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Palladium-Catalyzed Cyclocarbonylation of Arynes with Methyl Allyl Carbonates: Selective Synthesis of 1*H*-Inden-1-ones

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A selective protocol for the synthesis of 2-methylene-3-substituted-2,3-dihydro-1*H*-inden-1-ones and 2-benzylidene-2,3-dihydro-1*H*-inden-1-ones has been developed via palladium-catalyzed cyclocarbonylation reactions of arynes with allyl carbonates and carbon monooxide (CO). It is noteworthy that the selectivity of this new route is depended on both substrates and ligands.

The transition metal-catalyzed carbonylation reaction is one of the most common methods for the introduction of a carbonyl group into important molecules in organic synthesis and industry.[1−3] Among the most useful carbonylation processes, transition metal-catalyzed cyclocarbonylation reactions are particularly interesting due to directly creating carbocycles and heterocycles.[1−3] Although benzyne chemistry has been advanced recently due to the use of *o*-silyl aryltriflates as the aryne precursors,[3−7] only one paper has been reported on the catalytic carbonylation of arynes to date.[3] In 2001, Chatani and Murai employed arynes as one of the reaction partners to react with CO in the presence of Co, Rh, or Pd catalysis. Particularly, they found that treatment of arynes with CO and allyl acetates afforded the corresponding 2-methylene-1*H*-inden-1-ones in moderate to good yields (Scheme 1). On the other hand, inden-1-ones are important frameworks found in numerous natural products and pharmaceutically active compounds, as well as being valuable intermediates in organic synthesis.[8] As a continuing interest in benzyne chemistry,[7] we here report a novel palladium-catalyzed cyclocarbonylation route to selectively constructing inden-1-ones using *o*-silyl aryltriflates, methyl allyl carbonates, and CO as the reaction partners (Scheme 1).

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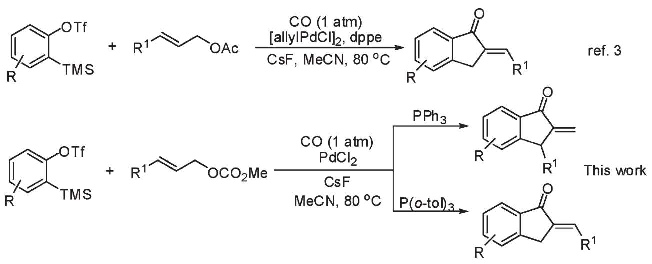
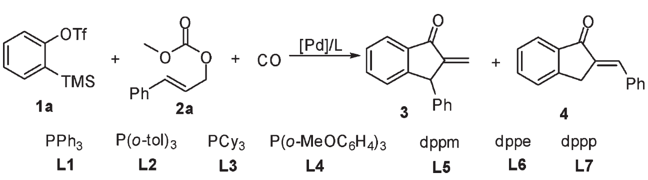
SCHEME 1



We began our investigation with the reaction of 2-(trimethylsilyl)phenyl triflate (**1a**) (0.25 mmol) with cinnamyl methyl carbonate (**2a**) (0.2 mmol) and CO (1 atm, bubbling) in the presence of [allylPdCl]$_2$, dppe, and CsF (the reported conditions[3]). Unfortunately, a mixture of products, including a trace amount of the target 1*H*-inden-1-ones **3** and **4**, was determined by GC-MS analysis. After a series of trials, we were pleased to find that [allylPdCl]$_2$ combined with PPh$_3$ could give the desired 2-methylene-3-phenyl-2,3-dihydro-1*H*-inden-1-one (**3**) in 10% yield along with a trace amount of another product **4**, (*E*)-2-benzylidene-2,3-dihydro-1*H*-inden-1-one (entry 1, Table 1).[9] Encouraged by these results, the effect of Pd catalysis was examined (entries 2−10). The results demonstrated that in the presence of PPh$_3$ ligand PdCl$_2$ was the most efficient catalyst among [allylPdCl]$_2$, Pd(OAc)$_2$, and Pd(PPh$_3$)$_4$ (entries 1−4). Treatment of substrate **1a** with carbonate **2a**, CO, PdCl$_2$, and PPh$_3$ enhanced the yield of **3** sharply to 73% (entry 2). Interestingly, PdCl$_2$ combined with a more bulky ligand, P(*o*-tol)$_3$, selectively afforded another product **4** in 74% yield (entry 5). However, the other ligands, such as PCy$_3$, P(*o*-MeOC$_6$H$_4$)$_3$, dppm, dppe, and dppp, displayed lower selectivity, providing a mixture of products **3** and **4** in good total yields (entries 6−10). Subsequently, the reaction temperature effect was tested in the presence of PdCl$_2$ and PPh$_3$, and the best results were obtained at 80 °C (entries 2 and 11−13). Among the solvents and fluorides examined, MeCN combined with CsF was the most effective (entries 2 and 14−17). It was found that the reaction could not take place without Pd catalysts (entry 18). However, cinnamyl acetate, the reported effective substrate,[3] could not undergo the reaction with triflate **1a** and CO in the presence of PdCl$_2$ and PPh$_3$.

