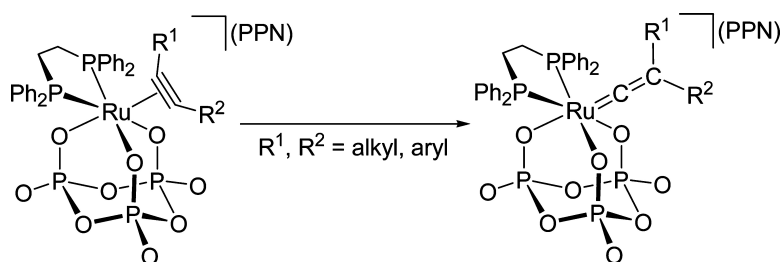Communication

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Formation of Vinylidenes from Internal Alkynes at a Cyclotriphosphato Ruthenium Complex

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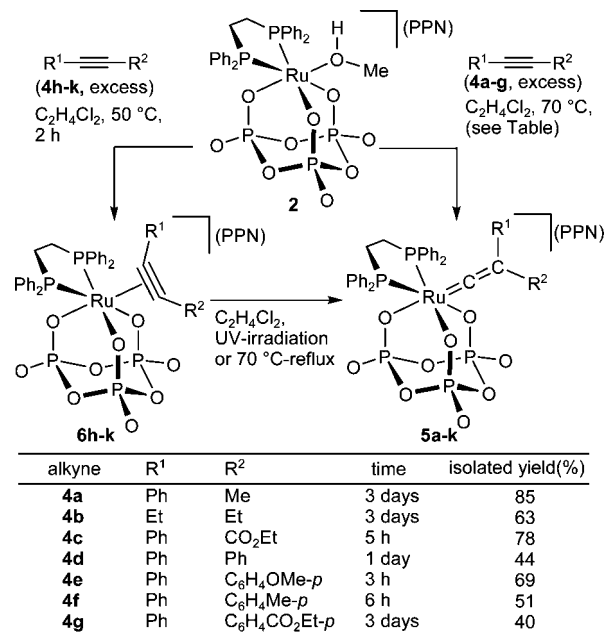Received October 13, 2008; E-mail: yo-ishii@kc.chuo-u.ac.jp

Terminal alkynes are readily converted into the corresponding vinylidenes at transition metal complexes by a direct 1,2-hydrogen shift, C−H oxidative addition−1,3-hydrogen shift, sequential protonation−deprotonation, and other mechanisms.[1] This tautomerization is now recognized as the key step in many metal-promoted or -catalyzed transformations of alkynes.[2] Heteroatom-substituted alkynes such as silyl-,[3] stannyl-,[4] thio-,[5] and iodoalkynes[6] are also known to undergo similar rearrangement. In contrast, migration of carbon substituents of internal alkynes has been limited to very few rearrangements of acylalkynes,[7] although the reverse process, i.e., the conversion of disubstituted vinylidenes to the η^2-internal alkynes, has been described in the literature.[8] In the course of our study on the transition metal cyclophosphato complexes which are structurally related to the hydroxyapatite-supported metal catalysts,[9] we have revealed that this class of organometallic complexes exhibits unique structural and chemical properties based on the circular array of P−O groups as an effective σ-donor set.[10] Now we have found that a ruthenium cyclotriphosphato ($P_3O_9^{3-}$) complex with a labile MeOH ligand can affect the vinylidene rearrangement of general internal alkynes via the 1,2-migration of alkyl, aryl, and acyl groups.

Coordination chemistry of ruthenium P_3O_9 complexes has not been explored extensively, but photochemical ligand substitution of the benzene complex $(PPN)[Ru(P_3O_9)(C_6H_6)]$ (1; PPN = $(Ph_3P)_2N^+$)[11] was found to be a versatile entry to reactive ruthenium species. Thus, UV-irradiation of 1 in MeOH−CH_2Cl_2 in the presence of dppe (dppe = $Ph_2PCH_2CH_2PPh_2$; 1.2 equiv) led to isolation of the MeOH complex $(PPN)[Ru(P_3O_9)(MeOH)(dppe)]$ (2) in 71% yield as orange crystals. An X-ray diffraction study of 2·3MeOH has confirmed its molecular structure with an octahedral geometry in which three facial coordination sites are occupied by the axial oxygen atoms of the P_3O_9 ligand (see Supporting Information). The MeOH ligand in 2 is highly labile and readily replaced by N_2 in CH_2Cl_2 to form $(PPN)[Ru(P_3O_9)-(N_2)(dppe)]$ (3), which exhibits a $\nu_{N\equiv N}$ band at 2154 cm^{-1} in the IR spectrum. On dissolution in MeOH under argon, 3 is quickly converted back to 2.

