

## Palladium-Catalyzed Addition of Mono- and Dicarboxyl Compounds to Conjugated Dienes

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An intermolecular, palladium-catalyzed addition of the  $\alpha$ -C–H bond of monocarbonyl and 1,3-dicarbonyl compounds to dienes has been developed, and an exploration of the scope of these reactions with a broad range of carbonyl compounds and nitriles was conducted. The combination of CpPd(allyl) and the commercially available 1,3-bis(dicyclohexylphosphino)propane (DCyPP) catalyzed the 1:1 addition of the C–H bonds of these substrates to dienes in high yields. These reactions included unusual additions of the C–H bonds of ketones, lactones, esters, and nitriles to dienes, as well as the more common additions of cyanoesters, malononitrile, and  $\alpha$ -sulfonyl esters. Reactions of these substrates with both cyclic and acyclic dienes are reported. Reactions catalyzed by complexes of nonracemic chiral ligands were also conducted, and the first enantioselective version of this reaction was achieved with a Josiphos ligand with enantioselectivities up to 81%.

### Introduction

The development of highly efficient, catalytic addition reactions is an important synthetic goal because these reactions occur without byproducts.<sup>1</sup> During studies of the hydroamination of dienes and vinylarenes with alkyl- and arylamines,<sup>2</sup> we became interested in the reactions between dienes and substrates with C–H bonds that are similar in acidity to the N–H bonds of amines.<sup>3</sup> Takahashi et al.<sup>4</sup> described the addition of 1,3-dicarbonyl compounds to dienes in the early 1970s; however, the scope of carbonyl compound and diene was narrow. Furthermore, the reactions yielded mixtures of 1,2- and 1,4-addition products and 2:1 telomerization products. The telomerization can be suppressed by using catalysts with bidentate phosphine ligands instead of monodentate ligands.<sup>4</sup>

In 1986 Moberg and co-workers<sup>5</sup> reported a Ni(0)-catalyzed addition of active methylene compounds, such as diethylmalonate and acetoacetate, to 1,3-conjugated dienes. The catalyst was prepared in situ by reduction of Ni(acac)<sub>2</sub> with trimethylaluminum in the presence of PBu<sub>3</sub> at –50 °C. Jolly and co-workers<sup>6</sup> later published an improved protocol for the addition of 1,3-dicarbonyl

compounds to butadiene and methyl-substituted 1,3-dienes, such as isoprene, in the presence of ( $\eta^2$ -butadiene)[bis(dialkylphosphino)ethane]palladium as catalyst. This catalyst simplified the system by eliminating additional reagents, such as triethylaluminum or alkoxides. Trost and co-workers reported intermolecular additions of bis(phenylsulfonyl)methane and 1,3-dicarbonyl compounds to dienes in the presence of  $[(\pi\text{-allyl})\text{PdCl}]_2$ , dppp [1,3-bis-(diphenylphosphino)propane], and NaOMe as a reducing reagent<sup>7</sup> and enantioselective additions to alkenes catalyzed by  $[(\pi\text{-allyl})\text{PdCl}]_2$  and the ligand developed by their group.<sup>8</sup>

More recently, Widenhoefer and co-workers<sup>9</sup> have published intramolecular reactions of the  $\alpha$ -C–H bonds of ketones to olefins to form products of both oxidative processes and addition reactions. These reactions were conducted with Pd(II) catalysts, such as (RCN)<sub>2</sub>PdCl<sub>2</sub>. Intermolecular reactions between 1,3-dicarbonyl compounds and ethylene and propylene have also been achieved with similar palladium and analogous platinum catalysts.<sup>10</sup> Most recently, Yao and Li<sup>11</sup> reported a gold-catalyzed addition of 1,3-dicarbonyl compounds to vinylarenes. Finally, Murahashi and co-workers have reported ruthenium-catalyzed Michael additions and aldol reactions<sup>12</sup> of substrates with acidic C–H bonds, such as malononitrile.<sup>13</sup>

<sup>†</sup> These authors contributed equally to this work.

