

Carbon–Carbon Bond Formation Involving Reactions of Alkynes with Group 9 Metals (Ir, Rh, Co): Preparation of Conjugated Olefins[†]

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Received September 29, 2000

ABSTRACT

Stable alkynyl complexes of iridium(III) ($L_n\text{Ir}\equiv\text{R}$) that are prepared from the reactions of terminal alkynes readily undergo the intramolecular C–C bond-forming reactions between the alkynyl and adjacent hydrocarbyl ligands to yield conjugated olefins. These reactions are initiated by electrophiles (H^+ , Me^+) that attack the β carbon of the alkynyl ligand to increase the electrophilicity of the α carbon of the alkynyl ligand. The C–C bond is then formed between the α carbons of the alkynyl and adjacent hydrocarbyl ligands.

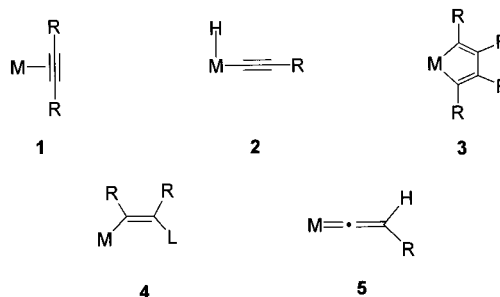
Introduction

Carbon–carbon bond formation is probably the most useful transformation in synthetic chemistry. Transition-metal-mediated C–C bond-forming reactions involving alkynes have been extensively investigated on the basis of the fact that they produce a variety of interesting organic compounds, such as conjugated olefins,¹ unsaturated cyclic hydrocarbons,² α,β -unsaturated aldehydes,³ unsaturated cyclic ketones,⁴ enynes,⁵ alkyne polymers,⁶ arenes,⁷ heteroarenes,⁸ and others.⁹

Reactions of alkynes with transition metals and the related reactions of metal complexes containing vinyli-

dene, allenylidene, allenyl, and propargyl ligands have been summarized recently in excellent reviews that cover the relevant reactions with mostly group 4, 8, and 10 metals.¹⁰ This account summarizes the C–C bond formation mediated by iridium-alkynyls, mostly based on our recent works.

Alkynes react with transition metals to yield stable complexes in several ways: (i) reactions of internal alkynes mostly yield π -alkyne complexes (**1**); (ii) those of terminal alkynes frequently yield alkynyl complexes (**2**); (iii) metallocyclopentadienes (**3**) are obtained from the reactions of internal and terminal alkynes, depending on the metals and the alkyne substituents; and (iv) alkynes are inserted into the M–L (L: $\text{C}=\text{C}=\text{CR}'_2$,^{11a} $\text{C}\equiv\text{C}-\text{R}'$,^{11b} H,¹² Cl,¹³ SiR'_3 ,¹⁴ NR'_3 ,^{1b,8b,15,16c} PR'_3 ,¹⁶ and AsR'_3 ^{16b,c}) bonds to produce alkenyl complexes (**4**). It is well-known that hydrido-alkynyl complexes (**2**) readily undergo hydride transfer reactions to yield metal vinylidenes (**5**), which are also obtained directly from the rearrangement of π -coordinated terminal alkynes.^{10b} Those metal complexes, **1–5**, are the key intermediates in the C–C bond-forming reactions mediated by metals that react initially with alkynes.



Reactions of Metal-Alkynyls

Proton-Mediated Coupling between Alkynyl, Alkyl, and Alkenyl Ligands. Metal-alkynyls (**2**) are in general obtained by oxidative addition of terminal alkynes to metals ($\text{M} + \text{H}-\text{C}\equiv\text{C}-\text{R} \rightarrow \text{H}-\text{M}-\text{C}\equiv\text{C}-\text{R}$) and by ligand (L) substitution reactions with alkynyl groups in the presence

[†] Dedicated to Professor L. Vaska on the occasion of his 75th birthday.

Chong Shik Chin, born in Seoul, Korea, in 1941, received his B.S. in 1965 from Yonsei University, Korea, and his Ph.D. from Clarkson University in 1977 with L. Vaska, who inspired him to work with group 9 metals. He was a postdoctoral research associate of M. D. Curtis at the University of Michigan before he went in 1979 to Sogang University, where he is currently a professor of inorganic chemistry. He spent a sabbatical year at the University of California, San Diego (1985–1986) with G. N. Schrauzer. He has been a member of the Korean Academy of Science and Technology since 1994 and is the President of the Korean Chemical Society for 2001. His current research interests include C–C bond formation through activation of alkynes and nitriles with iridium and rhodium compounds containing Cp^* (Me_5C_5), TPPTS ($\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) (water-soluble), CO, and PPh_3 .

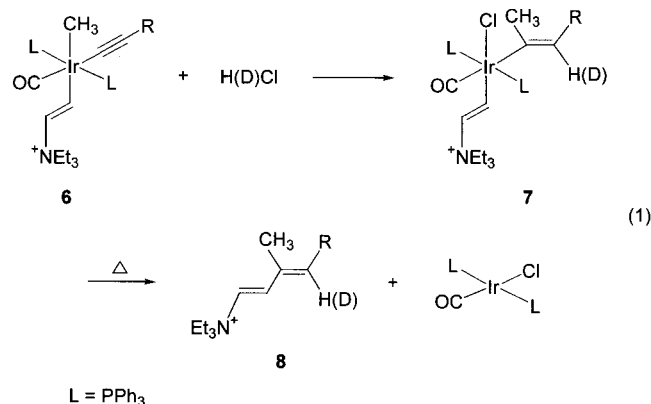
Gyongshik Won, born in Taejon, Korea, in 1964, received his B.S. from Chungnam University in 1990 and his M.S. from the Sogang University in 1992. He then moved to Hansol Paper Company (Korea) where he worked for five years before he returned to Sogang University in 1997 to complete his Ph.D. in 2000 with Chong Shik Chin. He was awarded the scholarship from the Daewoo Foundation in 1997 for his graduate work. His research has focused on C–C bond formation and polymerization of alkynes with iridium and rhodium compounds. He recently joined the research group of K. G. Caulton at Indiana University as a postdoctoral research associate.

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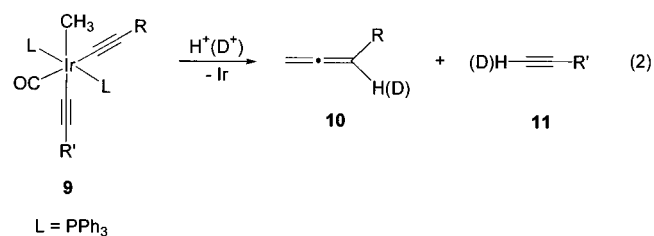
of terminal alkynes and base, $B ([M-L]^+ + H-C\equiv C-R + B \rightarrow M-C\equiv C-R + BH^+ + L)$.^{1,17} These alkynyl ligands are then capable of coupling with other adjacent hydrocarbyl ligands in the presence of a proton, as shown in eq 1. Reactions of **6** containing three different hydrocarbyl groups may provide valuable information on the selectivity of the coupling between the hydrocarbyl ligands. In this example, exclusive coupling of the alkynyl and alkyl ligands occurs in the proton-mediated reactions of **6** to produce the *cis*-bis(alkenyl) complexes **7** (eq 1), whereas



no coupling of the alkynyl and alkenyl groups has been observed.^{1b} Deuterium labeling experiments (eq 1) clearly suggest that the initial proton attack on the β carbon of the alkynyl group of **6** leads to this C–C coupling. The subsequent C–C coupling between the two *cis*-alkenyl ligands by reductive elimination reactions of **7** to yield 1,3-dienes (**8**) is somewhat surprising, since the alkyl-alkenyl-alkynyl iridium **6** does not undergo any reductive elimination reaction in the absence of a proton.

