Internal Alkyne-to-vinylidene Isomerization at Cationic Ruthenium and Iron Complexes

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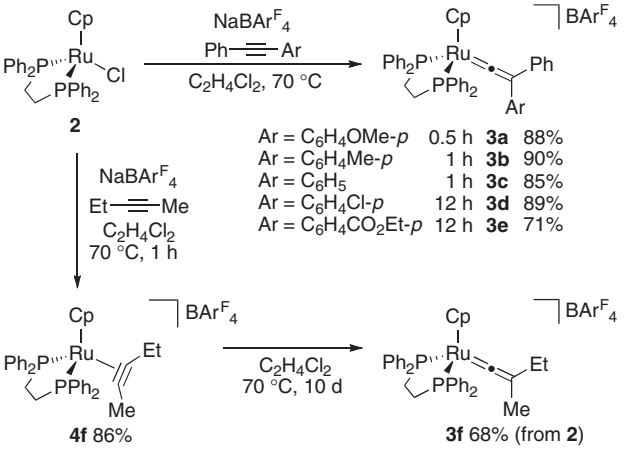
Cationic ruthenium and iron complexes $[CpM(PP)]^+$ ($Cp = \eta^5$-C_5H_5; M = Ru and Fe; $PP = Ph_2PCH_2CH_2PPh_2$, $2PPh_3$) can affect vinylidene rearrangement of general internal alkynes via the 1,2-migration of aryl and alkyl groups. Judging from the migratory aptitude of substituted aryl groups, the present reaction is viewed as an uncommon electrophilic rearrangement.

It is well known that terminal alkynes are readily converted into the corresponding vinylidenes at transition-metal complexes by several distinct mechanisms,[1] and this rearrangement has been utilized as the key step in many metal-promoted or -catalyzed transformations of alkynes.[2] In contrast, migration of carbon substituents of internal alkynes has been observed in very few rearrangements of acylalkynes,[3] though vinylidene rearrangement of heteroatom-substituted ($-SiR_3$,[4] $-SnR_3$,[5] $-SR$,[6] and $-I$[7]) internal alkynes has recently been receiving considerable attention. In the course of our studies on transition-metal cyclophosphato complexes[8] which are structurally related to hydroxyapatite-supported metal catalysts,[9] we have revealed that a ruthenium cyclotriphosphato ($P_3O_9^{3-}$) complex (PPN)[Ru(P_3O_9)(MeOH)(dppe)] (**1**; PPN = $(Ph_3P)_2N^+$; dppe = $Ph_2PCH_2CH_2PPh_2$) can affect the vinylidene rearrangement of general internal alkynes via the 1,2-migration of alkyl, aryl, and acyl groups.[8d] The findings prompted us to examine whether more commonly used CpRu and CpFe ($Cp = \eta^5$-C_5H_5) complexes can affect the internal alkyne-to-vinylidene isomerization.

Initially, we examined the reaction of [CpRuCl(dppe)] (**2**) with PhC≡CC$_6$H$_4$OMe-*p* which was found to be the most reactive in the reaction with **1**.[8d] When **2** was allowed to react with PhC≡CC$_6$H$_4$OMe-*p* (4 equiv) in the presence of $NaBAr^F_4$ (1.2 equiv; Ar^F = 3,5-$(CF_3)_2C_6H_3$) in 1,2-dichloroethane ($C_2H_4Cl_2$) at 70 °C for 0.5 h, the vinylidene complex [CpRu(=C=C(Ph)-C$_6$H$_4$OMe-*p*)(dppe)][BAr^F_4] (**3a**) was obtained in 88% yield as red crystals (Scheme 1).[10] Use of $NaBAr^F_4$ was essential for the selective formation of **3a**; either $AgPF_6$ or $NaBPh_4$ instead of $NaBAr^F_4$ resulted in the formation of a complex mixture containing **3a**. Complex **3a** exhibits $^{13}C\{^1H\}$ NMR signals at δ 350.4 (t, $^2J_{PC}$ = 16 Hz) and 133.3 (s) characteristic of the α and β carbons of a vinylidene ligand, respectively. The molecular structure of **3a** has been established unambiguously by X-ray analysis to confirm that migration of an aryl group took place to form the disubstituted vinylidene ligand (Figure 1, left).[10] The metrical features including the Ru–C1 and C1–C2 bond distances of 1.838(4) and 1.327(6) Å, respectively, and the Ru–C1–C2 bond angle of 173.3(2)° fall in the range of common Ru^{II}–vinylidene complexes.[11] Similar reactions were also observed with other internal alkynes to give the corresponding vinylidene complexes **3b**–**3e** in high yields.

