Review

Development of New Cycloaddition Reactions Based on the Unique Reactivity of Unsaturated Hydrocarbons

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Received April 4, 2005

We discovered that the reactivity of some conjugated and electron-deficient hydrocarbons was quite different in the presence of transition metal catalysts. In this review we report our development and applications of the highly selective palladium and nickel-catalyzed cycloaddition reactions of unsaturated hydrocarbons such as conjugated enynes, electron-deficient allenes, and electron-deficient methylenecyclopropanes. Some homocoupling reactions as well as co-cyclization reactions were described. The efficient synthesis of 4—7 membered carbocycles was achieved.

Key words   cycloaddition; transition metal; catalyst; unsaturated hydrocarbon; carbon–carbon bond

1. Introduction

The rapid development of various transition-metal catalyzed reactions induced the innovation of organic synthesis. A large number of unique and efficient reactions developed by organometallic chemists has been widely used for the synthesis of various organic compounds such as drugs, natural products, and functionalized materials. The catalytic coupling reactions between unsaturated hydrocarbons such as cyclotrimerization of alkynes[1—7] and Diels–Alder-type reactions[3,4] are particularly attractive, since complicated molecules are obtained in one step from simple unsaturated hydrocarbons, which are usually less reactive compared to compounds bearing leaving groups such as a halogen atom (Chart 1). The reactions proceed with high atom economy[8]: the product incorporates all of the atoms of the substrates and no unwanted products (such as inorganic salts) are produced, which is another attractive feature. On the other hand, the selective formation of the desired products is rather difficult, and the development of a new and selective reaction of this type is highly desirable.

Our approach for the development of new cycloaddition reactions is based on the serendipitous finding that the reactivity of some conjugated and electron-deficient hydrocarbons was quite different in the presence of transition metal catalysts. In this review we report our development and ap-

plications of the highly selective palladium and nickel-catalyzed cycloaddition reactions of unsaturated hydrocarbons.

2. Palladium-Catalyzed Cyclodimerization of Conjugated Enynes

The construction of the benzene ring by the transition metal-catalyzed cyclotrimerization of alkynes is a very useful approach for the synthesis of benzene derivatives.[1—7] Though conjugated enynes were considered as substituted alkynes ("vinylalkynes") and some nickel-catalyzed cyclotrimerizations have been reported,[9] the products of the palladium-catalyzed reactions of some enynes turned out to be quite different. The highly selective "cyclodimerization" of the enynes proceeded, and the formation of polysubstituted benzenes was observed (Chart 2). Pd(0) complexes, typically Pd(PPh$_3$)$_4$, were good catalysts for the reaction. The results of the reactions of 2-substituted enynes were summarized in Table 1.[10]

The wide applicability of this reaction has been demonstrated by the synthesis of various polysubstituted benzenes. For example, cyclophanes were prepared by the intramolecular cyclization of bisenynes (Chart 3).[10—13] The reactivity of ethoxycarbonylenynes was much higher compared to alkylenynes, and some cyclodimerization reactions proceeded at rt (Table 2). (*Z*)-Enynes were generally more reactive compared to (*E*)-enynes (Table 2, entries 1—2). Though the reactivity of disubstituted enynes was generally low and

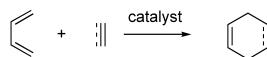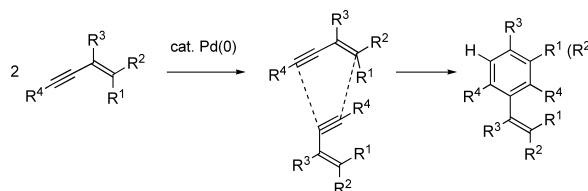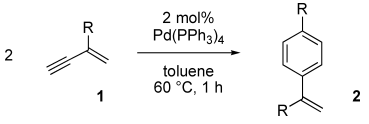Cyclotrimerization of Alkynes
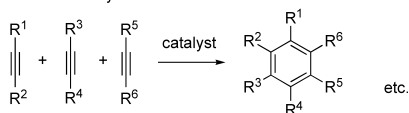
Diels-Alder-type Reaction

Chart 1

Chart 2

the benzannulation did not proceed, the reaction proceeded when an electron-withdrawing group was present (Table 2, entries 4—7).[14,15] The difference in the reactivity has been utilized for the synthesis of polysubstituted benzenes by the cross-coupling reactions between two different enynes (Chart 4).[16] A selective intramolecular reaction was also carried out (Chart 5). This reaction has been applied to the synthesis of **8**, one of the phthalides, some of which are known as biologically active natural products (Chart 6).[17] We also carried out this reaction in fluorous biphasic system in the presence of perfluoro-tagged palladium catalyst (Chart 7). The benzannulation proceeded when we carried out the reaction of **9** in a

mixture of heptane and hexafluoropropene trimer. On cooling, the perfluoro-tagged palladium catalyst and the product **10** could be recovered in the fluorous phase and the heptane
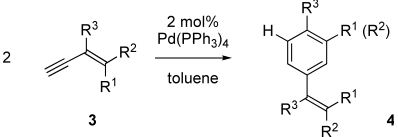
Chart 3