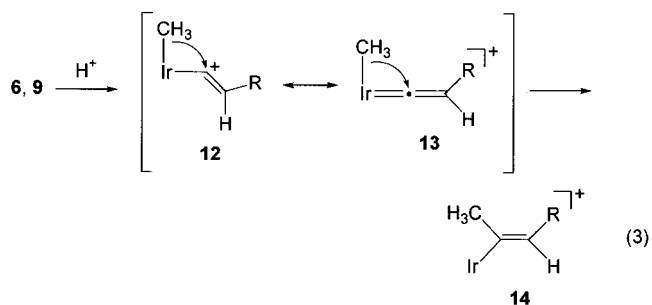
The facile reductive elimination of **8** from **7** may be understood by the formation of a relatively stable four coordinated iridium(I) complex IrCl(CO)(PPh₃)₂. It may also be said that the C–C bond formation reaction (reductive elimination of hydrocarbons) does not occur between the hydrocarbyl ligands of complex **6** in the absence of a proton, probably because the Ir–alkynyl bond in **6** is so strong (much stronger than the Ir–vinylidene bond in **7**) that any reductive elimination reaction involving the alkynyl ligand may not readily occur.

Competitive protonation at either the α or β carbon of the alkynyl ligands is seen in the reaction of the bis-alkynyl complex **9**. Whereas protonation of the alkynyl group *cis* to the CH₃ ligand occurs at the β carbon to yield the allenes (**10**), protonation of the alkynyl group *trans* to the CH₃ ligand also occurs at the α carbon to yield small amounts of the respective alkynes (**11**) (eq 2),^{1b} which is

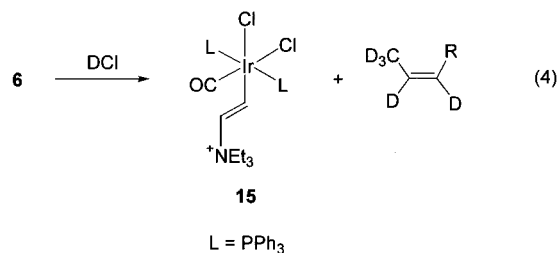


clearly confirmed by deuterium labeling experiments. Formation of allenes (**10**) can be rationalized by the initial protonation at the β carbon of the alkynyl group, followed by methyl-group migration to give an alkenyl species, as shown in eq 1.^{1b} β -Hydrogen elimination from the methyl group of the alkenyl complex (see Scheme 1) generates the allenes.

Protonation at the β carbon of an alkynyl ligand ($M-C\equiv CR$) apparently increases the electrophilicity of the α carbon (e.g., **12**) and is also well-known to yield metal-vinylidenes ($M=C=CHR$).^{10b} Although vinylidene complexes have not been observed in the above reactions, they cannot be excluded and, in fact, are viable intermediates in the reactions of eqs 1 and 2 (eq 3).^{1b}



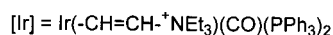
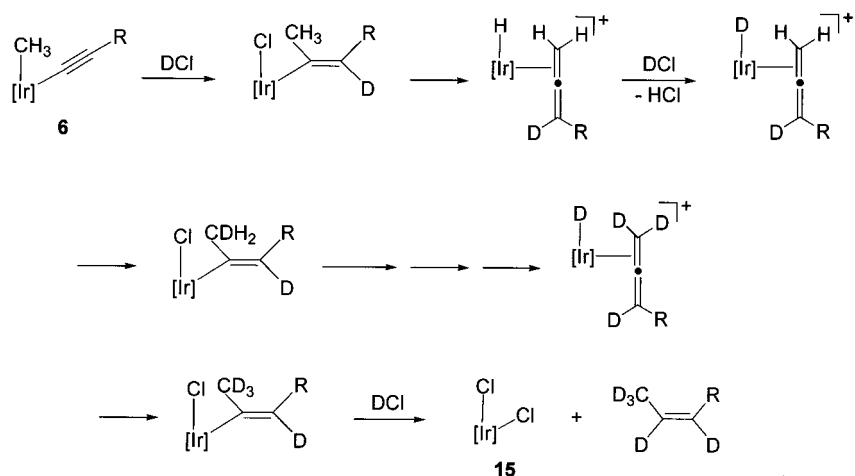
Although complex **7** can be isolated in high yield at the early stage of the reaction of **6** with HCl, further reaction of **7** with HCl at room temperature yields *cis*-CH₃CH=CHR exclusively and the dichloro complex **15** (eq 4).^{1b} The H/D exchange between the CH₃ group and DCl readily and extensively occurs during the formation of the *cis* olefins to yield *d*₅ olefins, *cis*-CD₃CD=CDR (eq 4).^{1b}



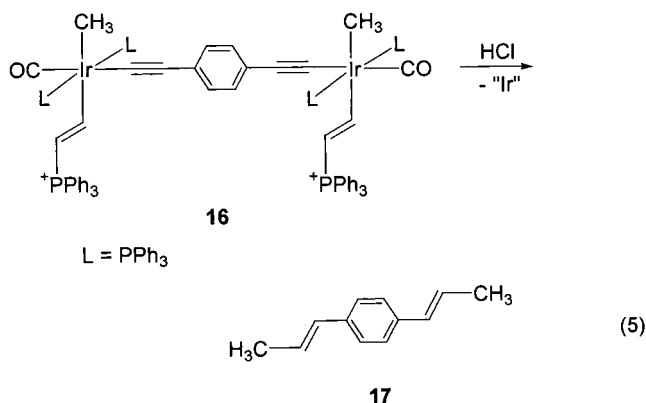
Iridium allenes ($H-Ir-\eta^2-H_2C=C=CHR$ in Scheme 1) have been suggested as the intermediates that rapidly undergo H/D exchange with DCl.^{1b} That allenes are not found from the reactions of **6** with HCl and *cis* olefins are not seen from the reactions of **9** may be understood in terms of relative stability of the metal complexes that are expected to be produced with the formation of allenes (eq 2) and *cis* olefins (eq 4). Trichlorocarbonyl complex IrCl₃(CO)(PPh₃)₂ and hydridoalkenyl complex $[IrHCl(CH=CH-NEt_3)(CO)(PPh_3)_2]^+$ are the expected products if *cis* olefins and allenes are produced from the reactions of **9** (eq 2) and **6** (eq 4) with HCl, respectively. These two complexes have never been reported thus far and have never been found from our experiments.

Related binuclear alkynyl-alkyl complexes are no exception to the proton-initiated C–C bond formation between the alkynyl and alkyl groups (eq 5). Complex **16**

Scheme 1

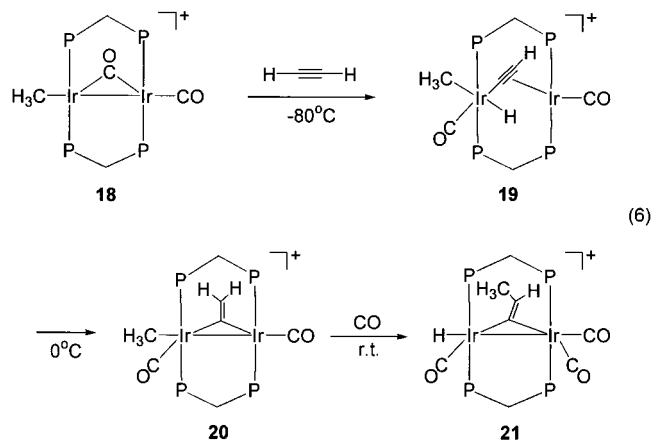


does not undergo the reductive elimination (C–C coupling between the alkynyl and alkyl groups) in the absence of H^+ . The diene ($\text{CH}_3\text{CH}=\text{CH}-p\text{-C}_6\text{H}_4-\text{CH}=\text{CHCH}_3$, **17**) is obtained from the reaction of **16** with HCl in high yield.¹⁸ The yield of the diene **17** seems dependent on the trans ligand ($-\text{CH}=\text{CH}-\text{PPh}_3$) to the CH_3 group.¹⁸ A variety of other products (such as $\text{CH}_3\text{CH}=\text{CH}-p\text{-C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$, $\text{CH}_3\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4-\text{CH}=\text{CHCH}_2\text{Cl}$, $\text{CH}_3\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4-\text{CH}=\text{CHCH}_3$, and $\text{CH}_3\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4-\text{CH}=\text{CHCl}$) are obtained with the trans ligand being CH_3CN .¹⁸ Identification of the deuterium-containing product (**17-d**₄, $\text{CH}_3\text{CD}=\text{CD}-p\text{-C}_6\text{H}_4-\text{CD}=\text{CDCH}_3$) unambiguously suggests the same reaction procedure (the initial proton attack on the β carbon of the alkynyl group followed by migration of the CH_3 group to the α carbon) as shown in eq 3.

