

Carbon–Carbon Bond Formation Reaction of Zirconacyclopentadienes with Alkynes in the Presence of Ni(II)-complexes

Tamotsu Takahashi,* Fu-Yu Tsai, Yanzhong Li, Kiyohiko Nakajima,† and Martin Kitora

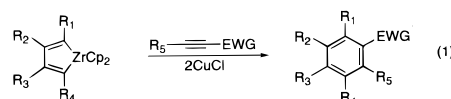
Contribution from the Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo 060-0811, Japan, and CREST, Science and Technology Corporation (JST), Sapporo 060-0811, Japan

Received March 8, 1999

Abstract: Zirconacyclopentadienes, prepared from two alkynes or a diyne, reacted with the alkyl-, trimethylsilyl-, or alkoxy-substituted third alkyne as well as an alkyne with an electron-withdrawing group in the presence of a stoichiometric amount of NiBr₂(PPh₃)₂ to give benzene derivatives in good yields. Heteroatom-containing diynes such as dipropargylbenzylamine and propargyl-homopropargylbenzylamine gave isoindoline and tetrahydroisoquinoline derivatives in good to high yields. This procedure was also used for the selective preparation of benzene derivatives from three different alkynes. The use of trimethylsilyl-substituted alkyne as the first, second or third alkyne afforded desilylated benzene derivatives. The reaction of zirconacyclopentadienes with allenes gave benzene derivatives as a mixture of two isomers.

Introduction

Transition-metal-catalyzed or -mediated coupling of three alkynes to give benzene derivatives has been well established in organic synthesis.^{1,2} Despite intense research in this area, the problem of the selective intermolecular coupling of three alkynes has remained virtually unsolved. Recently, we have reported that this problem can be overcome by the reaction of zirconacyclopentadienes, which can be selectively prepared from two different alkynes,³ with alkynes bearing electron-withdrawing groups in the presence of a stoichiometric amount of CuCl (eq 1).⁴ This method was the first example of the one-pot formation of benzene derivatives from three different alkynes in high yields (83–95%) with excellent selectivities.^{4a} However, the critical limitation of this method is that at least one electron-withdrawing



group is required for the third alkyne, since the major reaction step of this method is Michael addition of the dienylcopper species to the third alkyne. Therefore, consequently, an alkyne with electron-donating groups such as alkyl, trimethylsilyl, and alkoxy groups cannot be used for this reaction.

One reasonable approach to overcome this difficulty is development of an insertion reaction of the third alkyne into a dienylmetal and such insertion reaction can be expected for the late transition-metal compounds such as nickel. Therefore, we have investigated a novel and general reaction system using zirconacyclopentadienes and the late transition-metal compounds. In this paper we would like to report a novel reaction of zirconacyclopentadienes with the third alkynes which have electron-donating groups as well as an electron-withdrawing group in the presence of Ni(II)-complexes to afford benzene derivatives (eq 2). This can be a *general one-pot procedure for the selective synthesis of benzene derivatives by intermolecular coupling of alkynes or by intramolecular coupling of diynes.*

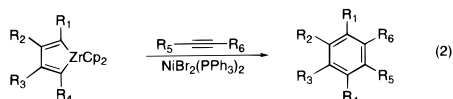
(4) For formation of benzene derivatives from three different alkynes via transmetalation of zirconacyclopentadienes to organocopper, see (a) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kitora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672–1680. (b) Takahashi, T.; Kitora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 361–362. For other examples of transmetalations of zirconacycles to organocopper compounds, see: (c) Takahashi, T.; Kitora, M.; Kasai, K.; Suzuki, N.; Nakajima, K. *Organometallics* **1994**, *13*, 4183–4185. (d) Kasai, K.; Kitora, M.; Suzuki, N.; Takahashi, T.; *J. Chem. Soc., Chem. Commun.* **1995**, 109–110. (e) Takahashi, T.; Kitora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 1503–1504. (f) Takahashi, T.; Hara, R.; Nishihara, Y.; Kitora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154–5155. (g) Takahashi, T.; Xi, Z.; Kitora, M.; Xi, C.; Nakajima, K. *Tetrahedron Lett.* **1996**, *37*, 7521–7524. (h) Takahashi, T.; Nishihara, Y.; Hara, R.; Huo, S.; Kitora, M. *Chem. Commun.* **1997**, 1599–1600. (i) Kitora, M.; Umeda, C.; Ishida, T.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 8355–8358. (j) Kitora, M.; Xi, C.; Takahashi, T. *Tetrahedron Lett.* **1998**, *39*, 4321–4324. (k) Takahashi, T.; Sun, W.-H.; Liu, Y.; Nakajima, K.; Kitora, M. *Organometallics* **1998**, *17*, 3841–3843.

* Department of Chemistry, Aichi University of Education, Igaya, Kariya, 448-8542, Japan, and CREST, Science and Technology Corporation (JST), Kariya 448-8542, Japan

(1) (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49–92. (b) Grotjahn, D. B. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science Ltd: Oxford, 1995; Vol 12; pp 741–770. (c) Schore, N. E. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds; Pergamon Press Ltd: Oxford, 1991; Vol. 5; pp 1129–1162. (d) Harrington, P. J. *Transition Metals in Total Synthesis*, John Wiley & Sons: New York, 1990; pp 200–240. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119. (f) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556.

(2) (a) Boese, R.; Van Sickle, A. P.; Vollhardt, K. P. C. *Synthesis* **1994**, 1374–1382. (b) Saa, C.; Crotts, D. D.; Hsu, G.; Vollhardt, K. P. C. *Synlett* **1994**, 487–489. (c) Lecker, S. H.; Nguyen, N. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 856–858. (d) Hillard, R. L., III; Parnell, C. A.; Vollhardt, K. P. C. *Tetrahedron* **1983**, *39*, 905–911. (e) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253–5261. (f) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549–4552.

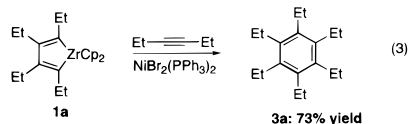
(3) (a) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444–4447. (b) Takahashi, T.; Xi, Z.; Rousset, C. J.; Suzuki, N. *Chem. Lett.* **1993**, 1001–1002. For other methods see: (c) Takahashi, T.; Swanson, D. R.; Negishi, E. *Tetrahedron Lett.* **1987**, *28*, 623–626. (d) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874. (e) Wagenen, B. C. V.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 3495–3498. (f) Takahashi, T.; Kageyama, V.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687–690.



Transmetalation of zirconacycles to other organometallic compounds has been used for further C–C bond formations. In particular, transmetalation from zirconacycles to copper or lithium has been intensively investigated by our group and others.^{4–6} The transmetalation reaction of zirconacycles to nickel compounds has not been reported yet, although the coupling reaction of alkenylzirconocene with organic halides or Michael addition to α,β -enones in the presence of nickel compounds is known.⁷

Results and Discussion

Reaction of Zirconacyclopentadienes with Alkyl-, Aryl-, Trimethylsilyl-, or Alkoxy-Substituted Alkynes. Addition of 1 equiv of $\text{NiBr}_2(\text{PPh}_3)_2$ to a mixture of tetraethylzirconacyclopentadiene **1a** and 3-hexyne in THF at 20 °C resulted in the formation of hexaethylbenzene **3a** in 1 h in 73% yield (eq 3)



along with the precipitation of metallic nickel. It is in sharp contrast to the reaction of **1a** in the presence of CuCl where 3-hexyne does not react with **1a**.

This result encouraged us to investigate the reactions of both mono- and bicyclic zirconacyclopentadienes with alkyl-, aryl-, trimethylsilyl-, or alkoxy-substituted alkynes. The results are summarized in Table 1. The reaction of tetraethylzirconacyclopentadiene with 4-octyne (entry 1) gave **3b** as a single product. The reaction of bicyclic zirconacyclopentadienes gave the corresponding indan (entries 2–4) and tetrahydronaphthalene derivatives (entry 5). It is interesting to note that terminal alkynes could be used as well (entries 6 and 7). In the case of CuCl -mediated coupling reaction, the use of terminal alkynes did not give a satisfactory result even with an electron-withdrawing

(5) (a) Lipshutz, B. H.; Segi, M. *Tetrahedron* **1995**, *51*, 4407–4420. (b) Honda, T.; Mori, M. *Organometallics* **1996**, *15*, 5464–5466. (c) Dekura, F.; Honda, T.; Mori, M. *Chem. Lett.* **1997**, 825–826.