Table 1. Palladium-Catalyzed *homo*-Benzannulation of 2-Substituted Enynes

Entry	Enyne	R	Yield of **2** (%)
1	**1a**	n-C$_6$H$_{13}$	77
2	**1b**[a]	CH$_3$	70
3	**1c**	(CH$_3$)$_2$CH(OH)(CH$_2$)$_2$	81
4	**1d**	CH$_3$CO(CH$_2$)$_2$	82

a) Compound **1b** (2 mmol) reacted in the presence of 1 mol% Pd catalyst.

Chart 4

Chart 5

Table 2. Palladium-Catalyzed *homo*-Benzannulation of Electron-Deficient Enynes

Entry	Enyne	R^1	R^2	R^3	Temp. (°C)	Time (h)	Yield of **4** (%)
1	**3a**	COOEt	H	H	rt	2	88
2	**3b**	H	COOEt	H	80	2	43
3	**3c**	CONMe$_2$	H	H	45	4	62
4	**3d**	COOEt	H	n-C$_6$H$_{13}$	80	2	73
5	**3e**	H	COOEt	n-C$_6$H$_{13}$	80	3	38
6	**3f**	CN	H	n-C$_5$H$_{11}$	80	1.5	84
7	**3g**	H	CN	n-C$_5$H$_{11}$	80	5	53
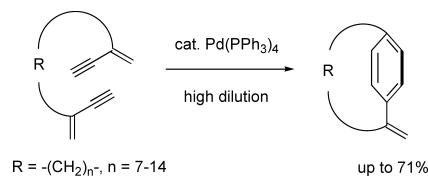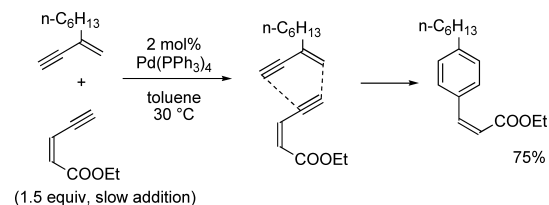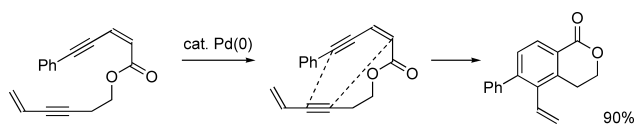
Shinichi Saito was born in Japan in 1968. He studied at Tokyo University, where he obtained his B.Sc. degree in 1990 and Ph.D. degree in 1995 under the supervision of Professor Koichi Shudo. In 1994, he had a chance to study at the University of Utah as a Nagai Foundation Fellow under the supervision of Professor Peter J. Stang. After he spent one year as a postdoctoral fellow under the supervision of Professor Yoshinori Yamamoto at Tohoku University, he moved to Toyama Medical and Pharmaceutical University and joined Professor Toru Koizumi's group as an Assistant Professor. In 1998, he returned to Tohoku University and joined Professor Yamamoto's group as an Assistant Professor. In 2001, he moved to Dr. Yasuo Wakatsuki's group as a RIKEN Special Researcher for Basic Science Program. One year later, he was appointed as a lecturer and became a primary investigator in Tokyo University of Science, where he was promoted to Associate Professor in 2005. He has received The Pharmaceutical Society of Japan Award for Young Scientists in 2005. His current research interests are primarily directed toward the development of novel transition-metal catalyzed reactions and their applications.
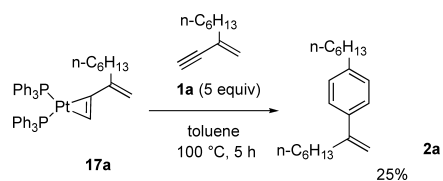
Shinichi Saito