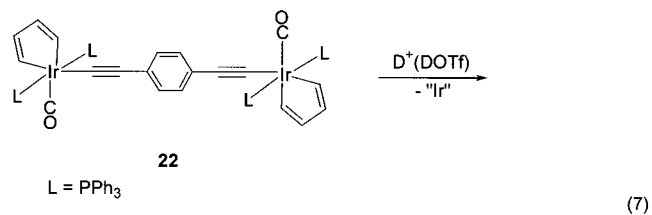


An interesting example of C–C bond formation has also been observed in the reaction of $\text{HC}\equiv\text{CH}$ with the related binuclear alkyl-iridium(I) complex **18**.¹⁹ The oxidative addition of $\text{HC}\equiv\text{CH}$ to the $\text{Ir}-\text{CH}_3$ of **18** produces the binuclear $\text{H}-\text{Ir}(\text{III})/\text{Ir}(\text{I})$ complex with $\mu-\eta^1:\eta^2-\text{C}\equiv\text{CH}$ ligand that is converted into the bridging vinylidene ligand (**20**) at lower temperature. Then, the exchange between the methyl ligand and the hydrogen of the bridging vinylidene ligand in **20** (C–C bond formation between the β carbon of the bridging vinylidene ligand and the methyl

ligand) occurs in the presence of CO to give a hydrido- μ -methylvinylidene complex **21** (eq 6).¹⁹



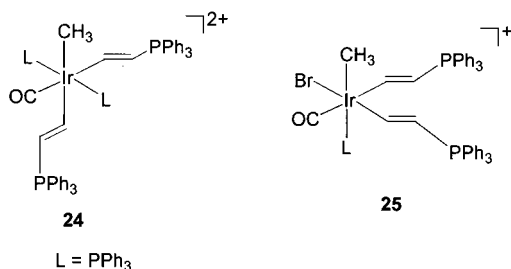
Somewhat unexpected C–C bond formation has been observed from the reaction of a binuclear alkynyliridacyclopentadiene, **22**²⁰ (eq 7). Proton attack does not seem



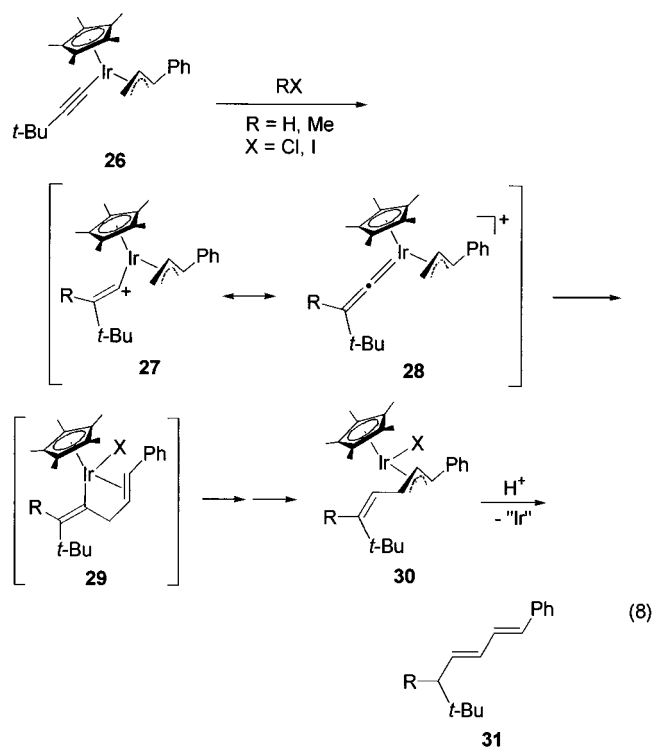
to occur on the β carbon of the alkynyl groups of **22** (no conjugated 1,3,5-trienes, such as $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-p\text{-C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$, have been observed from the reactions of **22** with HCl).²¹ Instead, the proton seems to attack the α carbons of the alkenyl groups to initiate the C–C bond formation (reductive elimination) to yield the dienyne **23** in high yield, which

is supported by the deuterium-containing product dienyne (**23-d₂**). It seems unprecedented that the proton selectively attacks the α carbon of the alkenyl group of alkynyl-alkenyl complexes.

Alkynes are inserted into Ir–P bonds to yield complexes containing alkenyl ligands Ir–CR=CR'–⁺PPh₃.¹⁶ These alkenyl complexes with an adjacent alkyl ligand (**24** and **25**)^{16a} do not undergo any C–C bond-forming reaction between the alkyl and alkenyl ligands, for which no plausible explanation is provided yet. We have prepared more than two dozen such compounds similar to **24** and **25**, none of which have been found to undergo the C–C coupling reactions between hydrocarbyl ligands under various experimental conditions.

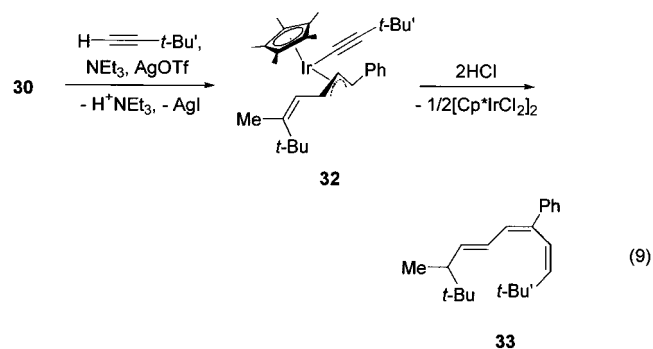


Electrophile (H⁺, Me⁺)-Mediated Coupling between Alkynyl and η^3 - or η^1 -Allyl Ligands. Electrophiles (H⁺, Me⁺) also mediate the coupling between alkynyl and η^3 -allyl groups coordinated to iridium (**26**) to yield η^3 -pentadienyl complexes **30** (eq 8).^{1a} The α carbon of the

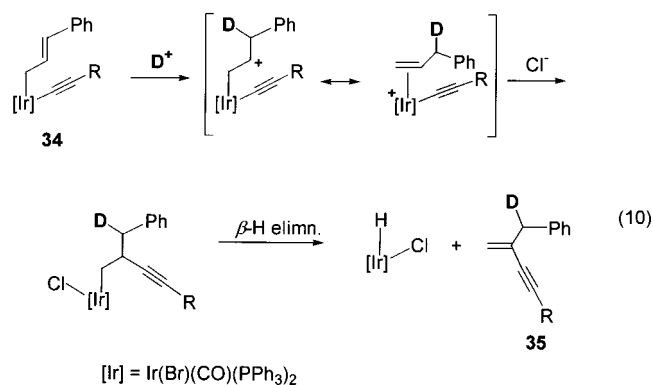


alkynyl group becomes more electrophilic (as shown in **27**) by the attack of the electrophile on the β carbon of the alkynyl ligand and accepts the nucleophilic terminal carbon of the allyl group to form a new C–C bond. A C–C coupling between the α carbons of the vinylidene and η^1 -

allyl groups may not be excluded, since the coordination of X[−] to the metal may cause a conversion of the η^3 -allyl complex to the η^1 -allyl one. It is most likely that the η^3 -pentadienyl (η^2 -alkene- η^1 -alkenyl) complexes **29** are formed initially immediately after the C–C bond formation step and then undergo the 1,3-hydrogen shift reaction, probably through β -hydrogen elimination, to yield another type of η^3 -pentadienyl complexes **30**, which can be isolated in high yield under controlled reaction conditions.^{1a} The trans,trans-conjugated dienes (**31**) are obtained quantitatively from the reactions of **30** with aqueous HCl.^{1a} The terminal carbon of the allyl ligand in **32** also reacts with the newly added alkynyl group in the same manner as shown by eq 8 (**26** → **31**) to yield conjugated 1,3,5-trienes (**33**) (eq 9).^{1a} It is interesting to notice that the C–C coupling occurs preferably through the terminal carbon of the η^3 -allyl ligand in eqs 8 and 9, whereas a C–C bond is formed through the central carbon of the η^3 -allyl ligand of the related complex [Cp*Ir(η^3 -CH₂CHCH₂)(η^2 -CR=CR)]⁺ in the reaction with a nucleophile.²²