(6) For the reaction of zirconacyclopentadienes with organolithium, see: (a) Takahashi, T.; Huo, S.; Hara, R.; Noguchi, Y.; Nakajima, K.; Sun, W.-H. *J. Am. Chem. Soc.* **1999**, *121*, 1094–1095. For the reaction of zirconacyclopentadienes with organolithium compounds, see: (b) Luker, T.; Whitby, R. J. *Tetrahedron Lett.* **1994**, *35*, 785–788. (c) Luker, T.; Whitby, R. J. *Tetrahedron Lett.* **1994**, *35*, 9465–9469. (d) Luker, T.; Whitby, R. J. *Tetrahedron Lett.* **1995**, *36*, 4109–4112. (e) Gordon, G. J.; Whitby, R. J. *Synlett* **1995**, 77. (f) Fillery, S.; Gordon, G. J.; Luker, T.; Whitby, R. J. *Pure Appl. Chem.* **1997**, *69*, 639–644. (g) Kondakov, D. Y.; Negishi, E. J. *Chem. Soc., Chem. Commun.* **1996**, 963.

(7) For transmetalations of organozirconium compounds to organonickel compounds, see: (a) Loots, M. J.; Schwartz, J. J. *Am. Chem. Soc.* **1977**, *99*, 8045–8046. (b) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 3168–3170. (c) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Speigel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254–2256. (d) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333–1340. (e) Dayrit, F. M.; Gladkowski, D. E.; Schwartz, J. J. *Am. Chem. Soc.* **1980**, *102*, 3976–3978. (f) Dayrit, F. M.; Schwartz, J. J. *Am. Chem. Soc.* **1981**, *103*, 4466–4473. (g) Coffen, D. L.; Manchand, P. S.; Truesdale, L. K. *Eur. Patent Appl. Ep 153689*, 1985; *Chem. Abstr.* **1986**, *104*, 186231v. (h) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393–2401. (i) Hauske, J. R.; Dorff, P.; Julin, S.; Martinelli, G.; Bussolari, J. *Tetrahedron Lett.* **1992**, *33*, 3715–3716. (j) Hauske, J. R.; Dorff, P.; Julin, S.; DiBrino, J.; Spencer, R.; Williams, R. J. *Med. Chem.* **1992**, *35*, 4284–4296. (k) Sun, R. C.; Okabe, M.; Coffen, D. L.; Schwartz, J. *Org. Synth.* **1993**, *71*, 83–88.

Table 1. Ni-Complex-Mediated Reaction of Zirconacyclopentadienes with Alkyl-, Aryl-, or Trimethylsilyl-Substituted Alkynes

Entry	Zirconacyclopentadiene	Alkyne	Product	Yields (%) ^a
1		$\text{Pr}-\text{C}\equiv\text{C}-\text{Pr}$		70 (49)
2		$\text{Et}-\text{C}\equiv\text{C}-\text{Et}$		76 (63)
3		$\text{Pr}-\text{C}\equiv\text{C}-\text{Pr}$		81 (67)
4		$\text{Et}-\text{C}\equiv\text{C}-\text{Et}$		90 (76)
5		$\text{Pr}-\text{C}\equiv\text{C}-\text{Pr}$		66 (46)
6		$\text{Pr}-\text{C}\equiv\text{C}-\text{H}$		70 (60)
7		$\text{Ph}-\text{C}\equiv\text{C}-\text{H}$		78 (64)
8		$\text{Me}-\text{C}\equiv\text{C}-\text{SiMe}_3$		- (53)

^a GC yields. Isolated yields are given in parentheses.

group. The reaction with trimethylsilylpropyne (entry 8) afforded the desired product; however, it was rather unstable and underwent desilylation during the isolation by column chromatography. Desilylated compound **3i** was obtained as a pure product in 53% yield. It is noteworthy that in all cases the formation of homotrimerization products of the third alkynes was not observed.

As far as nickel complexes were concerned, $\text{NiBr}_2(\text{PPh}_3)_2$ gave the best result. The use of other nickel complexes such as $\text{NiCl}_2(\text{dppf})$, $\text{NiBr}_2(\text{dppb})$, and NiBr_2 did not give benzene derivatives due to the poor solubility of the Ni complexes. $\text{NiCl}_2(\text{dppf})$, $\text{NiBr}_2(\text{dppb})$, and NiBr_2 were not soluble in THF at room temperature. In a mixture of THF and CH_2Cl_2 , use of $\text{NiBr}_2(\text{dppb})$ gave **3a** in 39% yield. $\text{NiCl}_2(\text{dppf})$ afforded precipitated solid at reflux in THF (vide infra).

To know the generality of this reaction, we investigated the reactions of **1a** with alkynes with an electron-withdrawing group such as COOEt and COMe groups and with an electron-donating group such as EtO and BuO groups. The results are shown in Table 2. In all cases the yields were comparable. The reaction of **1a** with both ethoxycarbonyl- and methylcarbonyl-substituted alkynes (entries 3 and 4) completed in much shorter reaction time when compared with the procedure using CuCl .^{3a} Conjugated alkyne such as 3,5-octadiyne also gave the desired product, 1-pentaethylphenyl-1-butyne **3n** in 69% yield. Further reaction of **3n** with **1a** was not observed. The formation of arenes was also possible by the reaction with conjugated diynes (entry 5).

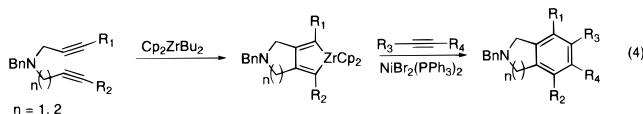
Table 2. Ni-complex-Mediated Reaction of Zirconacyclopentadienes with Functionalized Alkynes

Entry	Zirconacyclopentadiene	Alkyne	Product	Yields (%) ^a
1		EtO≡C–H		64 (32)
2		BuO≡C–Hex		66 (50)
3		Ph≡C–COOEt		78 (54)
4		Et≡C–COMe		68 (55)
5		Et≡C≡C–Et		69 (63)

^a GC yields. Isolated yields are given in parentheses.

Formation of Isoindolines and Tetrahydroisoquinoline.

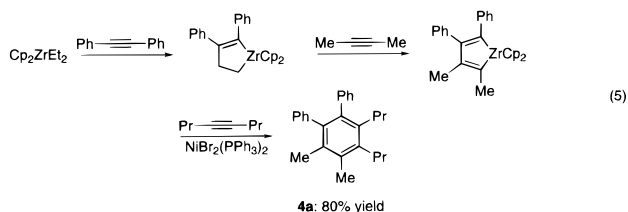
This Ni-mediated formation of arenes was applied to the synthesis of highly substituted benzo-type heterocycles with a 5-, 6-, and 7-membered ring (eq 4).⁸ Some representative



examples are given in Table 3. Isoindoline **3o**–**3r** (entries 1–4), tetrahydroisoquinoline **3s** and **3t** (entries 5 and 6), and benzoperhydrozepine **3u** (entry 7) derivatives were prepared.

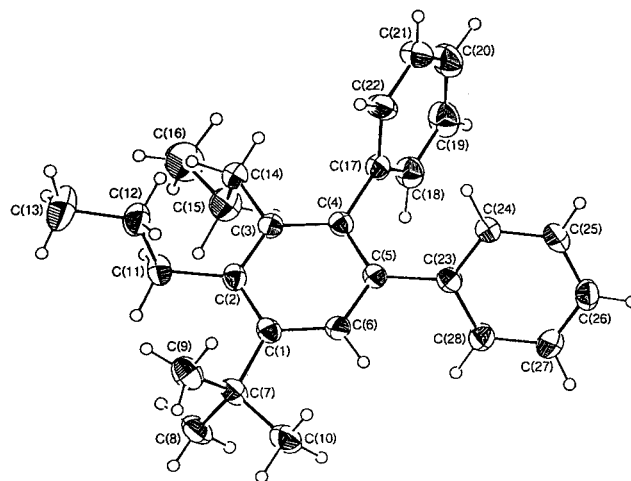
Preparation of Benzenes from Three Different Alkynes.

One attractive target of intermolecular coupling of three alkynes is the preparation of benzene derivatives from three different alkynes. We have already reported the zirconacyclopentadienes/CuCl system as mentioned above. However, the system with nickel compounds reported here is more general and useful for the preparation of benzene derivatives from three different alkynes (eq 5). This reaction can be done in one-pot.

