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Title: Competition between vinylidene rearrangement and 1,2-insertion of carbon-disubstituted internal alkynes at a Cp*Ir(III) complex

Even carbon-disubstituted internal alkynes can select the "vinylidene rearrangement route". Vinylidene rearrangement of diarylacetylenes in an aryl-Ir(III) complex has been shown to become a kinetically (and thermodynamically) more favorable path than common 1,2-insertion.

As featured in:
See Youichi Ishii et al. *Dalton Trans.*, 2015, 44, 17448.
**Competition between vinylidene rearrangement and 1,2-insertion of carbon-disubstituted internal alkynes at a Cp*Ir(III) complex†**

Yousuke Ikeda, a Shintaro Kodama, a Noriko Tsuchida b and Youichi Ishii a

Vinyldiene rearrangement is now recognized as one of the most valuable methods for the transformation of terminal alkynes.1 Details of this tautomerization involving mechanistic studies1,2 and applications to organic synthesis1 have been well discussed. The rich reactivities of vinylidenedes as well as the accumulated mechanistic information concerning their formation brought about interest in the vinyldiene rearrangement of more general alkynes.3,4 However, the tautomerization of internal alkynes is still not recognized as a common process,4,5 although a few examples of the internal alkyne-disubstituted vinyldiene rearrangement have been studied by us and other groups during the last decade.3,4 This is partly because the vinyldiene rearrangement of internal alkynes is a slower process than that of terminal alkynes, hence cannot compete necessarily the kinetic product. This also provides the first example of vinyldiene rearrangement of internal alkynes at metal complexes other than group 8 metals.

The iridium precursor 1 was readily synthesized by the reaction of [Cp*IrCl3]2 with 2-(2,3,4,5-tetrafluorophenyl)pyridine in the presence of NaOAc·3H2O and fully characterized by spectroscopic as well as crystallographic analysis (see ESI†). When 1 was allowed to react with diphenylacetylene and NaBARF1 in C6H6Cl2 (1,2-dichloroethane) at 50 °C for 4 h, the colour of the reaction mixture turned from yellow to dark purple (Scheme 1). Recrystallization of this mixture afforded the nine-membered iridacycle complex 2a with an Ir–(vinyl CH) agostic interaction as dark purple crystals in 87% isolated yield, and 2a was fully characterized by means of NMR analysis as well as a single-crystal X-ray diffraction study (Fig. 1, left). In the 1H NMR spectrum, the vinyl CH signal of 2a appears in a

†Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kassuga, Bunkyo-ku, Tokyo, Japan. E-mail: yoshiki@chuo-u.ac.jp; Fax: +81-3-3817-1895; Tel: +81-3-3817-1901

‡Department of Liberal Arts, Faculty of Medicine, Saitama Medical University, 38 Morohongo, Moroyama-machi, Iruma-gun, Saitama 350-0495, Japan. E-mail: n.tsuchi@saitama-med.ac.jp; Fax: +81-49-276-1901; Tel: +81-49-276-1901

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The formation of complexes \( \text{Cp}^*\text{Ir}\{\eta^2-\text{PhC(Ph)}\}]\) was fully characterized by spectroscopic reactions have so far been observed only at group 8 metal complexes.\(^3,4\) The thermodynamic product of this reaction is the \( \eta^1\)-pyrindosiquinolinium complex \( 4c\) (Scheme 2). A structurally related rhodium complex was already reported by Huang.\(^6\) Obviously complex \( 4c\) is formed from the 1,2-insertion of the alkynyl into the \( \text{Ir}^\text{II}\) core by the \( \text{Ir}^\text{III}\) metallocene complex instead of the vinylidene rearrangement, and this species was further isomerized to \( 4c\) through the reductive elimination (vide infra).

Surprisingly, as the reaction proceeded, isomerization of \( 4c\) to \( 2c\) was observed, and it was completed after 10 h (Scheme 3). Thus, complex \( 4c\) is kinetically formed at the early stage of this reaction, and on maintaining at 50 °C, \( 4c\) slowly isomerizes to \( 2c\), the thermodynamic product of this reaction. Similarly, \( \text{Cp}^*\text{Ir}(\text{i})\) complex \( 4a\) was observed at the early stage of the reaction of \( 3\) with \( \text{PhC}==\text{CPh}\) as a minor species and isomerized to \( 2a\) over 4 h (Scheme 3), although it could not be isolated in a pure form (Scheme 2).\(^{12}\) On the other hand, the has migrated across the \( \text{C}==\text{C}\) bond during the reaction. In addition, one Ph group is \textit{ortho}-metallated by the iridium center, and the H atom is transferred to the vinyl carbon (C1). These results clearly demonstrate that the formation of \( 2a\) occurred through the initial vinylidene rearrangement to generate the diphenylvinylidene intermediate followed by the \( 1,1\)-insertion of the vinylidene ligand into the \( \text{Ir}^\text{III}\) core to the \( \eta^1\)-position of the Ph group originated from the alkynyl (vide infra). Similarly, \( \eta^1\)-substituted diphenylacetylene derivatives \( p\text{-XC}6\text{H}4\text{C}==\text{C}6\text{H}4\text{C}==\text{CPh}\) \((X = \text{Me}, \text{Cl})\) were applied to this transformation, and the corresponding cyclometalated complexes \( 2b\) and \( 2c\) were formed in good yield under appropriate conditions (Scheme 1). Apparently, in this system, vinylidene rearrangement of internal alkynes was more favored than 1,2-insertion into the \( \text{Ir}^\text{III}\) core. It should also be mentioned that the present reaction provides the first example of the vinylidene rearrangement of carbon-disubstituted internal alkynes at an Ir complex,\(^10\) related reactions have so far been observed only at group 8 metal complexes.\(^3,4\)

