Pergamon

Tetrahedron 58 (2002) 8661–8667

TETRAHEDRON

Ir and Rh complex-catalyzed intramolecular alkyne–alkyne couplings with carbon monoxide and isocyanides

Takanori Shibata,* Koji Yamashita, Emi Katayama and Kentaro Takagi

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530, Japan

Received 16 August 2002; accepted 6 September 2002

Abstract—Intramolecular [2+2+1] cycloaddition of diynes with carbon monoxide was catalyzed by Vaska's complex ($IrCl(CO)(PPh_3)_2$) or IrCl(cod)(dppp), and cyclopentadienones were obtained in good to high yields. The first catalytic synthesis of iminocyclopentadienes was achieved by portionwise additions of isocyanides to a solution of diynes and Rh catalyst ($[RhCl(cod)]_2$).

1. Introduction

Transition metal complex-catalyzed cycloaddition is the most powerful and reliable method for the construction of various carbon skeletons.[1] In particular, carbonylative coupling is a fascinating tool for the synthesis of cyclic compounds possessing a carbonyl moiety. Compared with comprehensive study of carbonylative alkyne–alkene coupling (Pauson–Khand-(type) reaction),[2] however, the reports of carbonylative alkyne–alkyne coupling have been limited despite that it gives cyclopentadienones, potentially important intermediates.[3,4] After a pioneering work of $CpCo(PPh_3)_2$-mediated alkyne–alkyne coupling by Yamazaki and Hagihara,[5] $RhCl(PPh_3)_3$–,[6] $CpCo(CO)_2$–[7] and $Fe(CO)_5$-mediated[8] alkyne–alkyne couplings were reported for the synthesis of cyclopentadienones. But all these procedures are stepwise processes via organometallic intermediates, therefore, a stoichiometric amount of transition metal complexes is needed for the preparation of cyclopentadienones.[9]

Recently we reported the direct synthesis of cyclopentadienones by $Co_2(CO)_8$-mediated inter- and intramolecular carbonylative alkyne–alkyne coupling.[10] After our publication, $Co_2(CO)_8$-catalyzed tandem type reaction of diynes under a high pressure of carbon monoxide was reported, where cyclopentadienones (or their metal complexes) were not isolated and were used as an active intermediate for the second step.[11]

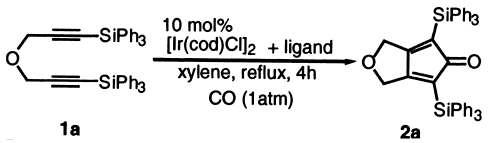
We here report the synthesis of cyclopentadienones by iridium complex-catalyzed carbonylative alkyne–alkyne coupling under an atmospheric pressure or a partial pressure (0.2 atm) of carbon monoxide.[12,13] Moreover, the first catalytic coupling of diynes with isocyanides for the synthesis of iminocyclopentadienes is also described.

2. Results and discussion

2.1. Ir complex-catalyzed alkyne–alkyne coupling of diynes with carbon monoxide

Based on our results of carbonylative alkyne–alkyne coupling mediated by $Co_2(CO)_8$,[10] we chose triphenylsilyl-substituted dipropargyl ether **1a** as a model diyne and examined a catalytic coupling. We found that iridium–phosphine complexes are efficient catalysts for carbonylative alkyne–alkene coupling,[14] therefore, we expected that they could work also in carbonylative alkyne–alkyne

Table 1. Optimization of mono- or bidentate phosphine ligands for the iridium complex-catalyzed carbonylative coupling of **1a**



1a **2a**

Ligand	Yield (%)	Ligand	Yield (%)
None	18	2dppe	37
$4PPh_3$	49	2dppp	52
$4P(4\text{-}FC_6H_4)_3$	42	2dppb	0
$4P(2\text{-furyl})_3$	10	2dppf	14

Coefficients at the head of ligands are molar ratio against $[Ir(COD)Cl]_2$. dppe: 1,2-Bis(diphenylphosphino)ethane. dppp: 1,3-Bis(diphenylphosphino)-propane. dppb: 1,4-Bis(diphenylphosphino)butane. dppf: 1,1′-Bis-(diphenylphosphino)ferrocene.

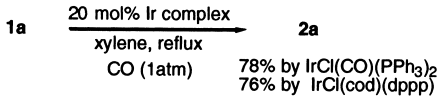
Keywords: alkynes; carbonylations; coupling reactions; diynes; iridium; rhodium.

* Corresponding author. Tel.: +81-86-251-7855; fax: +81-86-251-7831; e-mail: tshibata@cc.okayama-u.ac.jp

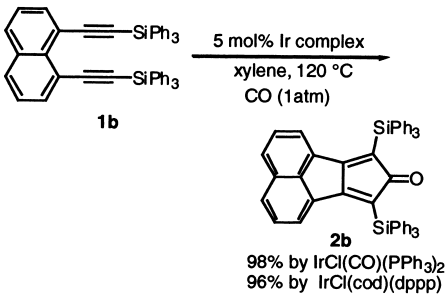
0040–4020/02/$ - see front matter
PII: S0040-4020(02)01122-5

coupling (Table 1). When phosphine-free iridium complex, $[IrCl(cod)]_2$, was used under an atmospheric pressure of CO, diyne **1a** was consumed to give a complex mixture but **2a** was obtained in 18%. As a result of screening of Ir–phosphine complexes, which were prepared in situ from $[IrCl(cod)]_2$ and monodentate phosphines, triphenylphosphine was the best ligand among them. Dppp was the best ligand among four bidentate phosphines we examined.

When isolated iridium–phosphine complex, Vaska's complex or IrCl(cod)(dppp),[15] was used as a catalyst, the yield was increased to ca. 80% (Eq. (1)). As for 1,8-dialkynylnaphthalene **1b**, the carbonylative coupling proceeded smoothly at a lower temperature by less amounts of the catalysts to give multicyclic compound **2b** in very high yield. (Eq. (2)).