With the two optimal reaction conditions in hand, the *o*-silyl aryltriflates and methyl allyl carbonates scope was explored for selectively synthesizing 1*H*-inden-1-ones (Tables 2 and 3). As shown in Table 2, 2-methylene-3-substituted-2,3-dihydro-1*H*-inden-1-ones were selectively prepared from the reactions of *o*-silyl aryltriflates (**1**) with methyl allyl carbonates (**2**) and CO with use of the PdCl$_2$/PPh$_3$ system. Initially, a variety of methyl allyl carbonates **2b**−**j** were examined by reacting with triflate **1a** and CO (Table 2, entries 1−9). The results demonstrated that several functional groups, such as methyl, methoxy, and chloro, on the aromatic ring at the terminal of allyl carbonates **2** were tolerated well, resulting in moderate yields (entries 1−5). Substrates **2b** or **2c** with a methyl group, for instance, underwent the cyclocarbonylation reaction with triflate **1a** and CO in 65%, and 59% yields, respectively (entries 1 and 2). Substrate **2f** bearing a methyl group and a chloro group successfully gave the desired product **9** in moderate yield (entry 5). It was noted that 30% yield was achieved from the reaction of methyl 3-(thiophen-2-yl)allyl carbonate (**2g**) with triflate **1a** and CO (entry 6). The optimal conditions were found to be compatible with aliphatic and terminal allyl carbonates **2h**−**j** (entries 7−9). For example, treatment of diene **2j** with triflate **1a**, CO, PdCl$_2$,and PPh$_3$ was carried out smoothly in 55% yield (entry 9). We were pleased to observe that a set of *o*-silyl aryltriflates **1b**−**e** were suitable for the reaction under the optimal conditions (entries 10−13), but the bulky triflate **1c** shifted the selectivity toward the (*E*)-2-benzylidene product **16** (entry 11). It is noteworthy that the unsymmetrical *o*-silyl aryltriflates **1b**−**e** afford the corresponding products regioselectively (entry 10−13). The results imply that the carbonylation reaction takes place regioselectively at the OTf position.

TABLE 1. Screening Conditions[a]



entry	fluoride	ligand	solvent	T (°C)	t (h)	yield[b] (%) 3	yield[b] (%) 4
1	[(allyl)PdCl]$_2$	**L1**	MeCN	80	6	10	trace
2	PdCl$_2$	**L1**	MeCN	80	4	73	trace
3	Pd(OAc)$_2$	**L1**	MeCN	80	6	30	trace
4	Pd(PPh$_3$)$_4$	**L1**	MeCN	80	6	trace	trace
5	PdCl$_2$	**L2**	MeCN	80	4	trace	74
6	PdCl$_2$	**L3**	MeCN	80	4	25	18
7	PdCl$_2$	**L4**	MeCN	80	4	24	52
8	PdCl$_2$	**L5**	MeCN	80	4	36	17
9	PdCl$_2$	**L6**	MeCN	80	4	48	25
10	PdCl$_2$	**L7**	MeCN	80	4	40	28
11	PdCl$_2$	**L1**	MeCN	100	8	27	trace
12	PdCl$_2$	**L1**	MeCN	50	8	64	trace
13	PdCl$_2$	**L1**	MeCN	rt	30	35	trace
14	PdCl$_2$	**L1**	THF	80	6	38	trace
15	PdCl$_2$	**L1**	toluene	80	24	trace	trace
16[c]	PdCl$_2$	**L1**	MeCN	80	24	trace	trace
17[d]	PdCl$_2$	**L1**	MeCN	80	24	27	trace
18		**L1**	MeCN	80	24	0	0