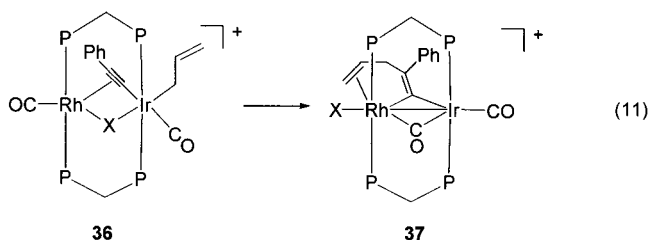


The reaction of an alkynyl- η^1 -allyl complex **34** with a proton shows an interesting C–C bond formation between the allyl and alkynyl ligands.²³ Proton attack on the γ carbon of the η^1 -allyl ligand induces the coupling between the β carbon of the allyl ligand and the α carbon of the alkynyl ligands to yield enynes **35** (eq 10). It is somewhat surprising not to see the initial attack of the proton on the β carbon of the alkynyl ligand of **34** to initiate the C–C coupling between the alkynyl and α carbon of η^1 -allyl ligand to produce dienes.



Another type of C–C coupling was recently reported between μ - η^1 : η^2 -alkynyl and η^1 -allyl ligands. Warming the binuclear Rh/Ir complexes **36** from −50 to 20 °C causes

an unusual C–C bond formation between the α carbon of the η^1 -allyl ligand and the β carbon of the bridging alkynyl group (eq 11).²⁴ The π coordination of the alkynyl ligand in **36** seems to make the β carbon electrophilic enough to accept the nucleophilic α carbon of the η^1 -allyl ligand to yield the bridging vinylidene complexes **37**.

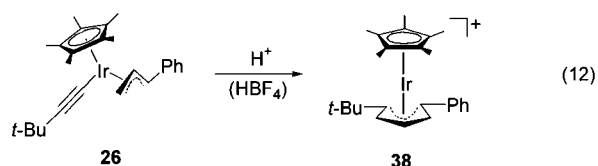


Unusual copper(III) complexes containing both η^1 -allyl ($-\text{CH}_2\text{CH}=\text{CH}_2$) and alkynyl ($-\text{C}\equiv\text{C}-\text{R}$) ligands were proposed in the catalytic allylation of alkynes as the intermediates that undergo the reductive elimination of 1,4-enynes ($\text{H}_2\text{C}=\text{CHCH}_2-\text{C}\equiv\text{C}-\text{R}$).²⁵ The proposed copper(III) intermediates may be so unstable that the typical reductive elimination rapidly occurs between the α carbons of the alkynyl and η^1 -allyl ligands to yield the 1,4-enynes.²⁵

It is also interesting to note that the hydrido- η^1 -allyl-alkynyl rhodium complexes, *mer*-Rh(H)($-\text{CH}_2\text{CH}=\text{CHR}$)($-\text{C}\equiv\text{CR}'$)L₃ (L₃ = (PPh₃)₂(CO)), obtained from the reaction of η^3 -allyl rhodium(I) complexes L₃Rh(η^3 -CH₂CHCHR) with terminal alkynes ($\text{H}-\text{C}\equiv\text{C}-\text{R}'$) selectively undergo the reductive elimination of olefins CH₃CH=CHR but yield no C–C bond formation product resulting from the coupling of the alkynyl and η^1 -allyl ligands.²⁶

An η^5 -pentadienyl complex **38** is obtained from the reaction of complex **26** with protic acid, such as HBF₄, in the absence of other bases (such as Cl[−] and CH₃CN) that readily are coordinated to the metal (eq 12).²⁷ Ring closing (C–C bond formation), however, has not been found between the terminal carbons of the η^5 -pentadienyl group

of **38** in the reaction of complex **26** with the proton. On the other hand, cyclization has been frequently observed from the reactions of η^3 -allyl- π -alkyne complexes of group 9 metals (e.g., **39**) with nucleophiles.^{2c,d,22,28,29}

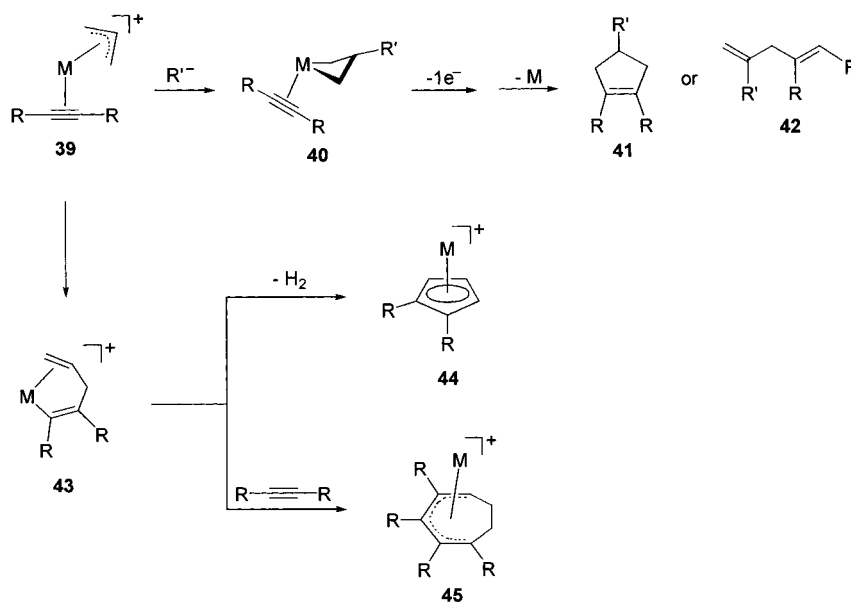


Both cyclic and linear polyenes are produced from the intramolecular coupling reactions between the π -alkyne and η^3 -allyl ligands.^{2c,d,22,28,29} Stryker et al. have studied the allyl/alkyne cycloaddition reactions ([3 + 2] and [3 + 2 + 2]) in the presence of group 9 metals (Co, Rh, Ir) to prepare five- and seven-membered polyenyl rings, cyclopentenes, and dienes (Scheme 2).^{2c,d,22} Linear polyenes are also produced in the presence of non-group 9 metals,²⁹ which is beyond the scope of this Account.

