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Reversibility of Disubstituted Vinylidene−Internal Alkyne Isomerization at Cationic Ruthenium and Iron Complexes

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Summary: The cationic disubstituted vinylideneruthenium complexes $[CpRu\{=C=C(Ph)R\}(dppe)][BAr^F{}_4]$*, which are prepared directly from internal alkynes via 1,2-migration of carbon substituents, are shown to undergo disubstituted vinylidene-to-internal alkyne isomerization on reaction with a monophosphine. The observation provides the first examples in which the reversible conversion between internal alkynes and disubstituted vinylidenes is experimentally confirmed, and the kinetic and mechnistic investigations indicated that an uncommon electrophilic 1,2-migration of the carbon substituents takes place in the internal alkyne−disubstituted vinylidene interconversion.*

It is well recognized that terminal alkynes are readily and reversibly interconvertible with monosubstituted vinylidenes at transition-metal complexes, and this rearrangement has in fact been utilized in many metal-promoted or -catalyzed transformations of alkynes as the key step.[1] In contrast, prior to our study, migration of carbon substituents in internal alkynes leading to the disubstituted vinylidenes was limited to very few rearrangements of acylalkynes,[2] although similar rearrangements of silyl-,[3] stannyl-,[4] sulfenyl-,[5] and iodo-substituted[6] alkynes have appeared in the literature. Very recently, we have demonstrated that several iron and ruthenium complexes can affect the vinylidene rearrangement of a wide variety of internal alkynes to give disubstituted vinylidene complexes such as $[CpRu\{=C=C(Ph)Ar\}(dppe)][BAr^F{}_4]$ (**1**; Cp = η^5-C_5H_5, dppe = $Ph_2PCH_2CH_2PPh_2$, Ar^F = 3,5-$(CF_3)_2C_6H_3$).[7] We have also disclosed that this transformation involves an uncommon electrophilic 1,2-migration of carbon substituents at the intermediary η^2-alkyne complexes. Meanwhile, the reverse process, i.e., the conversion of vinylidenes to alkynes, is well documented for the monosubstituted vinylidene complexes, especially the $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2]$ system.[8] However, similar conversions of η^1-vinylidenes with two carbon substituents into the η^2 internal alkynes have scarcely been explored. The only example reported so far is the *irreversible conversion* of the η^1-vinylidene in $[CpFe(CO)_2\{=C=C(Ph)Me\}](OTf)$ (Tf = SO_2CF_3) into the corresponding η^2-alkyne complex,[9] although the reversible migration of a silyl group was observed in the (β,β-bis(silyl)-vinylidene)chromium complex $[Cr(\eta^6\text{-}C_6Me_6)(CO)_2\{=C=C(SiMe_3)_2\}]$[3b] and ($\beta$-silyl-$\beta$-arylvinylidene)rhodium complex *trans*-$[RhCl\{=C=C(ferrocenyl)SiMe_3\}(P\text{-}i\text{-}Pr_3)_2]$.[3c] Now, we have experimentally demonstrated for the first time that the transformation between alkynes and vinylidenes via carbon substituent migration is potentially reversible (Scheme 1).

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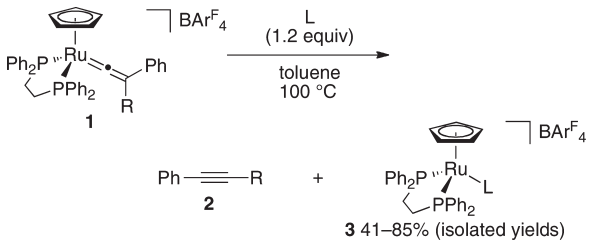
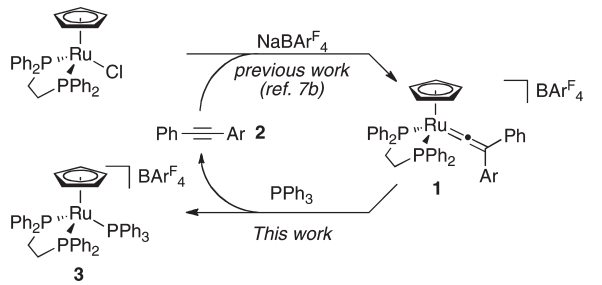
Table 1. Reaction of Disubstituted Vinylidene Complexes 1 with L[a]



