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Unexpected Formation of the Vinyl−Phosphonio Complex [CpRu(PPh$_3$)(C$_6$H$_4$PPh$_2$CH═CH$_2$)][PF$_6$] from a Vinylidene Complex via Nucleophilic Addition and Ortho Metalation of Triphenylphosphine

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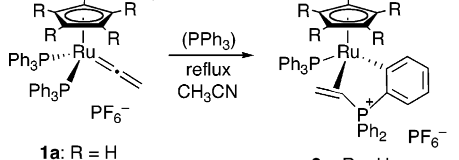
Summary: The reaction of Ru−vinylidene complexes with triphenylphosphine led to the formation of vinyl−phosphonio complexes in good yields. The results obtained by using a deuterium-labeled complex and a methyldiphenylphosphine analogue indicated that the present reaction proceeded via nucleophilic addition to the α-carbon of the vinylidene group, followed by ortho metalation of the phenyl ring on the cationic phosphorus atom.

Introduction

During the past decade, the chemistry of Ru−vinylidene complexes has become increasingly attractive, because it has been disclosed that the catalytic organic transformation of terminal alkynes often proceeds via a vinylidene intermediate.[1] Representative examples of such a catalytic reaction include dimerization,[2] coupling with alkene and pyridine,[3] cyclization of alkynes,[4] and addition of heteroatom nucleophiles to alkynes.[5] The reactivity of Ru−vinylidene complexes has been studied extensively in order to not only understand the reaction mechanism but also obtain fundamental information for the development of new catalytic reactions. For example, a nucleophile usually attacks the α-carbon of vinylidene ligands to produce a Fischer-type carbene complex,[6] whereas an electrophile attacks the β-carbon to generate a carbyne complex.[7] In the course of our studies on Ru−vinylidene complexes,[8] we discovered the formation of vinyl−phosphonio complexes, in which one of the phenyl groups on the cationic phosphorus atom is bound to the Ru atom at the ortho position and the vinyl group is in the π-coordination mode. In contrast to the report that the reactions of vinylidene complexes of metals other than Ru with phosphine led to addition at the α-carbon to give σ-alkenyl complexes,[9] there have been reports that the Ru−vinylidene complexes show unusual reactivity toward phosphine. For example, the reactions of the Ru−vinylidene complexes with phosphine and phosphite resulted in formal addition at the β-carbon[10] and the displacement of the vinylidene ligand,[11] respectively. We report herein our experimental results of the reaction of Ru−vinylidene complexes, yielding vinyl−phosphonio complexes.

Results and Discussion

Heating of an acetonitrile solution of the vinylidene complex **1a** at 80 °C led to the slow formation of the new complex **2a** (eq 1). After 24 h, the conversion was approximately 50%, and 5 days was needed for the complete consumption of **1a** to give **2a** in quantitative



1a: R = H
1b: R = Me

2a: R = H
2b: R = Me

(1)

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(1) For recent reviews, see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193−195*, 977. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

(2) (a) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (b) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Johar, P. S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 987. (c) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616. (d) Matsuzaka, H.; Takagi, Y.; Ishii, Y.; Nishio, M.; Hidai, M. *Organometallics* **1995**, *14*, 2153. (e) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968. (f) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.

(3) (a) Murakami, M.; Ubukata, M.; Ito, Y. *Tetrahedron Lett.* **1998**, *39*, 7361. (b) Murakami, M.; Hori, S. *J. Am. Chem. Soc.* **2003**, *125*, 4720.

(4) (a) Onitsuka, K.; Katayama, H.; Sonogashira, K.; Ozawa, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2267. (b) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (c) Murakami, M.; Ubukata, M.; Ito, Y. *Chem. Lett.* **2002**, 294.

(5) (a) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518. (b) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (c) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579. (d) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247. (e) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680. (f) Tokunaga, M.; Suzuki, T.; Koga, N.; Fukushima, T.; Horiuchi, A.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 11917. (g) Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **2002**, *124*, 2528. (h) Fukumoto, Y.; Dohi, T.; Masaoka, H.; Chatani, N.; Murai, S. *Organometallics* **2002**, *21*, 3845. (i) Jérôme, F.; Monnier, F.; Lawicka, H.; Dérien, S.; Dixneuf, P. H. *Chem. Commun.* **2003**, 696.