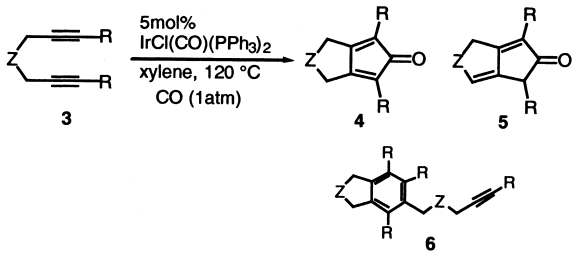
(1)



(2)

Not only silyl-substituted diynes, but aryl-substituted diynes could be submitted to the carbonylative coupling (Table 2). The reactions were examined under a CO atmosphere in xylene at 120°C. Both Vaska's complex and IrCl(cod)(dppp) efficiently catalyzed the coupling of dipropargylmalonate **3a**, but isomerized product **5a** and hexasubstituted benzene **6a** were also obtained by the latter catalyst (entries 1 and 2). Using Vaska's complex as a catalyst, the carbonylative coupling of other diynes was examined. Diethyl and di-*t*-Bu dipropargylmalonates **3b**,**c** were transformed into the corresponding cyclopentadienones **4b**,**c** exclusively (entries 3 and 4). Electron-donating and -withdrawing substituents on the aryl moiety did not deter the carbonylative coupling but electron-withdrawing groups destabilized cyclopentadienones (entries 5–7). From diyne **3d**, cyclopentadienone **4d** was a sole product. In the reaction of **3e**, part of obtained cyclopentadienone **4e** was isomerized to give **5e** in the course of purification. The carbonylative coupling of **3f** gave **5f** in the course of reaction and **4f** was so unstable that it could not be fully characterized. 1,6-Diyne **3g** and dipropargyl ether **3h** were also good substrates for the present carbonylative coupling (entries 8, 9). Under the same reaction conditions, diyne **3i** possessing alkyl substituents on its terminal was readily consumed. No carbonylated product could be detected, however, benzene derivative **6i** was detected from the complex mixture (entry 10). When less amounts (2 mol%) of the catalyst were used, **4c** was obtained in the same yield as entry 4 (entry 11). In intramolecular reactions, better results were generally obtained in dilute solution of substrates.[10] But this Ir complex-catalyzed intramolecular coupling efficiently proceeded under the conditions of the fourfold concentration of diyne at larger reaction scale (entry 12). Even by use of only 0.5 mol% of catalyst, the catalytic coupling proceeded (entry 13). Rate acceleration in the carbonylative coupling was observed by reduction of CO pressure.[16] Under a partial pressure (0.2 atm) of CO, diyne **3c** was readily consumed to give the coupling products in higher yield (entry 14).

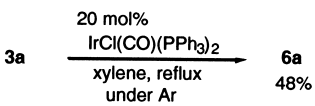
Table 2. Iridium complex-catalyzed carbonylative coupling of various diynes



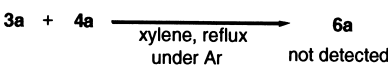
Entry[a]	R	Z	3	Time (h)	Yield (%)	4/5
1	Ph	$C(CO_2Bn)_2$	**3a**	5	86 (**4a**)	
2[b]	Ph	$C(CO_2Bn)_2$	**3a**	5	75 (**4a**+**5a**)	14:1
3	Ph	$C(CO_2Et)_2$	**3b**	5	99 (**4b**)	
4	Ph	$C(CO_2t\text{-}Bu)_2$	**3c**	4	92 (**4c**)	
5	4-$MeOC_6H_4$	$C(CO_2Bn)_2$	**3d**	6	94 (**4d**)	
6	4-ClC_6H_4	$C(CO_2Bn)_2$	**3e**	2	99 (**4e**+**5e**)	4:1
7	4-$MeO_2C\ C_6H_4$	$C(CO_2Bn)_2$	**3f**	7	89 (**4f**+**5f**)	1:2
8	Ph	CH_2	**3g**	5	79 (**4g**)	
9	Ph	O	**3h**	6	65 (**4h**)	
10[c]	Me	$C(CO_2Bn)_2$	**3i**	2	0	
11[d]	Ph	$C(CO_2t\text{-}Bu)_2$	**3c**	4	92 (**4c**)	
12[e]	Ph	$C(CO_2t\text{-}Bu)_2$	**3c**	4	90 (**4c**)	
13[f]	Ph	$C(CO_2t\text{-}Bu)_2$	**3c**	7	54 (**4c**)	
14[g]	Ph	$C(CO_2t\text{-}Bu)_2$	**3c**	1	98 (**4c**+**5c**)	24:1

[a] The reaction was carried out using 0.1–0.2 mmol of diyne at the concentration of 0.025 M.
[b] IrCl(cod)(dppp) was used in place of $IrCl(CO)(PPh_3)_2$ and **6a** (6%) was also obtained.
[c] **6i** (<32%) was detected in the complex mixture.
[d] 2 mol% of $IrCl(CO)(PPh_3)_2$ was used.
[e] The reaction was carried out using 2 mmol of diyne **3c** at the concentration of 0.1 M in the presence of 2 mol% of $IrCl(CO)(PPh_3)_2$.
[f] 0.5 mol% of $IrCl(CO)(PPh_3)_2$ was used in refluxed xylene.
[g] The reaction was examined under an atmosphere of CO (0.2 atm) and argon (0.8 atm).

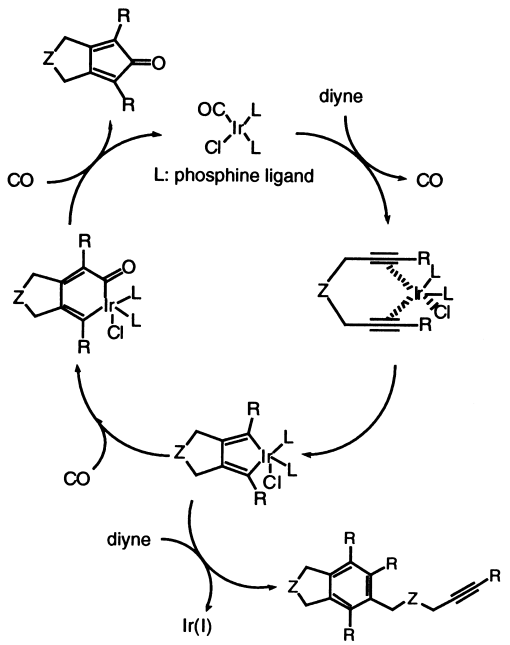
A plausible mechanism is shown in Scheme 1. From the π-complexation of diyne with Ir(I), the formation of iridacyclopentadiene, CO insertion, and reductive elimination of Ir(III) follow. When an intermolecular insertion of a diyne to the metallacycle precedes the carbonyl insertion, a benzene derivative is provided.[17] Actually, the present coupling of **3a** was examined under an argon atmosphere, hexasubstituted benzene **6a** was a major product (Eq. (3)) and thermal [4+2] cycloaddition between **3a** and **4a** did not proceed (Eq. (4)). However, the possibility of metal catalyzed [4+2] cyclization of **3a** and **4a** along with the aromatization cannot be fully eliminated.[11]