On the other hand, treatment of **2** with EtC≡CMe (7 equiv) at 70 °C for 1 h resulted in the formation of the η^2-alkyne com-



Scheme 1.

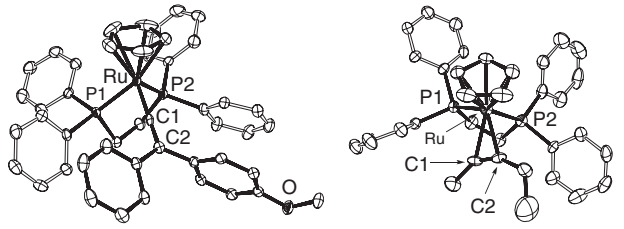
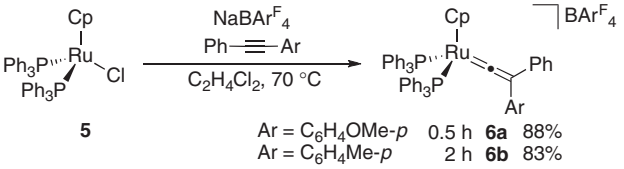


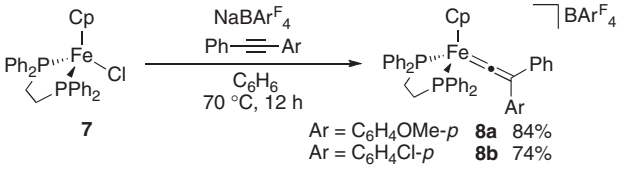
Figure 1. ORTEP drawings of **3a** (left) and **4f** (right). Anionic part and hydrogen atoms are omitted for clarity.

plex [CpRu(EtC≡CMe)(dppe)][BAr^F_4] (**4f**) in 86% isolated yield as yellow needles (Scheme 1), which was characterized by the $^{13}C\{^1H\}$ NMR signals at δ 77.8 and 82.1 (coordinated C≡C) and the IR absorption at 1951 cm^{-1} ($\nu_{C\equiv C}$) as well as by crystallographic study (Figure 1, right).[10] The alkyne complex **4f** was further transformed into the corresponding vinylidene complex **3f** as the sole product by heating in $C_2H_4Cl_2$ for 10 d. Unlike the P_3O_9–alkyne complexes (PPN)[Ru(P_3O_9)(RC≡CR)(dppe)],[8d] **4f** was not converted into **3f** by UV irradiation.

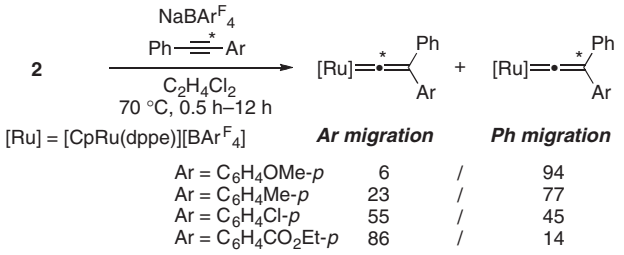
Similar vinylidene formation took place at the PPh_3 complex [CpRuCl(PPh_3)$_2$] (**5**) to give [CpRu(=C=C(Ph)Ar)-(PPh_3)$_2$][BAr^F_4] (**6**) in high yields (Scheme 2).[10] This result indicates that the vinylidene rearrangement of internal alkynes enjoys considerably high applicability as a synthetic method for disubstituted vinylidenes.[12]



Scheme 2.