To gain deeper insight into this reaction, we monitored the progress of the formation of \( 2c\) at 50 °C in DCl by means of \( ^1\text{H}\) NMR.\(^{11}\) After 30 min, \( 1\) was consumed completely, and two \( \text{Cp}^*\) signals were observed at \( \delta 1.58\) and 1.63 in the intensity ratio of 1 : 2.1. The former signal is assigned to \( 2c\), whereas the latter species was isolated in 50% yield as yellow crystals by column chromatography on silica gel and characterized unambiguously by X-ray diffraction study (see ESI†) as the \( \text{Ir}(\text{i})\) \( \eta^1\)-pyrindosiquinolinium complex \( 4c\) (Scheme 2). A structurally related rhodium complex was already reported by Huang.\(^6\)

Fig. 1 ORTEP drawings of \( 2a\) (left) and \( 3\) (right). Anionic part and hydrocarbon atoms except for H1 of \( 2a\) are omitted for clarity. Selected bond lengths (Å) and angles (°): \( 2a\), Ir1–N1, 2.121(5); Ir1–C1, 2.213(5); Ir1–C4, 2.026(6); Ir1–C9, 122.5(6); C2–C3–C4, 1.461(9); C1–C2–C3, 114.0(5); C1–C2–C9, 123.0(6); C3–C2–C9, 122.5(6); C2–C1–C15, 119.3(5). \( 3\), Ir1–N1, 2.085(3); Ir1–C1, 2.033(5); Ir1–C4, 2.056(4); C1–C2, 1.346(6); Ir1–C1–C2, 120.3(3); Ir1–C1–C15, 112.8(3); C2–C1–C15, 126.0(4); C1–C2–C3, 112.5(4); C1–C2–C9, 125.4(4); C3–C2–C9, 121.7(4).

using its \( ^{13}\text{C}[^1\text{H}]\) NMR signal exhibited notable high-field shift \((\delta 4.16)\) as an agostic CH, whereas its \( ^{13}\text{C}\) signal at 49.3. It is interesting to note that these spectroscopy data are in marked difference to those of the related \((\text{o-vinyl})\text{aryliridium complex}\ [\text{Cp}^*\text{Ir}[\text{o-\text{C}_6\text{H}_4\text{C(Ph)}==\text{CPh}]\text{(PM}_{3}\text{)]\text{[BARF}_4]}]\) which shows its vinyl CH signal at \( \delta -0.30\) in the \( ^1\text{H}\) NMR and \( \delta 86.4\) in the \( ^{13}\text{C}[^1\text{H}]\) NMR spectra.\(^7\) The molecular structure of \( 2a\) shows that the Ir1–C1 distance at 2.214(5) Å is explicitly shorter than common agostic iridium–CH distances,\(^7,8\) suggesting that the iridium center of \( 2a\) interacts more strongly with the C1 atom than the common Ir–CH agostic interaction. In fact, complex \( 2a\) easily dissociates the agostic vinyl proton by stirring in MeOH at room temperature for 30 min to form the neutral iridium[III] complex \( 3\) in 73% isolated yield (Scheme 1). Complex \( 3\) was fully characterized by spectroscopic as well as crystallographic analysis (Fig. 1, right). Importantly, the two Ph groups of \( 2a\) are bound to the same carbon atom (C2), indicating that one of the Ph groups of diphenylacetylene

![Scheme 1 Reaction of 1 with diphenylacetylene derivatives and NaBARF₄, and deprotonation of 2a to form 3.](image1)

![Scheme 2 Formation of complexes 4.](image2)
formation of 2b was so fast that the corresponding 4b could not be observed.