When 2 was allowed to react with 1-phenyl-1-propyne (4a, 2.6 equiv) in $C_2H_4Cl_2$ at 70 °C for 3 days, the vinylidene complex $(PPN)[Ru(P_3O_9)(=C=C(Ph)Me)(dppe)]$ (5a) was obtained in 85% yield as green crystals (Scheme 1; see Supporting Information for experimental details). Complex 5a exhibits $^{13}C\{^1H\}$ NMR signals at δ 369.0 (t, $^2J_{PC}$ = 20 Hz) and 118.2 (s) characteristic of the α and β carbons of a vinylidene ligand, respectively. The molecular structure of 5a·2MeOH has been established unambiguously by an X-ray diffraction study to confirm that either Me or Ph migration took place to form the disubstituted vinylidene ligand (see Supporting Information). The metrical features including the Ru−C_α and C_α−C_β bond distances of 1.842 (4) and 1.277(5) Å, respec-

tively, and the Ru−C_α−C_β bond angle of 178.4(3)° are comparable to common Ru(II)−vinylidene complexes.[12] Similar reactions were also observed with other internal alkynes such as 4b−4g, providing the first example of alkyne-to-vinylidene rearrangement of general internal alkynes. At present, the role of the P_3O_9 ligand is not fully understood, but we consider that its σ-donor character favors the formation of a π-acidic vinylidene ligand. It should be noted that the rate of the reaction is strongly dependent on the substituents; the reactions of 4a, 4b, and 4g are relatively slow and take a long time (3 days) to go to completion, while those of 4c, 4e, and 4f are completed within 3−6 h under the same conditions (70 °C). Intermediate complexes could not be isolated in any of these reactions.
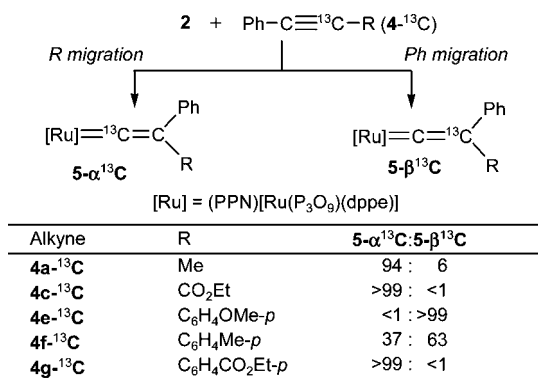
Scheme 1

alkyne	R¹	R²	time	isolated yield(%)
4a	Ph	Me	3 days	85
4b	Et	Et	3 days	63
4c	Ph	CO₂Et	5 h	78
4d	Ph	Ph	1 day	44
4e	Ph	C₆H₄OMe-p	3 h	69
4f	Ph	C₆H₄Me-p	6 h	51
4g	Ph	C₆H₄CO₂Et-p	3 days	40

On the other hand, treatment of 2 with alkynes 4h−4k (4h: R¹ = R² = CO_2Me; 4i: R¹ = R² = CO_2Et; 4j: R¹ = Me, R² = CO_2Et; 4k: R¹ = Et, R² = CO_2Et) at 50 °C resulted in the formation of the η^2-alkyne complexes $(PPN)[Ru(P_3O_9)(R^1C\equiv CR^2)(dppe)]$ (6h−6k) in 66−85% isolated yields, which were characterized by the $^{13}C\{^1H\}$ NMR signals at δ 72−87 (coordinated C≡C) and the IR absorption at 1920−1950 cm^{-1} ($\nu_{C\equiv C}$) as well as by a crystallographic study of 6j. These alkyne complexes were further transformed into the corresponding vinylidene complexes 5h−5k in 54−85% isolated yields either by heating in $C_2H_4Cl_2$ (up to 5 days) or more effectively by UV-irradiation at room temperature.[3a,d]

Obviously, in these cases, the vinylidene rearrangement is much slower than the alkyne coordination.