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.2 mmol), [Pd] (5 mol %), ligand (10 mol %), CsF (2 equiv), CO (1 atm, bubbled), and solvent (2 mL). [b] Isolated yield. [c] *n*-Bu$_4$NF (2 equiv) instead of CsF. [d] KF (2 equiv) instead of CsF in the presence of 18-crown-6 (2 equiv).

The synthesis of the (*E*)-2-benzylidene products[9] was subsequently investigated in the presence of PdCl$_2$ and P(*o*-tol)$_3$, and the results are summarized in Table 3. To our delight, moderate yields of the 2-benzylidene products were still achieved from the reactions of triflate **1a** with allyl carbonates **2d**, **2i**, or **2k** in the presence of PdCl$_2$ and P(*o*-tol)$_3$ (entries 1−3). Two other *o*-silyl aryltriflates **1c** and **1e** reacted with carbonate **2a** and CO were also examined under the same conditions, and the 2-benzylidene products **16** and **21** were selectively prepared in 70% and 63%, respectively (entries 4 and 5).

We also tested the product **3** as a synthetic intermediate to introduce a new group to this framework by the Heck reaction (Scheme 2). In the presence of Pd(OAc)$_2$, Ag$_2$CO$_3$,

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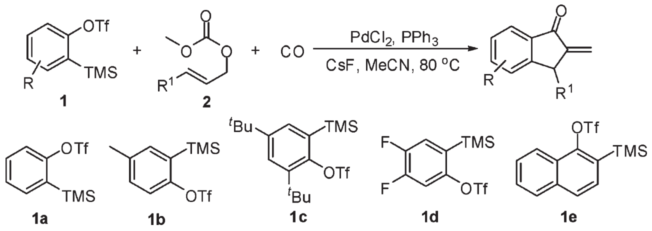
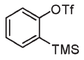
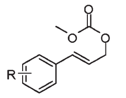
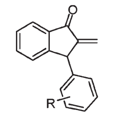
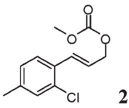
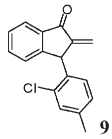
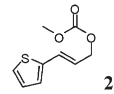
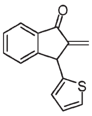
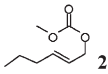
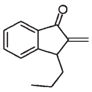
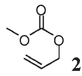
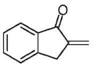
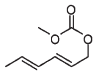
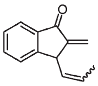
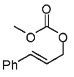
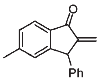
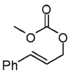
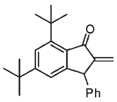
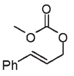
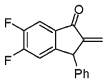
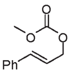
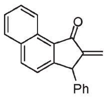
(9) The constructions of the products are based upon the chemical shift of the olefinic proton by comparison with the authoritative data, see: (a) References 3 and 8. (b) Minatiti, A.; Zheng, X.; Buchwald, S. L. *J. Org. Chem.* **2007**, *72*, 9253.

TABLE 2. $PdCl_2/PPh_3$-Catalyzed Carbonylation of *o*-Silyl Aryltriflates (1) with Methyl Allyl Carbonates (2)[a]

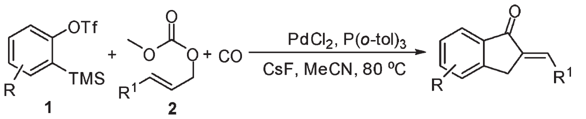


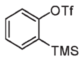
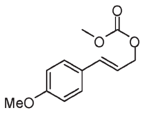
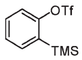
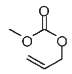
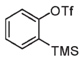
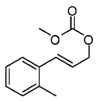
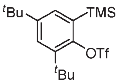
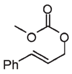
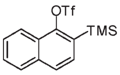
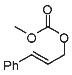
Entry	1	2	Product	Isolated Yield[b]
				