entry	1	R	L	time	2	GC yield (%)
1	**1a**	C_6H_4OMe-*p*	PPh_3	1 h	**2a**	95
2	**1b**	C_6H_4Me-*p*	PPh_3	4 h	**2b**	99
3	**1c**	C_6H_5	PPh_3	23 h	**2c**	91
4	**1d**	C_6H_5Cl-*p*	PPh_3	22 h	**2d**	51
5	**1e**	$C_6H_4CO_2Et$-*p*	PPh_3	137 h	**2e**	81
6	**1f**	Me	PPh_3	34 days	**2f**	21
7	**1g**	COPh	PPh_3	3 h	**2g**	91
8	**1c**	C_6H_5	PMe_2Ph[b]	23 h	**2c**	92
9	**1c**	C_6H_5	PMe_3[b]	19 h	**2c**	89
10	**1c**	C_6H_5	$P(OPh)_3$	23 h	**2c**	99
11	**1c**	C_6H_5	MeCN[c]	24 h		no reacn

[a] Conditions: $[\mathbf{1}]_0 = 10.0$ mM, $[L]_0 = 12.0$ mM, in toluene, at 100 °C. [b] $[L]_0 = 20.0$ mM. [c] Neat, at reflux temperature.

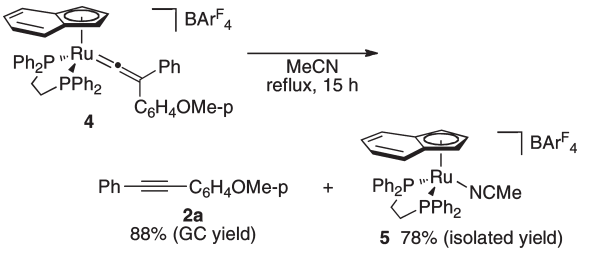
Scheme 1



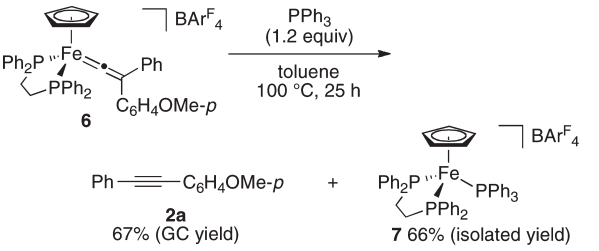
The migratory aptitude of the alkyl and aryl substituents in this rearrangement has been investigated.

When the disubstituted vinylidene complex [CpRu{=C=C(Ph)C_6H_4OMe-*p*}(dppe)][BAr^F_4] (**1a**) was allowed to react with PPh_3 (1.2 equiv) in toluene at 100 °C for 1 h, a color change from red to pale yellow was observed, and the $^{31}P\{^1H\}$ NMR analysis of the solution indicated the complete consumption of **1a**. GC analysis of the reaction mixture showed liberation of the internal alkyne PhC≡CC_6H_4OMe-*p* (**2a**) from **1a** in 83% yield. The organometallic product [CpRu(dppe)(PPh_3)][BAr^F_4] (**3**) was isolated in good yield as pale yellow crystals, which was confirmed by spectroscopic and elemental analysis as well as by an X-ray study (structure not shown). As summarized in Table 1, diarylalkynes **2b**−**e** with various substituents at the para position were also obtained in good yields from the (aryl)(phenyl)-substituted vinylidenes (entries 2−5), where the electron-donating substituents enhanced the reaction rate. *β*-Alkyl and *β*-acyl groups were tolerated in the reaction (entries 6 and 7), but the conversion of **1f** was much slower than for diarylvinylidene complexes. Similar reactions with other tertiary phosphines such as PMe_2Ph, PMe_3, and $P(OPh)_3$ proceeded smoothly to give the corresponding alkyne and phosphine-ligated complexes [CpRu(dppe)(*P*)][BAr^F_4] (*P* = PMe_2Ph, PMe_3, $P(OPh)_3$) (entries 8−10). In the absence of a phosphine ligand,

Scheme 2



Scheme 3



disubstituted vinylidenes were stable in MeCN (entry 11), whereas the indenylruthenium disubstituted vinylidene complex [(η^5-C_9H_7)Ru{=C=C(Ph)C_6H_4OMe-*p*}(dppe)][BAr^F_4] (**4**) reacted with MeCN to give **2a** and the Ru−NCMe complex [(η^5-C_9H_7)Ru(dppe)(NCMe)][BAr^F_4] (**5**) (Scheme 2).[10] Since **1** and **4** are directly obtained by the reaction of [CpRuCl(dppe)] and [(η^5-C_9H_7)RuCl(dppe)] with internal alkynes **2** in the presence of $NaBAr^F_4$,[7b] these observations provide the first examples in which the reversible conversion between internal alkynes and disubstituted vinylidenes has been experimentally confirmed.