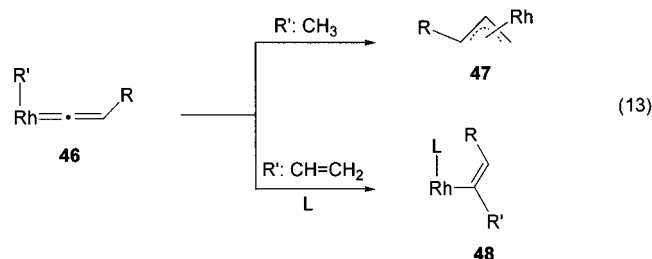
Although an intramolecular C–C coupling occurs between the terminal carbon of the η^3 -allyl and π -alkyne ligands (**39** → **43**), a new C–C bond is also formed between the central carbon of the η^3 -allyl group and an incoming nucleophile, R' (**39** → **40**).^{22,28b}

The η^3 -1,4-pentadien-1-yl complexes **43** [Cp*Ir(η^3 -CR=CR-CH₂CH=CH₂)]⁺, unlike the related η^5 -pentadienyl complex **38** that does not undergo further C–C bond formation reaction,²⁷ further undergo intramolecular (**43** → **44**) C–C bond forming reactions. It should also be noted that a variety of anomalous rearrangement reactions occur to yield several unexpected products in the reactions of related complexes, for which detailed studies were carried out to elucidate the mechanisms for those rearrangements.^{2c,d,28a} (See the cited references for the detailed mechanisms.) Interestingly, 1,4-dienes (RCH=CR-CH₂CH=CH₂) are obtained in the reactions of **39** with H⁺ in the presence of a ligand CH₃CN.^{28a}

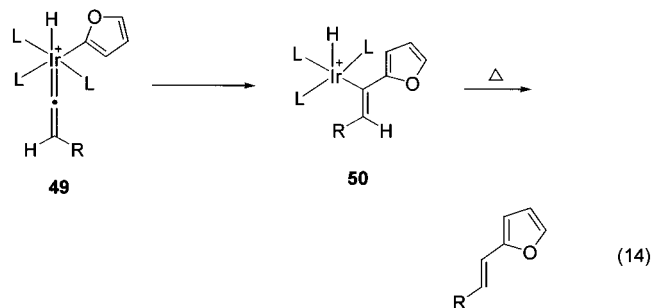
Scheme 2



Other Related Alkyne Transformation Mediated by Group 9 Metals. Vinylidene and allenylidene complexes are obtained from the reactions of alkynes with rhodium and iridium complexes and readily undergo intramolecular C–C coupling reactions when they also have other carbyl ligands adjacent to the vinylidene and allenylidene ligands.^{30–32} For example, rhodium vinylidene–alkyl and –alkenyl complexes **46** yield η^3 -allyl (**47**) and η^1 -alkenyl (**48**) complexes through the coupling between the vinylidene and alkyl or alkenyl ligands (eq 13).^{30b} Iridium



hydrido-alkenyl-vinylidene complexes **49** preferably undergo the C–C coupling between the *cis*-vinylidene and alkenyl ligands to produce 2-alkenyl furan (eq 14), but neither alkyne (HC≡CR) nor furan was produced.³² A variety of unsaturated cyclic compounds are selectively produced by intermolecular C–C bond formation between alkynes and alkenes and by an intramolecular C–C coupling reaction of enynes in the presence of transition metals.^{33–37}



Group 9 metal complexes show excellent catalytic activity for both hydroformylation and silylformylation of alkynes,³ as they do for hydroformylation of alkenes.³⁸ Cyclooligomerization of alkynes (cyclization of alkynes to prepare arenes,^{2f,7a,c,39–41} cyclobutadienes/cyclooctatetraenes,^{40c} and fulvenes⁴²), condensation of two alkynes and one nitrile to prepare pyridines,^{8a,43,44} linear oligomerization of alkynes (dimerization of terminal alkynes to prepare enynes,^{1e,5b–h,10b,39a} linear trimerization of alkynes to prepare dienyne^{1c,36a,45}), and polymerization of terminal alkynes⁶ are also very important reactions of alkynes and are known to be successfully mediated by group 9 metal compounds.

Conclusions

This account summarizes some of our recent work involving the electrophile-mediated intramolecular C–C bond-forming reactions of newly prepared alkynyl/alkenyl/alkyl/

η^3 - and η^1 -allyl iridium complexes along with other chemistry relevant to our work.

Alkynyl complexes are prepared from reactions of group 9 metals with terminal alkynes. These alkynyl complexes readily undergo C–C bond-forming reactions in the presence of electrophiles that attack the β carbon of the alkynyl ligand to initiate the C–C coupling between the alkynyl ligand and adjacent hydrocarbyl ligands, such as alkyl, alkenyl, and allyl ligands. Further investigation of the selectivity for the C–C coupling between such coordinated hydrocarbyl ligands would provide very useful information that may be utilized in synthetic chemistry, especially in the field of conjugated polyolefins.

The authors thank the Korea Science and Engineering Foundation, Korea Research Foundation, and Ministry of Education for their financial supports of the studies that produced many results cited in this account.

References

- (1) (a) Chin, C. S.; Maeng, W.; Chong, D.; Won, G.; Lee, B.; Park, Y. J.; Shin, J. M. Electrophile (H⁺, Me⁺)-Mediated Carbon–Carbon Bond Formation between η^3 -Allyl and Alkynyl groups Coordinated to “Cp*Ir”. *Organometallics* **1999**, *18*, 2210–2215. (b) Chin, C. S.; Cho, H.; Won, G.; Oh, M.; Ok, K. M. Reaction of an (Alkyl)(alkenyl)-(alkynyl)iridium(III) Complex with HCl: Intramolecular C–C Bond Formation from Alkyl, Alkenyl, and Alkynyl Groups Coordinated to “Ir(CO)(PPh₃)₂”. H/D Exchange between CH₃ and DCl. *Organometallics* **1999**, *18*, 4810–4816. (c) Comstock, M. C.; Shapley, J. R. Synthesis and Reactivity of Ir(CO)(η^2 -C₂R₂)(η^5 -C₉H₇) (R = Ph, Tol). Alkyne Coupling and Arene C–H Bond Activation Forming a Substituted Butadiene Ligand. *Organometallics* **1997**, *16*, 4816–4823. (d) O’Connor, J. M.; Chen, M.-C.; Frohn, M.; Rheingold, A. L.; Guzei, I. A. Diazoketones Undergo Reaction with a Cobalt Alkyne Complex to Give Highly Functionalized Conjugated Dienes. *Organometallics* **1997**, *16*, 5589–5591. (e) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. Palladium-Catalyzed Additions of Terminal Alkynes to Acceptor Alkynes. *J. Am. Chem. Soc.* **1997**, *119*, 698–708.
- (2) For example, see (a) Older, C. M.; Stryker, J. M. The Mechanism of Carbon–Carbon Bond Activation in Cationic 6-Alkylcyclohexadienyl Ruthenium Hydride Complexes. *J. Am. Chem. Soc.* **2000**, *122*, 2784–2797. (b) Waters, M. L.; Bos, M. E.; Wulff, W. D. Mechanistic Studies on the Reaction of Fischer Carbene Complex with Alkynes: Does the Alkyne Insertion Intermediate Form Irreversibly? *J. Am. Chem. Soc.* **1999**, *121*, 6403–6413. (c) Dzwiniel, T. L.; Etkin, N.; Stryker, J. M. Carbon–Carbon Bond Activation by Electrophilic Complexes of Cobalt: Anomalous [3 + 2] Allyl/Alkyne Cycloaddition Reactions and [5 + 2] Cyclopentenyl/Alkyne Insertion-Ring Expention Reactions. *J. Am. Chem. Soc.* **1999**, *121*, 10640–10641. (d) Etkin, N.; Dzwiniel, T. L.; Schweibert, K. E.; Stryker, J. M. Cobalt-Mediated Intermolecular Allyl/Alkyne [3 + 2 + 2] Cycloaddition Reactions. A Practical Metal Template for Convergent Synthesis of Functionalized Seven-Membered Rings. *J. Am. Chem. Soc.* **1998**, *120*, 9702–9703. (e) Mao, F.; Schüt, D. M.; Tyler, D. R. Catalysis by 18 + δ Compounds. Cyclooligomerization of Acetylenes Catalyzed by Co(CO)₃L₂. *Organometallics* **1996**, *15*, 4770–4775. (f) Lamata, M. P.; José, E. S. Unprecedented Rhodium-Mediated Trimerization of Alkynes HC≡CR (R = Ph, *p*-Tolyl) Leading to (η^4 -Cyclobutadiene)rhodium Complexes. *Organometallics* **1996**, *15*, 4852–4856.
- (3) (a) Ishii, Y.; Miyashita, K.; Kamita, K.; Hidai, M. Selective Hydroformylation of Internal Acetylenes by PdCl₂(PCy₃)₂: Remarkable Synergistic Effect of Cobalt. *J. Am. Chem. Soc.* **1997**, *119*, 6448–6449. (b) Johnson, J. R.; Cuny, G. D.; Buchwald, S. L. Rhodium-Catalyzed Hydroformylation of Internal Alkynes to α,β -Unsaturated Aldehydes. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1760–1761. (c) Monteil, F.; Matsuda, I.; Alper, H. Rhodium-Catalyzed Intramolecular Silylformylation of Acetylenes: A Vehicle for Complete Regio- and Stereoselectivity in the Formylation of Acetylenic Bonds. *J. Am. Chem. Soc.* **1995**, *117*, 4419–4420. (d) Doyle, M. P.; Shanklin, M. S. Highly Regioselective and Stereoselective Silylformylation of Alkynes Under Mild Conditions Promoted by Dirhodium(II) Perfluorobutylate. *Organometallics* **1994**, *13*, 1081–1088.