A preliminary kinetic study on the conversion of **6k** to **5k** at 70 °C in the presence of excess **4k** by means of $^{31}P\{^1H\}$ NMR clearly indicated that the reaction obeys first-order kinetics with an apparent rate constant (k) of 3.09×10^{-5} s^{-1}. This result demonstrated that the reaction proceeds via an intramolecular process, which is further supported by the fact that crossover of the alkyne substituents was not observed in the reactions with unsymmetric alkynes, especially **4f**. On the other hand, judging from the normal $\nu_{N\equiv N}$ value of **3**,[13] the oxidative addition of an internal alkyne to the 16e [Ru^{II}(P$_3$O$_9$)(dppe)]$^-$ fragment to form the (alkyl/aryl)(alkynyl) complex seems unlikely. Therefore we presume that the present vinylidene rearrangement involves the 1,2-alkyl/aryl shift of the intermediary alkyne complex. Theoretical studies on the terminal alkyne-to-vinylidene rearrangement have also suggested that the 1,2-hydrogen shift mechanism is most commonly operative with a Ru(II) center.[14]

To gain deeper insight into the reaction mechanism, the migratory aptitude of alkyl, aryl, and acyl groups has been investigated by using ^{13}C-enriched alkynes PhC≡^{13}CR (**4**-^{13}C, 25.9% ^{13}C). Migration of the R group gives rise to the α-^{13}C labeled vinylidene complex (**5**-α^{13}C), while the Ph migration leads to the β-^{13}C labeled product (**5**-β^{13}C) (Scheme 2). When complex **1** was reacted with **4a**-^{13}C, the $^{13}C\{^1H\}$ NMR analysis of the reaction mixture indicated that the ^{13}C content of the α-carbon in the product is 9.84 times as high as that of β-carbon, which implies that the ratio of Me and Ph migration is 94:6 (see Supporting Information). Detailed analysis of analogous reactions with a series of **4**-^{13}C disclosed that the migratory aptitude of alkyne substituents is in the order CO$_2$Et, C$_6$H$_4$CO$_2$Et-p > Me > Ph > C$_6$H$_4$Me-p > C$_6$H$_4$OMe-p.

Scheme 2[a]

Alkyne	R	**5**-α^{13}C:**5**-β^{13}C
4a-^{13}C	Me	94 : 6
4c-^{13}C	CO$_2$Et	>99 : <1
4e-^{13}C	C$_6$H$_4$OMe-p	<1 : >99
4f-^{13}C	C$_6$H$_4$Me-p	37 : 63
4g-^{13}C	C$_6$H$_4$CO$_2$Et-p	>99 : <1

^{a} Reaction conditions: C$_2$H$_4$Cl$_2$, 70 °C.

The above result clearly shows that electron-withdrawing groups enhance the migratory aptitude. Quite interestingly, this order is opposite to that of common organic nucleophilic rearrangements, in which the migrating group behaves as a formal carbanion.[15] Although we must await further investigation to elucidate the detailed reaction mechanism, the above result seems to suggest a mechanism involving the electrophilic 1,2-shift of the carbon substituents. This interpretation is in good agreement with the theoretical calculation results on the vinylidene rearrangement of a terminal alkyne at RuCl$_2$(PH$_3$)$_2$, where the migrating hydrogen behaves as a proton.[14a,16] In contrast, however, it should be noted that only Ph group migration has been observed in the vinylidene-to-alkyne rearrangement of [Cp(CO)$_2$Fe=C=C(Me)Ph]$^+$ (Cp = η^5-C$_5$H$_5$).[8] It is also interesting to note that the reaction rate of the

vinylidene rearrangement is not parallel with the migratory aptitude of the substituents. Especially in the series of 1-aryl-2-phenylacetylenes, the orders of reactivity and migratory aptitude are opposite to each other. We consider the rate of the vinylidene formation is strongly controlled by the stability of the intermediate alkyne complexes rather than the migratory aptitude of each substituent.

In conclusion, we have developed the first internal alkyne-to-vinylidene isomerization with high generality by using ruthenium P$_3$O$_9$ complex **2** and determined the migratory aptitude of alkyl, aryl, and acyl groups. Detailed mechanisms and synthetic applications of this reaction are now under investigation.

Supporting Information Available: Experimental details and crystallographic data for **2**·3MeOH, **5a**·2MeOH, and **6j**·2C$_2$H$_4$Cl$_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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