiometry of the cuprate had a significant role. Thus, a 2:1 ratio of Grignard reagent to copper salt (Bu$_2$Cu(I)(MgBr)$_2$) was necessary to achieve good yields and a fast reaction (complete within minutes) (Table 1, entries 6 and 8). A 1:1 ratio resulted in incomplete conversion and a low yield of **2** even after several hours (Table 1, entry 5). The choice of halide in the Grignard reagent influenced the yield of **2**, and better results were obtained with n-BuMgBr than with n-BuMgI (Table 1, entries 6 and 7).

Catalytic Reaction. The use of catalytic amounts of copper in the cross-coupling reaction between dienyl triflates and organolithium or Grignard reagents was next investigated. Lithium reagents, however, were found to be totally unreactive, whereas Grignard reagents showed excellent reactivity, leading to fast and clean reactions in the presence of catalytic amounts of a copper-(I) salt. The choice of copper catalyst, temperature, and solvent had a large effect on the yield of the coupling product **2** when **1** was reacted with n-BuMgBr (Table 2).

A control reaction in the absence of copper salt did not result in any formation of the desired product (Table 2, entry 1). The use of CuBr and CuCN afforded **2** in modest yields (Table 2, entries 2 and 3), whereas CuCl·2 LiCl[18] and CuI gave the best results (Table 2, entries 6 and 7). Variation of the amount of CuI or CuCl·2 LiCl between 10 and 1 mol % had no significant effect on the yield of **2** (Table 2, entries 8−10).

The choice of temperature was crucial. At −60 °C no reaction at all was observed (Table 2, entry 11). Apparently, this temperature is too low to allow formation of a reactive cuprate species. The yields were roughly equal at −20 and 0 °C (Table 2, entries 7 and 12). At 0 °C, however, the reaction did not go to completion, due to thermal decomposition of the cuprate.[19] The reaction
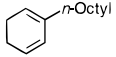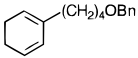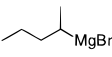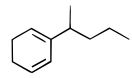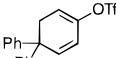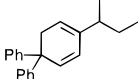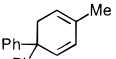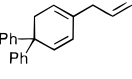
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Table 3. Synthesis of 2-Substituted 1,3-Dienes Employing Catalytic Amounts of CuI

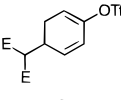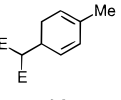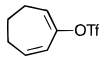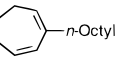| entry[a]	substrate	RMgX	CuI (%)	T (°C)	product	yield[b] (%)
1	**1**	n-OctylMgBr	10	-20	**8**	59
2			1			60
3		BnO(CH₂)₄MgBr	10	-20	**9**	60
4		(sec-pentyl)MgBr	1	-20	**10**	80
5	**5**	(isobutyl)MgBr	5	-20	**11**	79
6		MeMgBr	5	0	**12**	95[c]
7		allylMgCl	5	-10	**13**	91[c]
8[d]	**6**	MeMgBr[e]	10	0	**14**	96
9	**7**	n-OctylMgBr	5	-20	**15**	55

[a] All reactions where run in THF with 1.5 equiv of Grignard reagent, according to the general procedure given in the experimental section, unless otherwise stated. [b] Isolated yield after column chromatography. [c] CH₂Cl₂ used to extract the product due to its low solubility in ether and pentane. [d] E = -CO₂Me. [e] 3 equiv MeMgBr used.

mixture turned black within a few minutes. The mode of addition (**1** and n-BuMgBr) can be varied between slow addition (30 min) of the Grignard reagent to **1** and CuI in THF, slow addition of **1** to the Grignard reagent and CuI in THF, or fast addition of both reagents to CuI in THF, without any significant change of the yield of **2**.