- (4) (a) Trost, B. M.; Brown, R. E.; Toste, F. D. A Ruthenium-Catalyzed Hydrative Cyclization and [4 + 2] Cycloaddition of Yne-enones. *J. Am. Chem. Soc.* **2000**, *122*, 5877–5878. (b) Trost, B. M.; Toste, F. D. Ruthenium-Catalyzed Cycloisomerization of 1,6- and 1,7-Enynes. *J. Am. Chem. Soc.* **2000**, *122*, 714–715 and references therein. (c) Jeong, N.; Sung, B. K.; Choi, Y. K. Rhodium(I) Catalyzed Asymmetric Intramolecular Pauson–Khand-Type Reaction. *J. Am. Chem. Soc.* **2000**, *122*, 6771–6772. (d) Jeong, N.; Lee, S.; Sung, B. K. Rhodium(I) Catalyzed Intramolecular Pauson–Khand Reaction. *Organometallics* **1998**, *17*, 3642–3644.
- (5) (a) Ohmura, T.; Yorozuya, S.; Yamamoto, Y.; Miyaura, N. Iridium-Catalyzed Dimerization of Terminal Alkynes to (E)-Enynes, (Z)-Enynes, or 1,2,3-Butatrienes. *Organometallics* **2000**, *19*, 365–367. (b) Wang, J. Q.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. Selective Dimerization of Terminal Alkynes Promoted by the Cationic Actinide Compound [(Et₂N)₃U][BPh₄]. Formation of the Alkyne π -Complex [(Et₂N)₂U(C \equiv C^tBu)(η^2 -HC \equiv C^tBu)][BPh₄]. *Organometallics* **1999**, *18*, 2407–2409. (c) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. Ruthenium-Catalyzed Dimerization of Terminal Alkynes Initiated by a Neutral Vinylidene Complex. *Organometallics* **1996**, *15*, 5275–5277. (d) Yi, C. S.; Liu, N. Homogeneous Catalytic Dimerization of Terminal Alkynes by C₅Me₅Ru(L)H₃ (L = PPh₃, PCy₃, PMe₃). *Organometallics* **1996**, *15*, 3968–3971. (e) Chin, C. S.; Won, G.; Song, J. Selective Dimerization and Trimerization of Phenylacetylene with Rhodium and Iridium Complexes. *Bull. Korean Chem. Soc.* **1994**, *15*, 961–966.
- (6) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. Well-Controlled Polymerization of Phenylacetylenes with Organorhodium(I) Complexes: Mechanism and Structure of the Polyenes. *J. Am. Chem. Soc.* **1999**, *121*, 12035–12044.
- (7) For example, see (a) Sigman, M. S.; Fatland, A. W.; Eaton, B. E. Cobalt-Catalyzed Cyclotrimerization of Alkynes in Aqueous Solution. *J. Am. Chem. Soc.* **1998**, *120*, 5130–5131. (b) Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. C₃-Symmetric Hexakis(trimethylsilyl)[7]phenylene [⁺Tris(bisphenylene)cyclobutadiene]cyclohexatriene⁺, a Polycyclic Benzenoid Hydrocarbon with Slightly Curved Topology. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478–1481. (c) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. Mechanism of Acetylene Cyclotrimerization Catalyzed by the fac-IrP₃⁺ Fragment: Relationship between Fluxionality and Catalysis. *Organometallics* **1994**, *13*, 2010–2023.
- (8) For example, see (a) Takahashi, T.; Tsai, F.-Y.; Kitora, M. Selective Formation of Substituted Pyridines from Two Different Alkynes and a Nitrile: Novel Coupling Reaction of Azazirconacyclopentadienes with Alkynes. *J. Am. Chem. Soc.* **2000**, *122*, 4994–4995. (b) Li, Y.; Marks, T. J. Organolanthanide-Catalyzed Intra- and Intermolecular Tandem C–N and C–C Bond-Forming Processes of Aminodialkenes, Aminodialkynes, Aminoalkenynes, and Aminoalkynes. New Regioselective Approaches to Pyrrolizidine, Indolizidine, Pyrrole, and Pyrazine Skeletons. *J. Am. Chem. Soc.* **1998**, *120*, 1757–1771. (c) Li, Y.; Marks, T. J. Coupled Organolanthanide-Catalyzed C–N/C–C Bond Formation Processes. Efficient Regiospecific Assembly of Pyrrolizidine and Indolizidine Skeletons in a Single Catalytic Reaction. *J. Am. Chem. Soc.* **1996**, *118*, 707–708.
- (9) (a) Ohmura, T.; Yamamoto, Y.; Miyaura, N. Rhodium- or Iridium-Catalyzed trans-Hydroboration of Terminal Alkynes, Giving (Z)-1-Alkenylboron Compounds. *J. Am. Chem. Soc.* **2000**, *122*, 4990–4991. (b) Lo, H. C.; Grotjahn, D. B. Selective C–C Bond Formation on the First Ketene–Alkyne Complexes. *J. Am. Chem. Soc.* **1997**, *119*, 2958–2959.
- (10) (a) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. What Do Titano- and Zirconocenes Do with Diynes and Polyynes? *Acc. Chem. Res.* **2000**, *33*, 119–129. (b) Bruneau, C.; Dixneuf, P. H. Metal Vinylidenes in Catalysis. *Acc. Chem. Res.* **1999**, *32*, 311–323. (c) Chen, J.-T. Addition reactions of mononuclear η^3 -allenyl/propargyl transition metal complexes: a new class of potent organometallic carbon electrophiles. *Coord. Chem. Rev.* **1999**, *190–192*, 1143–1168. (d) Bruce, M. I. Transition Metal Complexes Containing Allenylidene, Cumulenylidene, and Related Ligands. *Chem. Rev.* **1998**, *98*, 2797–2858.
- (11) (a) Ilg, K.; Werner, H. An Unprecedented Type of Insertion of an Alkyne into a Metal–Carbon Bond. *Organometallics* **1999**, *18*, 5426–5428. (b) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. Carbostannylation of Alkynes Catalyzed by an Iminophosphine–Palladium Complex. *J. Am. Chem. Soc.* **1998**, *120*, 2975–2976.
