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Rh(I)-Catalyzed Carbonylative Cyclization Reactions of Alkynes with 2-Bromophenylboronic Acids Leading to Indenones

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Abstract: The Rh-catalyzed reaction of alkynes with 2-bromophenylboronic acids involves carbonylative cyclization to give indenones. The key steps in the reaction involve the addition of an arylrhodium(I) species to an alkyne and the oxidative addition of C−Br bonds on the adjacent phenyl ring to give vinylrhodium(I) species **II**. The regioselectivity depends on both the electronic and the steric nature of the substituents on the alkynes. A bulky group and an electron-withdrawing group favor the α-position of indenones. In the case of silyl- or ester-substituted alkynes, the regioselectivity is extremely high. The selectivity increases in the order $SiMe_3$ > COOR ≫ aryl ≫ alkyl. The reaction of norbornene with 2-bromophenylboronic acids under 1 atm of CO gives the corresponding indanone derivative. The reaction of alkynes with 2-bromophenylboronic acids under nitrogen gives naphthalene derivatives, in which two molecules of alkynes are incorporated. A vinylrhodium complex similar to **II** can also be generated by a different route by employing 2-bromophenyl(trimethylsilyl)acetylene and arylboronic acids in the presence of Rh(I) complex as the catalyst, resulting in the formation of indenones. The reaction of 1-(2-bromophenyl)-hept-2-yn-1-one with $PhB(OH)_2$ in the presence of Rh(I) complex also resulted in carbonylative cyclization to give an indan-1,3-dione derivative.

Introduction

The use of organoboron reagents in transition metal-catalyzed reactions has generated considerable interest in organic synthesis because of their unique reactivities, the diversity of transformations that can be achieved, and the extremely high functional group compatibility.[1] A variety of reactions in which organoboron reagents are used has been developed thus far as efficient methods for the formation of carbon−carbon bonds. Among them, the addition of arylboronic acids to alkynes, catalyzed by Rh,[2−9] Ni,[10] and Pd complexes,[11] has been the subject of extensive study. Hayashi found that the reaction of alkynes with arylboronic acids catalyzed by Rh(I) complexes gives styrene derivatives and that the reaction does not proceed via the direct protonation of an initially generated vinylrhodium complex, but a 1,4-shift of the hydride in the vinylrhodium complexes takes place prior to the direct protonation.[2a] In addition to protonolysis,[2] vinylrhodium complexes are reported to undergo nucleophilic attack on various intramolecular electrophiles,[3] such as aldehydes,[4] ketones,[4,5] esters,[4a,6] nitriles,[7] α,β-unsaturated esters,[8] and allyl ethers.[9] A 1,4-shift of a hydride not only in rhodium complexes but also palladium and platinum complexes has been of considerable interest in the sense of organic chemistry as well as organometallic chemistry.[12] A 1,4-shift of other functional groups X, such as alkoxy, alkylthio, or halides, in **II** leading to **III** is also interesting, which might lead to new

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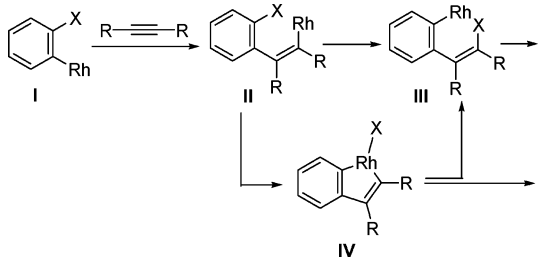
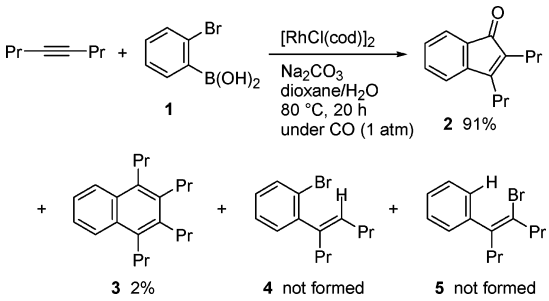
10.1021/ja070107n CCC: $37.00

Scheme 1. A Working Hypothesis (1,4-Shift or Oxidative Addition)



Scheme 2. Reaction of 4-Octyne with **1** under CO

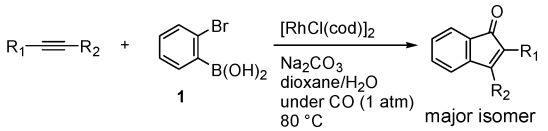


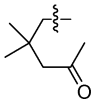
reactions (Scheme 1). The shift would proceed via the Rh(III) species **IV**, formed by the oxidative addition of C−X bonds to the generated vinylrhodium complexes **II**. There have been no reports, however, on catalytic reactions involving **III** or **IV** as a key species, when this project was started.[13] In this report, we wish to report on some Rh(I)-catalyzed carbonylative cyclization reactions of alkynes with 2-bromophenylboronic acid (**1**), in which the oxidative addition of C−Br bonds on the adjacent phenyl ring to the generated rhodium species **II** (X = Br) leading to **IV** is involved as a key step. A carbonylation reaction takes place to give indenones in a regioselective manner under an ambient pressure of CO. In addition, we found that a similar vinylrhodium intermediate could be generated by the addition of arylrhodium species to 2-bromophenyl(trimethylsilyl)acetylene followed by olefin isomerization, which also leads to the formation of indenones.