The scope of the reaction was explored utilizing a catalytic amount of CuI and 1.5 equiv of RMgBr in THF. The desired 2-substituted 1,3-dienes were formed in good to excellent yields when different alkyl or allyl Grignard reagents were employed (Table 3). Longer alkyl chains (Table 3, entries 1−3), give yields comparable to the GLC yields obtained for the coupling of **1** with n-BuMgBr. Introduction of a methyl substituent can be done in almost quantitative yields (Table 3, entries 6 and 8). It is noteworthy that also a secondary alkyl Grignard reagent can be used (Table 3, entries 4 and 5). In comparison, the cuprate derived from s-BuLi and CuI was totally unreactive in an attempted stoichiometric cross coupling. An allyl group can also be introduced in nearly quantitative yield (Table 3, entry 7). Compound **14**

(Table 3, entry 8) is a key intermediate[20] in a total synthesis of the natural product paeonilactone A.[21] The malonate functionality in **6** did not interfere with the cross-coupling reaction with MeMgBr; however, 3 equiv of the Grignard reagent had to be used due to deprotonation of the malonate during the reaction.

Aryl Grignard reagents generally gave high yields in the cross-coupling reaction (Table 4), but the aryl-substituted cyclohexadiene products are rather unstable compounds and special precautions have to be taken during their isolation.[22]

Dienyl phosphates such as **20a** and **20b** are attractive as alternative substrates to dienyl triflates. Cross couplings of related vinyl phosphates with organocuprates

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Table 4. Synthesis of 2-Aryl-Substituted 1,3-Dienes from Cyclic Dienyl Triflates and ArMgBr

entry[a]	dienyl triflate	product	yield[b] (%)
1	**1** (OTf)	**3** (Ph)	92
2		**16** (Me, Me)	86
3		**17** (t-Bu, t-Bu)	88
5	**7** (OTf)	**18** (Ph)	94
6		**19** (OMe)	87

[a]Reactions were run at 0 °C in THF with 1.5 equiv of ArMgBr according to the general procedure in the Experimental Section. [b]Isolated yield, after bulb to bulb distillation for aryl-substituted cyclohexadienes and after column chromatography for aryl-substituted cycloheptadienes.
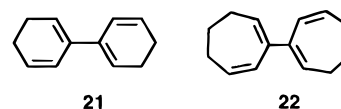
are known.[23] Unfortunately, **20** showed low reactivity in our system. Dienyl phosphate **20a** was totally unreactive toward both organolithium and Grignard reagent-derived cuprates. However, **20b** reacted with *n*-BuMgBr under standard catalytic conditions, but the reaction was slower than for the corresponding triflate **1**, and the yield of **2** was low (34% by GLC after several hours). An attempted coupling between **20b** and PhMgBr failed to give the cross-coupling product and **20b** was recovered. This shows the remarkable leaving-group ability of the triflate group.

20 a R=Et
b R=Ph
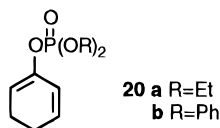
Mechanism. The modest yields in the case of couplings between **1** and butyl Grignard reagent (and other alkyl Grignards, except methyl) are explained by the formation of cyclohexadiene (ca 20%), bicyclohexadienyl (**21**) (5–10% for catalytic couplings with *n*-BuMgBr), and octane (20–30%). With **7** as substrate the symmetrical coupling product **22** can be isolated. These side products are in agreement with those previously observed in couplings between vinyl halides and copper reagents.[24]

21 **22**

The formation of octane can partly be explained by thermal or oxidative decomposition of the cuprate[19] or by decomposition of the Grignard reagent,[25] but a control experiment under the usual reaction conditions, without dienyl triflate **1**, afforded much less octane. The amount of **21** formed in couplings with stoichiometric lithium cuprates was shown to be temperature dependent with larger amounts being formed at lower temperature (up to 20%). Compound **21** and other side products were not detected for reactions that give higher yields of the cross-coupling product. We propose a mechanism involving an intermediate Cu(III) species obtained by oxidative addition of the dienyl triflate to a cuprate (Scheme 1). This oxidative addition most likely proceed via a π-olefin– copper complex followed by a nucleophilic vinylic substitution.[26] The products obtained from the reaction of **1** with *n*-BuMgBr (**2**, octane, 1,3-cyclohexadiene, and octane) can then arise via different reductive eliminations from the Cu(III) species. A reductive elimination where one R group couples to the diene gives the cross-coupling product. An undesired reductive coupling of the R groups would produce octane when R = *n*-Bu and leave a (cyclohexadien-2-yl)copper complex. The latter may produce 1,3-cyclohexadiene or react in a second cycle with RMgBr and dienyl triflate to produce **21**.