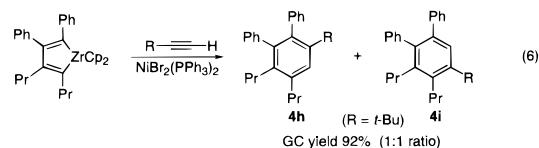


Results are summarized in Table 4. For example, the preparation of benzene having methyl, ethyl, and propyl groups **4c** (entry 3) was achieved in good yield (63%) in a simple reaction sequence. On the other hand, the reaction of unsymmetrically substituted zirconacyclopentadiene with a terminal acetylene such as *tert*-butylacetylene resulted in the formation

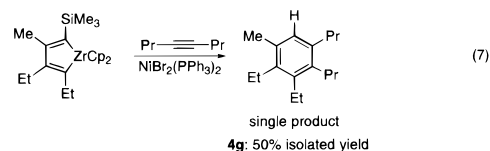
(8) Transition-metal-mediated formation of benzo-type nitrogen-containing heterocycles from diynes, for Rh, see: (a) Muller, E. *Synthesis* **1974**, 761. For Ni, see: (b) Chiusoli, G. P.; Pallini, L.; Terenghi, G. *Transition Met. Chem.* **1983**, *8*, 189. For Co, see: (c) ref 2d.

**Figure 1.**

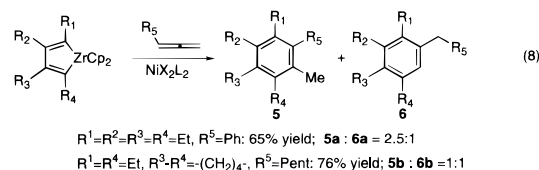
of two regioisomers **4h** and **4i** in a 1:1 ratio (eq 6). This is



because the terminal alkyne could not recognize the difference between the phenyl group and the propyl group of the zirconacyclopentadienes by this system. Compound **4i** was isolated as crystals, and its single-crystal X-ray analysis was performed to confirm the structure (Figure 1). The problem of the regioselectivity of the reaction with a terminal alkyne can be circumvented by the preparation of unsymmetrical trimethylsilyl-substituted zirconacyclopentadienes followed by desilylation. It is well-known that trimethylsilylacetylene affords unsymmetrical zirconacyclopentadienes by the reaction with other alkynes such as 3-hexyne and 4-octyne with an excellent regioselectivity. These zirconacyclopentadienes were converted into benzene derivatives with the third alkynes in the presence of a nickel compound. These products upon isolation underwent facile desilylation to give the corresponding pentasubstituted benzenes **4f** and **4g** (eq 7) as single products.



Reaction with Allenes. The nickel-mediated reaction proceeds also with allenes; however, in this case a mixture of compounds **5** and **6** was obtained as shown (eq 8). The



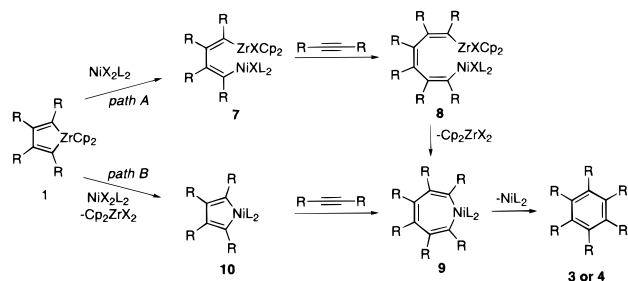
formation of **5** arises from the attack to the internal double bond of the allene moiety, and the formation of **6** arises from the attack to the terminal double bond of the allene moiety.

Reaction Mechanism. Monitoring the reaction by ¹H NMR did not show any significant intermediate except the formation of zirconocene dibromide. However, the following two reaction

Table 3. Ni-complex-Mediated Formation of Benzoheterocycles from Zirconacyclopentadienes

Entry	Zirconacyclopentadiene	Alkyne	Product	Yields (%) ^a
1		Et-C≡C-Et		(3o) 88 (70)
2		Et-C≡C-Et		(3p) 92 (68)
3		Ph-C≡C-COOEt		(3q) 90 (66)
4		Ph-C≡C-Ph		(3r) 78 (60)
5		Et-C≡C-Et		(3s) 78 (65)
6		MeOOC-C≡C-COOMe		(3t) 64 (55)
7		Et-C≡C-Et		(3u) 66 (58)

^a NMR yields. Isolated yields are given in parentheses.

Scheme 1

mechanisms, path A and path B, are plausible (Scheme 1). In path A, one of the Zr–C bonds transmetalates to give a bimetallic intermediate **7** in which one alkyne inserts into the C–Ni bond giving a bimetallic triene intermediate **8**. Intramolecular transmetalation of the second Zr–C bond affords the nickelacycloheptatriene **9** and zirconocene dibromide. Reductive coupling of **9** gives the benzene derivatives. In path B, both Zr–C bonds transmetalate simultaneously to give nickelacyclopentadiene **10** and zirconocene dibromide. The insertion of an alkyne into one of the C–Ni bonds affords the nickelacycloheptatriene **9**. Then compound **9** undergoes reductive elimination to give benzene derivatives **3–4** and a Ni⁰-complex that decomposes to metallic nickel and free ligands.

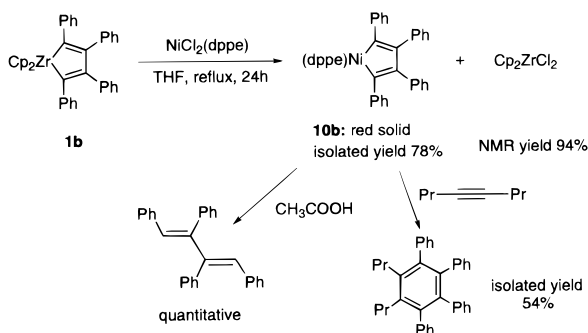
When tetraphenylzirconacyclopentadiene **1b** was treated with NiCl₂(dppf) at reflux in THF for 24 h, brick-red solid **10b** was precipitated along with the formation of Cp₂ZrCl₂ in 94% NMR yield as shown in Scheme 2. IR spectrum of the red solid showed the characteristic resonance at 1585 cm⁻¹ which was consistent with that observed for tetraphenylnickelacyclopentadiene **10b** which has been prepared by the reaction of NiCl₂-

Table 4. Formation of Arenes from Three Alkynes

Entry	Alkynes	Product	Yields (%) ^a
1	Ph-C≡C-Ph, Me-C≡C-Me, Pr-C≡C-Pr		(4a) 80 (62)
2	Ph-C≡C-Ph, Pr-C≡C-Pr, Et-C≡C-Et		(4b) 74 (60)
3	Pr-C≡C-Pr, Me-C≡C-Me, Et-C≡C-Et		(4c) 63 (55)
4	Ph-C≡C-Ph, Me-C≡C-Me, Et-C≡C-Et		(4d) 76 (58)
5	Bu-C≡C-Bu, Me-C≡C-Me, Et-C≡C-Et		(4e) 65 (44)
6	Me ₃ Si-C≡C-Me, Pr-C≡C-Pr, Et-C≡C-Et		(4f) .. (43)
7	Me ₃ Si-C≡C-Me, Et-C≡C-Et, Pr-C≡C-Pr		(4g) .. (50)
8	Me ₃ Si-C≡C-Me, Et-C≡C-Et, Me-C≡C-COOEt		(4j) 1:1 (4k) 50 (43)
9	Me ₃ Si-C≡C-Me, Pr-C≡C-Pr, Ph-C≡C-COOEt		(4i) 1:1 (4m) 45 (40)

^a GC yields. Isolated yields are given in parentheses.

Scheme 2



(dppe) with 1,4-dithio-1,2,3,4-tetraphenyl-1,3-butadiene.⁹ Treatment of the red solid **10b** with acetic acid gave 1,2,3,4-tetraphenyl-1,3-butadiene quantitatively and the reaction with 4-octyne afforded the corresponding 1,2-dipropyl-3,4,5,6-tetraphenylbenzene in 54% isolated yield as expected.¹⁰

This result clearly suggests that zirconacyclopentadienes reacted with nickel complexes to form nickelacyclopentadienes and Cp_2ZrX_2 and strongly supports the path B in Scheme 1. However, the existence of the path A cannot be ruled out.

Experimental Section

General Information. All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. THF was distilled from sodium benzophenone ketyl. Zirconocene dichloride was purchased from Aldrich Chemical Co., Inc. Butyllithium (1.6 M solution in hexane) was purchased from Kanto Chemical Co. Ltd. Alkynes were purchased from TCI Co. Ltd. Nickel(II) complexes,^{10a} phenylpropadiene, and 1,2-octadiene¹¹ were prepared according to the previously published procedure.

