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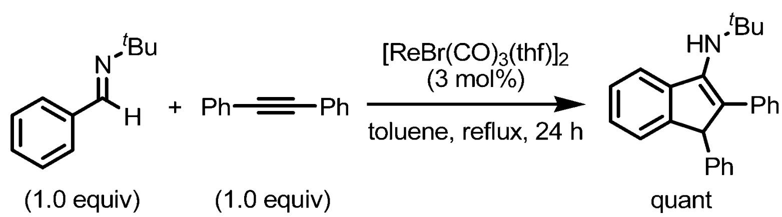

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Rhenium-Catalyzed Formation of Indene Frameworks via C−H Bond Activation: [3+2] Annulation of Aromatic Aldimines and Acetylenes

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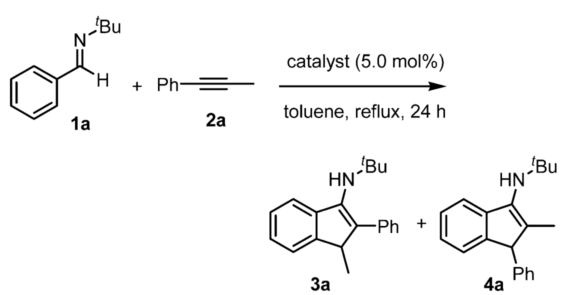
Indene derivatives are useful compounds serving as building blocks for many functional materials,[1] medicines,[2] and organic compounds.[3] They can also be used as ligands for transition metals by deprotonation.[4] There have been many reports on the synthesis of indene derivatives using transition metal compounds.[5] Among them, indene derivatives are obtained stoichiometrically by reactions of *ortho*-manganated aryl ketones with acetylenes.[6] If the starting *ortho*-metalated aryl ketones can be prepared by catalytic C−H bond activation,[7] and then successive insertion, intramolecular cyclization, and reductive elimination can occur, this indene formation will become a catalytic process. In this paper, by using a rhenium complex as the catalyst and changing the substrate from aromatic ketones to aldimines, we succeed in the first catalytic synthesis of indene derivatives via C−H bond activation followed by insertion and intramolecular addition.

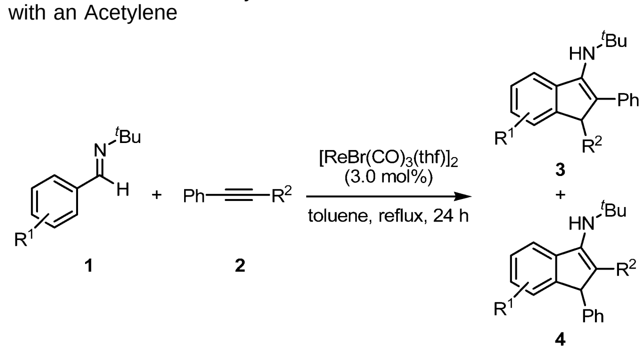
The formation of indene derivatives was examined by the reaction of aromatic aldimine **1a** (0.50 mmol) with acetylene **2a** (0.50 mmol) in toluene (1.0 mL) in the presence of a possible catalyst (5.0 mol %) under reflux conditions for 24 h (eq 1).[8−10] First, we examined a popular rhodium(I) complex, $RhCl(PPh_3)_3$, and a ruthenium complex, $Ru_3(CO)_{12}$, but the reactions did not occur and aldimine **1a** remained unchanged in both cases. Although the ruthenium complex has been reported to catalyze C−H bond activation and successive insertion of the 1-trimethylsilyl-1-propyne,[11] the process stops at this stage, and further intramolecular cyclization does not occur. Among the catalysts examined, a rhenium(I) complex, $ReCl(CO)_5$, was found to catalyze the desired reaction and gave two isomeric indene derivatives, **3a** and **4a**, though the yields were low (both 17% yields). The result suggested that the rhenium complex has a similar ability for C−H bond activation as $Ru_3(CO)_{12}$, and the formed alkenyl−rhenium species has sufficient nucleophilicity to add to the aldimine. The yields and selectivity were improved by changing the ligand of the rhenium complex from chloride to bromide and changing two carbon monoxides to THFs. In this case, the indene derivative **3a** was obtained quantitatively with $[ReBr(CO)_3(thf)]_2$ under the same reaction conditions.[12,13]