Results and Discussion

We first examined the rearrangement of the Br group, because C−Br bonds are known to undergo oxidative addition to Ph−Rh(I) species.[14] We were pleased to discover a new carbonylation reaction using 2-bromophenylboronic acid (**1**). When 4-octyne (1 mmol) was treated with 2-bromophenylboronic acid (**1**, 1.5 mmol) in the presence of $[RhCl(cod)]_2$ (0.025 mmol) and Na_2CO_3 (2 mmol) in dioxane/H_2O (100/1, 2 mL) at 80 °C under a CO atmosphere (1 atm, CO balloon) for 20 h, 2,3-dipropylinden-1-one (**2**) was isolated in 91% yield, along with 1,2,3,4-tetrapropylnaphthalene (**3**) in 2% (Scheme 2). Unlike other known reactions,[2] the styrene derivative **4** was not detected. Furthermore, a protonation product **5**, derived from a 1,4-Br shift, was also not detected. The use of a base was required for the reaction to proceed. Among the bases examined,

Table 1. Rh(I)-Catalyzed Reaction of Alkynes with 2-Bromophenylboronic Acids (**1**) under CO[a]



entry	R_1	R_2	products[b]
1	Ph	Ph	**6** 97%[c]
2	Ph	Me	**7** 93% (15:1)
3	4-$MeOC_6H_4$	Bu	**8** 82% (4:1)
4	Ph	Bu	**9** 82% (7:1)
5	4-$NO_2C_6H_4$	Bu	**10** 91% (10:1)
6	2,6-$Me_2C_6H_3$	Bu	**11** 83% (60:1)
7	Me_3Si	Me	**12** 92%
8	Me_3Si	Ph	**13** 95%
9	Me_3Si	Me_3Si	**14** 60%
10	COOMe	Ph	**15** 80% (25:1)[c]
11	Me_3Si	COOEt	**16** 67% (1.5:1)
12	—$(CH_2)_{10}$—		**17** 71%
13	^{t}Bu	—≡—Bu^t	**18** 83% (40:1)
14		Me	**19** 62% (10:1)[d]

[a] Reaction conditions: alkyne (1 mmol), 2-bromophenylboronic acid (**1**, 1.5 mmol), $[RhCl(cod)]_2$ (0.05 mmol), Na_2CO_3 (2 mmol) in dioxane/H_2O (100/1, 2 mL) at 80 °C for 20 h under CO (1 atm of balloon). [b] Isolated yields. Numbers in parentheses are the ratio of regioisomers. [c] $[RhCl(cod)]_2$ (0.025 mmol) was used. [d] 40 h.

Na_2CO_3 gave the best results: Cs_2CO_3 (50%), KOH (20%), Cy_2-NMe (31%). Certain other rhodium complexes were also found to be active. For example, $[RhCl(CO)_2]_2$ gave **2** in 70% yield. Interestingly, a Rh(0) complex also shows catalytic activity. When $Rh_4(CO)_{12}$ was used as the catalyst, **2** was produced in 77% yield. However, rhodium phosphine complexes, such as $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$, were not active.

Various internal alkynes having aryl, alkyl, ester, and silyl groups could be used to give the corresponding indenones in high yields, as shown in Table 1. The reaction generally proceeded in a regioselective manner, and a sterically bulky group or an electron-withdrawing group on alkynes favored the α-position of indenones. The steric and electronic nature of the substituents on the phenyl ring also had an effect on the regioselectivity of the reaction (entries 3−6). The substitution of an electron-withdrawing group at the 4-position on the phenyl ring increased the selectivity (entries 3−5). The substitution of a methyl group at the 2-position on the phenyl ring also dramatically increased the regioselectivity (entries 4 and 6). In the case of trimethylsilylacetylene derivatives, high regioselectivities were observed, and no regioisomers were detected by GC analysis and ^{1}H NMR measurements (entries 7 and 8). An ester group is also a good directing group (entry 10). Silyl and ester groups are comparable, but a silyl group is a slightly