(3)

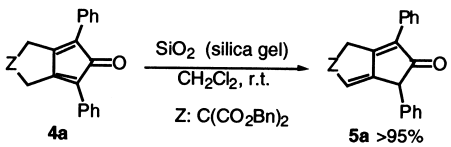


(4)



Scheme 1.

An acidic treatment of **4a** promoted the isomerization of the carbon–carbon double bond and bicyclic enone **5a** was obtained almost quantitatively (Eq. (5)). This is another route for preparing bicyclo[3.3.0]octa-1,5-diene-3-one skeleton, which has been synthesized by intramolecular carbonylative allene–alkyne coupling.[18]



(5)

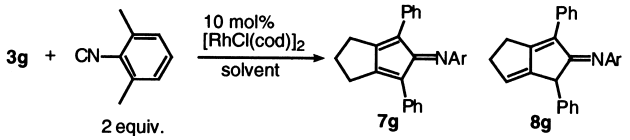
2.2. Rh complex-catalyzed alkyne–alkyne coupling of diynes with isocyanides

Compared with the comprehensive study of carbonylative cyclization, the reports of isocyanide-inserted cyclization have been limited. Actually, a pioneering work of Ni(0)-mediated alkyne–alkyne coupling with isocyanide was published in 1989,[19] but no catalytic coupling has been reported as far as we know.[20]

We examined a coupling of diyne **3c** with isocyanide using Vaska's complex (20 mol%). When an equivalent amount of 2,6-dimethylphenylisocyanide was added, no reaction proceeded. In the presence of 0.4 equiv. of the isocyanide, no isocyanide-inserted product could be detected and a benzene derivative was a major product. These results imply that migratory insertion of isocyanide into iridacyclopentadiene is an unfavorable process.

We changed a transition metal catalyst from iridium to rhodium complex. At first, a phosphine-free rhodium complex was examined in a coupling of diyne **3g** with isocyanide (Table 3). When THF was used as a solvent, iminocyclopentadiene **7g** was obtained in low yield but most of diyne **3g** was recovered. The reaction in dibutyl ether gave a better result but no reaction proceeded in xylene (entries 2 and 3). In diglyme and TMU (*N*,*N*,*N*′,*N*′-tetramethylurea), diyne **3g** was completely consumed and a catalytic coupling proceeded, although part or most of **7g** was isomerized to **8g** in the course of reaction (entries 4 and 5). These results suggested that coordinating solvents are suitable for the isocyanide-inserted coupling by rhodium complex.

Table 3. Rh complex-catalyzed coupling of diynes **3g** with isocyanide in various solvents



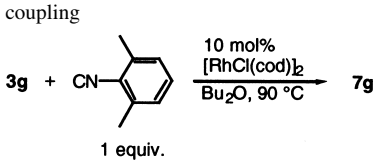
Entry	Solvent	Temperature (°C)[a]	Yield (%)	7g/8g
1	THF	70	5 (**7g**)	
2	Bu_2O	140	13 (**7g**)	
3	Xylene	145	0	
4	Diglyme	150	45 (**7g**+**8g**)	2:1
5	TMU	180	53 (**7g**+**8g**)	1:5

[a] Temperature of oil bath.

After screening of reaction conditions, we were pleased to find that portionwise addition of isocyanide realized a catalytic coupling of the diyne with the isocyanide: when 0.2 equiv. amounts of isocyanide were added five times at the interval of 10 min to a dibutyl ether solution[21] of $[RhCl(cod)]_2$ (10 mol%) and **3g** at 90°C, **7g** was obtained in 74% yield along with recovery of **3g** (19%) (Table 4, entry 1). The remaining **3g** was not consumed by the further addition of isocyanide. The interval of additions was important for the high conversion of diyne and 15 min gave the best yield of 83% along with recovery of **3g** (10%) (entry 2). By the longer interval of 20 min, the yield decreased and more amounts of diyne **3g** were recovered (39%) (entry 3). The addition of isocyanide by portions of 0.1 equiv. did not give the better result (entry 4). In each entry, isomerized product **8g** could not be detected.

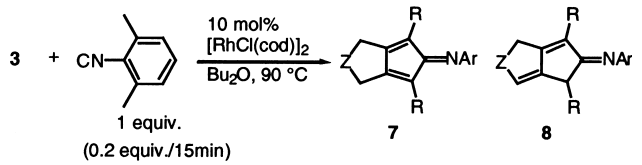
Several diynes were examined by the portionwise addition of isocyanide (Table 5). Dipropargylmalonate **3c** was transformed into the corresponding iminocyclopentadiene **7c** in high yield (entry 1). The coupling of trimethylsilyl-substituted diyne **3j** also proceeded to give **7j** (entry 2). It is

Table 4. Portionwise addition of isocyanide in Rh complex-catalyzed alkyne–alkyne coupling



Entry	Addition of ArNC	Time (h)	Yield (%)
1	0.2 equiv./10 min	1	74
2	0.2 equiv./15 min	1.5	83
3	0.2 equiv./20 min	2.0	55
4	0.1 equiv./10 min	2.5	70