- (12) (a) Pickin, K. A.; Welker, M. E. Reactions of Cobaloximes with Alkenyl Triflates and Halides as a New Method for the Preparation of Cobalt-sp² Carbon Bonds. *Organometallics* **2000**, *19*, 3455–3458. (b) Chin, C. S.; Lee, H.; Kim, M.; Park, H.; Park, Y. J. Acetylenes react with *cis*-dihydrido complex, [Ir(H)₂(CH₃CN)₂(PPh₃)₂]⁺ to give *cis*-bis(alkenyl) complex, [Ir(–CH=CH₂)₂(NCCH₃)₂(PPh₃)₂]⁺. Detailed results will be reported elsewhere.
- (13) Hua, R.; Shimada, S.; Tanaka, M. The First Example of Rhodium(I)-Catalyzed Regio- and Stereoselective Chloroesterification of Alkynes with Chloroformate Esters. *J. Am. Chem. Soc.* **1998**, *120*, 12365–12366.
- (14) (a) Adams, R. D.; Barnard, T. S. Catalytic Hydrosilylation of Diarylalkynes by Layer-Segregated Platinum–Ruthenium Cluster Complexes Pt₃Ru₆(CO)₂₀(μ_3 -RC₂R)(μ_3 -H)(μ -H). *Organometallics* **1998**, *17*, 2567–2573. (b) Matsuda, I.; Fukuta, Y.; Tsuchihashi, T.; Nagashima, H.; Itoh, K. Rhodium-Catalyzed Silylformylation of Acetylenic Bonds: Its Scope and Mechanistic Considerations. *Organometallics* **1997**, *16*, 4327–4345. (c) Ojima, I.; Tzamaridou, M.; Tsai, C.-Y. Extremely Chemoselective Silylformylation and Silylcarbocyclization of Alkynals. *J. Am. Chem. Soc.* **1994**, *116*, 3643–3644.
- (15) Chin, C. S.; Lee, H.; Oh, M. Reactions of Iridium(III) Compounds with Alkynes in the Presence of Triethylamine: The First Example of M–CH=CH–NR₃. *Organometallics* **1997**, *16*, 816–818.
- (16) (a) Chin, C. S.; Lee, M.; Oh, M.; Won, G.; Kim, M.; Park, Y. J. *cis*-Bis(alkenyl) iridium(III) Compounds by Apparent Insertion of Two Acetylenes into Two Ir–P Bonds: Crystal Structures of *cis*,*trans*-[IrCl(–CH=CH⁺PPh₃)₂(CO)(PPh₃)₂]²⁺ and [Ir(OClO₃)(CH₃)(H₂O)(CO)(PPh₃)₂]⁺. *Organometallics* **2000**, *19*, 1572–1577, and references therein. (b) Chin, C. S.; Park, Y.; Kim, J.; Lee, B. Facile Insertion of Alkynes into Ir–P (Phosphine) and Ir–As (Arsine) Bonds: Second and Third Alkyne Addition to Mononuclear Iridium Complexes. *J. Chem. Soc., Chem. Commun.* **1995**, 1495–1496. (c) Chin, C. S.; Chong, D.; Kim, M.; Lee, H. New η^3 -Allyl-Alkenyl- and η^3 -Allyl-Alkynyl-Ir–Cp* Compounds from Reactions of [Cp*Ir(η^3 -CH₂CHCHPh)(NCMe)]⁺ with Alkynes. *Bull. Korean Chem. Soc.* **2001**, *22*, 739–742.
- (17) Chin, C. S.; Yoon, J.; Song, J. Oxidative Addition of Phenylacetylene to [Ir(CO)(RCN)(PPh₃)₂]ClO₄: Preparation, Kinetics, and Mechanism. *Inorg. Chem.* **1993**, *32*, 5901–5904, and references therein.
- (18) Chin, C. S.; Kim, M.; Lee, H.; Park, H. Alkynyl Group Bridged Di- and Tri-Nuclear Iridium Complexes Containing Other Carbonyl Ligands: Conjugated Olefins from C–C Bond Formation between Carbonyl Ligands at “Ir(CO)(PPh₃)₂”. *The 10th Japan-Korea Joint Symposium on Organometallic and Coordination Chemistry*, University of Tsukuba, Tsukuba, Japan, June 19–22, 2001. Detailed data will be reported elsewhere.
- (19) Torkelson, J. R.; McDonald, R.; Cowie, M. C–H Bond Activation and C–C Bond Formation in the Reactions of the Methyl Complex [Ir₂(CH₃)(CO)₂(Ph₂PCH₂PPh₂)₂][CF₃SO₃] with Alkynes. *Organometallics* **1999**, *18*, 4134–4146.
- (20) Ok, K. M. M.S. Thesis, Intermediates of the Catalytic Polymerization of Terminal Alkynes with Iridium Compounds: Iridium(III)-Alkyne Adducts and Oligomers of Alkynes, Sogang University, Korea, 1997. The structure of complex **22** has been unambiguously determined by X-ray diffraction data analysis.
- (21) Chin, C. S.; Lee, H. Unpublished results.
- (22) (a) Schwiebert, K. E.; Stryker, J. M. Synthesis and Isolation of Highly Reactive η^3 -Allyl Alkyne Complexes of Iridium via the Inner-Sphere η^3 -Allyl Triflate Complex (C₅Me₅)Ir(η^3 -C₃H₅)OTf. Facile Conversion to Alkyne Metallacyclobutane Complexes by Nucleophilic Addition. *Organometallics* **1993**, *12*, 600–602. (b) Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. Synthesis of Substituted π -Cyclopentadienyl Complexes of Ruthenium, Rhodium, and Iridium by a Novel Reaction of Intramolecular Condensation of π -Allyl Ligand and Alkyne. X-ray Structure of [η -C₆H₄Ru(η -C₅H₅Ph₂-1,2)]BF₄. *J. Organomet. Chem.* **1985**, *281*, 349–364.
- (23) Chin, C. S.; Won, G.; Kim, M. Proton Mediated Carbon–Carbon Bond Formation between the β -Carbon of η^1 -Allyl and α -Carbon of Alkynyl Groups Coordinated to “IrBr(CO)(PPh₃)₂”. *Bull. Korean Chem. Soc.* **2001**, *22*, 255–256.
- (24) George, D. S. A.; Hiltz, R. W.; McDonald, R.; Cowie, M. An Unusual Example of Allyl-to-Alkynyl Migration in a Phenylacetylide-Bridged Heterobinuclear Complex of Rhodium and Iridium. *Organometallics* **1999**, *18*, 5330–5343.
- (25) Grushin, V. V.; Alper, H. Copper(II) and Phase Transfer Catalyzed Allylation of Alkynes. *J. Org. Chem.* **1992**, *57*, 2188–2192.
- (26) Choi, J.; Osakada, K.; Yamamoto, T. Single and Multiple Insertion of Aryllallene into the Rh–H Bond to Give (π -Allyl)rhodium Complexes. *Organometallics* **1998**, *17*, 3044–3050.
- (27) Yoon, T. M.S. Thesis, Mechanistic Studies for Carbon–Carbon Bond Formation between η^3 -Allyl and alkynyl Groups Coordinated to “Cp*Ir”, Sogang University, Korea, 2000. The structure of complex **38** has been unambiguously determined by X-ray diffraction data analysis.