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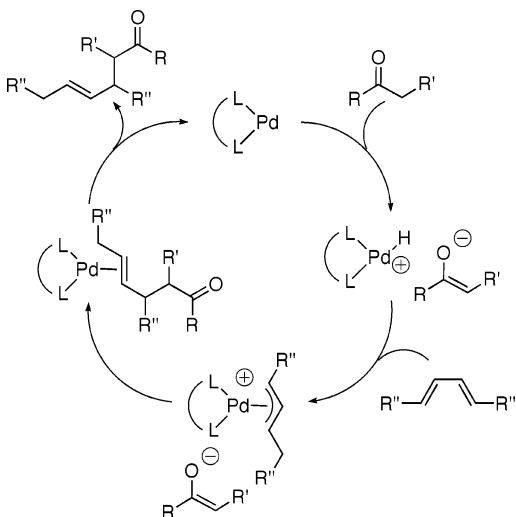
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## SCHEME 1



The additions of substrates with acidic C–H bonds to dienes could occur by the mechanism in Scheme 1. An electron-rich metal center could deprotonate a weakly acidic substrate in an endo- or exothermic step, depending on acidity, to generate a hydride that would insert diene to generate an allyl intermediate. Alternatively, the carbonyl compound could protonate a complex between the diene and the  $L_2Pd(0)$  fragment, and the resulting complex could undergo insertion to generate the same allyl intermediate. Subsequent attack of the enolate on the allyl intermediate would generate the final addition product. The step that forms the bond in the product would be related to that of allylic substitution, but the intermediate would be generated without the need for a leaving group or external base.

To the best of our knowledge, no intermolecular, enantioselective addition of C–H bonds across 1,3-dienes has been developed. More commonly, the allylic products have been prepared by substitution chemistry.<sup>14</sup> Yet the factors that control enantioselectivity of the addition process would be related to those that control enantioselectivity in allylic substitution because the intermediate that forms the C–C bond in the product by the mechanism of Scheme 1 would be the same as the one that forms the C–C bond in enantioselective allylic alkylation.

This paper delineates our progress toward developing the addition of substrates with mildly acidic C–H bonds, often termed pronucleophiles,<sup>15</sup> to substrates with conjugated carbon–carbon multiple bonds. We show that the scope of this process can be extended to the intermolecular addition<sup>16</sup> of benzylic ketones, lactones, esters, lactams, and nitriles and that the addition of 1,3-dicarbonyl compounds<sup>17</sup> to dienes can be conducted enantioselectively.

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## Results and Discussion

**In Situ Catalyst Preparation and Effects of Catalyst Structure.** The most efficient previous catalyst for the addition of 1,3-dicarbonyl compounds to dienes,  $(\eta^2-1,3\text{-butadiene})Pd(\text{Pr}^i_2\text{PC}_2\text{H}_4\text{Pr}^i_2)$ ,<sup>6</sup> is difficult to generate and isolate. Thus, we hoped to increase the scope of the C–H addition process and to develop a more convenient catalyst system. Because  $\text{CpPd}(\text{allyl})$  is a known precursor to  $Pd(0)$ <sup>18</sup> and can be synthesized easily from commercially available  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  and  $\text{NaCp}$ , we tested combinations of this precursor and bidentate phosphine ligands for the reaction of pronucleophiles with dienes.

To optimize the reactions with this precatalyst, we conducted the addition of 2,4-pentanedione to 1,3-cyclohexadiene (1.5 equiv) in several solvents and with a wide range of bidentate phosphine ligands at room temperature with 1% catalyst under concentrated conditions. In contrast to reactions catalyzed by  $(\eta^2-1,3\text{-butadiene})Pd(\text{Pr}^i_2\text{PC}_2\text{H}_4\text{Pr}^i_2)$  that were dependent on solvent,<sup>19</sup> reactions catalyzed by a combination of bidentate ligands and  $\text{CpPd}(\text{allyl})$  occurred in similar yield and with similar rates in tetrahydrofuran (THF), toluene, acetone, 1,2-dimethoxyethane (DME), dichloromethane (DCM), *N,N*-dimethylacetamide, dioxane, and *tert*-amyl alcohol. The small solvent effect may result from the small quantity of solvent (see Experimental Section for details). However, reactions conducted in DME were fastest and were slightly faster than those conducted in THF and dioxane.