Chart 6

Chart 9

Chart 7
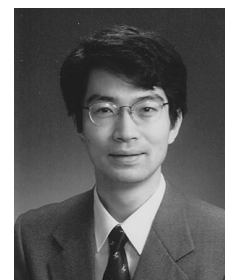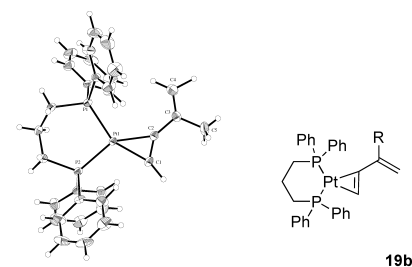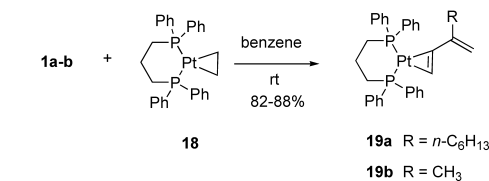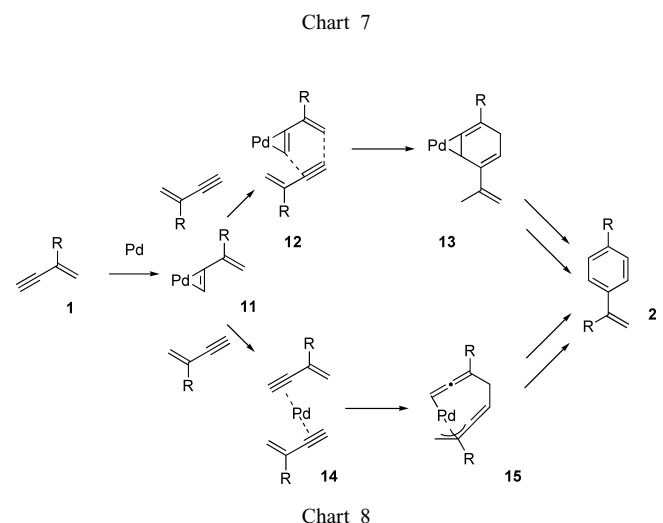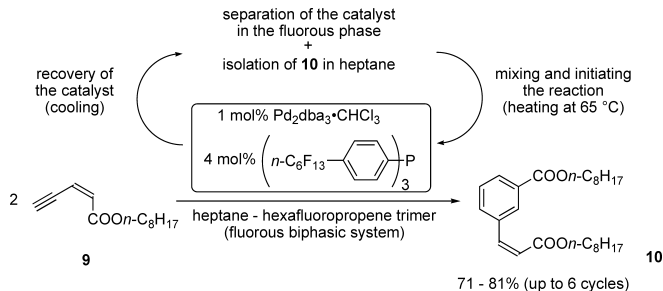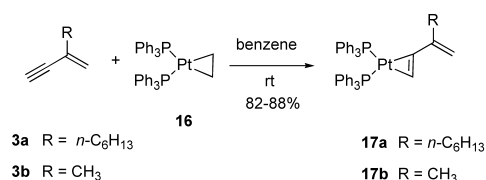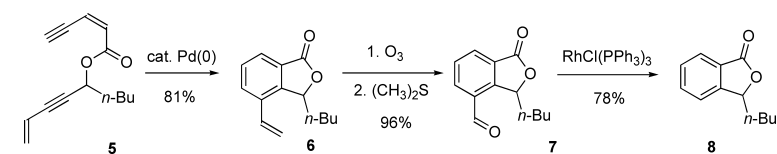
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Fig. 1.   X-Ray Structure of a Pt-Enyne Complex **19b**

Chart 8

Chart 10

phase, respectively. The palladium catalyst could be reused easily.[18]

At present the mechanism of the reaction is unclear, and a possible mechanism is shown in Chart 8. Thus, the enyne **1** might react with the Pd(0) complex and a Pd(0)-enyne complex **11** might be generated. A Diels–Alder-type reaction may proceed and complex **13** might be formed. The hydride shift and reductive elimination of the Pd species might follow, and the final product **2** might be isolated. Alternatively, a palladacycle **15** could be postulated as an intermediate of this reaction. In order to obtain supporting evidences for the mechanism postulated in Chart 8, we prepared a Pt-enyne π complexes **17a, b** and **19a, b** by the reaction of Pt-ethylene complexes **16**, **18** with the corresponding enynes (Chart 9).[19] These complexes correspond to the platinum analogue of the Pd intermediate **11**, and we confirmed the structure of **19b** by an X-ray crystallographic analysis (Fig 1). Since complex **17a** reacted with enyne to give **2a**, we assume that a Pd-enyne π complex is formed as an intermediate in the benzannulation reaction (Chart 10).[19] A recent interesting study reported by Nakao, Shirakawa, Hiyama, and coworkers showed that a stannylative benzannulation occurred by the Pd-catalyzed reaction of enynes (or enynes and diynes) with hexabutyldistannoxane (Chart 11).[20] Since it has been postulated that the cyclic allene (1,2,4-cyclohexatriene) was converted
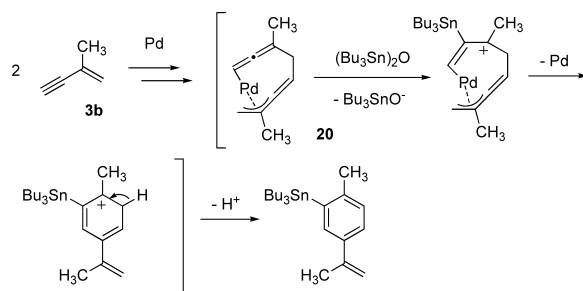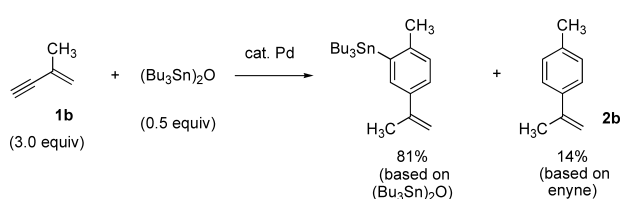
Chart 11

Chart 12

to the benzene ring or reacted as a nucleophile,[21,22] their results (stannylative benzannulation), combined with our results (benzannulation), might indicate the intermediacy of a strained allene such as **20** (Chart 12).