Table 5. Rhodium complex-catalyzed coupling of various diynes with isocyanide

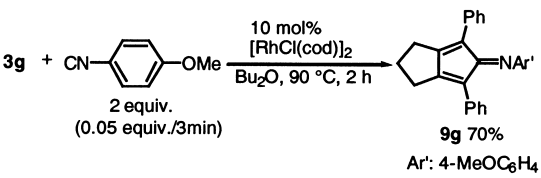


Entry	R	Z	3	Time (h)	Yield (%)	7/8
1	Ph	$C(CO_2t\text{-}Bu)_2$	**3c**	1.5	89 (**7c**)	
2	TMS	$C(CO_2Bn)_2$	**3j**	1.5	74 (**7j**)	
3	Me	$C(CO_2Bn)_2$	**3i**	1.5	73 (**7i**+**8i**)	2:1
4[a]	Ph	O	**3h**	0.5	92 (**7h**)	
5[b]	Ph	CH_2	**3g**	3.5	80 (**7g**+**8g**)	3:1

[a] Isocyanide was added by the interval of 5 min.
[b] Using 2.5 mol% of catalyst, 0.05 equiv. amounts of isocyanide were added 20 times by the interval of 10 min.

noteworthy that methyl-substituted diyne **3i** was also a good substrate for isocyanide-inserted coupling (entry 3). Dipropargyl ether **3h** was rather active and shortening of the addition interval from 15 to 5 min was needed (entry 4). Less amounts (2.5 mol%) of $[RhCl(cod)]_2$ were sufficient for alkyne–alkyne coupling with isocyanide but part of formed iminocyclopentadiene was isomerized to **8g**, probably because of prolonged reaction time (entry 5).

4-Methoxyphenylisocyanide was used in the coupling of diyne **3g**. As a result of optimization of reaction conditions, the addition of smaller portions (0.05 equiv.) by a shorter interval (3 min) gave a good result (Eq. (6)). Compared with 2,6-dimethylphenylisocyanide, 4-methoxyphenylisocyanide is a less bulky and more electron-rich isocyanide possessing strong ability of coordination to the metal, therefore, the addition of smaller portions was needed for keeping the catalyst active.



(6)

3. Conclusions

We developed catalytic intramolecular alkyne–alkyne couplings with carbon monoxide and isocyanide. Carbonylative coupling was efficiently catalyzed by Vaska's complex ($IrCl(CO)(PPh_3)_2$) and various diynes were transformed into bicyclic cyclopentadienones in good to high isolated yields. Rhodium complex ($[RhCl(cod)]_2$) realized the first catalytic synthesis of iminocyclopentadienes by alkyne–alkyne coupling with isocyanides. The portionwise addition of isocyanides by an appropriate interval in Bu_2O was very important for the catalytic coupling.

4. Experimental

4.1. General

IR spectra were recorded with JASCO FT/IR-5000 or Hitachi 260-10 spectrometer. ^1H NMR spectra (200 MHz) were measured with Varian VXR-200 spectrometer using tetramethylsilane (TMS) as an internal standard. High resolution mass spectra (HRMS) were obtained with JEOL JMS-SX102A mass spectrometer. Dry xylene was reagent grade and degassed prior to use. Dibutyl ether was distilled from calcium hydride and degassed prior to use. 2,6-Dimethylphenylisocyanide was reagent grade and 4-methoxyphenylisocyanide was prepared according to the literature.[22]

4.2. Syntheses of diynes

Diynes **1a** and **1b** were prepared by the reaction of dipropargyl ether or 1,8-ethynylnaphthalene with chlorotriphenylsilane according the same procedures in the literature.[10] Diynes **3a**, **3i**, **3j** were prepared by dialkylation of dibenzyl malonate with 3-bromo-1-phenylprop-1-yne, 1-bromobut-2-yne, 3-bromo-1-(trimethylsilyl)prop-1-yne, respectively, using NaH. Diynes **3b** and **3c** were prepared by dialkylation of diethyl or di-*tert*-butyl malonate with 3-bromo-1-phenylprop-1-yne using NaH. Diynes **3d**–**3f** were prepared by the reaction of dibenzyl dipropargylmalonate with 4-iodoanisole, 1-chloro-4-iodobenzene, methyl 4-iodobenzoate, respectively, using Sonogashira coupling.[23] Diynes **3g** and **3h** were prepared according to the literature.[8b,24]

4.3. Typical experimental procedure for alkyne–alkyne coupling with carbon monoxide (Table 2, entry 1)

$IrCl(CO)(PPh_3)_2$ (4.2 mg, 0.005 mmol) was placed in a flask. Under an atmospheric pressure of CO, a xylene solution (5 mL) of dipropargylmalonate **3a** (56.5 mg, 0.11 mmol) was added, then the resulting mixture was stirred at 120°C for 5 h. The solvent was removed under a reduced pressure and the crude products were purified column chromatography using neutral silica gel to give cyclopentadienone **4a** (51.0 mg, 0.094 mmol, 86%).

4.4. Typical experimental procedure for alkyne–alkyne coupling with isocyanide (Table 4, entry 2)

$[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol) was placed in a flask and a dibutyl ether solution (2 mL) of 1,7-diphenylhepta-1,6-diyne **3g** (24.7 mg, 0.21 mmol) was added, then the resulting mixture was stirred at 90°C. A dibutyl ether solution (0.2 mL) of 2,6-dimethylphenylisocyanide (2.7 mg, 0.021 mmol) was added five times at the interval of 15 min. After the last addition of the isocyanide, the resulting solution was stirred for further 30 min. The solvent was removed under a reduced pressure and the crude products were purified by thin layer chromatography to give iminocyclopentadiene **7g** (31.3 mg, 0.17 mmol, 83%).

4.4.1. Bis(3-triphenylsilyl-2-propynyl) ether (1a). White solid. Mp 116.5–117.0°C. ^1H NMR ($CDCl_3$) δ (ppm)=4.48 (s, 4H), 7.31–7.47 (m, 18H), 7.62–7.67 (m, 12H); ^{13}C

NMR ($CDCl_3$) δ (ppm)=57.4, 87.6, 105.1, 128.0, 130.0, 133.0, 135.5; IR (KBr disk) 2175 cm^{-1}; HRMS found *m/z* 610.2139, calcd for $C_{42}H_{34}OSi_2$: 610.2148.