Scheme 1
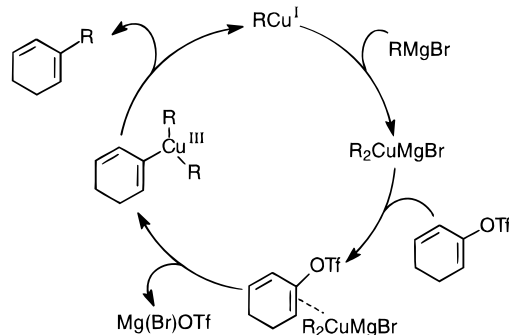
Conclusion

In conclusion, we have developed a general method for the synthesis of 2-substituted cyclic 1,3-dienes. The availability of various α,β-unsaturated ketones, as well as the easy access to various Grignard reagents from the corresponding halides, should make this method widely applicable in organic synthesis. The use of catalytic amounts of copper makes product isolation easier, gives a cleaner reaction, and is of course advantageous in an economical and environmental sense.[16] An investigation on the use of acyclic dienyl triflates is on its way and would add to the generality of this method.

Experimental Section

NMR spectra were recorded for CDCl$_3$ solutions (^{1}H at 400 MHz and ^{13}C at 100.5 MHz) using tetramethylsilane (0.0 ppm) or residual CHCl$_3$ (7.26 ppm) as internal standards in ^{1}H NMR

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and CDCl$_3$ (77.0 ppm) in ^{13}C NMR. Mass spectra were obtained in GC/MS or direct inlet mode (EI, 70 eV). Ether and THF were dried over Na−benzophenone prior to use. Diisopropylamine was dried over CaH$_2$ and distilled immediately before use. 2-Cyclohexen-1-one and 4,4-diphenyl-2-cyclohexen-1-one were purchased from Aldrich. *N*-Phenylbis-(trifluoromethanesulfonimide) (Tf$_2$NPh) was obtained from Lancaster. Grignard reagents were bought from Aldrich (MeMgBr, PhMgBr, allylMgBr) or prepared by standard procedures as solutions in ether or THF. Grignard reagents and organolithium reagents were always standardized before use.[27] 2-Cycloheptenone was prepared from cycloheptene via allylic oxidation,[28] followed by hydrolysis and oxidation, or from cycloheptanone by the method of Trost et al.[29] 4-(Dicarbomethoxymethyl)-2-cyclohexenone[20] was prepared in several steps from 1,3-cyclohexadiene via 1-acetoxy-4-(dicarbomethoxymethyl)-2-cyclohexene.[30] All copper-mediated reactions were run under an argon atmosphere. Slow addition was performed by the use of a syringe pump. Merck silica gel 60 (240−400 mesh) was used for flash chromatography.

1,3-Cyclohexadien-2-yl Triflate (1).[31] General Procedure for the Synthesis of Cyclic Dienyl Triflates. A solution of LDA (14.4 mmol) in THF (20 mL) was prepared from diisopropylamine (1.89 mL, 14.4 mmol) and *n*-butyllithium (1.6 M in hexane, 9.0 mL, 14.4 mmol) at 0 °C under N$_2$. The resulting solution was cooled to −78 °C by means of a dry ice/acetone bath. 2-Cyclohexenone (1.26 g, 13.1 mmol) in THF (20 mL) was added dropwise, and the reaction mixture was stirred for 30 min at −78 °C. A solution of Tf$_2$NPh (5 g, 14.0 mmol) dissolved in THF (20 mL) was then added. After complete addition, the reaction mixture was warmed to 0 °C and stirred at this temperature until the reaction was judged complete according to TLC (1−2 h). The solvent was evaporated, and the crude material was dissolved in ether and washed with water twice. The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude product was purified by column chromatography (pentane) to yield 2.41 g (80%) of **1** as a colorless liquid, which had an ^{1}H NMR spectrum in accordance with a literature spectrum:[31] ^{1}H NMR δ 6.01 (dtd, J = 0.8, 4.3, 10.1 Hz, 1H), 5.82 (dq, J = 2.2, 10.1 Hz, 1H), 5.68 (ddt, J = 4.7, 2.2, 0.8 Hz, 1H), 2.43−2.35 (m, 2H), 2.29−2.20 (m, 2H); ^{13}C NMR δ 145.9, 131.5, 120.9, 118.6 (q, J(^{13}C,^{19}F) = 320 Hz), 114,6, 21.6, 21.4.

