



Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

C. R. Chimie 8 (2005) 1386–1391



<http://france.elsevier.com/direct/CRAS2C/>

Account / Revue

Formation of metal–carbon σ -bonds via reactions of alkynes with iridium and their reactivity toward carbon–carbon bond formation with neighboring hydrocarbyl ligands

Chong Shik Chin *, Hyungeui Lee

Chemistry Department, Sogang University, 121-742 Seoul, South Korea

Received 27 April 2004; accepted 29 November 2004

Available online 23 May 2005

Abstract

In this account we summarize our recent works on the synthesis of iridium-unsaturated hydrocarbyls that contain metal–carbon σ -bonds and their reactions to produce unsaturated organic compounds regio- and stereospecifically. Iridium–carbon σ -bonds are made during the formation of iridium complexes such as metal-alkynyls, -alkenyls, -carbenes (vinylidenes), -alkyls and carbonyls from reactions of terminal alkynes with iridium. The β -carbon of alkynyl ligand is in general so nucleophilic that it is readily attacked by electrophiles to make the α -carbon of the alkynyl ligand reactive with the nucleophilic carbon of the neighboring hydrocarbyl ligand to form new C–C bonds between hydrocarbyl ligands. These C–C bond forming reactions selectively produce interesting unsaturated organic compounds such as conjugated polyenes, polyene-yne, cross-conjugated polyenes and *cis*-olefins. **To cite this article:** C. S. Chin, H. Lee, C. R. Chimie 8 (2005).

© 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Résumé

Nous avons rassemblé dans cette revue nos travaux récents sur la synthèse d'hydrocarbyles d'iridium insaturés contenant une liaison métal–carbone σ et leurs réactions pour produire des composés organiques insaturés de manière régio- ou stéréospécifique. Des liaisons σ iridium–carbone se créent durant la formation de complexes d'iridium tels que métal–alcynyles, –alcényles, –carbènes (vinylidènes), –alkyles et carbonyles, à partir de réactions d'alcynes terminaux avec de l'iridium. Le carbone des ligands alcynyles est généralement si nucléophile qu'il est facilement attaqué par des électrophiles, rendant le carbone du ligand alcynyle réactif avec le carbone nucléophile du ligand hydrocarbyle voisin pour former de nouvelles liaisons C–C entre les ligands hydrocarbyles. Ces réactions formant des liaisons C–C sélectivement produisent des composés organiques insaturés intéressants, tels que des polyènes conjugués, des polyènes-yne, des polyènes conjugués croisés et des oléfines *cis*. **Pour citer cet article :** C. S. Chin, H. Lee, C. R. Chimie 8 (2005).

© 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Keywords: Hydrocarbyl ligand; Metal–carbon σ -bond; C–C bond formation; Insertion of alkynes; Iridium–alkynyls; Iridium–alkenyls; Iridium–carbenes

Mots clés : Ligand hydrocarbyle ; Liaison métal–carbone σ ; Formation de liaisons C–C ; Insertion d'alcynes ; Alcynyles–iridium ; Alcényls–iridium ; Carbènes–iridium

* Corresponding author.

E-mail address: cschin@sogang.ac.kr (C.S. Chin).