The effects of varying the ligand were more pronounced. As shown in Table 1, the reactions catalyzed by the combination of 1,3-bis(dicyclohexylphosphino)propane (DCyPP; entry 8) or 1,3-bis(diisopropylphosphino)propane (entry 7) and  $\text{CpPd}(\text{allyl})$  occurred fastest. As shown by Jolly, the hydrocarbon chain bridging the two phosphorus atoms significantly affects the rate of reaction. In contrast to previous findings,<sup>6</sup> however, we found that reactions conducted with ligands containing a three-carbon bridge occurred up to twice as fast as reactions with a two-carbon bridge. On the basis of this series of studies, experiments to explore the reaction scope were performed with a ratio of pronucleophile to diene between 1:1.5 and 1:4 in DME with a 1:1 mixture of DCyPP and  $\text{CpPd}(\text{allyl})$  as catalyst.

**Increased Scope of Nucleophiles.** Because the published additions of C–H bonds to dienes<sup>4–7</sup> have been conducted with a limited scope of pronucleophiles (see Chart 1), we evaluated the catalyst generated from DCyPP and  $\text{CpPd}(\text{allyl})$  for reactions of monocarbonyl compounds and nitriles, in addition to the more standard reactions of the 1,3-dicarbonyl compounds.

As shown in Table 2, a variety of 1,3-dicarbonyl compounds,  $\alpha$ -cyanocarbonyl compounds, and malononitrile (entries 1–7) reacted with dienes in high yields to form the desired addition products. In some cases, the product from a 1:2 ratio of pronucleophile and diene was

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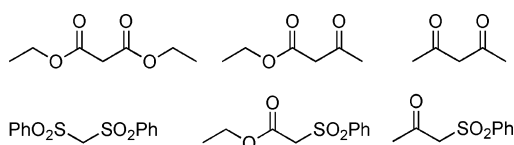
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**TABLE 1. Relative Rates of Reaction with Catalysts Generated from a Series of Alkylbisphosphines**

Entry	Phosphine	Relative Conversion <sup>a</sup>	Entry	Phosphine	Relative Conversion <sup>a</sup>
1		0.01	9		1.02
2		0.01	10		1.4
3		0.31	11		1.41
4		1	12		1.28
5		0.46	13		0.02
6		0.69	14		0.06
7		2.08	15		0.01
8		2.20	16		0.00

<sup>a</sup> Relative conversion was measured as the ratio of the moles of product after 7.5 h at room temperature to moles of nucleophile added at  $t = 0$  for reactions with the ligand shown vs reactions with dippe as ligand.

### CHART 1. Substrates That Underwent Additions of C–H Bonds to Dienes in Previous Work

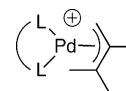


generated when the reactions were conducted at higher temperatures. For example, the reaction of malononitrile with 1,3-cyclohexadiene at room temperature occurred to form a 5:1 ratio of mono- and diaddition products and to generate 68% isolated yield of monoaddition product, but reaction of the same substrates at 80 °C formed the diallyl product in 97% yield (entry 6).

Monocarbonyl compounds and nitriles also underwent intermolecular additions to cyclohexadiene, as shown in Table 2. Reaction of the lactone isochroman-3-one (entry 8) as well as the ketone 2-tetralone (entry 9) with cyclohexadiene occurred to give the desired addition products in high yields. Reactions with purely aliphatic esters and ketones did not occur, suggesting that the acidity remains important in controlling the scope of the reaction. Activated nitriles (entries 7 and 10) also reacted to give the addition products in high yields at elevated

temperatures. In all three cases, the monoaddition products were obtained exclusively.