5,5-Diphenyl-1,3-cyclohexadien-2-yl triflate (5) was obtained from 4,4-diphenyl-2-cyclohexenone following the procedure above: viscous oil; 89% yield after column chromatography (pentane/ether 99:1): ^{1}H NMR δ 7.31−7.17 (m, 10H), 6.45 (dd, J = 0.8, 10.1 Hz, 1H), 5.98 (dd, J = 2.2, 10.1 Hz, 1H), 5.80 (dtd, J = 4.8, 2.3, 0.8 Hz, 1H), 3.06 (d, J = 4.8 Hz, 2H); ^{13}C NMR δ 146.6, 145.3, 139.1, 128.2, 127.2, 126.7, 120.1, 118.5 (q, J(^{13}C,^{19}F) = 321 Hz), 113.7, 47.7, 36.3; IR (CDCl$_3$) 3062, 1657, 1597, 1492, 1423, 1228, 1137, 1090, 861 cm^{-1}.

4-Dimethylmalonate-1,3-cyclohexadien-2-yl triflate (6)[20] was obtained from 4-(dicarbomethoxymethyl)-2-cyclohexenone[20] following the general procedure above, with the exception that 2.1 equiv of LDA was used and the reaction mixture was stirred for 3 h at −78 °C before addition of Tf$_2$NPh: clear oil; 55% yield after column chromatography (pentane/ether 75:25); ^{1}H NMR δ 5.98 (dd, J = 10.2, 4.3 Hz, 1H), 5.89 (dt, J = 10.2, 2.0 Hz, 1H), 5.68 (dt, J = 2.1, 4.9 Hz, 1H), 3.74 (dd, J = 5.2, 0.6 Hz, 6H), 3.51 (d, J = 9.0 Hz, 1H), 3.15 (m, 1H), 2.56 (m, 1H), 2.33 (m, 1H); ^{13}C NMR δ 168.1, 168.0, 145.3, 132.0, 122.0, 118.5 (q, J(^{13}C,^{19}F) = 319 Hz), 114.0, 53.6, 52.7, 52.6, 32.0, 25.5.

1,3-Cycloheptadien-2-yl triflate (14)[32] was obtained from 2-cycloheptenone following the above procedure: colorless liquid; 79% yield after column chromatography (pentane). Spectral data were consistent with those previously reported.[32]

Typical Procedure for Cross-Couplings of 1 with Preformed Lithium Organo Cuprates (Table 1). To a slurry of CuX (1 mmol) in THF or ether (10 mL) at −20 °C, under an argon atmosphere, was added RLi (2 mmol) via syringe. After 30 min, the temperature was adjusted to the value indicated in Table 1 and **1** (0.5 mmol) was added via syringe. The reaction mixture was stirred until completion as judged by TLC. Aqueous NH$_4$Cl and ether were added to quench the reaction. *n*-Decane (0.5 mmol) was added as internal standard, and a sample was taken for GLC analysis. The aqueous layer was extracted with pentane/ether (50:50) twice, and the combined organic layers were subsequently washed with brine and dried (MgSO$_4$). The diene obtained was isolated after evaporation of the solvent in vacuo, followed by column chromatography or bulb-to-bulb distillation.

Typical Procedure Employing Stoichiometric Amounts of a Preformed Magnesium Dibutylcuprate in the Reaction with 1 (Table 1). To a slurry of CuX (0.6 mmol) in THF (10 mL) at −20 °C under an argon atmosphere was added BuMgY (1.3 mmol) via syringe. After 30 min, the temperature was adjusted to the value indicated in Table 1, and **1** (0.5 mmol) was added via syringe. The reaction mixture was stirred until completion (usually within minutes) as judged by TLC. Aqueous NH$_4$Cl and ether were added to quench the reaction. *n*-Decane (0.5 mmol) was added as internal standard, and a sample was taken for GLC analysis. The aqueous layer was extracted with pentane/ether (50:50) twice, and the combined organic layers were subsequently washed with brine and dried (MgSO$_4$). Crude **2** (as a mixture with *n*-octane and **20**) was obtained by evaporation of the solvent in vacuo.