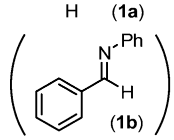


(1)

Then, we explored the substituents of aldimines (Table 1). By the reaction of 1-phenyl-1-propyne (**2a**) with aldimine **1b** instead of **1a**, the selectivity reversed and the indene derivative **4b** was obtained selectively (entry 2). The reaction did not proceed with the oxime or hydrazone of an aldehyde instead of the aldimine. Treatment of diphenylacetylene (**2b**) and aldimine **1a** with $[ReBr(CO)_3(thf)]_2$ afforded the indene derivative quantitatively (entry 3). Aldimines bearing electron-donating groups, such as methoxy and methyl groups at the *para*-position of the aldimine, gave the corresponding indene derivatives in excellent yields (entries 4 and 5). A reaction of an aldimine possessing a *para*-phenyl group with **2b** gave the indene derivative **3b** in good yield (entry 6). However, an aldimine bearing an electron-withdrawing trifluoromethyl group at the *para*-position gave the corresponding indene derivative in low yield (entry 7). In contrast to the *para*-substituents, the yields decreased when substituents were attached to the *ortho*-position of the aldimines. For example, the indene derivative was obtained in 40% yield by the reaction of an aldimine bearing *ortho*-methyl group with **2b** (entry 8), and an aldimine with an *ortho*-methoxy

Table 1. Rhenium-Catalyzed Reaction of an Aromatic Aldimine with an Acetylene



entry	imine (R^1)	acetylene (R^2)	% yield[a]	3:4[b]
1	H (**1a**)	Me	95 (>99)	>99:<1
2[c]	 (**1b**)	Me	89 (>99)	<1:>99
3	H	Ph	96 (>99)	
4	*p*-MeO	Ph	89 (96)	
5	*p*-Me	Ph	95 (>99)	
6	*p*-Ph	Ph	83 (93)	
7	*p*-CF_3	Ph	14 (16)	
8	*o*-Me	Ph	40 (52)	
9	*o*-MeO	Ph	0 (0)	
10[d]	H	*n*-C_6H_{13}	64 (68)	>99:<1
11	H	$SiMe_3$	81 (87)	<1:>99

[a] Isolated yield. The yield determined by ^1H NMR is reported in parentheses. [b] The ratios of indene derivatives **3** and **4**. [c] 1-Phenyl-1-propyne (1.1 equiv), 135 °C. [d] At 135 °C.

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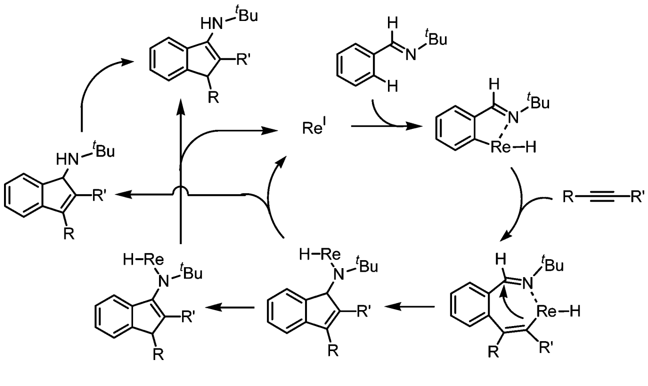
Scheme 1. Proposed Mechanism of the Formation of Indene Derivatives



group did not afford the corresponding indene derivative (entry 9). The reaction of **2b** with benzaldehyde or acetophenone did not proceed at all. The imine nitrogen atom could coordinate more strongly to the rhenium center than the oxygen atoms and promoted the C−H bond activation. In the case of the reaction of **2b** with a hydrazone derived from acetophenone, indene was not formed because the internal cyclization did not proceed after C−H bond activation and insertion of the acetylene.

From our experiments, it was found that acetylenes bearing at least one aryl group gave the corresponding indene derivatives (entries 10 and 11). Indene derivatives could not be obtained by the reaction of aldimine with 6-dodecyne, 1-trimethylsilyl-1-propyne, bis(trimethylsilyl)acetylene.