¹H and ¹³C NMR spectra were recorded for CDCl_3 or C_6D_6 (containing 1% TMS) solutions at 25 °C on Bruker NMR spectrometer. GC analysis was performed on Shimadzu GC-14A equipped with fused silica capillary column Shimadzu CBP1-M25-O25 and Shimadzu C-R6A-Chromatopac integrator.

Typical experimental procedure. To a solution of zirconacyclopentadiene **1** (1.0 mmol)^{4,12} in 20 mL THF were added the third alkyne (1.5 mmol) and $\text{NiBr}_2(\text{PPh}_3)_2$ (0.74 g, 1.0 mmol) at room temperature. The mixture was stirred for 1 h, quenched with 3N HCl, and extracted with hexane. The combined organic extracts were dried (MgSO_4) and concentrated in vacuo. Column chromatography on silica gel (hexane) afforded products. For the isolation of the following compounds mixtures of hexane/ Et_2O were used: **3j**, **3l**, and **3m** (19/1); **3o**, **3q**, and **3r** (4/1); **3p** and **3s** (6/1); **3t** and **3u** (5/1).

Hexaethylbenzene (3a): White solid. GC yield: 73%. Isolated yield: 57%. ¹H and ¹³C NMR were in agreement with the published data.¹³

1,2,3,4-Tetraethyl-5,6-dipropylbenzene (3b). White solid. GC yield: 70%. Isolated yield: 49%. ¹H NMR, (CDCl_3 , Me_4Si) δ 1.05 (t, $J = 7.2$ Hz, 6H), 1.18 (t, $J = 7.3$ Hz, 12H), 1.52–1.58 (m, 4H), 2.49–2.65 (m, 4H), 2.61 (q, $J = 7.1$ Hz, 4H), 2.63 (q, $J = 7.0$ Hz, 4H); ¹³C NMR (CDCl_3 , Me_4Si) δ 15.19 (2C), 15.75 (4C), 22.17 (2C), 22.31 (2C), 24.88 (2C), 32.08 (2C), 136.79 (2C), 137.74 (2C), 137.90 (2C). Anal. Calcd for $\text{C}_{20}\text{H}_{34}$: C, 87.52; H, 12.48. Found: C, 87.38; H, 12.55.

4,5,6,7-Tetraethylindan (3c): Colorless oil. GC yield: 76%. Isolated yield: 63%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.15 (t, $J = 7.5$ Hz, 6H), 1.18

(t, $J = 7.5$ Hz, 6H), 2.0–2.1 (m, 2H), 2.61 (q, $J = 7.5$ Hz, 4H), 2.66 (q, $J = 7.5$ Hz, 4H), 2.89 (t, $J = 7.5$ Hz, 4H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.67 (2C), 16.17 (2C), 21.78 (2C), 23.58 (2C), 24.41, 31.73 (2C), 135.68 (2C), 137.79 (2C), 140.41 (2C); HRMS calcd for $\text{C}_{17}\text{H}_{26}$ 230.2033; found 230.2037.

4,7-Diethyl-5,6-dipropylindan (3d): Colorless oil. GC yield: 81%. Isolated yield: 67%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 7.3$ Hz, 6H), 1.34 (t, $J = 7.5$ Hz, 6H), 1.71–1.74 (m, 4H), 2.20–2.27 (m, 2H), 2.74–2.78 (m, 4H), 2.79 (q, $J = 7.5$ Hz, 4H), 3.08 (t, $J = 7.4$ Hz, 4H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.65 (2C), 15.04 (2C), 23.71 (2C), 24.40, 25.31 (2C), 31.62 (2C), 31.74 (2C), 135.73 (2C), 136.67 (2C), 140.30 (2C); HRMS calcd for $\text{C}_{19}\text{H}_{30}$ 258.2346; found 258.2340.

4-Butyl-5,6-diethyl-7-phenylindan (3e): Pale yellow oil. GC yield: 90%. Isolated yield: 76%. ¹H NMR (CDCl_3 , Me_4Si) δ 0.94 (t, $J = 7.5$ Hz, 3H), 0.99 (t, $J = 7.5$ Hz, 3H), 1.21 (t, $J = 7.5$ Hz, 3H), 1.47–1.56 (m, 4H), 1.89–1.96 (m, 2H), 2.45–2.53 (m, 4H), 2.61–2.65 (m, 2H), 2.71 (q, $J = 7.5$ Hz, 2H), 2.92 (t, $J = 7.5$ Hz, 2H), 7.19–7.22 (m, 2H), 7.25–7.29 (m, 1H), 7.33–7.37 (m, 2H); ¹³C NMR (CDCl_3 , Me_4Si) δ 13.97, 15.97, 16.18, 21.91, 22.89, 23.52, 24.51, 30.59, 32.08, 32.78, 32.98, 126.24, 127.94 (2C), 129.28 (2C), 136.15, 136.56, 137.72, 138.05, 140.13, 140.51, 141.85; HRMS calcd for $\text{C}_{23}\text{H}_{30}$ 306.2346; found 306.2351.

4,7-Diethyl-5,6-dipropyltetrahydronaphthalene (3f): Colorless oil. GC yield: 66%. Isolated yield: 46%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.26 (t, $J = 7.3$ Hz, 6H), 1.34 (t, $J = 7.5$ Hz, 6H), 1.70–1.80 (m, 4H), 1.95–2.10 (m, 4H), 2.72–2.78 (m, 4H), 2.81 (q, $J = 7.5$ Hz, 4H), 2.90–2.97 (m, 4H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.49 (2C), 15.12 (2C), 21.86 (2C), 23.26 (2C), 25.05 (2C), 27.08 (2C), 31.90 (2C), 132.95 (2C), 136.16 (2C), 138.05 (2C); HRMS calcd for $\text{C}_{20}\text{H}_{32}$ 272.2502; found 272.2503.

1,2,3,4-Tetraethyl-5-propylbenzene (3g): Colorless oil. GC yield: 70%. Isolated yield: 60%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.01 (t, $J = 7.3$ Hz, 3H), 1.15 (t, $J = 7.5$ Hz, 6H), 1.17 (t, $J = 7.5$ Hz, 3H), 1.22 (t, $J = 7.5$ Hz, 3H), 1.60–1.66 (m, 2H), 2.53–2.59 (m, 2H), 2.59–2.70 (m, 8H), 6.86 (s, 1H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.53, 15.59 (2C), 15.67, 15.93, 21.74, 21.81, 22.06, 24.79, 25.65, 35.26, 127.35, 137.36, 137.47, 138.10, 139.24, 139.76; HRMS calcd for $\text{C}_{17}\text{H}_{28}$ 232.2190; found 232.2187.

5-Phenyl-4,7-diethylindan (3h): Pale yellow oil. GC yield: 78%. Isolated yield: 64%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.00 (t, $J = 7.5$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H), 2.08–2.15 (m, 2H), 2.53 (q, $J = 7.5$ Hz, 2H), 2.59 (q, $J = 7.6$ Hz, 2H), 2.91 (t, $J = 7.4$ Hz, 2H), 2.95 (t, $J = 7.4$ Hz, 2H), 6.88 (s, 1H), 7.28–7.37 (m, 5H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.23, 14.62, 23.62, 24.85, 26.19, 31.19, 31.69, 126.37, 127.62, 127.80 (2C), 129.39 (2C), 134.85, 136.73, 140.23, 141.58, 142.69, 142.84; HRMS calcd for $\text{C}_{19}\text{H}_{22}$ 250.1720; found 250.1717.

4,7-Diethyl-5-methyltetrahydronaphthalene (3i): Pale yellow oil. Isolated yield: 53%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.05 (t, $J = 7.6$ Hz, 3H), 1.14 (t, $J = 7.6$ Hz, 3H), 1.71–1.74 (m, 4H), 2.24 (s, 3H), 2.49 (q, $J = 7.6$ Hz, 2H), 2.56 (q, $J = 7.6$ Hz, 2H), 2.60–2.65 (m, 2H), 2.68–2.73 (m, 2H), 6.80 (s, 1H); ¹³C NMR (CDCl_3 , Me_4Si) δ 13.32, 14.30, 19.41, 21.81, 22.95, 23.30, 25.41, 26.46, 26.87, 127.38, 132.64, 132.68, 134.75, 138.06, 139.33; HRMS calcd for $\text{C}_{15}\text{H}_{22}$ 202.1720; found 202.1716.