The reaction was further expanded by Gevorgyan, Yamamoto, and co-workers to the corss-benzannulation reaction between conjugated enynes and diynes. The scope and limitation of these reactions have been summarized as reviews.[1,23—25]

3. Nickel-Catalyzed Cyclodimerization of Electron-Deficient Enynes

While the enhanced reactivity of some electron-deficient enynes such as ethoxycarbonylenynes has been utilized for the synthesis of various benzene derivatives (*vide supra*), we observed the formation of completely different cyclodimer in the reactions of some electron-deficient enynes. For example, the Pd-catalyzed reaction of perfluoroalkylenyne **21a** gave **22a**, along with the expected benzene derivative **23a** (Chart 13). We turned our attention to the screening of the reaction condition which selectively gave the bicyclic product **22a**. Since the formation of an analogous cyclobutane derivative **24** has been reported in the Ni-catalyzed reactions of 1,3-butadiene (Chart 14),[26] we carried out the reaction in the presence of a Ni(0) catalyst and the selective formation of **22a** was achieved (Chart 15).[27] A series of electron-deficient enynes was used as the substrates for the reaction and the results were summarized in Table 3.[14,15,27] Thus, 2-perfluoroalkylenynes generally gave the corresponding bicyclic

compounds in good to high yields in the presence of Ni(PPh$_3$)$_4$ at rt (entries 1, 3, 4), and a difluoroenyne **21d** gave **22d** in 27% yield (entry 5). Unfortunately, the reaction did not proceed efficiently (or selectively) when other electron-deficient enynes such as **21e, f** were employed: the formation of a complex mixture was generally observed when Ni(PPh$_3$)$_4$ was used, and compound **23e** (or **23f**) was isolated as the major product when Pd(PPh$_3$)$_4$ was selected as the catalyst (entries 6—9). The presence of an electron-withdrawing group is essential for the formation of the bicyclic compound, and the attempted Ni(0)-catalyzed reaction of a 2-alkylenyne was unsuccessful, providing a complex mixture of oligomeric compounds (entry 10). We also carried out the nickel-catalyzed reactions of 1-perfluoroalkyl- and 1-cyanoenynes. The cyclotrimerization proceeded selectively, and the formation of the benzene derivatives was observed (Chart 16).[28]

The formation of **22** might proceed as shown in Chart 17. Nickelacyclopentadiene **26** (or **27**) is a generally accepted intermediate in the cyclotrimerization of alkynes, and a similar
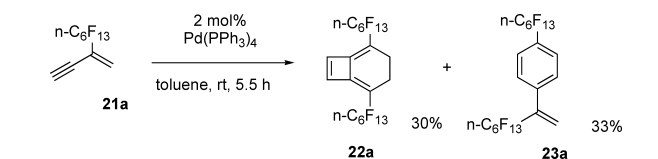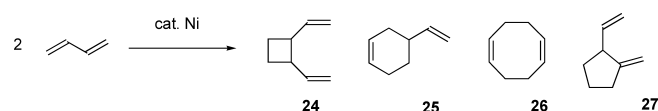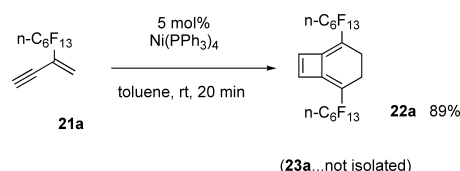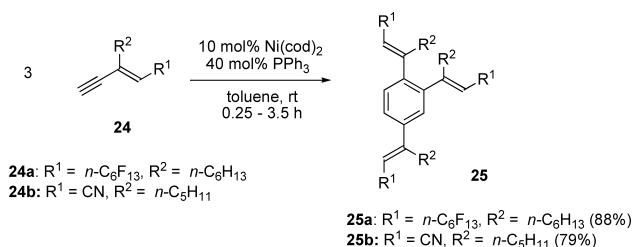
Chart 15

Chart 13

Chart 14

Chart 16

Table 3. Palladium and Nickel-Catalyzed Cyclodimerization of Electron-Deficient Enynes