Not only the ruthenium complexes **1** and **4** but also the disubstituted vinylideneiron complex [CpFe(=C=C(Ph)C_6H_4-OMe-*p*)(dppe)][BAr^F_4] (**6**),[7b] which can be derived directly from [CpFeCl(dppe)] and **2a** in the presence of $NaBAr^F_4$, undergoes vinylidene-to-alkyne rearrangement on treatment with PPh_3 in toluene at 100 °C to give alkyne **2a** and the PPh_3-ligated complex [CpFe(dppe)(PPh_3)][BAr^F_4] (**7**) (Scheme 3). It should be noted that only the disubstituted vinylidene-to-alkyne rearrangement was observed at $[CpFe(CO)_2]^+$, as already mentioned,[9] while $[CpFe(dppe)]^+$ can promote both conversions.

The kinetic aspects of the reaction were revealed by following the conversion of the disubstituted vinylidene complex **1c** into the phosphine complex **3** by means of $^{31}P\{^1H\}$ NMR spectroscopy at 100 °C. No intermediate species was detected, and the reaction could be treated as first order in the concentration of **1c**. As given in Table 2, the observed rate constant (k_{obs}) was estimated as $[4.65(6)] \times 10^{-5}$ s^{-1} in the presence of 1.2 equiv of PPh_3 (entry 1), and this value was not affected at this temperature either by the concentration of added PPh_3 (entries 1−4) or by that of added **2c** (entry 5). In addition, essentially the same k_{obs} values were obtained even

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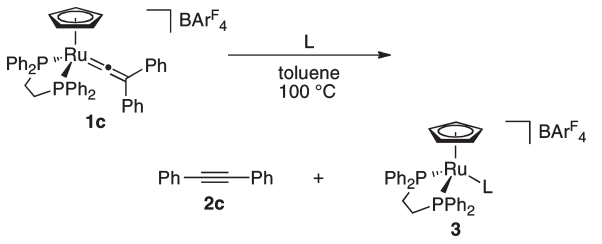
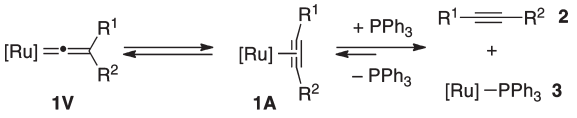
Table 2. Effect of Concentration and Types of Phosphine on the First-Order Rate Constants k_{obs} for the Conversion of 1c into 3[a]



entry	L	$[L]_0$ (mM)	$10^5 k_{obs}$ (s^{-1})
1	PPh_3	10.3	4.65(6)
2	PPh_3	26.3	4.61(5)
3	PPh_3	41.6	4.60(4)
4	PPh_3	83.1	4.67(5)
5[b]	PPh_3	25.2	4.67(7)
6	PMe_2Ph	23.2	4.67(8)
7	PMe_3	26.0	4.68(6)
8	$P(OPh)_3$	25.9	4.68(5)

[a] Reaction conditions: $[\mathbf{1c}]_0 = 8.47 \pm 0.12$ mM, $[\mathbf{2c}]_0 = 0$ mM, in toluene, at 100 °C for 10 h (ca. 80% conversion of **1c**). [b] $[\mathbf{2c}]_0 = 25.2$ mM.

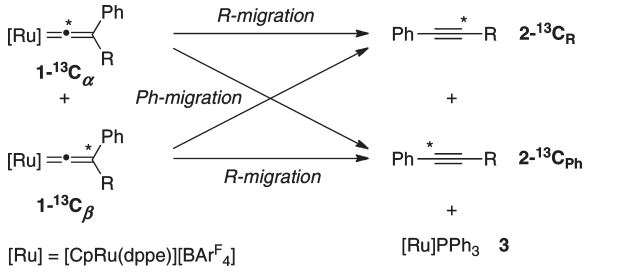
Scheme 4



when different phosphines were used (entries 2 and 6−8). On the basis of these observations, the present reaction is deduced to be a two-step successive reaction involving the intramolecular isomerization of the starting disubstituted vinylidene complex (**1V**) to the η^2 internal alkyne intermediate (**1A**) followed by ligand substitution to give **3a** (Scheme 4). Judging from the coordinatively saturated nature of **1A**, the latter process is considered to proceed by a dissociative mechanism, but the zero-order dependence on the concentration of added phosphine and internal alkyne indicates that the isomerization process from **1V** to **1A** is the rate-determining step. This view agrees with the fact that the concentration of **1A** remains lower than the observation limit by $^{31}P\{^1H\}$ NMR.