1-Ethoxy-2,3,4,5-tetraethylbenzene (3j): Pale yellow oil. GC yield: 64%. Isolated yield: 32%. ¹H NMR (CDCl_3 , Me_4Si) δ 1.13 (t, $J = 7.5$ Hz, 6H), 1.16 (t, $J = 7.5$ Hz, 3H), 1.22 (t, $J = 7.4$ Hz, 3H), 1.39 (t, $J = 7.0$ Hz, 3H), 2.58–2.69 (m, 8H), 4.00 (q, $J = 7.0$ Hz, 2H), 6.56 (s, 1H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.74, 15.10, 15.68, 15.83, 15.85, 19.52, 21.40, 22.10, 26.09, 63.31, 109.60, 128.55, 131.58, 140.02, 140.90, 155.05. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}$: C, 81.99; H, 11.18. Found: C, 81.85; H, 11.09.

1-Butoxy-2,3,4,5-tetraethyl-6-hexylbenzene (3k): Colorless oil. GC yield: 66%. Isolated yield: 50%. ¹H NMR (CDCl_3 , Me_4Si) δ 0.90 (t, $J = 7.0$ Hz, 3H), 1.00 (t, $J = 7.4$ Hz, 3H), 1.14–1.19 (m, 12H), 1.31–1.36 (m, 4H), 1.40–1.44 (m, 2H), 1.50–1.57 (m, 4H), 1.76–1.80 (m, 2H), 2.53–2.55 (m, 2H), 2.57–2.65 (m, 8H), 3.76 (t, $J = 6.5$ Hz, 2H); ¹³C NMR (CDCl_3 , Me_4Si) δ 14.05, 14.08, 15.70, 15.87, 15.90, 15.96, 19.39, 20.18, 22.04 (2C), 22.16, 22.72, 27.45, 30.26, 31.47, 31.74, 32.76, 73.48, 132.10, 133.19, 135.61, 138.85, 139.01, 154.21; HRMS calcd for $\text{C}_{24}\text{H}_{42}\text{O}$ 346.3234; found 346.3264.

(9) Eisch, J. J.; Galle, J. E.; Aradi, A. A.; Boleslawski, M. P. *J. Organomet. Chem.* **1986**, 312, 399.

(10) (a) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719–724. (b) Hoberg, H.; Richter, W. *J. Organomet. Chem.* **1980**, 195, 355. (c) Eisch, J. J.; Galle, J. E.; *J. Organomet. Chem.* **1975**, 96, C23.

(11) Allenes were prepared according to the known procedure: Brandsma, L.; Verkruijse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.

(12) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, 27, 2829–2832.

(13) Jhingon, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, 52, 1161–1165.

Ethyl 2-phenyl-3,4,5,6-tetraethylbenzene carboxylate (3l): White solid. GC yield: 78%. Isolated yield: 54%. ^1H and ^{13}C NMR were in agreement with the published data.^{4a}

Pentaethylacetophenone (3m):¹⁴ White solid. GC yield: 68%. Isolated yield: 55%. ^1H NMR (CDCl_3 , Me_4Si) δ 1.14 (t, $J = 7.5$ Hz, 6H), 1.17 (t, $J = 7.5$ Hz, 9H), 2.40–2.50 (m, 4H), 2.51 (s, 3H), 2.61–2.70 (m, 6H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 15.67 (2C), 15.72, 16.24 (2C), 21.48 (2C), 21.95, 23.54 (2C), 33.25, 133.68 (2C), 138.24 (2C), 140.77, 141.50, 209.24.

1-(Butyn-1-yl)-2,3,4,5-pentaethylbenzene (3n): Pale yellow oil. GC yield: 69%. Isolated yield: 63%. ^1H NMR (CDCl_3 , Me_4Si) δ 1.19 (t, $J = 7.6$ Hz, 3H), 1.21 (t, $J = 7.5$ Hz, 6H), 1.25 (t, $J = 7.5$ Hz, 3H), 1.51 (t, $J = 7.5$ Hz, 6H), 2.47 (q, $J = 7.5$ Hz, 2H), 2.61–2.67 (m, 6H), 2.84 (q, $J = 7.5$ Hz, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.42, 14.19, 14.87 (2C), 15.79 (2C), 15.82, 22.23 (2C), 22.25, 24.82 (2C), 78.37, 96.97, 121.40, 137.19 (2C), 139.71, 142.04 (2C); HRMS calcd for $\text{C}_{20}\text{H}_{30}$ 270.2346, found 270.2340.

N-Benzyl-4,5,6,7-tetraethylisoindoline (3o): Colorless oil. NMR yield: 88%. Isolated yield: 70%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.98 (t, $J = 7.6$ Hz, 6H), 1.12 (t, $J = 7.5$ Hz, 6H), 2.37 (q, $J = 7.6$ Hz, 4H), 2.61 (q, $J = 7.5$ Hz, 4H), 3.82 (s, 2H), 3.93 (s, 4H), 7.1–7.6 (m, 5H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 15.23 (2C), 16.57 (2C), 22.01 (2C), 23.71 (2C), 58.90 (2C), 60.79, 127.27, 128.73 (2C), 128.81 (2C), 134.17 (2C), 137.28 (2C), 138.30 (2C), 140.51; HRMS calcd for $\text{C}_{23}\text{H}_{31}\text{N}$ 321.2455, found 321.2453.

N-Butyl-4,5,6,7-tetraethylisoindoline (3p): Colorless oil. NMR yield: 92%. Isolated yield: 68%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.96 (t, $J = 7.3$ Hz, 3H), 1.06 (t, $J = 7.6$ Hz, 6H), 1.14 (t, $J = 7.5$ Hz, 6H), 1.35–1.48 (m, 2H), 1.50–1.65 (m, 2H), 2.47 (q, $J = 7.6$ Hz, 4H), 2.63 (q, $J = 7.5$ Hz, 4H), 2.65 (t, $J = 7.3$ Hz, 2H), 3.92 (s, 4H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 14.10, 14.99 (2C), 16.35 (2C), 20.71, 21.79 (2C), 23.54 (2C), 31.32, 56.12, 58.74 (2C), 133.83 (2C), 137.01 (2C), 138.02 (2C); HRMS calcd for $\text{C}_{20}\text{H}_{33}\text{N}$ 287.2611, found 287.2619.

N-Butyl-5-carboxyethyl-6-phenyl-4,7-diethylisoindoline (3q): Colorless oil. NMR yield: 90%. Isolated yield: 66%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.72 (t, $J = 7.1$ Hz, 3H), 0.84 (t, $J = 7.6$ Hz, 3H), 0.98 (t, $J = 7.3$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H), 1.40–1.50 (m, 2H), 1.50–1.65 (m, 2H), 2.30 (q, $J = 7.4$ Hz, 2H), 2.60 (q, $J = 7.4$ Hz, 2H), 2.65 (t, $J = 7.2$ Hz, 2H), 3.82 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 2H), 3.92 (s, 2H), 6.95–7.25 (m, 3H), 7.25–7.45 (m, 2H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 13.80, 14.32, 14.67, 15.17, 20.87, 23.95, 24.94, 31.52, 56.10, 58.33, 58.71, 60.28, 127.15, 127.79(2C), 130.45(2C), 132.57, 134.24, 134.37, 138.33, 138.97, 139.99, 140.61, 169.43; HRMS calcd for $\text{C}_{25}\text{H}_{33}\text{NO}_2$ 379.2510, found 379.2511.

N-Butyl-5,6-diphenyl-4,7-diethylisoindoline (3r): Colorless oil. NMR yield: 78%. Isolated yield: 60%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.94 (t, $J = 7.5$ Hz, 6H), 1.00 (t, $J = 7.3$ Hz, 3H), 1.45–1.55 (m, 2H), 1.55–1.65 (m, 2H), 2.40 (q, $J = 7.4$ Hz, 4H), 2.70 (t, $J = 7.2$ Hz, 2H), 4.03 (s, 4H), 6.80–7.20 (m, 10H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 14.35, 14.96 (2C), 20.94, 24.68 (2C), 31.60, 56.30, 58.93(2C), 126.19 (2C), 127.51 (4C), 130.86 (4C), 133.94 (2C), 138.71 (2C), 140.50 (2C), 141.40 (2C); HRMS calcd for $\text{C}_{28}\text{H}_{33}\text{N}$ 383.2611, found 383.2614.