Entry	Enyne	R^1	R^2	R^4	Catalyst[a]	Time (h)	Yield of **22** (%)	Yield of **23** (%)
1	**21a**	H	n-C$_6$F$_{13}$	H	Ni(PPh$_3$)$_4$[b]	0.33	88	0
2	**21a**	H	n-C$_6$F$_{13}$	H	Pd(PPh$_3$)$_4$	5.5	33	30
3	**21b**	H	PhCF$_2$	H	Ni(PPh$_3$)$_4$	0.33	55	0
4	**21c**	H	n-C$_5$H$_{11}$CF$_2$	H	Ni(PPh$_3$)$_4$	0.83[c]	52	0
5	**21d**	F	n-C$_9$H$_{19}$	H	Ni(PPh$_3$)$_4$	20	27	0
6	**21e**	H	CN	n-C$_6$H$_{13}$	Ni(PPh$_3$)$_4$	—[d]	—[d]	—[d]
7	**21e**	H	CN	n-C$_6$H$_{13}$	Pd(PPh$_3$)$_4$[e]	16	29	39
8	**21f**	H	COOMe	n-C$_6$H$_{13}$	Ni(PPh$_3$)$_4$	—[d]	—[d]	—[d]
9	**21f**	H	COOMe	n-C$_6$H$_{13}$	Pd(PPh$_3$)$_4$[e]	5[f]	0	68
10	**3b**	H	n-C$_6$H$_{13}$	H	Ni(PPh$_3$)$_4$	—[d]	—[d]	—[d]

a) Ni(PPh$_3$)$_4$ was prepared *in situ* by the reaction of Ni(cod)$_2$ and PPh$_3$.   *b*) The reaction was carried out in the presence of 5 mol% of the catalyst.   *c*) A solution of **21c** was added dropwise to a solution of the catalyst for 30 min and stirred for 20 min at 0 °C.   *d*) A complex mixture was formed immediately.   *e*) The reaction was carried out in the presence of 2 mol% of the catalyst.   *f*) The reaction was carried out at 30 °C.

Chart 17

Chart 18

Table 4.   Nickel-Catalyzed [2+2] Cycloaddition of Electron-Deficient Allenes

Entry	Allene	EWG	Temp. (°C)	Time (h)	Yield of 30 (%)
1	29a	n-C$_6$F$_{13}$	rt	0.5	79
2	29b	C$_6$F$_5$	rt	0.5	81
3	29c	COOEt	−10-−15	0.5	71
4[a]	29d	CON(Me)Ph	0	3	66
5	29e	COEt	−10-−15	3[b]	34
6	29f	COPh	−10-−15	1.5[b]	36
7	29g	SO$_2$Ph	rt	1.5[b]	36

a) The reaction was carried out in the presence of Ni(cod)$_2$ (10 mol%) and PPh$_3$ (20 mol%).   *b)* A solution of allene was slowly added to a solution of the Ni catalyst.
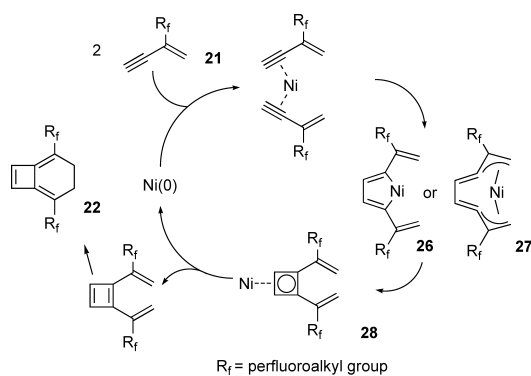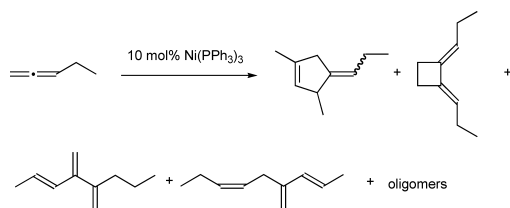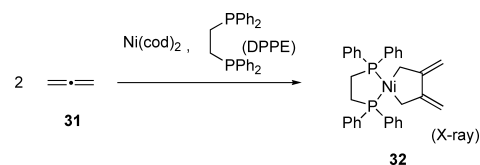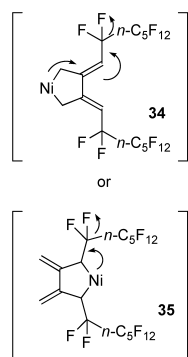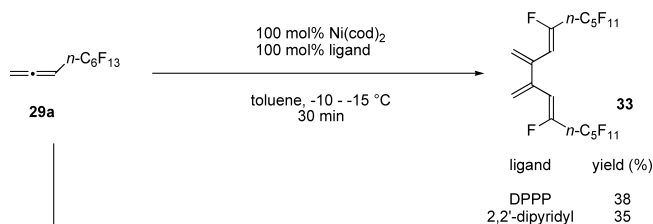

Chart 19

Chart 20

nickelacycle would be generated. Though the insertion of another reactant usually follows, the reductive elimination of the nickel species would proceed in this reaction, providing the cyclobutadiene complex **28** as another intermediate.[29] The further isomerization of **28** should lead to the formation of **22**. In the reaction of 1-perfluoroalkylenynes, the reductive elimination of Ni species from the corresponding nickelacyclopentadiene is slow, and the insertion of another enyne to **26** (or **27**) would proceed, leading to the formation of the benzene derivatives.