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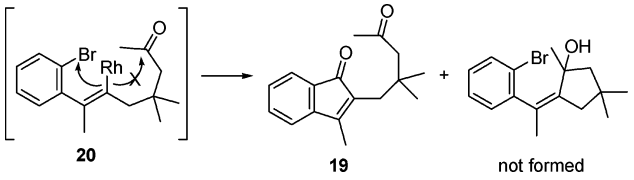
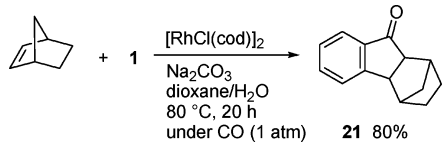
Scheme 3. C−Br versus C=O



Scheme 4. Reaction of Norbornene with **1** under CO



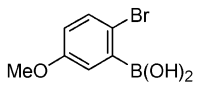
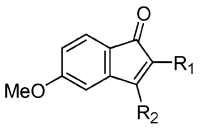
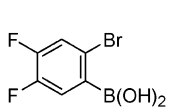
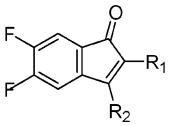
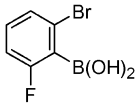
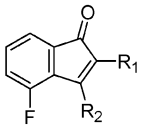
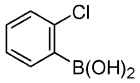
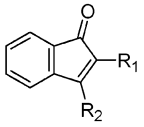
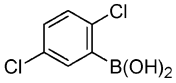
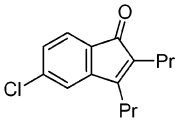
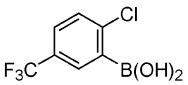
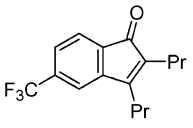
stronger directing group (entry 11). The selectivity increases in the order of $SiMe_3$ > COOR ≫ aryl ≫ alkyl. Terminal alkynes could not be used in this reaction.[15] The result for entry 14 shows that the generated vinylrhodium species **20** does not react with the intramolecular ketone functionality, unlike the known reaction (Scheme 3).[4,5]

The reaction of alkenes with **1** was next examined. However, styrene and cyclopentene did not undergo carbonylative cyclization, but norbornene gave the corresponding ketone **21** in high yield (Scheme 4).

Because the generation of the benzyne−Pd complex from 2-bromophenylboronic ester and Pd(0) is known to occur,[16,17] we anticipated that the reaction would proceed by a [2 + 2 + 1] cycloaddition of the in situ generated benzyne, alkynes, and CO. In fact, we previously reported the $Co_4(CO)_{12}$- and $[RhCl(cod)]_2$-catalyzed carbonylative cycloaddition of benzyne leading to the formation of anthraquionone and fluorenone.[18] To exclude this possibility, reactions using substituted 2-bromophenylboronic acids were performed. The reaction of 4-octyne with 2-bromo-5-methoxyphenylboronic acid (**22**)[19] gave **23** as a single isomer (Table 2), the formation of which clearly supports the conclusion that the reaction does not involve benzyne as an intermediate. Other substituted 2-bromophenylboronic acids could be used for the carbonylation reaction, and indenones **24**−**32** were obtained in good to high yields, as shown in Table 2. Replacing 2-bromophenylboronic acid with a corresponding chloro analogue also gave indenone **2**, along with a small amount of styrene derivative (6%) as a byproduct; the latter would have been formed by protonation of the generated vinylrhodium complex, related to **II**.

Interestingly, the course of the reaction was found to be significantly affected by the nature of the atmosphere. Even under 1 atm of CO, indenone **2** was formed as a major product, and only a small amount (2%) of naphthalene derivative **3** was detected (Scheme 2). However, naphthalene derivatives were selectively produced when the reaction was carried out under N_2. After optimization of the reaction conditions, 1,2,3,4-tetrapropylnaphthalene (**3**) and 1,2,3,4-tetraphenynaphthalene (**35**) were produced in 76% and 77% isolated yields, respectively, when 4-octyne and diphenylacetylene (1 mmol) were reacted with **1** (0.75 mmol) in the presence of $[RhCl(cod)]_2$ (0.025 mmol) and Na_2CO_3 (1 mmol) in dioxane/H_2O (100/1, 1 mL) at 50 °C under N_2 for 20 h (Scheme 5).[20]

Table 2. Rh(I)-Catalyzed Reaction of Alkynes with 2-Bromoarylboronic Acids and CO[a]

boronic acid	R_1—≡—R_2		product[b]
 **22**	R_1 = Pr	R_2 = Pr	 **23** 88%
	R_1 = Me_3Si	R_2 = Me	**24** 92%[c]
	R_1 = Me_3Si	R_2 = Ph	**25** 69%[c]
	R_1 = COOMe	R_2 = Ph	**26** 47%
			
	R_1 = Pr	R_2 = Pr	**27** 81%
	R_1 = Me_3Si	R_2 = Me	**28** 83%[c]
	R_1 = Me_3Si	R_2 = Ph	**29** 85%[c]
			