1	1a	R = 4-Me **2b**	R = 4-Me **5**	65 (4 h)
2	1a	R = 3-Me **2c**	R = 3-Me **6**	59 (4 h)
3	1a	R = 4-MeO **2d**	R = 4-MeO **7**	58 (4 h)
4	1a	R = 2-MeO **2e**	R = 2-MeO **8**	67 (4 h)
5	1a	 **2f**	 **9**	54 (4 h)
6	1a	 **2g**	 **10**	30 (10 h)
7	1a	 **2h**	 **11**	63 (4 h)
8	1a	 **2i**	 **12**	33 (4 h)
9[c]	1a	 **2j**	 **13**	55 (4 h)
10	1b	 **2a**	 **14**	76 (4 h)
11[d]	1c	 **2a**	 **15**	trace (8 h)
12	1d	 **2a**	 **17**	40 (10 h)
13	1e	 **2a**	 **18**	63 (12 h)

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.2 mmol), $PdCl_2$ (5 mol %), PPh_3 (10 mol %), CsF (2 equiv), CO (1 atm, bubbled), and MeCN (2 mL) at 80 °C. [b] The reaction time is given in parentheses. [c] *Z*-/*E*-isomer = 1:2.6. [d] Product **16**, (*E*)-2-benzylidene-5,7-di-*tert*-butyl-2,3-dihydro-1*H*-inden-1-one, was obtained in 57% for 8 h.

and toluene, **3** was treated with iodobenzene smoothly to afford a Heck/isomerization product **22**, 2-benzyl-3-phenyl-1*H*-inden-1-one, in 53% yield.[10]

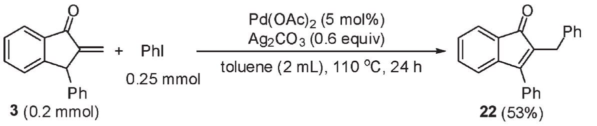
TABLE 3. $PdCl_2/P(o\text{-tol})_3$-Catalyzed Cycloarbonylation of *o*-Silyl Aryltriflates (1) with Methyl Allyl Carbonates (2)[a]



Entry	Triflate 1	Carbonate 2	Isolated Yield
1	 **1a**	 **2d**	45 (**20**)
2	 **1a**	 **2i**	58 (**12**)
3	 **1a**	 **2k**	53 (**19**)
4	 **1c**	 **2a**	70 (**16**)
5	 **1e**	 **2a**	63 (**21**)

[a] Reaction conditions: **1** (0.25 mmol), **2** (0.2 mmol), $PdCl_2$ (5 mol %), $P(o\text{-tol})_3$ (10 mol %), CsF (2 equiv), CO (1 atm, bubbled), and MeCN (2 mL) at 80 °C for 4 h.

SCHEME 2



A possible mechanism was proposed as outlined in Scheme 3 on the basis of the present results and the reported mechanism.[3-8] Reaction of Pd(0) with allyl carbonate **2** affords the allylPd(II) intermediate **B**, followed by addition of intermediate **B** to aryne **A**, which is generated in situ from **1** with CsF, gives intermediates **C** and/or **D** based on the properties of both ligand and substrates.[3] Insertion of CO into intermediates **C** and **D** takes place to yield intermediates **E** and **F**. The second cis-addition to the C−C double bond in intermediates **E** and **F** leads to intermediates **G** and **H**. Finally, reductive elimination of intermediates **G** and **H** affords the products and regenerates the active Pd(0) species. It is noteworthy that the steric hindrance effect of both arynes and ligands has a fundamental influence on the selectivity (intermediates **I** and **J**). In the presence of PPh_3, selectivity toward 2-methylene-1*H*-inden-1-ones may be that secondary cabon in intermediate **B** is more active (stable) than primary carbon, whereas $P(o\text{-tol})_3$ shifted the selectivity toward 2-substituted-methylene-1*H*-inden-1-ones due to its steric hindrance.