4.4.2. 1,8-Bis(triphenylsilylethynyl)naphthalene (1b). Light pink solid. Mp 192.5–193.0°C. ^1H NMR ($CDCl_3$) δ (ppm)=7.08–7.16 (m, 12H), 7.24–7.32 (m, 6H), 7.41–7.54 (m, 14H), 7.86 (dd, 2H, *J*=1.4, 8.2 Hz), 7.95 (dd, 2H, *J*=1.4, 7.2 Hz); IR (KBr disk) 2137 cm^{-1}. Anal. found C, 86.65; H, 5.21%, calcd for $C_{50}H_{36}Si_2$: C, 86.66; H, 5.24%.

4.4.3. 2,4-Bis(triphenylsilyl)-7-oxabicyclo[3.3.0]octa-1,4-dien-3-one (2a). Yellow solid. Mp 211.5–212.0°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=3.69 (s, 4H), 7.31–7.43 (m, 18H), 7.54–7.58 (m, 12H); IR (KBr disk) 1585, 1693 cm^{-1}; λ_{max} (CH_3CN) 258 nm (ε 5700), 396 nm (ε 1400); HRMS found *m/z* 638.2079, calcd for $C_{43}H_{34}O_2Si_2$: 638.2097.

4.4.4. 1-Oxo-2,5-bis(triphenylsilyl)cyclopenta-1,4-dieno[3,4-*a*]acenaphthene (2b). Red solid. Mp >300°C. ^1H NMR ($CDCl_3$) δ (ppm)=6.00 (d, 2H, *J*=7.2 Hz), 7.04 (d, 1H, *J*=7.4 Hz), 7.08 (d, 1H, *J*=7.4 Hz), 7.28–7.46 (m, 20H), 7.63–7.67 (m, 12H); IR (KBr disk) 1556, 1672 cm^{-1}. Anal. found C, 85.22; H, 5.01%, calcd for $C_{51}H_{36}OSi_2$: C, 84.96; H, 5.03%.

4.4.5. 4,4-Bis(benzyloxycarbonyl)-1,7-diphenylhepta-1,6-diyne (3a). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=3.31 (s, 4H), 5.19 (s, 4H), 7.24–7.27 (m, 20H); ^{13}C NMR ($CDCl_3$) δ (ppm)=23.8, 57.4, 67.6, 83.8, 83.9, 110.0, 123.0, 128.0, 128.1, 128.3, 128.5, 131.7, 135.2, 168.6; IR (neat) 1739 cm^{-1}; HRMS found *m/z* 512.1978, calcd for $C_{35}H_{28}O_4$: 512.1988.

4.4.6. 1,7-Diphenyl-4,4-bis(ethoxycarbonyl)hepta-1,6-diyne (3b). Spectral data were accorded with those in the literature.[25]

4.4.7. 4,4-Bis(*tert*-butoxycarbonyl)-1,7-diphenylhepta-1,6-diyne (3c). White solid. Mp 142°C. ^1H NMR ($CDCl_3$) δ (ppm)=1.49 (s, 18H), 3.15 (s, 4H), 7.25–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ (ppm)=23.5, 27.8, 57.8, 81.9, 83.3, 84.7, 123.3, 127.8, 128.1, 131.6, 168.0; IR (CH_2Cl_2) 1731 cm^{-1}; HRMS found *m/z* 444.2297, calcd for $C_{29}H_{32}O_4$: 444.2301.

4.4.8. 4,4-Bis(benzyloxycarbonyl)-1,7-bis(4-methoxyphenyl)hepta-1,6-diyne (3d). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=3.30 (s, 4H), 3.74 (s, 6H), 5.17 (s, 4H), 6.74–6.78 (m, 4H), 7.21–7.25 (m, 14H); ^{13}C NMR ($CDCl_3$) δ (ppm)=23.7, 55.1, 57.4, 67.4, 82.3, 83.7, 113.6, 115.1, 127.9, 128.2, 128.4, 133.0, 135.2, 159.3, 168.7; IR (CH_2Cl_2) 1746 cm^{-1}; HRMS found *m/z* 572.2209, calcd for $C_{37}H_{32}O_6$: 572.2199.

4.4.9. 4,4-Bis(benzyloxycarbonyl)-1,7-bis(4-chlorophenyl)-hepta-1,6-diyne (3e). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=3.27 (s, 4H), 5.18 (s, 4H), 7.20–7.27 (m, 18H); ^{13}C NMR ($CDCl_3$) δ (ppm)=23.8, 57.2, 67.6, 82.9, 84.8, 121.3, 128.1, 128.3, 128.4, 128.5, 132.9, 134.0, 135.1, 168.5; IR (CH_2Cl_2) 1739 cm^{-1}; HRMS found *m/z* 580.1207, calcd for $C_{35}H_{26}Cl_2O_4$: 580.1208.

4.4.10. 4,4-Bis(benzyloxycarbonyl)-1,7-bis[(4-methoxycarbonyl)phenyl]hepta-1,6-diyne (3f). Pale yellow solid. Mp 106–107°C. ^1H NMR ($CDCl_3$) δ (ppm)=3.32 (s, 4H), 3.91 (s, 6H), 5.20 (s, 4H), 7.27–7.34 (m, 14H), 7.91–7.95 (m, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm)=23.9, 52.2, 57.1, 67.7, 83.4, 86.9, 127.5, 128.1, 128.4, 128.5, 129.3, 129.4, 131.6, 135.0, 166.5, 168.4; IR (CH_2Cl_2) 1730, 1741 cm^{-1}; HRMS found *m/z* 628.2100, calcd for $C_{39}H_{32}O_8$: 628.2097.

4.4.11. 4,4-Bis(benzyloxycarbonyl)-1,7-dimethylhepta-1,6-diyne (3i). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=1.67 (t, 6H, *J*=2.5 Hz), 2.94 (q, 4H, *J*=2.5 Hz), 5.13 (s, 4H), 7.25–7.32 (m, 10H); ^{13}C NMR ($CDCl_3$) δ (ppm)=3.4, 22.9, 57.2, 67.3, 73.1, 79.1, 128.0, 128.2, 128.4, 135.3, 169.0; IR (neat) 1735 cm^{-1}; HRMS found *m/z* 388.1687, calcd for $C_{25}H_{24}O_4$: 388.1675.