	R_1 = Pr	R_2 = Pr	**30** 40%
	R_1 = Me_3Si	R_2 = Me	**31** 51%[c]
	R_1 = Me_3Si	R_2 = Ph	**32** 38%[c]
			
	R_1 = Pr	R_2 = Pr	**2** 66%
	R_1 = Me_3Si	R_2 = Ph	**13** 77%[c]
			
	R_1 = Pr	R_2 = Pr	**33** 73%
			
	R_1 = Pr	R_2 = Pr	**34** 70%

[a] Reaction conditions: alkyne (1 mmol), 2-bromoarylboronic acid (1.5 mmol), $[RhCl(cod)]_2$ (0.025 mmol), Na_2CO_3 (2 mmol) in dioxane/H_2O (100/1, 2 mL) at 80 °C for 20 h under CO (1 atm of balloon). [b] Isolated yields. [c] $[RhCl(cod)]_2$ (0.05 mmol) was used.

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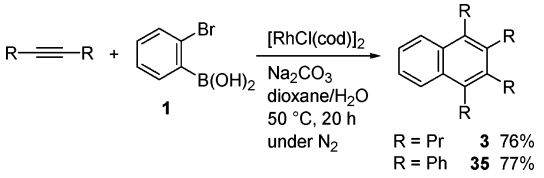
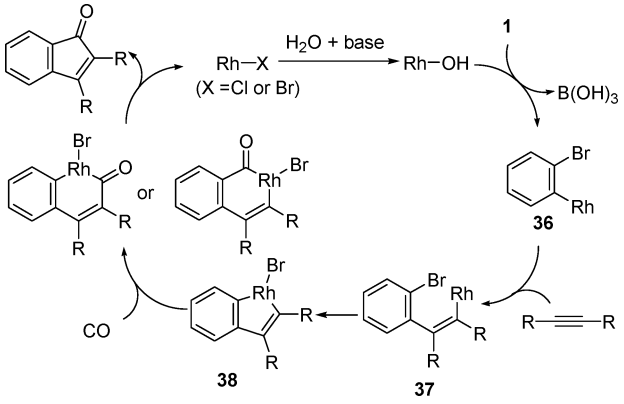
(19) 2-Bromo-5-methoxyphenylboronic acid was easily prepared by bromination of 3-methoxyphenylboronic acid. Kuivila, H. G.; Benjamin, L. E.; Murphy, C. J.; Price, A. D.; Polevy, J. H. *J. Org. Chem.* **1962**, *27*, 825−829. Other 2-haloarylboronic acids employed in Table 2 are commercially available.
(20) The reaction of 1-phenylpropyne with **1** gave the corresponding naphthalene in 77% yield as a 1:1 mixture of regioisomers.

Scheme 5. Reaction of Alkynes with **1** under N_2



Scheme 6. Proposed Reaction Mechanism



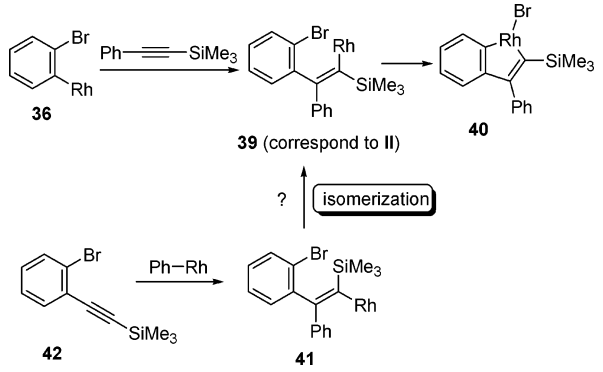
A proposed mechanism for the reaction is shown in Scheme 6. The arylrhodium(I) complex **36** is generated via the transmetalation of Rh−X (X = Cl, Br, or OH) with 2-bromophenylboronic acid **1**. The insertion of an alkyne gives the vinylrhodium(I) complex **37** (corresponding to **II**). When unsymmetric alkynes are used, rhodium favors attachment at the acetylenic carbon that contains a sterically bulky group or an electron-withdrawing group. The oxidative addition of C−Br on the adjacent phenyl ring to **37** produces the rhodium(III) species **38**.[13,14] The insertion of CO in **38** followed by reductive elimination gives indenones, with regeneration of the catalyst. In the case where the reaction is conducted under N_2, the insertion of a second molecule of an alkyne in **37** or **38** occurs, followed by reductive elimination to afford a naphthalene derivative.[21] The use of 2-chlorophenylboronic acid in place of **1** also gave indenones (Table 2), but styrene derivatives were also formed (<10%), although no styrene derivatives were obtained in the case of 2-bromophenylboronic acids. These results clearly show that complex **37** undergoes oxidative addition much faster than protonation (or a 1,4-H shift), as compared to the chloro analogue.