In summary, we have developed a new palladium-catalyzed cyclocarboynlation protocol for selectively preparing 2-methylene-3-substituted-2,3-dihydro-1*H*-inden-1-ones and

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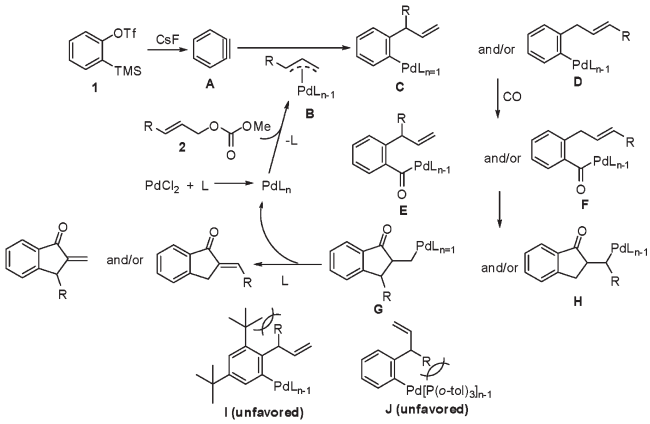
(10) Pan, D.; Chen, A.; Su, Y.; Zhou, W.; Li, S.; Jia, W.; Xiao, J.; Liu, Q.; Zhang, L.; Jiao, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4729.

SCHEME 3. A Working Mechanism



2-benzylidene-2,3-dihydro-1*H*-inden-1-ones. This work is the first to demonstrate that the selectivity of cyclocarbonylation between arynes and allyl carbonates can be controlled by changing ligands. Most importantly, these products with several functional groups can be employed as synthetic blocks to synthesize this class of compounds with a new structural feature readily for further elaboration.[10]

Experimental Section

Typical Experimental Procedure with the $PdCl_2/PPh_3$ System. Aryne **1** (0.25 mmol), allyl carbonate **2** (0.2 mmol), $PdCl_2$ (5 mol %), PPh_3 (10 mol %), CsF (2 equiv), and MeCN (2 mL) were added to a two-necked flask in turn. Then, CO was bubbled, and the solution was stirred at 80 °C for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was washed with brine, extracted with diethyl ether, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to afford the desired product.

2-Methylene-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3):[3] yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 7.0 Hz, 1H), 7.33−7.26 (m, 4H), 7.12 (d, J = 7.0 Hz, 2H), 6.43 (d, J = 2.0 Hz, 1H), 5.44 (d, J = 1.5 Hz, 1H), 4.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.4, 153.5, 149.0, 142.3, 137.4, 135.4, 128.8, 128.3, 128.1, 127.1, 126.5, 124.2, 121.1, 49.1; IR (KBr, cm^{-1}) 1679, 1654; LRMS (EI, 70 eV) *m*/*z* (%) 220 (M$^+$, 100), 191 (58), 165 (20), 115 (20).

Typical Experimental Procedure with the $PdCl_2/P(o\text{-tol})_3$ System. Aryne **1** (0.25 mmol), allyl carbonat **2** (0.2 mmol), $PdCl_2$ (5 mol %), $P(o\text{-tol})_3$ (10 mol %), CsF (2 equiv), and MeCN (2 mL) were added to a two-necked flask in turn. Then, CO was bubbled, and the solution was stirred at 80 °C for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was washed with brine, extracted with diethyl ether, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to afford the desired product.

(*E*)-2-Benzylidene-2,3-dihydro-1*H*-inden-1-one (4):[3] yellow solid; mp 105.0−107.0 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 1H), 7.68−7.60 (m, 4H), 7.55 (d, J = 7.5 Hz, 1H), 7.48−7.34 (m, 4H), 4.05 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.3, 149.6, 137.9, 135.3, 134.7, 134.6, 133.9, 130.7, 129.6, 128.9, 127.6, 126.1, 124.4, 32.4; IR (KBr, cm^{-1}) 1732, 1715, 1650; LRMS (EI, 70 eV) *m*/*z* (%) 220 (M$^+$, 65), 219 (100), 191 (43), 165 (13).

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Supporting Information Available: Analytical data and spectra (^{1}H and ^{13}C NMR) for all the products **3**−**14** and **16**−**22** and typical procedure for the palladium-catalyzed cyclocarbonylation reaction. This material is available free of charge via the Internet at http://pubs.acs.org.