N-Butyl-1,2,3,4-tetrahydro-6,7,8-triethyl-5-methylisoquinoline (3s): Colorless oil. NMR yield: 78%. Isolated yield: 65%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.94 (t, $J = 7.4$ Hz, 3H), 1.09 (t, $J = 7.5$ Hz, 3H), 1.11 (t, $J = 7.5$ Hz, 3H), 1.15 (t, $J = 7.5$ Hz, 3H), 1.3–1.48 (m, 2H), 1.5–1.65 (m, 2H), 2.03 (s, 3H), 2.44 (t, $J = 7.2$ Hz, 4H), 2.48–2.58 (m, 4H), 2.61–2.68 (m, 4H), 3.64 (s, 2H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 14.33, 14.74, 15.07, 15.27, 16.43, 21.00, 21.56, 22.26, 22.92, 29.14, 29.99, 51.33, 55.43, 58.74, 131.17, 131.71, 131.73, 135.68, 136.71, 137.98; HRMS calcd for $\text{C}_{20}\text{H}_{33}\text{N}$ 287.2611, found 287.2616.

N-Butyl-1,2,3,4-tetrahydro-6,7-dicarboxymethyl-8-ethyl-5-methylisoquinoline (3t): Yellow oil. NMR yield: 64%. Isolated yield: 55%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.94 (t, $J = 7.3$ Hz, 3H), 1.17 (t, $J = 7.5$ Hz, 3H), 1.25–1.4 (m, 2H), 1.4–1.55 (m, 2H), 2.09 (s, 3H), 2.35 (t, $J = 7.3$ Hz, 3H), 2.40 (s, 3H), 2.59 (q, $J = 7.5$ Hz, 2H), 3.47 (s, 2H), 3.56 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 14.28, 15.01,

16.01, 20.89, 22.81, 28.50, 29.76, 50.19, 51.74 (2C), 54.48, 58.23, 130.50, 131.18, 132.67, 136.06, 136.59, 137.00, 169.21, 169.23; HRMS calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_4$ 347.20947, found 347.2088.

N-Butyl-6,7,8,9-tetraethyl-3-benzoperhydroazepine (3u): Yellow oil. NMR yield: 66%. Isolated yield: 58%. ^1H NMR (C_6D_6 , Me_4Si) δ 0.92 (t, $J = 7.2$ Hz, 3H), 1.09 (t, $J = 7.5$ Hz, 6H), 1.15 (t, $J = 7.5$ Hz, 6H), 1.25–1.40 (m, 2H), 1.4–1.5 (m, 2H), 2.30 (t, $J = 7.3$ Hz, 2H), 2.5–2.55 (m, 4H), 2.64 (q, $J = 7.3$ Hz, 4H), 2.66 (q, $J = 7.4$ Hz, 4H), 2.9–3.0 (m, 4H); ^{13}C NMR (C_6D_6 , Me_4Si) δ 14.34, 16.14 (2C), 16.31 (2C), 21.02, 22.79 (2C), 23.07 (2C), 29.73, 30.97 (2C), 56.05 (2C), 59.08, 136.98 (2C), 137.27 (2C), 139.38 (2C); HRMS calcd for $\text{C}_{22}\text{H}_{37}\text{N}$ 315.29241, found 315.2917.

Representative Procedure from the Preparation of Benzenes from Three Different Alkynes. Formation of 1,2-Dimethyl-3,4-dipropyl-5,6-diphenylbenzene (4a). To solution of diethylzirconocene (1.25 mmol) in THF (5 mL) was added diphenylacetylene (178 mg, 1 mmol), and the reaction mixture was stirred at 0 °C for 3 h. After the addition of 2-butyne (108 mg, 2 mmol), the reaction mixture was warmed to room temperature for 1 h, followed by the removal of the solvent and unreacted 2-butyne. Then fresh THF (10 mL), 4-octyne (165 mg, 1.5 mmol), and $\text{NiBr}_2(\text{PPh}_3)_2$ (0.74 g, 1.0 mmol) were added at room temperature. The mixture was stirred for 1 h, quenched with 3 N HCl, and extracted with hexane. The combined organic extracts were dried (MgSO_4) and concentrated in vacuo. Column chromatography on silica gel (hexane) afforded the title compound as a colorless oil. GC yield: 80%. Isolated yield: 62%. ^1H NMR (CDCl_3 , Me_4Si) δ 0.70 (t, $J = 7.4$ Hz, 3H), 1.08 (t, $J = 7.4$ Hz, 3H), 1.36–1.41 (m, 2H), 1.62–1.66 (m, 2H), 1.98 (s, 3H), 2.32 (s, 3H), 2.34–2.38 (m, 2H), 2.70–2.74 (m, 2H), 6.89–6.97 (m, 6H), 6.98–7.03 (m, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.76, 14.93, 16.34, 18.36, 23.95, 24.85, 32.68, 33.27, 125.47, 125.52, 126.91 (2C), 127.15 (2C), 130.28 (2C), 130.48 (2C), 132.23, 134.18, 136.23, 138.22, 139.45, 139.64, 141.69, 142.02; HRMS calcd for $\text{C}_{26}\text{H}_{30}$ 342.2346, found 342.2345.

1,2-Diethyl-3,4-dipropyl-5,6-diphenylbenzene (4b): White solid. GC yield: 74%. Isolated yield: 60%. ^1H NMR (CDCl_3 , Me_4Si) δ 0.69 (t, $J = 7.4$ Hz, 3H), 0.92 (t, $J = 7.4$ Hz, 3H), 1.09 (t, $J = 7.3$ Hz, 3H), 1.28 (t, $J = 7.3$ Hz, 3H), 1.35–1.37 (m, 2H), 1.64–1.68 (m, 2H), 2.31–2.35 (m, 2H), 2.44 (q, $J = 7.3$ Hz, 2H), 2.65–2.69 (m, 2H), 2.76 (q, $J = 7.3$ Hz, 2H), 6.93–7.00 (m, 6H), 7.01–7.05 (m, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.83, 15.19, 15.68, 15.96, 22.45, 23.46, 24.71, 25.12, 32.14, 33.14, 125.40, 125.42, 126.83 (2C), 126.86 (2C), 130.50 (2C), 130.55 (2C), 136.62, 137.49, 138.12, 139.23, 139.77, 139.90, 141.77 (2C); Anal. Calcd for $\text{C}_{28}\text{H}_{34}$: C, 90.75; H, 9.25. Found: C, 90.68; H, 9.42.

1,2-Dimethyl-3,4-diethyl-5,6-dipropylbenzene (4c): Colorless oil. GC yield: 63%. Isolated yield: 55%. ^1H NMR (CDCl_3 , Me_4Si) δ 1.04 (t, $J = 7.3$ Hz, 3H), 1.05 (t, $J = 7.3$ Hz, 3H), 1.13 (t, $J = 7.5$ Hz, 3H), 1.17 (t, $J = 7.5$ Hz, 3H), 1.47–1.56 (m, 4H), 2.20 (s, 3H), 2.21 (s, 3H), 2.53–2.58 (m, 4H), 2.64 (q, $J = 7.5$ Hz, 2H), 2.68 (q, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.84, 14.89, 15.06, 15.94, 16.13, 16.32, 22.51, 22.93, 23.94, 25.08, 32.22, 32.68, 132.64, 132.78, 136.17, 136.96, 137.30, 137.94. Anal. Calcd for $\text{C}_{18}\text{H}_{30}$: C, 87.73; H, 12.27. Found: C, 87.61; H, 12.41.

1,2-Dimethyl-3,4-diethyl-5,6-diphenylbenzene (4d): Colorless solid. GC yield: 76%. Isolated yield: 58%. ^1H NMR (CDCl_3 , Me_4Si) δ 0.96 (t, $J = 7.4$ Hz, 3H), 1.25 (t, $J = 7.4$ Hz, 3H), 1.99 (s, 3H), 2.34 (s, 3H), 2.46 (q, $J = 7.4$ Hz, 2H), 2.82 (q, $J = 7.4$ Hz, 2H), 6.90–6.92 (m, 2H), 6.96–6.99 (m, 4H), 7.03–7.05 (m, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.84, 15.82, 16.13, 18.34, 22.99, 23.61, 125.48, 125.56, 126.96 (2C), 127.16 (2C), 130.26 (2C), 130.50 (2C), 132.31, 134.15, 137.18, 139.32, 139.37, 139.71, 141.65, 141.98. Anal. Calcd for $\text{C}_{24}\text{H}_{26}$: C, 91.67; H, 8.33. Found: C, 91.45; H, 8.42.

