1−ナフチルホスフィンから誘導されるビニルロジウム錯体における アルキンのβ−炭素脱離

β-Carbon Elimination to Give an Alkyne from a Vinylrhodium Complex Derived from 1-Naphthylphosphine

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1. Introduction

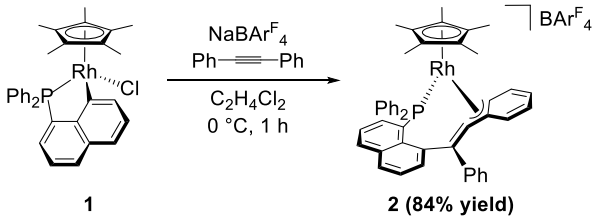
The migratory insertion of an unsaturated bond into a metal−carbon bond represents a prevalent elementary step in organometallic chemistry. Its reverse process, namely β-carbon elimination, has also attracted increasing attention in recent years, because this process can provide unique methods for the activation of a C−C bond. However, despite of many reports on β-carbon elimination reactions of alkyl−alkoxometal complexes, those of alkenylmetal species, the reverse processes of alkyne insertion, have scarcely been reported. Pioneering work by Etienne *et al.* showed that the R/R' exchange reaction of an alkylniobium complex [Tp*NbCl(R)(R'C≡CR")] proceeds via the sequential alkyne insertion−β-carbon elimination.[1] This laboratory also reported specific examples using late transition metals, where the alkyne insertion−β-carbon elimination process competes with the vinylidene rearrangement of the alkyne.[2,3] However, fundamental characteristics of this reaction still remain to be investigated. In this study, the author has focused his attention on more direct observation of the β-carbon elimination from alkenylmetal complexes to give alkynes, and found that a new rhodium complexes derived from 1-naphtylphosphine and PhC≡CPh is capable of alkenyl moiety exchange reaction under very mild conditions via β-carbon elimination.

2. Experimental Section

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. New organometallic compounds were characterized by NMR, X-ray diffraction, and elemental analyses.

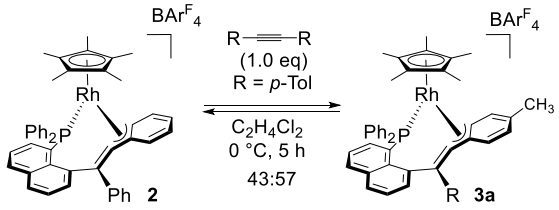
3. Results and Discussion

First, the author synthesized rhodium complex **2** by modifying a synthetic method for an analogous Ru(η^6-C_6Me_6) complex. [Cp*RhCl{$PPh_2(C_{10}H_6)$-κ-*P,C*}] (**1**) was reacted with 1.0 equivalent of PhC≡CPh in the presence of $NaBAr^F_4 \cdot 2H_2O$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$) to afford the desired (η^3-α-phenylvinyl)rhodium complex **2** as black purple crystals in 84% yield (Scheme 1).



Scheme 1. Synthesis of alkenyl rhodium complex **2**.

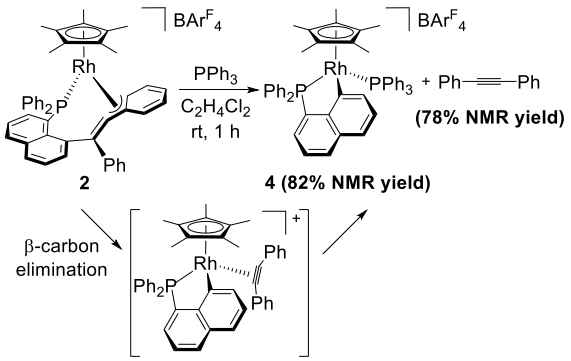
Then, complex **2** was treated with 1.0 equivalent of di(*p*-tolyl)acetylene in $C_2H_2Cl_2$ at 0 °C. After 5 h, $^{31}P\{^1H\}$ NMR analysis of the crude product showed a new signal at 39.7 ppm along with that attributable to the starting complex **2** (40.6 ppm) in the ratio of 43:57. The ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR signals derived from the novel complex was completely consistent with those of an authentic sample of **3a**, which was prepared by the reaction of the complex **1** and di(*p*-tolyl)acetylene. This



Scheme 2. Reaction of **2** with di(*p*-tolyl)acetylene.

result indicates that the alkenyl moiety of the complex **2** is readily exchanged on treatment with an alkyne.