The scope of this methodology extends to acyclic dienes. As shown in Table 3, reactions of the acyclic 2,3-dimethylbutadiene occurred to give high yields of the addition products. In contrast to reactions of 1,3-cyclohexadiene that form equivalent products from 1,2- and 1,4-additions, reactions of acyclic dienes generate different products from 1,4- and 1,2-additions. If the reactions occur by insertion of diene into a palladium hydride, as shown in Scheme 1, a single allyl complex shown below would be generated from 2,3-dimethylbutadiene. The enolate or nitrile anion would then add preferentially to the less substituted terminus of the  $\pi$ -allyl group.<sup>20</sup> In this case, the more sterically crowded substrates (entries 5 and 10) would react with higher selectivity for the 1,4-addition products over the 1,2-addition products.



A broad range of compounds with mildly acidic C–H bonds added to acyclic dienes. 1-Phenylbutan-2-one, the

TABLE 2. Reactions of Various Pronucleophiles with 1,3-Cyclohexadiene

Entry	Nucleophile	Catalyst Loading	Temp	Time	Yield <sup>a</sup>
1	<chem>PhSO2CH2SO2Ph</chem>	5%	80° C	7 h	89%
2	<chem>CC(=O)CC(=O)C</chem>	2%	80° C	20 h	77%
3	<chem>CCOC(=O)CC(=O)OCC</chem>	5%	80° C	18 h	90%
4	<chem>COC(=O)CC(=O)OC</chem>	5%	80° C	24 h	92%
5	<chem>NC#CC#N</chem>	5%	RT	19 h	68%
6	<chem>NC#CC#N</chem>	5%	80° C	8 h	97% <sup>b</sup>
7	<chem>c1ccc(cc1)C(=O)CC#N</chem>	5%	80° C	7 h	89%
8	<chem>O=C1OCc2ccccc21</chem>	2%	80° C	18 h	87%
9	<chem>O=C1OCc2ccc3ccccc3c21</chem>	2%	80° C	20 h	91%
10	<chem>C#CCc1ccc(cc1)C(F)(F)F</chem>	2%	80° C	20 h	94%

<sup>a</sup> Yields are for isolated material and are an average of two runs. RT, room temperature. <sup>b</sup> Yield of the dialkylation product.

ethyl ester of phenylacetic acid (entries 2 and 4), nitriles such as phenylacetone, benzoylacetonitrile, and phenylsulfonacetone (entries 6–8) all added to 2,3-dimethyl-1,3-butadiene in good yields and formed the monoaddition products with high selectivities. Even an aqueous solution of *N*-methyl acetoacetamide (65%) reacted in high yields after only 2 h (Table 3, entry 11). Clearly, the catalyst is not sensitive to moisture.

In contrast, oxindole (Table 3, entry 9) and malononitrile (entry 15) formed a mixture of mono- and diaddition products, even at early reaction times when the concentration of reagent exceeds that of product. Interestingly, only one of the two isomeric monoaddition products underwent a second addition to the diene. Thus, the ratio of 1:2 decreased to favor **2** as the reaction of oxindole (Table 3, entry 9) proceeded.

The reaction of *N*-methyloxindole occurred more sluggishly, perhaps due to a less acidic C–H bond, but occurred with selectivity that was similar to the reaction of the parent oxindole. The product from addition of two dienes formed well before all of the *N*-methyloxindole was consumed. In contrast, 1,3-dimethyloxindole (Table 3, entry 10) proceeded without any side reaction to provide the addition product in 97% yield.

Even though factors other than the  $pK_a$  of the C–H bond affected the scope of pronucleophile, the reactant with the more acidic C–H bond tended to react faster within the same class of substrate. A comparison of the reactions of cyclic and acyclic benzylic ketones (Table 3, entries 1 and 2) revealed this trend. In water, the cyclic ketone has a  $pK_a$  value of 12.9, whereas the acyclic analogue has a  $pK_a$  of 15.9.<sup>21</sup> Though the  $pK_a$  of  $\beta$ -tetralone in DMSO is not reported, the  $pK_a$  of 2-indanone ( $pK_a = 17.0$  in DMSO) is lower than that of dibenzyl ketone