- (28) (a) Schwiebert, K. E.; Stryker, J. M. Transition Metal-Mediated [3 + 2 + 2] Alkyl/Alkyne/Cycloaddition Reactions. A New Reactivity Pattern for the Synthesis of Seven-Membered Carbocycles. *J. Am. Chem. Soc.* **1995**, *117*, 8275–8276. (b) Schwiebert, K. E.; Stryker, J. M. Oxidatively Induced Metal-Mediated Cycloaddition. Cyclopentene Formation via Electrocatalyzed Insertion of Alkynes into Iridacyclobutanes. *J. Am. Chem. Soc.* **1994**, *116*, 11570–11571.
- (29) (a) Older, C. M.; Stryker, J. M. Oxidatively Induced Carbonylation and Cyclization of Ruthenium(II) Vinyl-Olefin Complexes Prepared via Alkyl/Alkyne Coupling. *Organometallics* **2000**, *19*, 3266–3268. (b) Barrado, G.; Hricko, M. M.; Miguel, D.; Riera, V.; Wally, H.; Garcia-Granda, S. Coupling of η^3 -Allyl and Alkyne in Molybdenum Carbonyl Complexes. *Organometallics* **1998**, *17*, 820–826, and references therein.
- (30) (a) Gil-Rubio, J.; Laubender, M.; Werner, H. Synthesis of Dinuclear Rhodium Complexes with 1,3-Butadienyldiyl Bridges. Coupling of the C₄ and the Two C₂ Units of a C₂RhC₄RhC₂ Chain. *Organometallics* **2000**, *19*, 1365–1372. (b) Wiedemann, R.; Wolf, J.; Werner, H. C–C Coupling Reactions as a Novel Synthetic Route to π -Allyl- and π -Butadienylnrhodium Complexes. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1244–1246, and references therein.
- (31) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. Novel C–C and C–C–P Coupling Reactions Using an Allenylidenerhodium Complex as a Precursor. *J. Am. Chem. Soc.* **1996**, *118*, 2495–2496.
- (32) Selnau, H. E.; Merola, J. S. The Chemistry of *mer*-(Me₃P)₃Ir(H)-(2-furyl)(Cl): Preferential Reaction of an Alkyne with an Ir–C Bond in the Presence of an Ir–H Bond. *Organometallics* **1993**, *12*, 3800–3801.
- (33) For example, see (a) Lautens, M.; Klute, W.; Tam, W. Transition Metal-Mediated Cycloaddition Reactions. *Chem. Rev.* **1996**, *96*, 49–92. (b) Frühauf, H.-W. Metal-Assisted Cycloaddition Reactions in Organotransition Metal Chemistry. *Chem. Rev.* **1997**, *97*, 523–596.
- (34) Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. Strained Cyclic Cumulene Intermediates in Diels–Alder Cycloadditions of Enynes and Diynes. *J. Am. Chem. Soc.* **1996**, *118*, 4218–4219.
- (35) (a) Saito, S.; Tanaka, T.; Koizumi, T.; Tsuboya, N.; Itagaki, H.; Kawasaki, T.; Endo, S.; Yamamoto, Y. Nickel(0)-Catalyzed Unprecedented Zipper Annulation of Certain Conjugated Enynes. *J. Am. Chem. Soc.* **2000**, *122*, 1810–1811. (b) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. Effective Synthesis of Aryl Ethers and Coumaranones Employing the Palladium-Catalyzed Enyne-Diyne [4 + 2] Cycloaddition Protocol. *J. Org. Chem.* **2000**, *65*, 568–572.
- (36) (a) Cao, P.; Wang, B.; Zhang, X. Rh-Catalyzed Enyne Cycloisomerization. *J. Am. Chem. Soc.* **2000**, *122*, 6490–6491. (b) Wender, P. A.; Dyckman, A. J.; Husfeld, C. O.; Scanio, M. J. C. A New and Practical Five-Carbon Component for Metal Catalyzed [5 + 2] Cycloadditions: Preparative Scale Syntheses of Substituted Cycloheptenones. *Org. Lett.* **2000**, *2*, 1609–1611. (c) Wender, P. A.; Takahashi, H.; Witulski, B. Transition Metal Catalyzed [5 + 2] Cycloadditions of Vinylcyclopropanes and Alkynes: A Homologue of the Diels–Alder Reaction for the Synthesis of Seven-Membered Rings. *J. Am. Chem. Soc.* **1995**, *117*, 4720–4721.
- (37) (a) Kim, S.-W.; Son, S. U.; Lee, S. I.; Hyeon, T.; Chung, Y. K. Cobalt on Mesoporous Silica: The First Heterogeneous Pauson–Khand Catalyst. *J. Am. Chem. Soc.* **2000**, *122*, 1550–1551. (b) Pagenkopf, B. L.; Livinghouse, T. Photochemical Promotion of the Intramolecular Pauson–Khand Reaction. A New Experimental Protocol for Cobalt-Catalyzed [2 + 2 + 1] Cycloadditions. *J. Am. Chem. Soc.* **1996**, *118*, 2285–2286. (c) Marco-Contelles, J. Asymmetric Pauson–Khand Reaction. Cobalt-Mediated Cycloisomerization of 1,6-Enynes in Carbohydrate Templates: Synthesis of Bis-Heteroannulated Pyranosides. *J. Org. Chem.* **1996**, *61*, 7666–7670.
- (38) (a) Esteruelas, M. A.; Nürnberg, O.; Olivan, M.; Oro, L. A.; Werner, H. Synthesis and Reactions of New Hydrosilyliridium(III) Complexes Containing the Diolefin Tetrafluorobenzobarrelene. *Organometallics* **1993**, *12*, 3264–3272. (b) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. Hydrosilylation of 1-Hexyne Catalyzed by Rhodium and Cobalt–Rhodium Mixed-Metal Complexes. Mechanism of Apparent Trans Addition. *Organometallics* **1990**, *9*, 3127–3133.
- (39) Reviews: (a) Grotjahn, D. B. Transition Metal Alkyne Complexes: Transition Metal-Catalyzed Cyclotrimerization. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. A., Wilkinson, G., Hegedus, L. S., Eds.; Pergamon: 1995; Vol. 12, pp 741–770. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p. 870. (c) Vollhardt, K. P. C. Transition-Metal-Catalyzed Acetylene Cyclizations in Organic Synthesis. *Acc. Chem. Res.* **1977**, *10*, 1–8.
- (40) Co: (a) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. Parallel Reaction Pathways in the Cobalt-Catalyzed Cyclotrimerization of Acetylenes. *J. Am. Chem. Soc.* **1977**, *99*, 1666–1668. (b) Vollhardt, K. P. C.; Bergman, R. G. A One-Step Synthesis of Benzocyclobutenes Involving Cooligomerization of Linear Mono- and Diacetylenes Catalyzed by η^5 -Cyclopentadienylcobalt Dicarboxylate. *J. Am. Chem. Soc.* **1974**, *96*, 4996–4998. (c) Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G.-Y. Theoretical Study of the Acetylene Trimerization with CpCo. *J. Am. Chem. Soc.* **1999**, *121*, 6055–6067. (d) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. The First Metallacyclopentadiene(Alkyne) Complexes and Their Discrete Isomerization to η^4 -Bound Arenes: The Missing Link in the Prevalent Mechanism of Transition Metal Catalyzed Alkyne Cyclotrimerizations, as Exemplified by Cyclopentadienylcobalt. *J. Am. Chem. Soc.* **1998**, *120*, 8247–8248 and references therein.
- (41) Ir: Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Foltling, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. An η^4 -Benzene Species Mediates Acetylene Cyclotrimerization. *J. Am. Chem. Soc.* **1991**, *113*, 5127–5129.
- (42) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S.; Adams, M.; Rheingold, A. L. [2 + 2 + 1] Alkyne Cyclotrimerizations: A Metallacyclopentadiene Route to Fulvenes. *J. Am. Chem. Soc.* **1997**, *119*, 9, 3631–3632.
- (43) (a) Varela, J. A.; Castedo, L.; Saá, C. One-Step Synthesis of Spiropyridines, a Novel Class of C₂-Symmetric Chiral Ligands, by Cobalt(I)-Catalyzed [2 + 2 + 2] Cycloadditions between Bis-Alkynenitriles and Alkynes. *Org. Lett.* **1999**, *1*, 2141–2143. (b) Varela, J. A.; Castedo, L.; Saá, C. One-Step Synthesis of Symmetrical 3,3'-Substituted 2,2'-Bipyridine Ligands by Cobalt(I)-Catalyzed [2 + 2 + 2] Cycloadditions. *J. Am. Chem. Soc.* **1998**, *120*, 12147–12148. (c) Heller, B.; Oehme, G. First Cobalt(I)-Catalyzed Heterocyclotrimerization of Ethyne with Nitriles to Pyridines in Water under Mild Conditions. *J. Chem. Soc., Chem. Commun.* **1995**, 179–180.
- (44) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. Coupling of Two Ethyne Molecules at Rhodium versus Coupling of Two Rhodium Atoms at Ethyne. 2. Implications for the Reactivity. Catalytic and Stoichiometric Functionalization Reactions of Ethyne. *Organometallics* **1991**, *10*, 645–651.
- (45) (a) Haskel, A.; Straub, T.; Dash, A. K.; Eisen, M. S. Oligomerization and Cross-Oligomerization of Terminal Alkynes Catalyzed by Organoactinide Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 3014–3024. (b) Haskel, A.; Wang, J. Q.; Straub, T.; Neyroud, T. G.; Eisen, M. S. Controlling the Catalytic Oligomerization of Terminal Alkynes Promoted by Organoactinides: A Strategy to Short Oligomers. *J. Am. Chem. Soc.* **1999**, *121*, 3025–3034.

AR000090C