4.   Nickel-Catalyzed Cyclodimerization of Electron-Deficient Allenes

The observed dramatic substituent effects on the mode of the reaction and the reactivity of conjugated enynes led us to consider the effect of substituents on the reactions of other unsaturated hydrocarbons. The nickel-catalyzed reaction of allenes has been extensively studied by Pasto *et al.* They carried out the nickel-catalyzed reactions of alkylallenes and observed the formation of a complex mixture of dimers, trimers, and oligomers (Chart 18).[30,31] To the best of our knowledge, only one example has been reported for the selective cyclodimerization of a substituted allene.[32] We carried out the reactions of electron-deficient allenes and observed the selective formation of the [2+2] cycloadduct. Thus, perfluorohexylallene cyclodimerized in the presence of Ni(cod)$_2$-PPh$_3$ and compound **30** was isolated in 79% yield.[33] The scope of this reaction was very wide, and other electron-deficient allenes gave the corresponding cyclodimers (Table 4).

Though the attempted isolation of an intermediate of the reaction was unsuccessful, the result of some stoichiometric reactions indicated the formation of a nickelacyclopentane as an intermediate of the reaction. Jolly and coworkers reported the formation of a nickelacycle **32** by the reaction of 2 eq of allene (1,2-propadiene) **31** with 1 equiv of Ni(0)-dppe complex, and the structure has been confirmed by an X-ray crys-

tallographic analysis (Chart 19).[34] We carried out the reaction of an electron-deficient allene **29a** in the presence of Ni(cod)$_2$-dppe and the reaction did not proceed catalytically. Instead, a stoichiometric reaction proceeded and the formation of a dimeric compound (**33**) was observed (Chart 20).[33] The formation of **33** could be explained by postulating a nickelacyclopentane such as **34** or **35** as the intermediate of this reaction.

The proposed mechanism of this reaction is summarized in Chart 21. A nickelacyclopentane **36** would be generated by the reaction of Ni(0) species with 2 eq of allenes. The complex may further interact with another allene molecule to
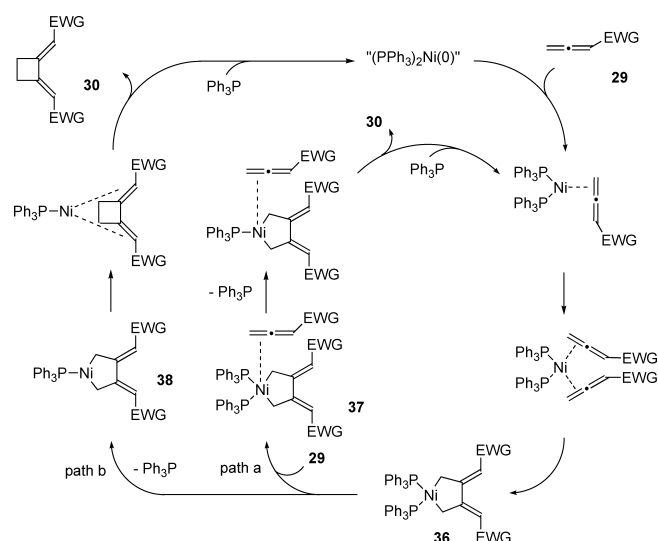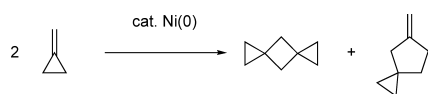
Chart 21

Table 5. Nickel-Catalyzed Cyclodimerization of Ethyl Cyclopropylideneacetate **39**

Entry	Ligand	Time (h)	Yield (%)			
			40	**41**	**42**	**43**
1	PPh$_3$	2	52	28	—	—
2	PPh$_3$	1[a]	0	74	—	—
3[b]	P(o-tol)$_3$	0.25	8	32	20	9
4[b]	—	42	2	6	21	2

a) The reaction was carried out at 80 °C. *b*) Yields determined by NMR.