To gain further insight into the isomerization mechanism, we next investigated the migratory aptitude of the substituents in disubstituted vinylidene complexes **1** using ^{13}C-enriched vinylidene complexes **1-^{13}C** (Table 3). Migrations of the R group in **1-^{13}C$_\alpha$** and phenyl group in **1-^{13}C$_\beta$** (denoted as R migration and Ph migration, respectively) give rise to the internal alkynes **2-^{13}C$_R$**, where the carbon atom next to the R group is labeled with ^{13}C. Similarly, Ph migration from **1-^{13}C$_\beta$** and R migration from **1-^{13}C$_\alpha$** leads to the formation of **2-^{13}C$_{Ph}$** with the ^{13}C-enriched carbon atom next to the phenyl group. Detailed $^{13}C\{^1H\}$ NMR analyses disclosed the ratio of R migration to Ph migration as shown in the table, where the migratory aptitude is in the order COPh > $C_6H_4CO_2Et$-*p* > C_6H_4Cl-*p*/C_6H_5 > C_6H_4Me-*p* > Me > C_6H_4OMe-*p*. In this regard, the order obtained for Ph/Me migration is in accordance with Ph migration at $[CpFe(CO)_2\{=C=C(Ph)Me\}](OTf)$ rather than Me migration.[9] Hammett analysis of the relative migratory aptitude of aryl groups

Table 3. Migratory Aptitude in the Reaction of 1-^{13}C with PPh_3[a]



R	time	R migration/Ph migration[b]
C_6H_4OMe-*p*	1 h	3/97
C_6H_4Me-*p*	4 h	25/75
C_6H_4Cl-*p*	44 h	50/50
$C_6H_4CO_2Et$-*p*	137 h	83/13
Me	34 days	15/85
COPh	3 h	> 99/< 1

[a] The reactions were performed as shown in Table 1. The asterisks represent ^{13}C-enriched carbon atoms. **2-^{13}C** were obtained in 8−86% GC yields and **3** in 68−89% isolated yields. [b] The ratios were estimated by $^{13}C\{^1H\}$ NMR analysis. See the Supporting Information for details.

indicates an almost linear correlation between σ_P and log[(Ar migration)/(Ph migration)] ($\rho = 2.8$).

The above order of the migratory aptitude is opposite to that of common nucleophilic rearrangements in organic chemistry, where the migrating group moves with its bonding electrons.[11] The derived ρ value denotes substantial development of negative charge in the transition state, reflecting that an electron-withdrawing group enhances migratory aptitude. These tendencies are also observed for internal alkyne−disubstituted vinylidene isomerization at an anionic $Ru(P_3O_9)$ complex[7a] and cationic CpRu and CpFe complexes.[7b] Therefore, we suggest that the η^2 internal alkyne−η^1 disubstituted vinylidene isomerization proceeds through an uncommon electrophilic 1,2-shift of the carbon substituents. In this context, it should be mentioned that the mechanism of vinylidene rearrangement of terminal alkynes at ruthenium complexes still remains a subject of discussion; migration of a proton is proposed for the rearrangement of $[RuCl_2(HC{\equiv}CH)(PH_3)_2]$,[12] while it has been suggested that migration of a hydride rather than a proton could be involved in the η^1 monosubstituted vinylidene to η^2-1-alkyne rearrangement at the indenylruthenium complex $[(\eta^5\text{-}C_9H_7)Ru(=C{=}CHAr)(PPh_3)_2][PF_6]$.[8g]

It should also be noted that the reactivity of disubstituted vinylidenes **1** for the present rearrangement is not controlled by the migratory aptitude of the substituents; **1a** with a C_6H_4OMe-*p* substituent, which shows the lowest migratory aptitude, is the fastest to react. Probably the stability of the vinylidene and η^2-alkyne complexes is increased by an electron-withdrawing group. A similar tendency was observed for the internal alkyne to vinylidene isomerization at $[(P_3O_9)Ru]^-$, $[CpRu]^+$, and $[CpFe]^+$ complexes.[7]

In summary, we have demonstrated the first reversible interconversion between internal alkynes and disubstituted vinylidenes at cationic ruthenium and iron complexes.

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The kinetics and migratory aptitude revealed that an uncommon electrophilic 1,2-shift of carbon substituents takes place in the present isomerization. Further studies on detailed mechanisms and synthetic applications of this reaction will be reported in due course.

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Supporting Information Available: Text, figures, and CIF files giving experimental procedures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.