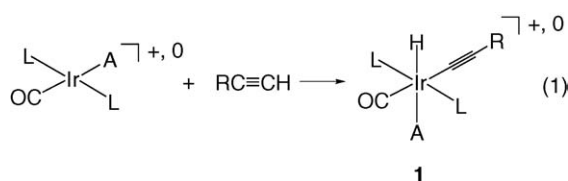
1. Introduction

Metal–carbon σ -bond is apparently the most important bond in organometallic compounds since so many metal-mediated organic syntheses involve steps of forming and breaking of metal–carbon bonds, and numerous well-known catalytic reactions by metal complexes usually include key intermediates having metal–carbon bonds. Among metal–carbon σ -bond containing compounds, metal-unsaturated hydrocarbyls draw more attention due to their applicability to diverse organic synthesis than metal-saturated hydrocarbyls. We have prepared, from reactions of alkynes with iridium, a variety of metal-unsaturated hydrocarbyls containing (i) three, four and five metal–carbon σ -bonds, (ii) all of sp , sp^2 and sp^3 carbons bound to one metal, and (iii) nitrogen, phosphorus and arsenic ylide ligands [1–7]. In this account, we summarize our recent works on the formation of iridium–carbon σ -bonds from reactions of alkynes with iridium producing a variety of iridium-unsaturated hydrocarbyls and the formation of new C–C bonds between the neighboring hydrocarbyl ligands to produce interesting unsaturated organic compounds.

2. Iridium-alkynyls

2.1. Oxidative addition of terminal alkynes: hydrido-alkynyl-iridium

Terminal alkynes are oxidatively added to four coordinated iridium(I) to give six coordinated *cis*-hydrido-alkynyl-iridium(III) (**1**) that are stable in general (Eq. (1)) [8,9].



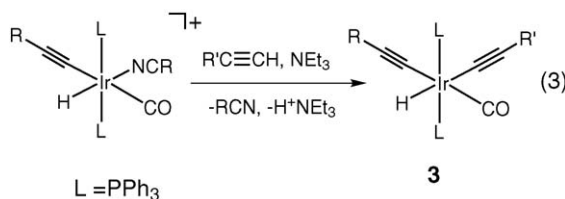
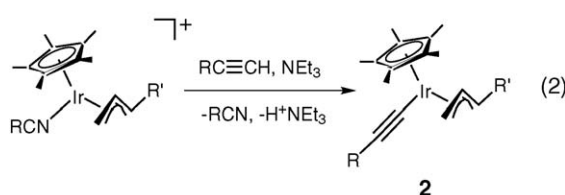
L = PPh₃, A = RCN, OClO₃[−]

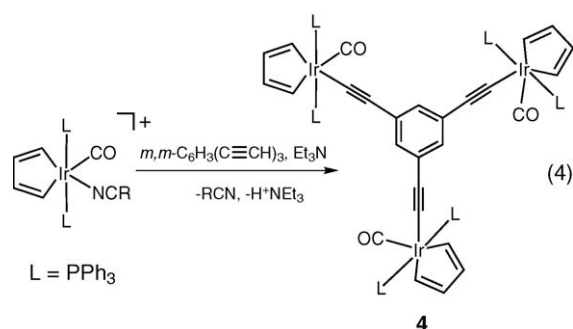
Metal-alkynyls have drawn much attention [10–12] since they are probably the key intermediates for metal-mediated oligomerization of alkynes that produces diverse forms of unsaturated oligomeric hydrocarbons such as cross-conjugated poly-olefin [3], poly-enynes [13,14], alkyne polymers [15] and aromatic com-

pounds [14,16]. In the metal-mediated oligomerization of alkynes, metal-hydrido moiety M–H also plays important roles being involved in the insertion step of an alkyne into the M–C bond (M–H + RC≡CH → M–CH=CHR [3]) and the termination step to give products (M(H)R → M + RH). When these hydrido-alkynyl complexes (**1**) have a labile ligand such as RCN, they show catalytic activity for reactions of alkynes such as oligomerization to give dimeric en-yne and cyclo-trimerization to give aromatics, and in the presence of H₂ hydrogenation of alkynes to give *cis*-olefins and saturated hydrocarbons [17].