Chart 22

Chart 23

give complex **37**, which would induce the dissociation of PPh$_3$, followed by the reductive elimination (path a). Since the catalytic reaction did not proceed when a bidentate ligand was bound to the nickel atom, we assume that the dissociation of the ligand is essential for the catalytic reaction to proceed. Alternatively, the simple dissociation of PPh$_3$ from **36** might take place, followed by the reductive elimination (path b). The electron-withdrawing group would enhance the reductive elimination of the Ni(0) species from the intermediates such as **37** or **38**.[35]

5. Nickel-Catalyzed Cyclodimerization of Ethyl Cyclopropylideneacetates

Methylenecyclopropanes are strained unsaturated hydrocarbons and the cleavage of the C–C σ bond and/or the addition of various compounds to the C=C double bond is frequently observed in the presence of a transition metal catalyst. While the unsubstituted methylenecyclopropane cyclodimerized in the presence of a Ni catalyst (Chart 22),[36—39] few examples have been reported for the cyclodimerization of substituted methylenecyclopropanes.[40—42]

We carried out the reaction of an electron-deficient methylenecyclopropane **39** (ethyl cyclopropylideneacetate) in the presence of Ni(cod)$_2$-PPh$_3$ and observed the formation of cyclodimers such as **40**—**43** (Table 5).[43] The reactivity of **39** was significantly higher than that of other methylenecyclopropanes: the Ni-catalyzed reaction of an alkylidenecyclopropane **44** was very sluggish, and the formation of a complex mixture was observed when the reaction was carried out at higher temperature (Chart 23).[43,44] The assumed mechanism of this reaction was shown in Chart 24. Thus, the Ni species would react with **39** and a nickelacyclopentene **46** would be generated. The cyclopropylmethyl-butenyl rearrangement[36] of **46** could occur, leading to the formation of the six-membered nickelacycle **47** (path a). Alternatively, the
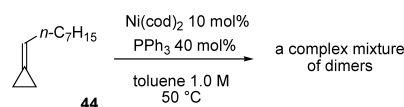
formation of **47** might be explained in terms of the formation of a nickelacyclobutane **45**, followed by the insertion of **39** (path b). The reductive elimination of the Ni species would follow, and compound **40** (or **41**) would be isolated as the product. The further rearrangement of **47** might also proceed, and the formation of **42** (or **43**) could be observed in this case (path c). The higher reactivity of **39** compared to alkylidenecyclopropanes could be explained in terms of the strong coordinating ability of **39** with the Ni(0) species, or the increased polarity of the cyclopropyl C–C bond.

6. Nickel-Catalyzed Cycloaddition of Electron-Deficient Methylenecyclopropanes with Alkynes

The Pd or Ni-catalyzed cross coupling reaction of methylenecyclopropanes with alkenes or alkynes is a well-known reaction. The [3+2] cycloaddition generally proceeded, and the formation the cyclopentane derivative was observed (Chart 25).[40—42] The high and unique reactivity of **39** prompted us to investigate the cross coupling reaction of **39** with various unsaturated hydrocarbons. The Ni-catalyzed reaction of **39** with alkenes gave the expected [3+2] cycloadduct in good yields (Chart 26).[43] On the other hand, the reaction of **39** with alkynes gave the unexpected [3+2+2] cycloadduct.[45] The results of the reactions of **39** with various alkynes were summarized in Table 6. Best results are obtained when bulky terminal alkynes were used as the substrates: the presence of a bulky substituent such as trimethylsilyl group was a requirement for the regioselective formation of **50**, and a mixture of isomeric compounds was observed when an *n*-alkyl group (*n*-hexyl group) was bound to the alkyne (entry 7). The reaction of ketone **51** also proceeded and a cycloheptatriene **52** was isolated (Chart 27).[44] The formation of **52** could be explained in terms of the isomerization of the initially formed cycloheptadiene **53**.

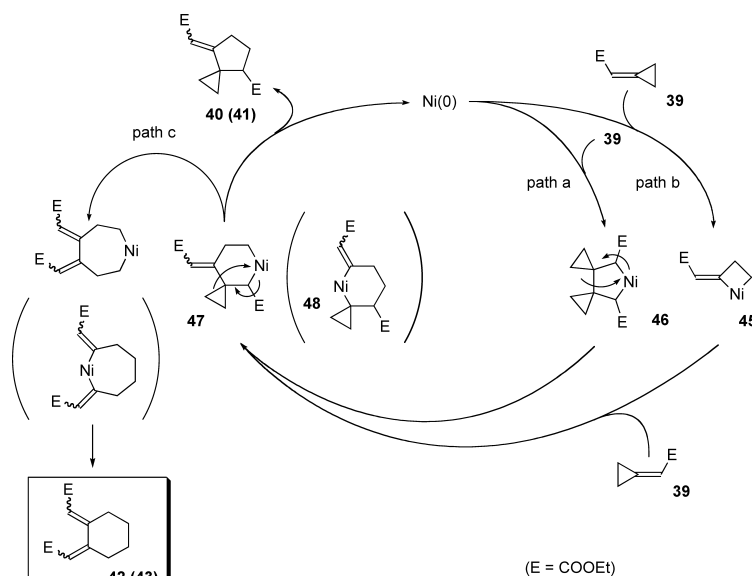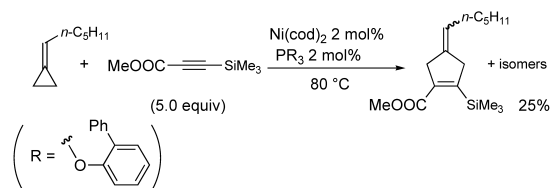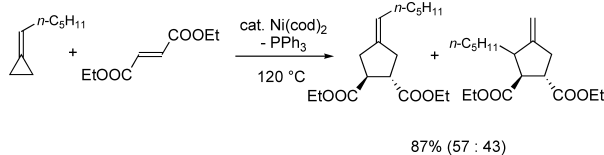Though the mechanism of this reaction is unclear, we as-