4.4.12. 4,4-Bis(benzyloxycarbonyl)-1,7-bis(trimethylsilyl)hepta-1,6-diyne (3j). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=0.11 (s, 18H), 3.04 (s, 4H), 5.12 (s, 4H), 7.25–7.33 (m, 10H); ^{13}C NMR ($CDCl_3$) δ (ppm)=−0.1, 24.0, 57.2, 67.4, 88.5, 100.9, 127.9, 128.2, 128.5, 135.2, 168.3; IR (neat) 1742, 2176 cm^{-1}; HRMS found *m/z* 504.2148, calcd for $C_{29}H_{36}O_4Si_2$: 504.2152.

4.4.13. 7,7-Bis(benzyloxycarbonyl)-2,4-diphenylbicyclo-[3.3.0]octa-1,4-dien-3-one (4a). Purple solid. Mp 133.0°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=3.51 (s, 4H), 5.15 (s, 4H), 7.18–7.41 (m, 16H), 7.60–7.64 (m, 4H); IR (CH_2Cl_2) 1712, 1732 cm^{-1}; λ_{max} (CH_3CN) 257 nm (ε 42000), 497 nm (ε 3600); HRMS found *m/z* 540.1917, calcd for $C_{36}H_{28}O_5$: 540.1937.

4.4.14. 2,4-Diphenyl-7,7-bis(ethoxycarbonyl)bicyclo-[3.3.0]octa-1,4-dien-3-one (4b). Red purple solid. Mp 137.0°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=1.28 (t, 6H, *J*=7.1 Hz), 3.52 (s, 4H), 4.24 (q, 4H, *J*=7.1 Hz), 7.24–7.44 (m, 6H), 7.65–7.69 (m, 4H); IR (neat) 1727 cm^{-1}; λ_{max} (CH_3CN) 258 nm (ε 45000), 495 nm (ε 4700); HRMS found *m/z* 416.1621, calcd for $C_{26}H_{24}O_5$: 416.1624.

4.4.15. 7,7-Bis(*tert*-buthoxycarbonyl)-2,4-diphenylbicyclo-[3.3.0]octa-1,4-dien-3-one (4c). Red purple solid. Mp 190.0°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=1.47 (s, 18H), 3.40 (s, 4H), 7.29–7.42 (m, 6H), 7.65–7.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm)=27.8, 35.8, 63.8, 82.5, 119.5, 127.2, 128.1, 128.5, 131.5, 158.7, 169.7, 201.9; IR (CH_2Cl_2) 1697, 1717 cm^{-1}; λ_{max} (CH_3CN) 258 nm (ε 34000), 495 nm (ε 3200). Anal. found C, 76.18; H, 6.84%, calcd for $C_{30}H_{32}O_5$: C, 76.25; H, 6.82%.

4.4.16. 7,7-Bis(benzyloxycarbonyl)-2,4-bis(4-methoxyphenyl)bicyclo[3.3.0]octa-1,4-dien-3-one (4d). Red purple solid. Mp 136.0°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=3.46 (s, 4H), 3.82 (s, 6H), 5.14 (s, 4H), 6.91 (d, 4H, *J*=9.0 Hz), 7.18–7.32 (m, 10H), 7.57 (d, 4H, *J*=9.0 Hz); IR (CH_2Cl_2) 1604, 1716, 1737 cm^{-1}; λ_{max} (CH_3CN) 265 nm (ε 50000), 497 nm (ε 4500); HRMS found *m/z* 600.2133, calcd for $C_{38}H_{32}O_7$: 600.2148.

4.4.17. 7,7-Bis(benzyloxycarbonyl)-2,4-bis(4-chlorophenyl)bicyclo[3.3.0]octa-1,4-dien-3-one (4e). Purple solid. Mp 177.0°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=3.47

(s, 4H), 5.15 (s, 4H), 7.18–7.36 (m, 14H), 7.55 (d, 4H, J=8.8 Hz); IR (CH_2Cl_2) 1721 cm^{-1}; λ_{max} (CH_3CN) 266 nm (ε 44000), 498 nm (ε 3400); HRMS found m/z 608.1161, calcd for $C_{36}H_{26}Cl_2O_5$: 608.1157.

4.4.18. 2,4-Diphenylbicyclo[3.3.0]octa-1,4-dien-3-one (4g). Purple oil. ^1H NMR ($CDCl_3$) δ (ppm)=2.11 (quint, 2H, J=7.1 Hz), 2.78 (t, 4H, J=7.1 Hz), 7.18–7.39 (m, 6H), 7.66 (d, 4H, J=7.4 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm)=27.1, 28.0, 118.8, 126.8, 127.9, 128.4, 132.0, 162.7, 203.3; IR (neat) 1599, 1707 cm^{-1}; λ_{max} (CH_3CN) 259 nm (ε 45000), 500 nm (ε 3900); HRMS found m/z 272.1210, calcd for $C_{20}H_{16}O$: 272.1201.

4.4.19. 2,4-Diphenyl-7-oxabicyclo[3.3.0]octa-1,4-dien-3-one (4h). Purple solid. Mp 104°C (dec). ^1H NMR ($CDCl_3$) δ (ppm)=4.93 (s, 4H), 7.26–7.50 (m, 6H), 7.57 (d, 4H, J=3.2 Hz); IR (CH_2Cl_2) 1601, 1715 cm^{-1}; λ_{max} (CH_3CN) 259 nm (ε 30000), 506 nm (ε 3200); HRMS found m/z 274.0993, calcd for $C_{19}H_{14}O_2$: 274.0994.

4.4.20. 7,7-Bis(benzyloxycarbonyl)-2,4-diphenylbicyclo-[3.3.0]octa-1,5-dien-3-one (5a). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=3.82 (s, 2H), 4.20 (s, 1H), 5.17 (s, 2H), 5.19 (s, 2H), 6.24 (s, 1H), 7.16–7.44 (m, 18H), 7.81 (d, 2H, J=6.8 Hz); IR (neat) 1704, 1729 cm^{-1}; HRMS found m/z 540.1943, calcd for $C_{36}H_{28}O_5$: 540.1937.