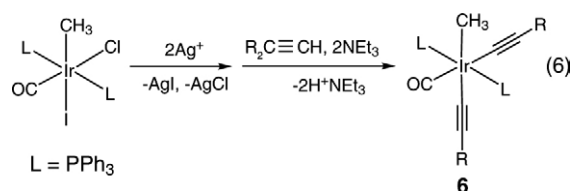
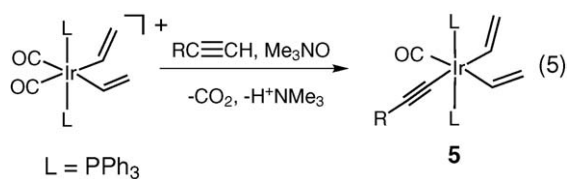
2.2. Alkynylation by substitution of labile ligand in the presence of base

Nitriles coordinated to late transition metals such as iridium(I, III) are so labile that they are readily replaced by alkynyl ligands in reactions of metal with alkynes in the presence of a base such as NEt₃ (Eqs. (2)–(4)) [14,18,19]. Complexes **2** are somewhat unique compounds since they have only the unsaturated hydrocarbyl ligands and react with electrophiles to undergo the carbon–carbon bond forming reactions between the alkynyl and allyl ligands to produce conjugated dienes (see Eq. (7) [18]). Complexes **3** and **4** are also interesting compounds since they have three and four Ir–C σ -bonds for each metal and yet they are so stable that they do not undergo any intra-molecular C–C bond forming reactions by themselves unless a strong electrophilic reagent such as H⁺ is added (see Eq. (8) [4,19]).





Relatively inert ligands such as CO and X⁻ (X = Cl, Br, I) are also effectively replaced with alkyne ligands by using removing agents, Me₃NO and Ag⁺, respectively (Eqs. (5) and (6)). Only one of the two CO ligands is substituted with an alkyne group in high yields in the reactions of alkynes in the presence of Me₃NO (Eq. (5)) [3] while both of halo ligands are effectively removed by Ag⁺ and replaced with alkyne groups in the presence of an amine NEt₃ (Eq. (6)) [20].



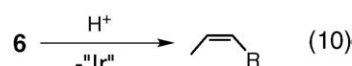
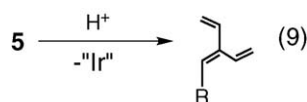
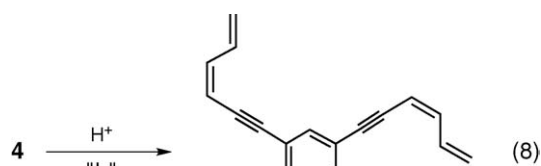
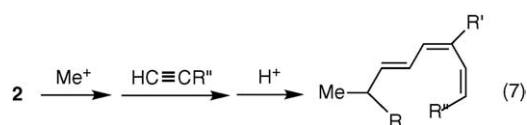
Complexes **5** and **6** are also interesting compounds as they have four Ir–C σ-bonds through the sp² and sp³ carbons, and undergo the C–C bond forming reactions between the hydrocarbyl ligands in the presence of H⁺ (see Eqs. (9) and (10)).

2.3. Reactivity of alkyne ligands

The β-carbon (Ir–C≡CR) of the alkyne ligands of **2–6** readily reacts with electrophiles (E⁺) such as H⁺ and Me⁺ to make the α-carbon (Ir–C⁺=CER) of the

resulting alkenyl ligand so electrophilic that it reacts with the nucleophilic carbon of a neighboring hydrocarbyl ligand to form a new C–C bond between hydrocarbyl ligands [3,4,12,18]. It has been well-known that the β-carbon of the alkyne ligand is so nucleophilic that it is readily attacked by electrophiles [21].

Interesting unsaturated organic compounds such as conjugated polyenes (Eq. (7)) [18], polyenynes (Eq. (8)) [4], cross-conjugated olefins (Eq. (9)) [3] and *cis*-olefins (Eq. (10)) [22] may be selectively obtained in high yields.