The above observation indicates that the rate of the formation of 2 is notably enhanced by introducing electron donating groups into the \( \text{para} \) positions of the diphenylacetylene. Recently we have shown both experimentally and theoretically that the internal alkyne-disubstituted vinylidene rearrangement at \([\text{CpRu(dppe)}]^+\) is facilitated by an electron-donating substituent,\(^{14b, c}\) and this tendency is in good agreement with the present observations, suggesting that the present vinylidene rearrangement at the \( \text{Ir(III)} \) center involves nucleophilic aryl migration in the rate determining step. In addition, the ppy-F\(_4\) ligand is essential for the formation of 2; the reaction of \([\text{Cp*IrCl(ppy)}]\) (5) with \( \text{PhC} = \text{COPh} \) in the presence of \( \text{NaBArF}_4 \) at 50 \( ^\circ \text{C} \) for 30 min resulted in selective formation of 6 as the sole product in 67% yield, and the corresponding vinylaryliridium species was not formed any more (Scheme 4). For a better understanding of the above observations, preliminary density functional theory (DFT) calculations on the cationic part of 2a and 4a were performed with the \( \text{B3PW91} \) functional. As expected, it was confirmed that 2a is more stable in energy than 4a by 8.52 kcal mol\(^{-1}\), which gives good explanation for the selective formation of 2 as the thermodynamic product (Scheme 5). Although we must await a more detailed theoretical study, several mechanisms are considered to be plausible for the conversion of 4 to 2. One is the \( \text{C} = \text{N} \) bond oxidative addition followed by the \( \beta\)-carbon elimination (back-reaction from 4) to regenerate the \( \eta^1\)-alkyne complex,\(^{13}\) which then undergo vinylidene rearrangement. \( \beta\)-Carbon elimination from a vinyl complex to form the corresponding \( \eta^2\)-alkyne complex is a rare process, but some examples are known in the literature.\(^{4f, 14}\) Alternatively, direct isomerization of the seven-membered iridacycle 5 may be operative. In this case, concerted migration of the iridium center and an aryl group (Fig. 2[a]) or an aryl group migration to eliminate \( \text{C}_9\text{H}_9\text{N} = \text{C}_6\text{F}_4\) anion followed by its nucleophilic attack at the vinylidene \( \alpha\)-carbon (Fig. 2[b]) is assumed to be involved.\(^{15}\)

Finally, we have investigated the reactivity of 1 with acyl alkyne, which is known to be a reactive substrate towards a vinylidene rearrangement.\(^{3, 4c}\) When a mixture of 1 with \( \text{PhC} = \text{CCOPh} \) and \( \text{NaBArF}_4 \) in \( \text{C}_2\text{H}_4\text{Cl}_2 \) was allowed to react at 50 \( ^\circ \text{C} \) for 30 min, a mixture of yellow and red crystals was obtained after recrystallization. X-ray diffraction studies disclosed that the yellow product is the ten-membered iridacycle 7, while the red one is attributed to the vinyliridium complex 8 (see ESI†).\(^{16}\) These complexes could be separated by column chromatography on silica gel and isolated in 36% and 38% yields, respectively.

Judging from these structures, the 1,2-insertion and vinylidene rearrangement of \( \text{PhC} = \text{CCOPh} \) competitively occurred to generate the seven-membered vinyliridium species 9 and the iridium vinylidene species 10. Complex 7 was formed from 9 by the 1,4-Ir migration from the vinyl to the \( \text{ortho} \) position of the COPh group, whereas 8 was produced by the 1,1-insertion of the vinylidene ligand in 10 into the \( \text{Ir} = \text{C}_6\text{F}_4 \) bond and the
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Scheme 6  Reactions of $1$ with PhC$_2$COPh and NaBAR$_4$.

final coordination of the oxygen atom of the carbonyl group (Scheme 6). Unlike the reaction with diarylalkynes, the ratio of $7$ and $8$ was not changed by further heating at $50 \, ^\circ$C.$^{17}$

In conclusion, we have revealed that the reaction of $[\text{Cp*Ir(ppy-}F_4\text{)}]^+$ with diphenylacetylene derivatives afforded the nine-membered metallacycle complex $2$ by way of the sequential vinylidene rearrangement, $1,1$-insertion of the vinylidene ligand, and the 1,4-Ir migration to the Ar group. Detailed analysis of this reaction disclosed that $2$ and the Ir(i) pyridosoquinoxaline complex $4$, the latter of which is a normal $1,2$-insertion–reductive elimination product, are competitively generated at the early stage of the reaction, but $4$ is gradually isomerized to $2$, indicating that $2$ is the thermodynamically favoured product. The present reaction provides not only the first example of the internal alkyne-disubstituted vinylidene rearrangement at an iridium complex but also a rare example of actual observation of the competition between vinylidene rearrangement and $1,2$-insertion of internal alkynes.

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Instead of CDCl$_3$, C$_2$H$_4$Cl$_2$ was used as the solvent for initial 30 min of this reaction because of the insolubility of NaBAR$_4$ for CDCl$_3$.

The structure of 4a was determined by a preliminary single-crystal X-ray diffraction study.

Preliminary DFT calculation indicated that the free energy barrier of activation for the $\beta$-carbon elimination is ca. 19 kcal mol$^{-1}$ (see ESI†), and therefore we consider that the formation of the $\eta^2$-alkyne complex from A is acceptable in the present reaction conditions, while we have not obtained satisfactory calculation results to explain the C–N bond oxidative addition yet.

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The $^1$H NMR analysis of the crude reaction mixture indicated that complexes 7 and 8 were formed in the ratio of 1.4 : 1.

When isolated 7 and 8 are dissolved in C$_2$H$_4$Cl$_2$ and kept at 50 °C overnight, no isomerization was observed for both complexes.