( $pK_a = 18.7$  in DMSO).<sup>22</sup> The reaction of the less acidic acyclic ketone required higher catalyst loading, higher temperature, and a longer reaction time. The same correlation was observed for reaction of the ethyl ester of phenylacetic acid ( $pK_a$  22.7 in DMSO) (Table 3, entry 4), and of the benzolactone ( $pK_a$  18.8 in DMSO) (Table 3, entry 3).<sup>23</sup> The benzolactone isochroman-3-one (Table 3, entry 3) reacted faster and in higher yield. The reactions of amides followed the same trend. The benzo-fused lactams (Table 3, entries 9 and 10) reacted readily, whereas *N*-methyl-2-phenylacetamide and *N,N*-diethyl-2-phenylacetamide did not react at all.

**Asymmetric Additions.** These C–H additions across conjugated dienes can generate products with a new stereocenter at a carbon that originated from the diene or the pronucleophile or both. We investigated both additions of symmetric carbon pronucleophiles to 1,3-cyclohexadiene (Scheme 2, top) and addition of a dissymmetric carbon pronucleophile to a terminal, acyclic diene (Scheme 2, bottom). More examples of allylic substitutions that occur with high enantioselectivities with prochiral allylic electrophiles are known than examples that occur with high enantioselectivities with prochiral nucleophiles.<sup>24</sup> Thus, the first approach was more likely to uncover an enantioselective addition of acidic C–H bonds across dienes.

To study enantioselective additions of carbonyl compounds to prochiral dienes, the addition of 2,4-pentadione to 1,3-cyclohexadiene was conducted. Because bidentate alkylphosphines generated more active catalysts for the addition process than did bidentate arylphosphines, a

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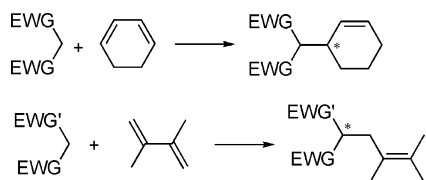
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**TABLE 3.** Addition of Substrates with Acidic C–H Bonds across 2,3-Dimethylbutadiene

Entry	Nucleophile	Catalyst Loading	Temp	Time	1:2	Yield <sup>a</sup>
1		2%	RT	8 h	96:4	77% <sup>b</sup>
2		5%	90° C	11 h	96:4	97%
3		2%	60° C	15 h	82:18	70% <sup>b</sup>
4		10%	90° C	10 d	100:0	72%
5		2%	60° C	19 h	100:0	98%
6		5%	60° C	11 h	48:52	91% <sup>c</sup>
7		5%	90° C	14 h	93:7	53%
8		2%	RT	22 h	100:0	90% <sup>b</sup>
9		2%	RT	6 h	57:43	52% <sup>b</sup>
10		2%	60° C	5 h	100:0	97%
11		5%	90° C	2 h	97:3	70%
12		2%	RT	8 h	94:6	78%
13		2%	RT	7 h	42:58	71% <sup>b</sup>
14		2%	RT	23 h	88:12	88%
15		5%	90° C	3 h	29:71	61%

<sup>a</sup> Yields are for isolated material and are an average of two runs. <sup>b</sup> The diaddition product was also isolated. <sup>c</sup> The yield is estimated from <sup>1</sup>H NMR spectroscopy because the mono- and diaddition products could not be separated.

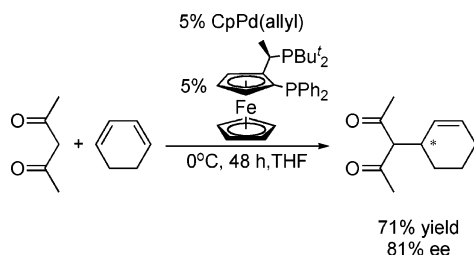
**SCHEME 2**

series of chiral, nonracemic, bidentate di- and trialkylphosphines were tested as ligands. A series of experiments conducted at room temperature with 1% catalyst in THF for 24 h showed that (*R*)-(-)-1-[(*S*)-2-diphenylphosphinoferrocenyl]ethyl-di-*tert*-butylphosphine<sup>25</sup> generated the product in 72% enantiomeric excess (ee) and