With the success of these processes, we sought to develop new carbonylation reactions, in which the same intermediate **II** could be generated by the addition of phenylrhodium species to 2-bromophenyl(trimethylsilyl)acetylene followed by isomerization, as shown in Scheme 7. The requisite substrates for testing this hypothesis were readily prepared in one step by the Sonogashira coupling of 2-bromoiodobenzene with silylacetylene, and various arylboronic acids would be expected to be applicable to the new carbonylation reactions. However, a critical issue for the success of the designed reaction is whether the facile isomerization of **41** to **39** takes place. This prompted us to examine the Rh-catalyzed reaction of 2-bromophenyl(trimethylsilyl)acetylene (**42**) with arylboronic acids.

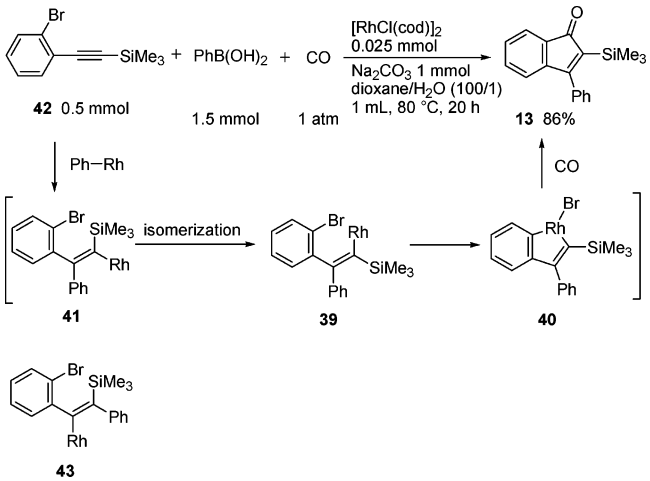
To our delight, the reaction of 2-bromophenyl(trimethylsilyl)acetylene (**42**) with $PhB(OH)_2$ and CO (1 atm) gave indenone

(21) An alternative mechanism for the formation of naphthalene derivatives involves the [4 + 2] cycloaddition of **38** with alkyne followed by demetalation.

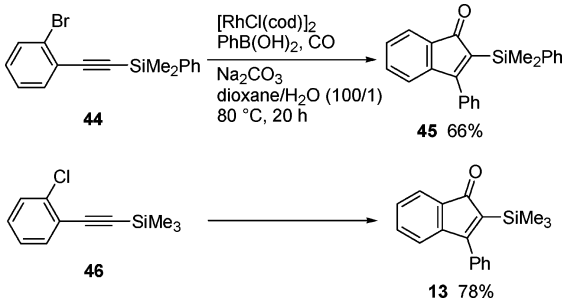
Scheme 7. An Alternative Route for Generating the Vinylrhodium(I) Complex **II**



Scheme 8. Reaction of 2-Bromophenyl(trimethylsilyl)acetylene (**42**) with Phenylboronic Acid and CO



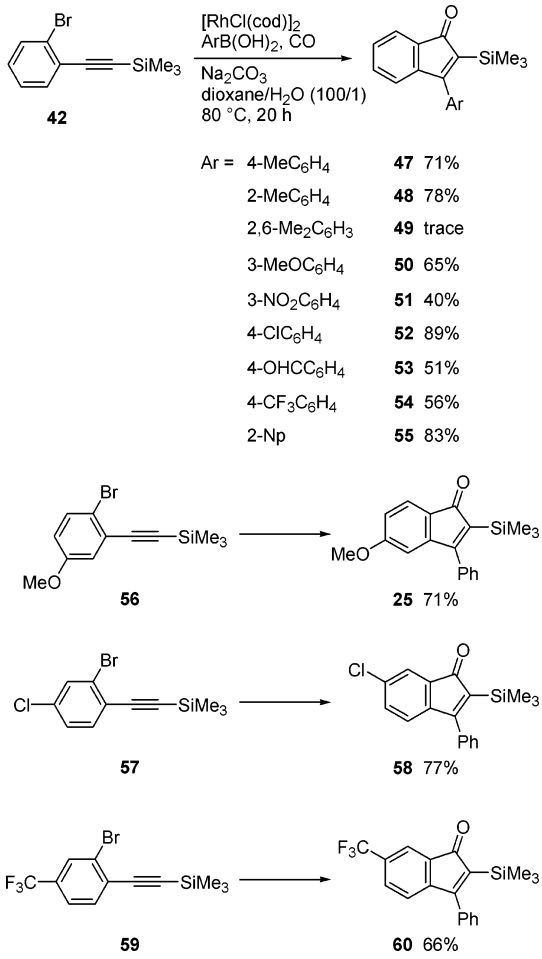
Scheme 9



13 as the sole product. When **42** (0.5 mmol) was treated with phenylboronic acid (1.5 mmol) in the presence of $[RhCl(cod)]_2$ (0.025 mmol) and Na_2CO_3 (1 mmol) in dioxane/H_2O (100/1, 1 mL) at 80 °C under a CO atmosphere (1 atm, CO balloon) for 20 h, 3-phenyl-2-trimethylsilylinden-1-one (**13**) was obtained in 86% isolated yield (Scheme 8). Because the addition of a Ph−Rh species to an alkyne is known to take place in a cis manner, the formation of **13** suggests that the initially generated vinylrhodium species **41** undergoes *E*−*Z* isomerization leading to **39**, as expected. The virtue of this protocol is that no regioisomeric indenones are formed, because the wrong isomers **43** cannot be converted to indenones even if they are formed.