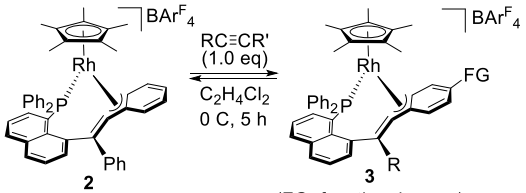
In order to gain insight into the reaction mechanism, *in situ* trapping of the rhodium intermediate was examined. When complex **2** was allowed to react with PPh_3 instead of an alkyne, PPh_3-coordinated rhodium complex **4** and free diphenylacetylene were obtained in 82 and 78% yield, respectively. Formation of complex **4** should result from ligand exchange of alkyne-coordinated rhodium complex generated by the β-carbon elimination of **2**. Thus, the exchange reaction of alkenyl unit is deduced to be mediated by the β-carbon elimination of alkenyl rhodium complex **2**.



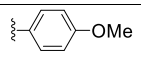
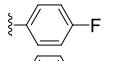
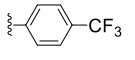
Scheme 3. Tapping experiment of the rhodium intermediate using PPh_3.

The author next examined scope of alkynes, and the results with aryl-substituted alkynes are shown in Table 1. A reaction with electron-rich di(*p*-anisyl)acetylene provided a mixture of **2** and **3b**, and the equilibrium ratio was identical with that of di(*p*-tolyl)acetylene (entry 1). In contrast, in the reactions with electron-deficient diarylalkynes, the equilibrium ratio of **3** significantly decreased (entries 2 and 3). These

Table 1. Scope of alkynes.



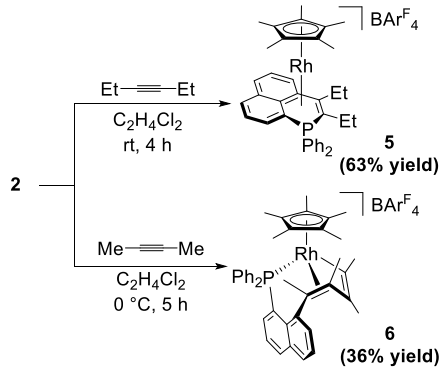
(FG=functional group)

entry	R	R'	Ratio (**2**:**3**)[a]
1			43:57
2			70:30
3			72:28
4[b]	Me	Ph	23:77

[a]Product ratios were determined by $^{31}P\{^1H\}$ NMR analysis.
[b]No regioisomer was observed by $^{31}P\{^1H\}$ NMR analysis.

electronic effects of aryl groups can be rationalized by assuming better η^3-coordination of the electron-rich C−(*p*-anisyl) and C−(*p*-tolyl) groups to the cationic Rh(III) center. Reaction with 1-phenyl-1-propyne proceeded with high regioselectivity to afford the corresponding alkenyl rhodium complex, in which the rhodium center is located on the phenyl side (entry 4). This selectivity also stems from the stable η^3-coordination of the C−Ph group.

In contrast, the reaction of **2** with 3-hexyne resulted in the formation of the η^4-phosphaphenalenium complex **5**, which was formed by the P–C reductive elimination following the alkyne exchange reaction. Moreover, when reacted with excess amount of 2-butyne, double insertion of the alkyne took place to give the nine-membered rhodacycle **6** (Scheme 5). In these cases, **2** was completely converted to **5** and **6**, suggesting their irreversibility.



Scheme 4. Reaction of **2** with dialkylacetylenes.

4. Conclusion

The author has investigated β-carbon elimination of metalacyclic alkenylrhodium complexes through their alkenyl moiety exchange reaction. Exchange reactions with arylalkynes gave equilibrium mixtures, while those with 3-hexyne and 2-butyne led to the exclusive formation of phosphaphenalenium complex **5** and nine-membered rhodacycle **6**, respectively.

References

(1) Etienne, M. e*t al*. *J. Am. Chem. Soc*. **1997**, *119*, 3218−3228. (2) Ishii, Y. *et al*. *Organometallics*, **2013**, *32*, 4353−4358. (3) Ishii, Y. *et al*. *Dalton Trans.* **2015**, *44*, 17448−17452.

Presentation List

(1) 100th CSJ Annual Meeting 2H2-35 (2020). (2) 70th Conf. of JSCC, 1D-13 (2020).