1,2-Dimethyl-3,4-diethyl-5,6-dibutylbenzene (4e): Colorless oil. GC yield: 65%. Isolated yield: 44%. ^1H NMR (CDCl_3 , Me_4Si) δ 0.97 (t, $J = 7.0$ Hz, 3H), 0.98 (t, $J = 7.0$ Hz, 3H), 1.13 (t, $J = 7.4$ Hz, 3H), 1.17 (t, $J = 7.4$ Hz, 3H), 1.45–1.51 (m, 8H), 2.20 (s, 3H), 2.21 (s, 3H), 2.55–2.61 (m, 4H), 2.64 (q, $J = 7.4$ Hz, 2H), 2.68 (q, $J = 7.4$ Hz, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.87, 13.90, 14.85, 15.93, 16.14, 16.30, 22.46, 22.93, 23.47, 23.60, 29.47, 29.98, 32.84, 33.96, 132.60, 132.74, 136.17, 136.99, 137.30, 137.92; HRMS calcd for $\text{C}_{20}\text{H}_{34}$ 274.2659; found 274.2659.

(14) (a) Hopff, H.; Wick, A. K. *Helv. Chim. Acta* **1960**, *43*, 1473–1480. (b) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 27–32.

1-Methyl-3,4-diethyl-5,6-dipropylbenzene (4f): Pale yellow oil. Isolated yield: 43%. ^1H NMR (CDCl_3 , Me_4Si) δ 1.03 (t, $J = 7.5$ Hz, 3H), 1.05 (t, $J = 7.5$ Hz, 3H), 1.14 (t, $J = 7.4$ Hz, 3H), 1.21 (t, $J = 7.4$ Hz, 3H), 1.49–1.53 (m, 4H), 2.27 (s, 3H), 2.51–2.63 (m, 8H), 6.84 (s, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.93, 15.01, 15.63, 15.74, 19.83, 21.83, 23.68, 25.10, 25.57, 31.78, 32.14, 128.46, 133.59, 136.98, 137.56, 138.63, 139.21; HRMS calcd for $\text{C}_{17}\text{H}_{28}$ 232.2190; found 232.2190.

1-Methyl-2,3-diethyl-4,5-dipropylbenzene (4g): Colorless oil. Isolated yield: 50%. ^1H NMR (CDCl_3 , Me_4Si) δ 1.00 (t, $J = 7.3$ Hz, 3H), 1.04 (t, $J = 7.4$ Hz, 3H), 1.13 (t, $J = 7.5$ Hz, 3H), 1.16 (t, $J = 7.5$ Hz, 3H), 1.46–1.53 (m, 2H), 1.56–1.63 (m, 2H), 2.27 (s, 3H), 2.49–2.57 (m, 4H), 2.63 (q, $J = 7.5$ Hz, 2H), 2.65 (q, $J = 7.5$ Hz, 2H), 6.83 (s, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.55, 14.58, 14.95, 15.94, 19.66, 22.14, 22.44, 24.77, 24.87, 31.39, 35.20, 129.20, 133.31, 136.33, 137.99, 138.15, 139.89; HRMS calcd for $\text{C}_{17}\text{H}_{28}$ 232.2190; found 232.2191.

1,2-Dipropyl-4-tert-butyl-5,6-diphenylbenzene (4h) and 1,2-Dipropyl-3-tert-butyl-5,6-diphenylbenzene (4i). Column chromatography afforded **4h** as a colorless liquid (23%), **4i** as a colorless solid (34%), and the mixture of **4h** and **4i** (10%). **4h:** ^1H NMR (CDCl_3 , Me_4Si) δ 0.62 (t, $J = 7.3$ Hz, 3H), 1.03 (t, $J = 7.3$ Hz, 3H), 1.12 (s, 9H), 1.24–1.28 (m, 2H), 1.66–1.71 (m, 2H), 2.17–2.21 (m, 2H), 2.60–2.64 (m, 2H), 6.79–7.07 (m, 10H), 7.34 (s, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.60, 14.73, 24.31, 24.79, 32.63, 32.87 (3C), 35.52, 36.46, 125.25, 125.52, 126.12 (2C), 126.66 (2C), 126.85, 130.54 (2C), 132.24 (2C), 136.21, 138.73, 139.00, 141.69, 142.68, 143.46, 144.58. **4i:** ^1H NMR (CDCl_3 , Me_4Si) δ 0.78 (t, $J = 7.4$ Hz, 3H), 1.13 (t, $J = 7.4$ Hz, 3H), 1.33–1.38 (m, 2H), 1.54 (s, 9H), 1.68–1.74 (m, 2H), 2.55–2.59 (m, 2H), 2.92–2.96 (m, 2H), 7.07–7.19 (m, 10H), 7.33 (s, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.84, 14.93, 24.83, 25.81, 32.36 (3C), 32.41, 33.43, 36.18, 125.56, 125.92, 126.00, 127.21 (2C), 127.28 (2C), 129.88 (2C), 130.87 (2C), 138.79, 138.96, 139.11, 141.15, 141.19, 143.01, 146.52. Anal. Calcd for $\text{C}_{28}\text{H}_{34}$: C, 90.75; H, 9.25. Found: C, 90.86; H, 9.45.

Ethyl 2,4-dimethyl-3-trimethylsilyl-5,6-diethylbenzene carboxylate (4j) and ethyl 2,5-dimethyl-3,4-diethyl-6-trimethylsilylbenzene carboxylate (4k). A 1:1 mixture of **4j** and **4k**. Colorless liquid. Combined GC yield: 50%. Isolated yield 43%. One isomer: ^1H NMR (CDCl_3 , Me_4Si) δ 0.27 (s, 9H), 1.00–1.20 (m, 6H), 1.25–1.40 (m, 3H), 2.15 (s, 3H), 2.37 (s, 3H), 2.45–2.70 (m, 4H), 4.20–4.35 (m, 2H); ^{13}C NMR δ 1.69 (3C), 14.17, 14.31, 15.68, 15.91, 16.30, 21.67, 22.55, 23.97, 60.71, 129.27, 132.07, 133.84, 137.85, 138.71, 141.20. The other isomer: ^1H NMR (CDCl_3 , Me_4Si) δ 0.34 (s, 9H), 1.00–1.20 (m, 6H), 1.25–1.40 (m, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 2.45–2.70 (m, 4H), 4.20–4.35 (m, 2H); ^{13}C NMR δ 4.00 (3C), 14.20, 14.39, 15.75, 16.02, 20.80, 22.37, 22.60, 24.21, 60.68, 129.30, 133.80, 136.73, 137.87, 138.77, 141.44; HRMS calcd for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ 306.2015; found 306.2017.

Ethyl 2-phenyl-3-trimethylsilyl-4-methyl-5,6-dipropylbenzene carboxylate (4l) and ethyl 2-phenyl-3,4-dipropyl-5-methyl-6-trimethylsilylbenzene carboxylate (4m): A 1:1 mixture of **4l** and **4m**. Colorless liquid. Combined GC yield: 45%. Isolated yield 40%. One isomer: ^1H NMR (CDCl_3 , Me_4Si) δ -0.01 (s, 9H), 0.48 (t, $J = 7.1$ Hz, 3H), 0.53 (t, $J = 7.1$ Hz, 3H), 0.70–0.80 (m, 4H), 1.16–1.30 (m, 4H), 2.15 (s, 3H), 2.18–2.31 (m, 4H), 3.35 (q, $J = 7.2$ Hz, 2H), 6.85–6.99 (m, 5H); ^{13}C NMR δ 1.97 (3C), 13.29, 14.70, 14.82, 21.11, 23.34, 24.36, 24.84, 32.80, 60.36, 127.28 (2C), 130.01, 130.09 (2C), 136.82, 137.01, 139.98, 140.18, 140.44, 141.92, 142.41, 170.87. The other isomer: ^1H NMR (CDCl_3 , Me_4Si) δ -0.43 (s, 9H), 0.34–0.39 (m, 6H), 0.60–0.70 (m, 4H), 0.93–1.0 (m, 4H), 1.16–1.30 (m, 2H), 1.95–2.00 (m, 2H), 2.14 (s, 3H), 3.50 (q, $J = 7.1$ Hz, 2H), 6.85–6.99 (m, 5H); ^{13}C NMR δ 2.52 (3C), 13.63, 14.97, 15.07, 21.59, 23.28, 31.68, 32.16, 33.62, 60.36, 126.72 (2C), 127.15, 130.49 (2C), 132.19, 133.55, 134.20, 136.24, 138.31, 138.80, 143.93, 170.57; HRMS calcd for $\text{C}_{25}\text{H}_{36}\text{O}_2\text{Si}$ 396.2483; found 396.2489.