The use of a dimethylphenylsilyl group in place of a trimethylsilyl, as in **44**, led to a slight decrease in the yield of the corresponding indenone **45** (Scheme 9). The replacement of Br by Cl also gave **13** in good yield.

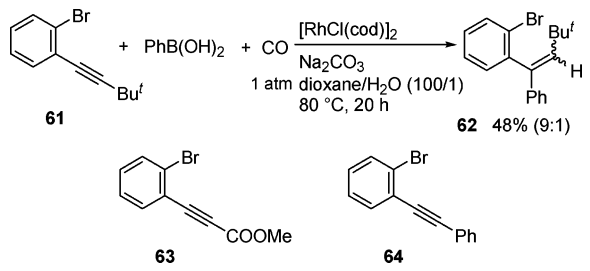
Scheme 10. Rh(I)-Catalyzed Reaction of 2-Bromophenyl(trimethylsilyl)acetylenes with Arylboronic Acids under CO



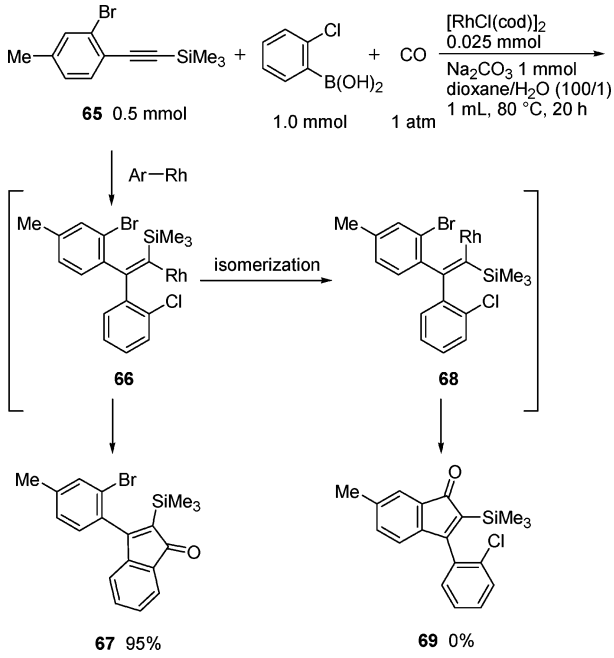
A variety of arylboronic acid derivatives can be used in the present carbonylation reaction, as shown in Scheme 10. Arylboronic acids having a methoxy group at the ortho and para positions on the phenyl ring gave the corresponding indenones in quite low yields (results not shown), because a facile protonation of the arylboronic acids took place under the reaction conditions used. In contrast, the *meta*-methoxy substrate gave the corresponding indenone **50** in 65% yield. The reaction shows high functional group compatibility. Even nitro and formyl groups were tolerated under the reaction conditions used herein.

We next examined the effect of a substituent on the acetylenic terminal carbon to determine whether the presence of a trimethylsilyl group at the terminal acetylenic carbon is necessary for *E*/*Z* isomerization, which is a crucial step for the reaction to proceed. The replacement of a trimethylsilyl group by a *tert*-butyl group, as in **61**, resulted in the predominant formation of styrene derivative **62**, and the corresponding indenone was not detected, showing that the required *E*/*Z* isomerization did not take place, but instead protonation took place prior to the isomerization (Scheme 11). An ester **63** and phenyl analogue **64** also did not give the corresponding indenones, and complex mixtures were obtained. These results indicate that the presence of a silyl group at the terminal acetylenic carbon is essential for the isomerization to proceed.[22,23]

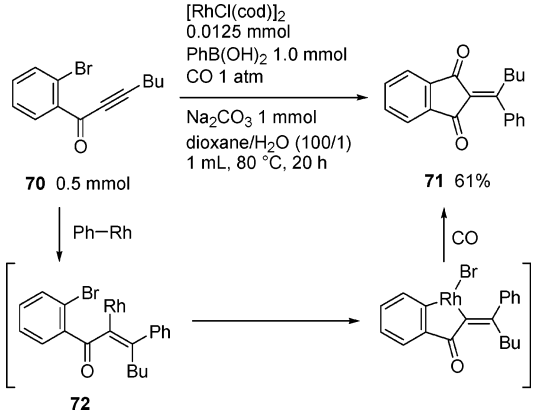
Scheme 11



Scheme 12



Scheme 13. Reaction of 1-(2-Bromophenyl)-hept-2-yn-1-one (**70**) with $PhB(OH)_2$ and CO



It was found that the *E*/*Z* isomerization of vinylrhodium complexes is a key step for the indenone synthesis. Next, the reaction of **65** with 2-chlorophenylbononic acid and CO was performed to examine if the isomerization is slow. If the oxidative addition of a C−Cl bond in the initially generated vinylrhodium complex **66** takes place, indenone **67** will be

(22) For a paper on isomerization of β-silyl-substituted vinylrhodium complexes, see: Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127−3133.