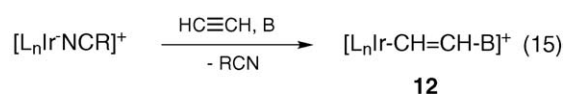


3. Iridium-alkenyls

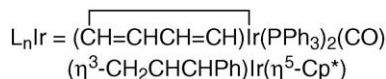
3.1. Oxidative coupling of terminal alkynes: iridacyclopentadienes

Terminal alkynes are added to [Ir(NCCH₃)(CO)(PPh₃)₂]⁺ by oxidative coupling to give stable *cis*-bis(alkenyl) complexes **7** [23] in high yields and these irida-cyclopentadienes **7** further react with alkynes to give alkyne trimerization products, *cis*-dienynes (linear trimers) and aromatic compounds (cyclotrimers) (Eq. (11)) [4]. Metalla-cyclopentadienes have been known to be obtained from reactions of metals not only with terminal alkynes (RC≡CH) but also substituted

been rarely reported except the recent works of ours [19,23]. Apparent insertion of alkynes into the Ir–B (B = NMe₃, PPh₃, AsPh₃) bonds occurs to give iridium complexes of nitrogen, phosphorus and arsenic ylides (Eq. (15)) [19,23,31]. These ylide compounds are prepared from reactions of Ir–NCR complexes with alkynes in the presence of B. Phosphorus ylides are also prepared from reactions of Ir–PPh₃ complexes with alkynes in the absence of excess PPh₃ in relatively high yields. We recently succeeded in preparing iridium complexes having three hydrocarbonyl ligands (**13** [Ir(CH₃)(–CH=CH–NEt₃)(–C≡CR)(CO)(PPh₃)₂]⁺), each of which is bound to the metal through σ-bond of sp³, sp² and sp carbon, respectively [22]. Complexes **13** are the first examples of metal complexes having alkyl, alkenyl and alkynyl ligands. It is interesting that nitrogen ylides of conjugated dienes ([*trans,cis*-Et₃N–CH=CH=CHR]⁺) are separated from the metal by the proton-initiated C–C bond forming reactions between the three sp³ (alkyl), sp² (alkenyl) and sp (alkynyl) carbons of the three hydrocarbonyl ligands of **13** [22].

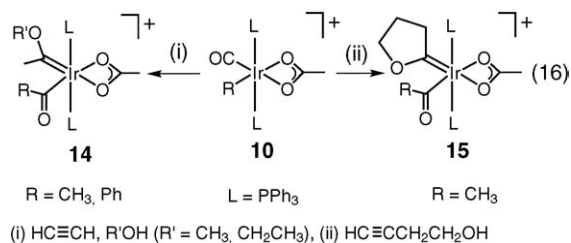


B = NEt₃, PPh₃, AsPPh₃



4. Iridium-carbenes

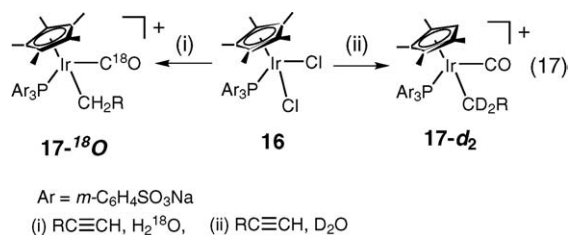
Metal-carbenes (vinylidenes) are frequently found and suggested as the early products during reactions of alkynes with metals [32–34] and Fisher-type metal-carbenes are produced from reactions of alkynes with metals in the presence of alcohols [35,36]. Iridium-alkoxycarbenes (**14**, **15**) are formed from reactions of alkynes in presence of alcohols or yn-ols (Eq. (16)) [6]. Formation of both metal-carbenes **14** and **15** is accompanied by CO insertion into Ir–R bond to provide vacant site for the carbene ligands. Metal vinylidenes (Ir=C=CH₂, Ir=C=CH–CH–OH) are the probable initial intermediates that are attacked by the alcoholic oxygen on the carbene carbon to produce the alkoxy-carbenes as previously suggested [6]. Reactivity of these iridium-carbenes is currently under investigation.