Chart 24

87% (57 : 43)

(5.0 equiv)   25%

$\left(R = \begin{array}{c} Ph \\ O \end{array} \right)$

Chart 25

39   (5.0 equiv)   71%
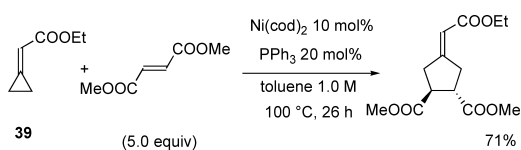
Chart 26

51 (1 mmol)   49c (5 mmol)
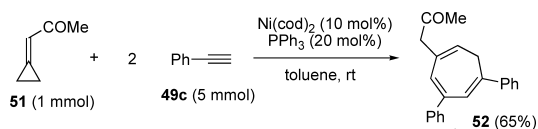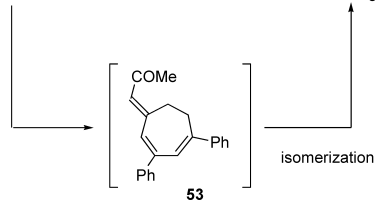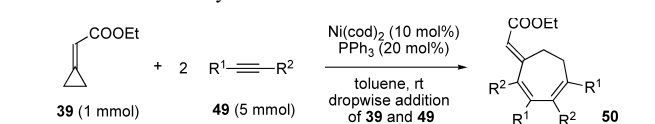

isomerization

53

Chart 27

Table 6. Nickel-Catalyzed [3+2+2] Cocyclization of Ethyl Cyclopropyli-
deneacetate 39 with Alkynes

Entry	Alkyne	R^1	R^1	Yield of 50 (%)
1	49a	$(CH_3)_3Si$	H	70
2	49b	$(CH_3)_3C$	H	89
3	49c	Ph	H	74
4	49d	$4\text{-}MeOC_6H_4$	H	72
5	49e	$4\text{-}FC_6H_4$	H	59
6	49f	$HO(CH_3)_2C$	H	56
$7^{a)}$	49g	$n\text{-}C_6H_{13}$	H	—
$8^{b)}$	49h	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	31

a) An inseparable mixture of cycloheptadiene derivatives, together with benzene de-
rivatives, was isolated.   *b*) To a mixture of Ni catalyst and 49h in toluene was added
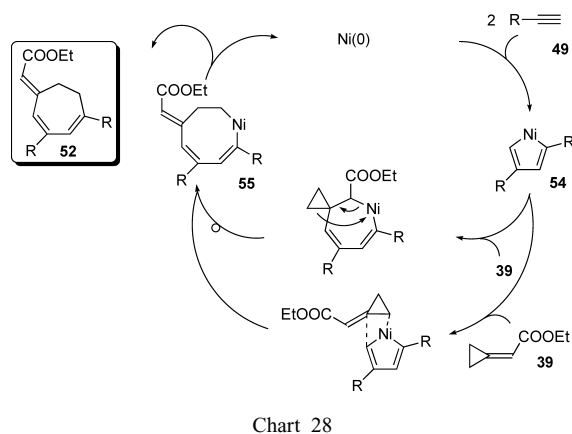dropwise a solution of 1 in toluene for 5 h.

Chart 28

sume that a nickelacyclopentadiene 54 is initially formed by
the reaction of alkynes with the Ni(0) species (Chart 28).[46]
The addition of the third alkyne to 54, which would usually

proceed in the cyclotrimerization of alkynes, is suppressed
probably due to the large steric hindrance, and the addition of
39 would selectively proceed. The product would be formed
by the reductive elimination of the Ni(0) species from the
eight-membered nickelacycle 55. Currently we are applying

this reaction to the synthesis of various cycloheptadienes.

7.   Conclusion

We developed a series of new and selective reactions of unsaturated hydrocarbons catalyzed by Pd or Ni complexes. The initial serendipitous findings were followed by the systematic explorations, which led us to the discovery of the importance of electronic effect on the reactivity. The discovered new reactions provided new pathways for the synthesis of complicated molecules, which are otherwise difficult to synthesize, in short steps and highly atom-economical manners.

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