(23) For a paper on isomerization of α-silyl-substituted vinyllithium, see: Negishi, E.-i.; Takahashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 3402−3408.

obtained. On the other hand, isomerization of **66** to **68** takes place prior to the oxidative addition of the C−Cl bond; the oxidative addition of a C−Br bond in **68** occurs leading to the formation of **69**. The result obtained was the exclusive formation of **67**, and **69** was not formed, showing that the isomerization of a vinylrhodium complex is not facile (Scheme 12).

The reaction of 1-(2-bromophenyl)-hept-2-yn-1-one (**70**) with $PhB(OH)_2$ in the presence of a Rh(I) complex also resulted in carbonylative cyclization to give indan-1,3-dione derivative **71** in good yield (Scheme 13). In this reaction, isomerization of the olefin is not required in the vinylrhodium complex **72**.

Conclusion

We report herein on the development of a new carbonylation reaction of alkynes with 2-bromophenylboronic acid (**1**)[24] leading to the formation of indenones.[25] The reaction involves the Rh-catalyzed regioselective addition of an arylrhodium(I) species to alkynes and the oxidative addition of C−Br bonds in the adjacent phenyl ring to the resulting vinylrhodium(I) species as key steps. The regioselectivity is generally high and is significantly affected by the steric and electronic factors. Sterically bulky and electron-withdrawing groups, such as silyl, *tert*-butyl, and ester groups, favor the attachment at the α-position of indenones. Similar vinylrhodium intermediates could be generated by the addition of arylrhodium species to 2-bromophenyl(trimethylsilyl)acetylene followed by olefin isomerization, which also leads to the formation of indenones.

Experimental Section

A few representative examples are listed here. Experimental procedures and spectroscopic data for new compounds can be found in the Supporting Information.

Typical Procedure for the Rh-Catalyzed Formation of Indenones. A 10-mL two-necked flask was charged with sodium carbonate (212.0 mg, 2.0 mmol), 2-bromophenylboronic acid (**1**, 301.2 mg, 1.5 mmol), $[RhCl(cod)]_2$ (12.3 mg, 0.025 mmol), 4-octyne (110.2 mg, 1.0 mmol), and 1,4-dioxane/H_2O (2 mL/0.02 mL), and a three-way stopcock, connected to a vacuum line and a balloon filled with carbon monoxide, was attached to the flask. The system was carefully evacuated and refilled with carbon monoxide and then filled with carbon monoxide (1 atm). It was then immersed in an oil bath at 80 °C. After 20 h, it was removed from the oil bath and cooled to room temperature. The contents were transferred to a round-bottom flask, and volatiles were removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent; hexane/EtOAc = 50/1) to give 2,3-dipropylinden-1-one (**2**) (195.0 mg, 91% yield) as a yellow oil.

5-Methoxy-3-methyl-2-trimethylsilylinden-1-one (24). Yellow solid. R_f 0.23 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$) δ: 0.28 (s, 9H), 2.25 (s, 3H), 3.85 (s, 3H), 6.64 (d, J = 7.5 Hz, 1H), 6.67 (s, 1H), 7.35 (d, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 0.0, 14.5, 55.7, 107.5, 110.3, 122.9, 125.1, 134.4, 149.7, 163.9, 166.2, 200.3. IR (KBr): 2989 m, 2898 m, 2833 m, 1695 s, 1597 s, 1560 s, 1475 m, 1433 m, 1408 m, 1375 s, 1338 m, 1296 s, 1250 s, 1228 s, 1190 m, 1172 s, 1126 m, 1084 s, 1041 s, 1030 s, 864 s, 841 s, 826 s, 760 m, 748 m, 711 m, 688 m, 631 s. MS, *m*/*z* (relative intensity, %): 246 (M^+, 27), 232 (19), 231 (100), 188 (13), 115 (20), 75 (10). Anal. Calcd for $C_{14}H_{18}O_2Si$: C, 68.25; H, 7.36; O, 12.99. Found: C, 68.19; H, 7.26.