(6) (a) Bruce, M. I.; Swincer, A. G.; Wallis, R. C. *J. Organomet. Chem.* **1979**, *171*, C5. (b) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471. (c) Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1986**, *317*, C25. (d) Davies, S. G.; Smallridge, A. J. *J. Organomet. Chem.* **1990**, *395*, C39.

(7) (a) Stüer, W.; Wolf, J.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 3421. (b) Gonzalez-Herrero, P.; Weberndoerfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672. (c) Beach, N. J.; Jenkins, H. A.; Spivak, G. J. *Organometallics* **2003**, *22*, 5179.

(8) Ajioka, Y.; Matsushima, Y.; Onitsuka, K.; Yamazaki, H.; Takahashi, S. *J. Organomet. Chem.* **2001**, *617−618*, 601.

10.1021/om049440f CCC: $27.50

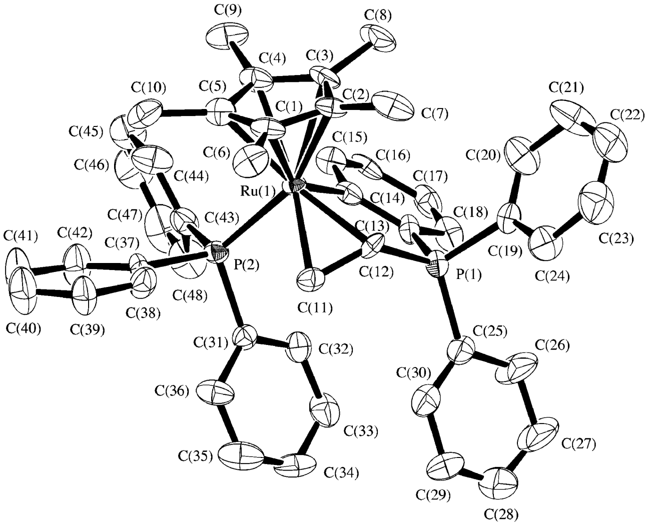
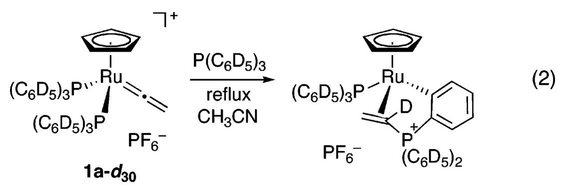


Figure 1. Molecular structure of the cation of complex **2b**. Hydrogen atoms are omitted for clarity.

yield. The ^{31}P NMR spectrum of **2a** showed two doublets at δ 56.7 ($J = 4$ Hz) and 39.7 ($J = 4$ Hz). The fairly small coupling constant suggested that **2a** had no CpRu(PPh$_3$)$_2$ skeleton. In the ^{1}H NMR spectrum, three characteristic signals were observed at δ 4.1, 3.7, and 1.7. As each signal was attributed to one proton, two of those signals would be due to the protons originating from the vinylidene ligands. The reaction of **1b**, which has a Cp* ligand instead of a Cp ligand, proceeded more quickly than that of **1a** under similar conditions. Heating of an acetonitrile solution of **1b** for 24 h resulted in complete consumption to give **2b** in 83% yield. The spectral data of **2b** were similar to those of **2a**. Fortunately, single crystals of **2b** were obtained by recrystallization from ethyl acetate−diethyl ether, and the structure was determined by X-ray analysis. As shown in Figure 1, complex **2b** has a three-legged piano-stool structure in which one phenyl group on the cationic phosphorus atom is bound to the Ru atom by a σ-bond at the ortho position and the vinyl group derived from the vinylidene ligand coordinates to the Ru atom in an η^2 fashion. Thus, one proton on the vinyl group would be derived from the phenyl group linking to the Ru atom.

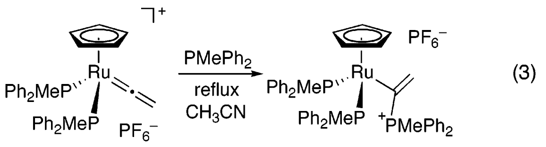
To confirm the origin of the hydrogen atom on the vinyl group, we performed the reaction using the triphenylphosphine-d_{15} complex **1a-*d*$_{30}$** (eq 2). The ^{1}H NMR spectrum of the resulting complex (**2a-*d*$_{30}$**) showed two signals due to the vinyl protons at δ 3.6 and 1.7. The small coupling constant ($J = 2.4$ Hz) between those two signals suggested that those protons were bound to the same carbon atom; this was unequivocally supported by 2D-NMR (HMQC) experiments. Therefore, the proton derived from the phenyl group of triphenylphosphine must be located on the α-carbon of the vinyl group.