Typical Procedure for Reactions of Cyclic Dienyl Triflates with Grignard Reagents Employing a Catalytic Amount of a Cu(I) Salt (Tables 3 and 4). CuI (2 mg, 0.01 mmol) was suspended in THF under an atmosphere of argon, at the temperature indicated in Table 3 or 4. The dienyl triflate (1 mmol) was added. The Grignard reagent (1.5 mmol) was then added via syringe, and the mixture was stirred at the chosen temperature until judged complete according to TLC (<15 min.). The reaction was quenched by addition of aqueous NH$_4$Cl and ether. *n*-Decane (1 mmol) was added as internal standard if the mixture was to be analyzed by GLC, and a sample was taken. Ether and water were added, and the water phase was extracted with ether twice. The combined organic layers were washed with brine, dried (MgSO$_4$), and evaporated in vacuo. The crude product was purified by the method stated for each compound below.

Data for Selected Cross-Coupling Products. 2-*n*-Butyl-1,3-cyclohexadiene (2) was purified by column chromatography (pentane) followed by bulb-to-bulb distillation: ^{1}H NMR δ 5.82 (m, 2H), 5.46 (m, 1H), 2.09 (m, 4H), 2.00 (m, 2H), 1.42−1.25 (m, 4H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 136.0, 127.3, 126.5, 119.9, 35.3, 30.6, 22.4, 22.35, 22.3, 14.0; IR 3032, 2930, 1466, 1165 cm^{-1}.

2-Phenyl-1,3-cyclohexadiene (3)[10,33] was purified by filtration through alumina followed by bulb-to-bulb distillation. Spectral data are consistent with those previously reported.[10,33]

2-Methyl-1,3-cyclohexadiene (4)[34] was purified by distillation. Spectral data are consistent with those previously reported.[34]

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2-[4-(Phenylmethoxy)butyl]-1,3-cyclohexadiene (9)[11a] was purified by column chromatography (pentane/ether 99:1). Spectral data are consistent with those previously reported.[11a]

5-(Dicarbomethoxymethyl)malonate-2-methyl-1,3-cyclohexadiene (14)[20] was isolated as a clear colorless oil after column chromatography (pentane/Et$_2$O 75:25): ^{1}H NMR δ 5.85 (app dt, $J = 9.6$, 1.5 Hz, 1H), 5.74 (dd, $J = 9.6$, 4.5 Hz, 1H), 5.42 (m, 1H), 3.72 (s, 3H), 3.48 (d, $J = 9.6$ Hz, 1H), 2.96 (m, 1H), 2.28 (m, 1H), 2.01 (m, 1H), 1.72 (app q, $J = 1.8$ Hz, 3H); ^{13}C NMR δ 168.8, 168.7, 131.4, 129.5, 126.6, 119.2, 54.1, 52.4, 52.3, 32.6, 26.5, 20.9; IR 2955, 1732, 1436, 1333, 1252, 1215, 1195, 1158 cm^{-1}.

Spectral Data for Side Products in the Cross-Coupling Reaction. 2,2′-Bis(1,3,cyclohexadienyl) (21).[35] Compound **21** is unstable and could not be isolated in pure form. Any attempts resulted in polymerization: ^{1}H NMR δ 6.20 (dq, $J = 9.9$, 1.7 Hz, 2H), 5.95 (dtd, $J = 9.9$, 4.3, 0.8 Hz, 2H), 5.88 (m, 2H), 2.23 (m, 4H), 2.12 (m, 4H); ^{13}C NMR δ 133.8, 127.6, 124.1, 120.0, 22.7, 22,1.

2,2′-Bis(1,3,cycloheptadienyl) (22): ^{1}H NMR δ 5.98 (m, 6H), 2.19 (m, 8H), 1.93 (m, 4H); ^{13}C NMR δ 140.4, 133.9, 129.5, 128.3, 31.2, 29.8, 28.7.

Supporting Information Available: Experimental and characterization data for compounds **8**, **10−13**, and **15−19**. Copies of ^{1}H and ^{13}C NMR spectra for compounds **2**, **5**, **6**, **8**, **10**, **11**, **14−19**, and **22** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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