5-Chloro-2,3-dipropylinden-1-one (33). Yellow oil. R_f 0.29 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, J = 7.3 Hz, 3H), 1.03 (t, J = 7.3 Hz, 3H), 1.48 (tq, J = 7.3 Hz, 7.7 Hz, 2H), 1.62 (tq, J = 7.3 Hz, 7.6 Hz, 2H), 2.23 (t, J = 7.7 Hz, 2H), 2.49 (t, J = 7.6 Hz, 2H), 6.98 (s, 1H), 7.11 (d, J = 7.8 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.1, 14.3, 21.1, 22.4, 24.9, 28.1, 119.8, 122.5, 127.3, 129.2, 136.2, 139.2, 147.6, 156.4, 197.0. IR (neat): 2962 m, 2933 m, 2871 m, 1711 s, 1604 m, 1585 m, 1464 m, 1410 w, 1360 m, 1261 w, 1227 w, 1159 w, 1113 w, 1066 m, 1009 w, 947 w, 910 w, 874 w, 829 m, 783 w, 744 w, 596 w. MS, *m*/*z* (relative intensity, %): 250 (M^+ + 2, 17), 248 (M^+, 46), 221 (33), 220 (22), 219 (100), 206 (24), 205 (32), 191 (39), 179 (29), 178 (35), 177 (67), 165 (21), 149 (37), 141 (29), 139 (25), 128 (52), 127 (53), 126 (23), 115 (31), 77 (25), 75 (29), 63 (33), 55 (21), 51 (24). Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89; Cl, 14.25. Found: C, 72.20; H, 6.74; Cl, 14.51.

3-(4-Chlorophenyl)-2-trimethylsilanylinden-1-one (52). Yellow solid. R_f 0.31 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$) δ: 0.06 (s, 9H), 6.85 (d, J = 6.4 Hz, 1H), 7.25−7.33 (c, 4H), 7.46−7.51 (c, 3H). ^{13}C NMR ($CDCl_3$) δ: 0.0, 120.8, 122.6, 128.9, 129.3, 129.4, 132.4, 133.2, 133.6, 135.3, 135.5, 147.1, 169.3, 201.6. IR (KBr): 2958 w, 1693 s, 1595 w, 1541 w, 1481 w, 1454 w, 1398 w, 1363 w, 1298 w, 1244 w, 1174 w, 1092 m, 1012 w, 862 m, 845 m, 795 w, 756 w, 719 w, 638 w, 611 w. MS, *m*/*z* (relative intensity, %): 314 (M^+ + 1, 10), 312 (M^+ − 1, 26), 299 (37), 298 (24), 297 (100), 281 (18), 277 (17), 203 (16), 202 (20), 189 (14), 176 (11), 131 (12), 75 (10), 73 (10), 62 (18). Anal. Calcd for $C_{18}H_{17}ClOSi$: C, 69.10; H, 5.48; Cl, 11.33; O, 5.11. Found: C, 68.92; H, 5.36; Cl, 11.68.

3-(4-Formylphenyl)-2-trimethylsilanylinden-1-one (53). Yellow solid. R_f 0.14 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$) δ: 0.05 (s, 9H), 6.81 (d, J = 6.4 Hz, 1H), 7.26−7.32 (c, 2H), 7.52−7.55 (c, 3H), 8.01 (d, J = 8.0 Hz, 2H), 10.10 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: −0.2, 120.8, 122.9, 128.7, 129.6, 123.0, 132.2, 133.5, 136.3, 136.9, 141.6, 147.0, 168.9, 191.9, 201.5. IR (KBr): 2949 w, 2831 w, 2736 w, 1699 s, 1611 m, 1549 m, 1495 w, 1456 w, 1365 w, 1298 m, 1284 w, 1250 m, 1205 m, 1184 m, 1092 m, 1011 w, 870 s, 847 s, 796 m, 754 m, 714 m, 611 w. MS, *m*/*z* (relative intensity, %): 307 (M^+ + 1, 11), 306 (M^+, 49), 292 (25), 291 (100), 278 (10), 277 (19), 263 (25), 248 (10), 247 (39), 218 (11), 217 (35), 204 (12), 203 (27), 202 (31), 201 (14), 189 (19), 176 (11), 145 (46), 123 (21), 75 (11), 73 (13), 59 (10), 53 (11). Anal. Calcd for $C_{19}H_{18}O_2Si$: C, 74.47; H, 5.92. Found: C, 74.25; H, 5.81.

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Supporting Information Available: Experimental procedures and spectroscopic data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JA070107N

(24) Recently, Rh(I)-catalyzed carbonylation of alkynes with $PhB(OH)_2$ leading to α,β-unsaturated γ-lactones was reported. Aksin, O.; Dege, N.; Artok, L.; Türkmen, H.; Cetinkaya, B. *Chem. Commun.* **2006**, 3187−3189.

(25) For papers on indenone synthesis, see: (a) Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.* **1993**, *58*, 4579−4583. (b) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941−6946. (c) Pletnev, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 9276−9287.