93% yield. Similar yields and ee values were obtained with 1,3-cyclohexadiene and dimethyl malonate (91% yield, 72% ee) as well as with diethyl-2-fluoromalonate (97% yield, 71% ee). Because the malonates were less reactive than the  $\beta$ -diketones, a higher catalyst loading of 5% was used. After optimization of solvent, reaction temperature, and catalyst loading, the reaction of 2,4-pentadione with 1,3-cyclohexadiene occurred in THF at 0 °C with 5 mol % catalyst over 48 h to give the addition product in a good yield of 71% and in 81% ee (Scheme 3).

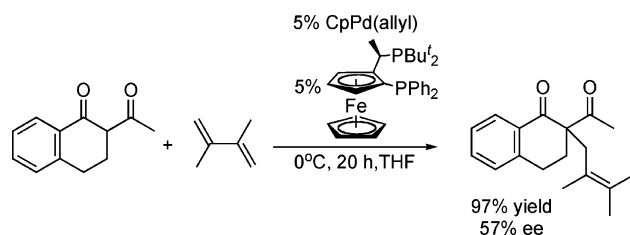
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## SCHEME 3



The reactions of prochiral pronucleophiles occurred with lower enantioselectivities. To date, the reaction of 2,3-dimethylbutadiene with the  $\beta$ -diketone in Scheme 4

## SCHEME 4



occurred with the best enantioselectivity. The addition product was isolated in an excellent yield of 97%, but the enantiomeric excess of the product was a modest 57%.

## Conclusion

New catalysts for the palladium-catalyzed addition of compounds with mildly acidic C–H bonds to conjugated dienes were developed, and these catalysts significantly expanded the scope of substrates that added to dienes. The scope of this reaction now includes benzylic ketones, amides, nitriles, and lactones as well as activated esters, nitriles, and sulfones. The reactions were conducted under conditions without base and with a catalyst generated in situ from CpPd(allyl) and commercially available DCyPP. The products from monoalkylation were obtained with higher regioselectivity than those in prior reports on related addition processes. Further, an enantioselective version of this addition reaction was developed; the reaction between 2,4-pentadione and 1,3-cyclohexadiene occurred with 81% ee in the presence of a catalyst generated from CpPd(allyl) and a Josiphos ligand with one di-*tert*-butylphosphino group and one diphenylphosphino group.

## Experimental Section

**General Methods.** Reactions were loaded in a drybox and were conducted in 4 mL vials sealed with a cap containing a poly(tetrafluoroethylene) (PTFE) septum. Yields refer to an average over two runs of isolated yields of compounds. Reagents and ligands were purchased from commercial suppliers. 1,3-Dimethyl oxindole<sup>26</sup> and CpPd(allyl)<sup>27</sup> were prepared by literature procedures.

**Reactions with 2,3-Dimethylbutadiene. Representative Procedure: 1-(2,3-Dimethylbut-2-enyl)-2-tetralone.** In a drybox, a screw-capped vial containing a small stir bar was charged with  $\beta$ -tetralone (292 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg,

0.0400 mmol) as a solution in 0.1 mL of DME, and CpPd(allyl) (8.5 mg, 0.040 mmol) as a solution in 0.05 mL of DME. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. After being stirred at room temperature for 8 h, the reaction mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the volatile materials were evaporated under reduced pressure. Automated column chromatography (diethyl ether/pentane gradient from 2/98 to 4/96) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 96:4 as slightly yellow oil (309.5 mg, 68% yield). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  7.22–7.13 (m, 3H), 6.89 (d,  $J$  = 7.3 Hz, 1H), 3.46 (dd,  $J$  = 9.6 and 6.1 Hz, 1H), 3.31–3.23 (m, 1H), 2.99 (ddd,  $J$  = 15.7, 6.4, and 3.4 Hz, 1H), 2.76 (ddd,  $J$  = 17.7, 5.4, and 3.4 Hz, 1H), 2.56–2.42 (m, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.19 (s, 3H); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta$  213.3 (1C), 137.1 (1C), 135.9 (1C), 128.9 (1C), 128.3 (1C), 127.6 (1C), 126.7 (1C), 126.4 (1C), 123.3 (1C), 53.3 (1C), 38.3 (1C), 37.7 (1C), 27.6 (1C), 20.6 (1C), 19.8 (1C), 18.6 (1C). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O: C, 84.16; H, 8.83. Found: C, 84.22; H, 9.10. Selected <sup>1</sup>H NMR of minor isomer: 7.01 (d,  $J$  = 8.1 Hz, 1H), 4.82 (s, 1H), 4.60 (s, 1H), 1.85 (s, 1H), 1.12 (s, 1H), 1.09 (s, 1H).