5. Alkyl-carbonyl-iridium from reactions with alkynes and water

Alkyl-carbonyl complexes, M(–CH₂R)(CO) are obtained from reactions of metal with alkynes (RC≡CH) in the presence of H₂O [37–40]. Plausible mechanisms involves the attack of H₂O on the α-carbon of the alkynyl ligand to give the acyl group (M–C≡CR + H₂O → M–C(OH)=CHR → M–COCH₂R) followed by the CO de-insertion (M–COCH₂R → M(–CH₂R)(CO)) [37–40]. We recently observed that a water-soluble η⁵-Cp*IrCl₂(PAr₃) (**16**, Cp* = C₅Me₅[–]; PAr₃ = P(*m*-C₆H₄SO₃Na)₃) reacts with alkynes in H₂O to give water-soluble alkyl-carbonyl-iridium complexes **17** (Eq. (17)) [41].

While no reaction is observed between **16** and olefins such as CH₂=CH₂ in H₂O, the reaction readily occurs to give water-soluble [Cp*(PAr₃)Ir(CH₃)(CO)]⁺ when Ag⁺ is added to the reaction mixture of **16** and CH₂=CH₂ in H₂O to produce in situ [η⁵-Cp*Ir(PAr₃)(OH₂)₂]²⁺ [22]. It has not been well understood yet how the elimination of Cl[–] ligands from **16** makes the reaction with CH₂=CH₂ to occur while it is not necessary for complex **16** to be reactive with alkynes (Eq. (17)). We found that the water-soluble **16** dissociates Cl[–] ligand in H₂O to some extent while the dissociation of Cl[–] ligand has not been reported for Cp*IrCl₂(Ph₃P) that is not water-soluble and does not react with alkynes and olefins at all.



6. Concluding remarks

A variety of hydrocarbyl-iridium complexes such as iridium-alkyls, -alkenyls, -alkynyls and -carbenes can be prepared from reactions with alkynes under appropriate conditions. Various types of conjugated polyenes and poly-en-yne can be prepared by the carbon–carbon coupling reactions between neighboring unsaturated hydrocarbyl ligands. Further investigation should be carried out to make these stoichiometric reactions above to occur catalytically.

Acknowledgements

The authors wish to thank the Korea Research Foundation (KRF) for their financial support of this study through the Basic Science Research Institute program (Grant No. KRF-2003-015-C00332).