4.4.21. 7,7-Bis(benzyloxycarbonyl)-2,4-bis[(4-methoxy-carbonyl)phenyl]bicyclo[3.3.0]octa-1,5-dien-3-one (5f). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=3.85 (s, 2H), 3.92 (s, 3H), 3.93 (s, 3H), 4.27 (s, 1H), 5.20 (s, 4H), 6.32 (s, 1H), 7.23–7.36 (m, 12H), 7.88 (d, 2H, J=8.4 Hz), 7.95 (d, 2H, J=8.4 Hz), 8.07 (d, 2H, J=8.4 Hz); IR (neat) 1611, 1717 cm^{-1}; HRMS found m/z 656.2032, calcd for $C_{40}H_{32}O_9$: 656.2046.

4.4.22. 2,2-Bis(benzyloxycarbonyl)-5-[2,2-bis(benzyloxy-carbonyl)-5-phenyl-4-pentynyl]-4,6,7-triphenylindan (6a). Colorless oil. ^1H NMR ($CDCl_3$) δ (ppm)=2.27 (s, 2H), 3.28 (s, 2H), 3.39 (s, 2H), 3.73 (s, 2H), 4.63 (d, 2H, J=12.4 Hz), 4.78 (d, 2H, J=12.4 Hz), 5.05 (s, 4H), 7.03–7.36 (m, 40H); IR (neat) 1737 cm^{-1}; HRMS found m/z 1024.3977, calcd for $C_{70}H_{56}O_8$: 1024.3975.

4.4.23. 7,7-Bis(*tert*-buthoxycarbonyl)-3-(2,6-dimethyl-phenylimino)-2,4-diphenylbicyclo[3.3.0]octa-1,4-diene (7c). Red solid. Mp 137–138°C. ^1H NMR ($CDCl_3$) δ (ppm)=1.44 (bs, 18H), 2.04 (s, 6H), 3.11–3.43 (brs, 4H), 6.44–6.65 (m, 3H), 6.75–7.80 (m, 10H); ^{13}C NMR ($CDCl_3$) δ (ppm)=18.8, 27.8, 34.3, 35.4, 64.0, 82.1, 121.8, 123.2, 124.8, 125.8, 126.7, 126.9, 127.3, 128.0, 129.3, 133.1, 147.6, 150.9, 157.7, 170.0, 170.1; IR (CH_2Cl_2) 1594, 1654, 1732 cm^{-1}; λ_{max} (CH_3CN) 246 nm (ε 30000), 446 nm (ε 3000); HRMS found m/z 575.3035, calcd for $C_{38}H_{41}NO_4$: 575.3036.

4.4.24. 3-(2,6-Dimethylphenylimino)-2,4-diphenylbicyclo-[3.3.0]octa-1,4-diene (7g). Spectral data were accorded with those in the literature.[19]

4.4.25. 3-(2,6-Dimethylphenylimino)-2,4-diphenyl-7-oxa-bicyclo[3.3.0]octa-1,4-diene (7h). Orange solid. Mp 167–168°C. ^1H NMR ($CDCl_3$) δ (ppm)=2.08 (s, 6H), 4.73–4.86 (brs, 4H), 6.57–6.73 (m, 3H), 6.82–7.62 (m, 10H); IR (CH_2Cl_2) 1590, 1618 cm^{-1}; λ_{max} (CH_3CN) 235 nm (ε 35000), 264 nm (ε 35000), 451 nm ε 4400); HRMS found m/z 377.1778, calcd for $C_{27}H_{23}NO$: 377.1780.

4.4.26. 7,7-Bis(benzyloxycarbonyl)-2,4-dimethyl-3-(2,6-dimethylphenylimino)bicyclo[3.3.0]octa-1,4-diene (7i). Orange oil. ^1H NMR (C_6D_6) δ (ppm)=1.10 (s, 3H), 1.92 (s, 3H), 2.00 (s, 6H), 3.01 (s, 2H), 3.11 (s, 2H), 5.14 (s, 4H), 6.87–7.00 (m, 3H), 7.21–7.31 (m, 10H); ^{13}C NMR ($CDCl_3$) δ (ppm)=9.7, 11.7, 18.3, 33.4, 33.6, 63.0, 67.5, 122.9, 124.5, 127.5, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 135.2, 148.3, 148.5, 170.7, 175.0; IR (neat) 1591, 1632, 1735 cm^{-1}; λ_{max} (CH_3CN) 239 nm (ε 27000), 401 nm (ε 840); HRMS found m/z 519.2407, calcd for $C_{34}H_{33}NO_4$: 519.2410.

4.4.27. 7,7-Bis(benzyloxycarbonyl)-3-(2,6-dimethyl-phenylimino)-2,4-bis(trimethylsilyl)bicyclo[3.3.0]octa-1,4-diene (7j). Orange oil. ^1H NMR (C_6D_6) δ (ppm)=0.33 (brs, 18H), 2.29 (s, 6H), 3.60 (s, 4H), 5.15 (s, 4H), 7.09–7.40 (m, 13H); ^{13}C NMR ($CDCl_3$) δ (ppm)=0.4, 18.9, 35.8, 63.1, 67.6, 123.0, 125.3, 127.7, 127.9, 128.3, 128.5, 135.1, 149.4, 170.6, 181.6; IR (neat) 1592, 1623, 1731 cm^{-1}; λ_{max} (CH_3CN) 247 nm (ε 31000), 407 nm (ε 1700); HRMS found m/z 635.2895, calcd for $C_{38}H_{45}NO_4Si_2$: 635.2887.

4.4.28. 2,4-Diphenyl-3-(4-methoxyphenylimino)bicyclo-[3.3.0]octa-1,4-diene (9g). Orange oil. ^1H NMR ($CDCl_3$) δ (ppm)=2.13 (tt, 2H, J=7.1, 7.1 Hz), 2.63 (t, 2H, J=7.1 Hz), 2.84 (t, 2H, J=7.1 Hz), 3.63 (s, 3H), 6.41–6.47 (m, 2H), 6.65–6.69 (m, 2H), 6.79–6.95 (m, 4H), 7.24–7.44 (m, 4H), 7.64 (d, 2H, J=7.4 Hz); IR (CH_2Cl_2) 1499, 1602 cm^{-1}; λ_{max} (CH_3CN) 249 nm (ε 26000), 445 nm (ε 4500); HRMS found m/z 377.1762, calcd for $C_{27}H_{23}NO$: 377.1780.