When the proposed reaction was carried out with $ReBr(CO)_5$ under an atmosphere of carbon monoxide (1.0 atm), an indene derivative was not obtained and the starting materials **1a** and **2a** were recovered quantitatively. This result and the fact that the catalytic activity of $[ReBr(CO)_3(thf)]_2$ is higher than that of $ReBr(CO)_5$ indicated that the formation step of one or more vacant coordination sites as a result of the carbonyl ligand(s) leaving the rhenium center is important to promote the reaction. The proposed reaction mechanism is as follows (Scheme 1): (1) coordination of a nitrogen atom of an imine to a rhenium center; (2) C−H bond activation (formation of *ortho*-metalated imine);[14−16] (3) insertion of an acetylene to the rhenium−carbon bond of the aryl−rhenium intermediate; (4) intramolecular nucleophilic attack of the formed alkenyl−rhenium moiety to a carbon atom of the imine; and (5) reductive elimination and 1,3-rearrangement of hydrogen atoms (or vice versa).

In summary, we have succeeded in the catalytic synthesis of indene derivatives via C−H bond activation by the reactions of aromatic aldimines with phenyl acetylenes. There are only a few precedents for the rhenium-catalyzed $C(sp^2)$−H bond activation.[17,18] In addition, to our knowledge, the intramolecular nucleophilic addition of organometallic species derived from C−H bond activation to an imine moiety has not been reported. Since this reaction needs only a catalytic amount of the metal reagent and a few reaction steps compared with the reported synthetic methods of indene derivatives, it will become a useful method to synthesize indene frameworks. Further reactions initiated by the C−H bond activation with rhenium catalysts are now in progress.

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Supporting Information Available: General experimental procedure, characterization data for indene derivatives, and X-ray crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The ^1H NMR yields were determined by using 1,1,2,2-tetrachloroethane as an internal standard.
(9) A detailed structure of the indene framework was determined by X-ray crystal structure analysis. See the Supporting Information.
(10) Heat and/or a rhenium catalyst promote interconversion of substituents at the 1,2-position of the indene framework, though the mechanism is not clear yet.
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(12) Methyl−rhenium complex $Re(CH_3)(CO)_5$ promoted the reaction, but the yield of **3a** was very low. The formation reaction of indene derivatives did not occur with the following catalysts: $Re_2(CO)_{10}$, $ReBr(CO)_3(CH_3CN)_2$, $ReCp^*(CO)_3$, $ReCl_3(PMe_2Ph)_3$, $MnBr(CO)_5$, and $RhCl(PPh_3)_3$.
(13) The highest yield and selectivity was obtained by using toluene as a solvent in the reaction of aromatic aldimine **1a** with acetylene **2a**. Results for the other solvents are as follows: hexane, >99% (**3a**:**4a** = 47:53); CH_2Cl_2, 35% (17:83); THF, 17% (<1:>99); DMI, 17% (41:59); DMF, <1%.
(14) There have been some reports on the synthesis of *ortho*-rhenated complexes. For *ortho*-rhenation of aromatic imines with $Re(CH_2Ph)(CO)_5$, see: (a) Böhm, A.; Sünkel, K.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1998**, *552*, 237. For *ortho*-rhenation of phenylpyridine derivatives with $Re(CH_2Ph)(CO)_5$, see: (b) Djukic, J.-P.; Maisse, A.; Pfeffer, M.; Dötz, K. H.; Nieger, M. *Organometallics* **1999**, *18*, 2786.
(15) Although we tried to prepare or isolate the rhenium−hydride intermediate by the quantitative reaction of $[ReBr(CO)_3(thf)]_2$ with aldimine, we could not observe the formation of the intermediate.
(16) A referee has proposed that electrophilic metalation is another possible mechanism for the formation of the aryl−rhenium complex and H^+. We examined the rhenium-catalyzed reaction by addition of a base (K_2CO_3 or tributylamine) and noticed that the reaction with the base proceeded without decreasing the yield. Thus, we are tempted to assume that the rhenium-catalyzed reaction proceeds via the C−H bond activation.
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