References

- [1] C.S. Chin, G. Won, D. Chong, M. Kim, H. Lee, *Acc. Chem. Res.* 35 (2002) 218.
- [2] C.S. Chin, M. Kim, H. Lee, *Organometallics* 21 (2002) 1679.
- [3] C.S. Chin, H. Lee, H. Park, M. Kim, *Organometallics* 21 (2002) 3889.
- [4] C.S. Chin, M. Kim, H. Lee, S. Noh, K.M. Ok, *Organometallics* 21 (2002) 4785.
- [5] C.S. Chin, H. Lee, S. Noh, H. Park, M. Kim, *Organometallics* 22 (2003) 2119.
- [6] C.S. Chin, M. Kim, M.K. Lee, H. Lee, *Organometallics* 22 (2003) 3239.
- [7] C.S. Chin, M. Kim, G. Won, H. Jung, H. Lee, *J. Chem. Soc., Dalton Trans.* (2003) 2325.
- [8] C.S. Chin, M. Oh, G. Won, H. Cho, D. Shin, *Polyhedron* 18 (1999) 811 (and references therein).
- [9] C.S. Chin, J. Yoon, J. Song, *Inorg. Chem.* 32 (1993) 5901.
- [10] M.C. Comstock, J.R. Shapley, *Organometallics* 16 (1997) 4816.
- [11] J.M. O'Connor, M.-C. Chen, M. Frohn, A.L. Rheingold, I.A. Guzei, *Organometallics* 16 (1997) 5589.
- [12] B.M. Trost, M.T. Sorum, C. Chan, A.E. Harms, G. R  hter, *J. Am. Chem. Soc.* 119 (1997) 698.
- [13] T. Ohmura, S. Yorozuya, Y. Yamamoto, N. Miyaura, *Organometallics* 19 (2000) 365 (and references therein).
- [14] C.S. Chin, G. Won, J. Song, *Bull. Korean Chem. Soc.* 15 (1994) 961.
- [15] Y. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* 121 (1999) 12035 (and references therein).
- [16] M.S. Sigman, A.W. Fatland, B.E. Eaton, *J. Am. Chem. Soc.* 120 (1998) 5130.
- [17] Unpublished results.
- [18] C.S. Chin, W. Maeng, D. Chung, G. Won, B. Lee, Y. Park, et al., *Organometallics* 18 (1999) 2210.
- [19] C.S. Chin, H. Lee, M. Oh, *Organometallics* 16 (1997) 816.
- [20] C.S. Chin, M. Lee, M. Oh, G. Won, M. Kim, Y. Park, *Organometallics* 19 (2000) 1572.
- [21] I. de los Rios, M.J. Tenorio, M.C. Puerta, P. Valerga, *J. Am. Chem. Soc.* 119 (1997) 6529 (and references therein).
- [22] C.S. Chin, H. Cho, G. Won, M. Oh, K. Ok, *Organometallics* 18 (1999) 4810.
- [23] C.S. Chin, Y. Park, J. Kim, B. Lee, *J. Chem. Soc. Chem. Commun.* (1995) 1495.
- [24] A.D. Burrows, M. Green, J.C. Jeffrey, J.M. Lyman, M.F. Mahon, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 3043 (For example, see).
- [25] J.M. O'Connor, A. Closson, K. Hiibner, R. Merwin, P. Gantzel, *Organometallics* 20 (2001) 3710.
- [26] C.S. Chin, H. Lee, M. Eum, S. Hong, *J. Organomet. Chem.* 690 (2005) 1306.
- [27] J.F. Corrigan, N.J. Taylor, A. Carty, *Organometallics* 13 (1994) 3778.
- [28] K. Yang, S.G. Bott, M.G. Richmond, *Organometallics* 13 (1994) 3767.
- [29] J. Takats, J. Washington, B.D. Santarsiero, *Organometallics* 13 (1994) 1078.
- [30] D.M. Hoffman, J.C. Huffman, D. Lappas, D.A. Wierda, *Organometallics* 12 (1993) 4321.
- [31] C.S. Chin, D. Chong, M. Kim, H. Lee, *Bull. Korean Chem. Soc.* 22 (2002) 739.
- [32] D. Amoroso, G.P.A. Yap, D.E. Fogg, *Organometallics* 21 (2002) 3335.
- [33] M. Saoud, A. Romerosa, M. Peruzzini, *Organometallics* 19 (2000) 4005.
- [34] S.M. Hansen, M.A.O. Volland, F. Rominger, F. Eisentrager, P. Hofman, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 1273.
- [35] M.F. Semmelhack, A. Lindenschmit, D. Ho, *Organometallics* 20 (2001) 4114.
- [36] H.D. Hansen, J.H. Nelson, *Organometallics* 19 (2000) 4740.
- [37] M.V. Jimenez, E. Sola, A.P. Martinez, F.J. Lahoz, L.A. Oro, *Organometallics* 18 (1999) 1125.
- [38] C. Bianchini, J.A. Casares, M. Peruzzini, A. Romerosa, F. Zanobini, *J. Am. Chem. Soc.* 118 (1996) 4585.
- [39] M.L. Buil, M.A. Esteruelas, A.M. Lopez, E. O  ate, *Organometallics* 16 (1997) 3169.
- [40] B.P. Sullivan, R.S. Smithe, E.M. Kober, T.J. Meyer, *J. Am. Chem. Soc.* 104 (1982) 4701.
- [41] C.S. Chin, D. Chong, B. Maeng, J. Ryu, H. Kim, M. Kim, H. Lee, *Organometallics* 21 (2002) 1739.