Acknowledgements

Financial support by Sumitomo Foundation and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology is gratefully acknowledged.

References

1. Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49–92. Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635–662. Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523–596.
2. Schore, N. E. *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12. pp 703–739. Geis, O.; Schmalz, H. G. *Angew. Chem., Int. Ed.* **1998**, *37*, 911–914. Jeong, N. *Transition Metals in Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley/VCH: Weinheim, 1998; Vol. 1. pp 560–577.
3. Ogliaruso, M.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261–367.
4. Synthetic application of cyclopentadienones: Yamashita, Y.;

Masumura, M. *Tetrahedron Lett.* **1979**, 1765–1768. Yamashita, Y.; Miyauchi, Y.; Masumura, M. *Chem. Lett.* **1983**, 489–492. Baraldi, P. G.; Barco, A.; Benetti, S.; Pollini, G. P.; Polo, E.; Simoni, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1049–1050. Chiusoli, G. P.; Costa, M.; Gerbella, M.; Salerno, G. *Gazz. Chim. Ital.* **1985**, *115*, 697–700. Chiusoli, G. P.; Costa, M.; Gerbella, M.; Reverberi, S.; Salerno, G.; Terenghi, M. G. *Gazz. Chim. Ital.* **1987**, *117*, 695–699. Gamba, A.; Gandolfi, R.; Oberti, R.; Sardone, N. *Tetrahedron* **1993**, *49*, 6331–6348. Kumar, U.; Neenan, T. X. *Macromolecules* **1995**, *28*, 124–130. Knölker, H.-J.; Baum, E.; Heber, J. *Tetrahedron Lett.* **1995**, *42*, 7647–7650. Jikyo, T.; Eto, M.; Harano, K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3463–3470. Jikyo, T.; Eto, M.; Harano, K. *Tetrahedron* **1999**, *55*, 6051–6066. Rainier, J. D.; Imbriglio, J. E. *Org. Lett.* **1999**, *1*, 2037–2039.

5. Yamazaki, H.; Hagihara, N. J. *Organomet. Chem.* **1967**, *7*, C21–C22.
6. Müller, E. *Synthesis* **1974**, 761–774.
7. Gesing, E. R. F.; Tane, J.-P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023–1024. Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883–892.
8. (a) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 202–203. (b) Pearson, A. J.; Shively, Jr. R. J.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096–4104. (c) Knölker, H.-J.; Heber, J.; Mahler, C. H. *Synlett* **1992**, 1002–1004. (d) Knölker, H.-J.; Heber, J. *Synlett* **1993**, 924–926. (e) Pearson, A. J.; Shively, Jr. R. J. *Organometallics* **1994**, *13*, 578–584. (f) Pearson, A. J.; Perosa, A. *Organometallics* **1995**, *14*, 5178–5183. (g) Pearson, A. J.; Yao, X. *Synlett* **1997**, 1281–1282.
9. The only example of a catalytic carbonylative coupling of *tert*-butyl-substituted alkynes for the synthesis of cyclopentadienone but in low yield: Kelly, E. A.; Wright, G. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 178–183.
10. Shibata, T.; Ohta, T.; Soai, K. *Tetrahedron Lett.* **1998**, *39*, 5785–5788. Shibata, T.; Yamashita, K.; Takagi, K.; Ohta, T.; Soai, K. *Tetrahedron* **2000**, *56*, 9259–9267.
11. Hong, S. H.; Kim, J. W.; Choi, D. S.; Chung, Y. K.; Lee, S.-G. *Chem. Commun.* **1999**, 2099–2100. Son, S. U.; Chung, Y. K.; Lee, S.-G. *J. Org. Chem.* **2000**, *65*, 6142–6144. Son, S. U.; Choi, D. S.; Chung, Y. K.; Lee, S.-G. *Org. Lett.* **2000**, *2*, 2097–2100.
12. For a preliminary communication of a part of this work: Shibata, T.; Yamashita, K.; Ishida, H.; Takagi, K. *Org. Lett.* **2001**, *3*, 1217–1219.
13. After our publication (Ref. 12), a trinuclear cobalt carbonyl complex was reported to be a catalyst for carbonylative alkyne–alkyne coupling under a high pressure of CO: Sugihara, T.; Wakabayashi, A.; Takao, H.; Imagawa, H.; Nishizawa, M. *Chem. Commun.* **2001**, 2456–2457.
14. Shibata, T.; Takagi, K. *J. Am. Chem. Soc.* **2000**, *122*, 9852–9853.
15. IrCl(cod)(dppp) was readily prepared by the reaction of $[IrCl(cod)]_2$ and dppp in hot toluene, following crystallization. Its structure was determined by X-ray measurement as its $CHCl_3$ complex. Crystallographic data of $IrCl(cod)(dppp)\cdot CHCl_3$ have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 157001 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.
16. Kobayashi, T.; Koga, Y.; Narasaka, K. *J. Organomet. Chem.* **2001**, *624*, 73–87.
17. Recently, Ir complex-catalyzed [2+2+2] cyclization of diynes and alkynes was reported: Takeuchi, R.; Tanaka, S.; Nakaya, Y. *Tetrahedron Lett.* **2001**, *42*, 2991–2994.
18. The first example of transition metal-mediated intramolecular carbonylative allene–alkyne coupling: Narasaka, K.; Shibata, T. *Chem. Lett.* **1994**, 315–318.
19. Tamao, K.; Kobayashi, K.; Ito, Y. *J. Org. Chem.* **1989**, *54*, 3517–3519.
20. Ti complex-catalyzed intramoleculer alkyne–alkene coupling with isocyanides, which were provided by the tautomeric equilibrium from the corresponding cyanides: Berk, S. C.; Grossmann, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8593–8601.
21. We chose dibutyl ether as a solvent because exclusion of diglyme and TMU from the reaction mixture was very difficult due to their high boiling points and polarity.
22. Walborsky, H. M.; Niznik, G. E. *J. Org. Chem.* **1972**, *37*, 187–190.
23. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467–4470.
24. Scheller, A.; Winter, W.; Müller, E. *Liebigs Ann. Chem.* **1976**, 1448–1454.
25. Yamamoto, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 582–588.