**Representative Reaction of 1,3-Cyclohexadiene: 3-Cyclohex-2-enyl-3-oxo-3-phenylpropionitrile.** The reaction was performed according to the representative procedure with 3-oxo-3-phenylpropionitrile (144.2 mg, 0.99 mmol), 1,3-cyclohexadiene (0.3 mL, 3.10 mmol), DCyPP (23.0 mg, 0.052 mmol), and CpPd(allyl) (11.3 mg, 0.052 mmol) in 1.0 mL of DME at 80 °C for 7 h. Column chromatography (hexane/diethyl ether 7/1) gave the title compound as a colorless oil (204 mg, 91% yield). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$  7.98–7.94 (m, 4H), 7.63–7.68 (m, 2H), 7.55–7.54 (m, 4H), 5.75–5.69 (m, 1H), 5.50–5.45 (m, 1H), 4.40 (d,  $J$  = 6.6 Hz, 1H), 4.30 (d,  $J$  = 6.5 Hz, 1H), 2.97 (m, 2H), 2.03 (m, 4H), 1.92–1.75 (m, 5H), 1.68–1.43 (m, 5H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>)  $\delta$  190.7, 190.6, 134.6, 134.5, 134.40, 134.38, 131.7, 131.5, 129.1, 129.0, 128.69, 128.67, 126.0, 125.1, 116.4, 116.3, 45.7, 45.2, 36.4, 36.3, 27.8, 26.0, 24.62, 24.60, 20.96, 20.7. Anal. Calcd for C<sub>15</sub>H<sub>15</sub>NO: C, 79.97; H, 6.71; N, 6.22; O, 7.10. Found: C, 79.72; H, 6.74.

**Representative Enantioselective Reaction: 3-Cyclohex-2-enylpentane-2,4-dione.**<sup>28</sup> In a drybox, a screw-capped vial containing a small stir bar was charged with (*R*)-(-)-1-[(*S*)-2-diphenylphosphinoferrocenyl]ethyl-di-*tert*-butylphosphine (54.2 mg, 0.0999 mmol), 1,3-cyclohexadiene (163 mg, 2.04 mmol), acetylacetone (200 mg, 2.00 mmol), CpPd(allyl) (21.3 mg, 0.100 mmol), and 50  $\mu$ L of THF. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. After being stirred at 0 °C for 48 h, the reaction mixture was dissolved in diethyl ether, and the resulting solution was evaporated under reduced pressure. Column chromatography (hexane/diethyl ether 10/1) afforded 3-cyclohex-2-enylpentane-2,4-dione as a colorless oil (243.0 mg, 81% ee, 71% yield). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>)  $\delta$  5.79 (m, 1H), 5.38 (ddm,  $J$  = 10 and 2 Hz, 1H), 3.63 (d,  $J$  = 10 Hz, 1H), 3.04 (m, 1H), 2.21 (s, 3H), 2.20 (s, 3H), 2.01 (m, 2H), 1.73 (m, 2H), 1.60 (m, 1H), 1.22 (m, 1H); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta$  204.0, 203.8, 130.0, 127.0, 74.8, 35.6, 30.1, 29.6, 26.6, 24.9, 20.6.

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**Supporting Information Available:** Procedures for isolation and data on characterization of reaction products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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