Scheme 3.



Scheme 4. Migratory aptitude of alkyne substituents. The asterisks represent ^{13}C-enriched carbon atoms.

Unexpectedly, the disubstituted vinylidene formation was also found to proceed with a CpFe system. Although [CpFeCl(dppe)] (**7**) failed to react with PhC≡CAr in $C_2H_4Cl_2$ in the presence of NaBAr$^F_4$, the desired vinylidene complexes [CpFe(=C=C(Ph)Ar)(dppe)][BAr$^F_4$] (**8**) were obtained in high yields by using benzene as the solvent (Scheme 3). Complexes **8** were fully characterized by spectroscopy as well as an X-ray diffraction study of **8a** (structure not shown).[13] This reaction provides the first example of the internal alkyne-to-vinylidene isomerization at an iron complex. It should be noted that the reverse process, that is, vinylidene-to-alkyne rearrangement was observed with the carbonyl complex [CpFe(CO)$_2$(=C=CR$_2$)]-(OTf) (Tf = SO_2CF_3).[14]

In order to shed light on the mechanistic aspects of the present reaction, the migratory aptitude of aryl groups has been investigated using ^{13}C-enriched alkynes PhC≡^{13}CAr (ca. 26% ^{13}C). Migration of the Ar group gives rise to the α-^{13}C-labeled vinylidene complex (Ar migration), whereas the Ph group migration leads to the β-^{13}C-labeled product (Ph migration) (Scheme 4). Detailed ^{13}C{^{1}H} NMR analysis[10] of the reaction products with a series of ^{13}C-labeled alkynes disclosed that the migratory aptitude of alkyne substituents is in the order C_6H_4-CO_2Et-*p* > C_6H_4Cl-*p* > C_6H_5 > C_6H_4Me-*p* > C_6H_4OMe-*p*. Hammett analysis of the relative migratory aptitude indicates a linear correlation between σ_p and log[(Ar migration)/(Ph migration)], where the ρ value is estimated to be 2.53 (R^2 = 0.97).

A similar tendency was observed in the vinylidene rearrangement with **1**,[8d] and the order of the migratory aptitude is opposite to that of common nucleophilic rearrangements in organic chemistry.[15] Obviously the electron-withdrawing group on an alkyne substituent increases the migratory aptitude through the stabilization of the negative charge on the migrating Ar group in the transition state; therefore, the results shown above suggest that an present rearrangement proceeds through the uncommon electrophilic 1,2-shift of the carbon substituents.[16]

In summary, we have revealed that commonly used CpRu and CpFe complexes can affect the internal alkyne-to-vinylidene isomerization and determined the migratory aptitude of aryl groups in the reaction of **2**. Detailed mechanisms and synthetic applications of this reaction will be reported in due course.

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12 It was noted that the reaction of [{CpRu(PPh$_3$)$_2$}$_2$(μ-N$_2$)][BAr$^F_4$]$_2$ with PhC≡CPh failed to give vinylidene complex.[3b]

13 **8a**: ^{1}H NMR: δ 3.01 (br, 2H, CH$_2$ of dppe), 3.23 (br, 2H, CH$_2$ of dppe), 3.69 (s, 3H, OCH$_3$), 5.22 (s, 5H, C$_5$H$_5$), 6.44–7.72 (m, 41H, Ar). ^{13}C{^{1}H} NMR: δ 360.8 (t, J = 33 Hz, Fe=C), 144.2 (Fe=C=*C*) ^{31}P{^{1}H} NMR: δ 94.5 (s, dppe). IR (cm^{-1}): 1621 (m, $\nu_{C=C}$). Anal. Calcd for $C_{78}H_{53}BF_{24}FeOP_2$: C, 58.89; H, 3.36%. Found: C, 58.63; H, 3.19%.

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