1-Phenyl-2,3,4,5-tetraethyl-6-methylbenzene (5a) and 1-benzyl-2,3,4,5-tetraethylbenzene (6a): A 2.5:1 mixture of **5a** and **6a**. Colorless liquid. Combined isolated yield: 53%. **5a:** ^1H NMR (CDCl_3 , Me_4Si) δ 0.90 (t, $J = 7.3$ Hz, 3H), 1.18 (t, $J = 7.6$ Hz, 3H), 1.22 (t, $J = 7.5$ Hz, 3H), 1.25 (t, $J = 7.4$ Hz, 3H), 1.89 (s, 3H), 2.36 (q, $J = 7.5$ Hz,

2H), 2.70 (q, $J = 7.4$ Hz, 4H), 2.73 (q, $J = 7.5$ Hz, 2H), 7.16–7.18 (m, 2H), 7.29–7.31 (m, 1H), 7.35–7.39 (m, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.59, 15.67, 15.93, 15.96, 17.39, 22.16, 22.31, 22.91, 23.51, 126.14, 127.98 (2C), 129.70 (2C), 132.00, 137.27, 137.77, 138.02, 139.09, 140.50, 142.85. Anal. Calcd for $\text{C}_{21}\text{H}_{28}$: C, 89.94; H, 10.06. Found: C, 90.03; H, 10.16. **6a:** ^1H NMR (CDCl_3 , Me_4Si) δ 1.08 (t, $J = 7.5$ Hz, 3H), 1.15–1.20 (m, 9H), 2.57–2.64 (m, 4H), 2.67–2.70 (m, 4H), 3.99 (s, 2H), 6.79 (s, 1H), 7.12–7.18 (m, 3H), 7.24–7.27 (m, 2H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 15.25, 15.59 (2C), 15.97, 21.76, 21.98, 22.18, 25.56, 39.18, 125.69, 128.24 (2C), 128.72 (2C), 128.75 (2C), 135.83, 138.09, 138.12, 140.18, 141.59.

5,6,7,8-Tetrahydro-2-pentyl-1,4-diethylnaphthalene (5b) and 5,6,7,8-tetrahydro-2-hexyl-1,4-diethylnaphthalene (6b): A 1:1 mixture of **5b** and **6b**. Colorless liquid. Combined isolated yield: 62%. **5b:** ^1H NMR (CDCl_3 , Me_4Si) δ 0.92 (t, $J = 7.1$ Hz, 3H), 1.09–1.15 (m, 6H), 1.38–1.48 (m, 6H), 1.75–1.78 (m, 4H), 2.26 (s, 3H), 2.56–2.66 (m, 6H), 2.71–2.75 (m, 4H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.45, 14.09, 14.59, 15.07, 21.93, 22.36, 22.53, 23.29, 23.31, 27.11, 27.20, 30.00, 30.38, 32.69, 131.38, 132.63, 132.66, 136.73, 137.70, 138.51. **6b:** ^1H NMR (CDCl_3 , Me_4Si) δ 0.90 (t, $J = 6.8$ Hz, 3H), 1.12 (t, $J = 7.3$ Hz, 3H), 1.20 (t, $J = 7.5$ Hz, 3H), 1.30–1.34 (m, 4H), 1.37–1.42 (m, 2H), 1.53–1.61 (m, 2H), 1.75–1.78 (m, 4H), 2.52–2.58 (m, 4H), 2.61 (q, $J = 7.5$ Hz, 2H), 2.67–2.70 (m, 2H), 2.74–2.77 (m, 2H), 6.85 (s, 1H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.12, 14.28, 14.42, 21.26, 22.69, 22.93, 23.30, 25.50, 26.49, 26.97, 29.76, 31.82, 32.04, 33.06, 126.42, 132.62, 134.95, 137.47, 137.65, 139.36; HRMS calcd for $\text{C}_{20}\text{H}_{32}$ 272.2502; found 272.2498.

X-ray Crystallographic Analysis of 1,2-dipropyl-3-tert-butyl-5,6-diphenylbenzene (4i). A single crystal of approximate dimensions of $0.24 \times 0.26 \times 0.40$ mm³ was cut out from the large crystal, placed on a glass fiber with epoxy resin, and mounted on an Enraf-Nonius CAD4 diffractometer. The cell parameters were obtained from the least-squares refinement of the setting angles of 25 carefully centered reflections. Crystallographic data: fw = 370.58, monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$, $a = 10.125(2)$ Å, $b = 24.829(2)$ Å, $c = 10.138(2)$ Å, $\beta = 114.56(2)^\circ$, $V = 2318.0(8)$ Å³, $D_x = 1.06$ g cm⁻³, and $\mu(\text{Cu K}\alpha) = 4.1$ cm⁻¹. The diffraction data were collected at room temperature by using graphite-monochromated Cu K α radiation ($\lambda = 1.54184$ Å). A total of 4984 reflections ($2\theta = 148.52^\circ$) were measured, of which 3658 reflections were unique with $|F_o| > 3\sigma(|F_o|)$. The structure was solved by direct methods (SHELX-86)¹⁵ and subsequently completed by Fourier recycling. All of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques using the Xtal 3.2¹⁶ crystallographic software package. All of the hydrogen atoms were located at the calculated positions with isotropic displacement parameters of their parent carbon atoms. Refinement of positional and thermal parameters converged at $R = 0.053$, $R_w = 0.068$, and GOF = 2.66.

Reaction of Tetraphenylzirconacyclopentadiene with NiCl₂(dppe). Formation of Tetraphenylnickelacyclopentadiene and Cp₂ZrCl₂. To a solution of tetraphenylzirconacyclopentadiene **1b** (2.0 mmol) in 20 mL THF was added NiCl₂(dppe) (2.0 mmol, 1.06 g). The mixture was refluxed under N₂ for 24 h, and a brick-red solid precipitated along with the formation of Cp₂ZrCl₂ in 94% NMR yield. After filtration the solid was washed several times with dry diethyl ether until the color of the filtrate disappeared. The brick-red solid **10b** was dried under vacuo to give the product in 78% (1.26 g) yield. IR $\nu_{\text{Ni-C=C}}$ 1585 cm⁻¹; MS m/z 813. The hydrolysis of this brick-red solid **10b** by acetic acid resulted in the formation of 1,2,3,4-tetraphenyl-1,3-butadiene in quantitative GC yield.

Reaction of Tetraphenylnickelacyclopentadiene 10b with 4-Octyne. Formation of 1,2-Dipropyl-3,4,5,6-tetraphenylbenzene. To a mixture of 20 mL of toluene and **10b** prepared from 1.0 mmol of NiCl₂(dppe) as described above was added 4-octyne (4.0 mmol, 0.58 mL). After refluxing in toluene for 12 h, the resulting mixture was diluted with 100 mL of a 1/1 (v/v) mixture of benzene and hexane and then

(15) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Determination*; University of Göttingen: Germany, 1986.

(16) Hall, S. R.; Flack, H. D.; Stewart, J. M. *Xtal 3.2, Program for X-ray Crystal Structure Analysis*; Universities of Western Australia, Geneva, and Maryland, 1992.

filtrated. Evaporation and column chromatography on silica gel (benzene/hexane = 1/3) afforded the product as a white solid in 54% yield. ^1H NMR (CDCl_3 , Me_4Si) δ 0.75 (t, $J = 7.2$ Hz, 6H), 1.43–1.49 (m, 4H), 2.49–2.53 (m, 4H), 6.71–6.75 (m, 10H), 7.04–7.22 (m, 10H); ^{13}C NMR (CDCl_3 , Me_4Si) δ 14.86, 24.67, 33.16, 124.81, 125.75, 126.26, 127.04, 130.59, 131.19, 138.28, 138.79, 140.94, 140.96, 141.27; HRMS calcd for $\text{C}_{36}\text{H}_{34}$ 466.2661; found 466.2675.

Acknowledgment. We thank the Inoue Foundation for an Inoue fellowship to support F.-Y. Tsai. A part of this work was

supported by the Ministry of Education, Science, Sport and Culture, Japan (09440212).

Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters and bond lengths and angles for **4i** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA990750C