1a-*d*$_{30}$ **2a-*d*$_{30}$**

When the reaction was performed in the presence of 1.5 equiv of triphenylphosphine, **1a** was completely consumed within 2 h to produce another complex (**3**), which was converted into **2a** after reaction for 18 h. The ^{1}H NMR spectrum of **3** revealed three signals at δ 3.8, 3.2, and 2.2, which were similar to those of **2a**, suggesting that **3** might have a vinyl group. Although **3** was surmised to be an intermediate of the present reaction, we could not determine its structure. The marked acceleration of the reaction by the addition of triphenylphosphine to a solution of **1a** indicated that the intermolecular attack of triphenylphosphine took place.

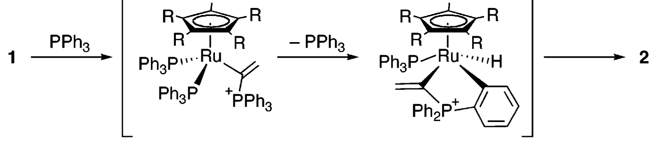
On the other hand, the reaction of **1c**, which is a methyldiphenylphosphine analogue of **1a**, with 1.5 equiv of methyldiphenylphosphine at room temperature produced a new complex (**4**), whereas no reaction took place by heating an acetonitrile solution of **1c** in the absence of additional methyldiphenylphosphine (eq 3). Although we could not isolate **4** in pure form, spectral data suggested that **4** was an alkenyl complex. For example, the FAB mass spectrum showed a peak (*m/z* 794) that corresponded to the product of the cationic part of **4** with one molecule of methyldiphenylphosphine. In the ^{1}H NMR spectrum, two doublet signals assignable to the protons of the noncoordinated olefin were observed at δ 6.1 and 6.0 with large coupling constants of $J = 39$ and 73 Hz, respectively, similar to those of an analogous alkenyl Fe complex.[9a] Although we examined further the reaction of **4** at high temperatures, no reaction was detected.



1c **4**

One plausible pathway for the formation of **2** is given in Scheme 1. At the first stage, phosphine, which is added to the system or generated by dissociation from another molecule of **1**, attacks the α-carbon of the vinylidene group to give an alkenyl complex.[9] After one of the two phosphine ligands is dissociated, ortho metalation takes place to give a Ru(IV) hydride complex. Reductive elimination followed by the coordination of

Scheme 1. Plausible Pathway[a]



[a] Counter-anions are omitted for clarity.

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(9) (a) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. (b) Senn, D. R.; Wong, A.; Patton, A. T.; Marsi, M.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6096. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241. (d) Ipaktschi, J.; Klotzbach, T.; Dülmer, A. *Organometallics* **2000**, *19*, 5281.

(10) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; Garcia-Granda, S. *Organometallics* **1997**, *16*, 3178.

(11) Bruce, M. I.; Hall, B. C.; Tiekink, E. R. T. *Aust. J. Chem.* **1997**, *50*, 1097.

the olefin produces **2**. This pathway agrees with the result of deuterium-labeled experiments.

In summary, we have described here the formation of vinyl−phosphonio complexes from the reaction of Ru−vinylidene complexes with phosphine. Our results may provide useful information for understanding the mechanism underlying the hydrophosphonation of alkyne. Further studies on the extension of these findings to the development of new catalytic reactions are in progress.

Experimental Section

All reactions were carried out under an argon atmosphere, whereas the workup was performed in air. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL JNM-LA400 and JEOL JNM-LA600 spectrometers. Chemical shifts are given in ppm based on $SiMe_4$ as the internal standard for ^{1}H and ^{13}C NMR and 85% H_3PO_4 as the external standard for ^{31}P NMR. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR instrument. FAB mass spectra were obtained on a JEOL JMS-600H spectrometer. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Complexes **1a**−**c** were prepared according to the literature method.[12]

Synthesis of [CpRu(PPh$_3$)(C$_6$H$_4$PPh$_2$CH=CH$_2$)][PF$_6$] (2a). To a solution of complex **1a** (150 mg, 0.17 mmol) in acetonitrile (10 mL) was added triphenylphosphine (68 mg, 0.26 mg), and the reaction mixture was refluxed for 18 h. After removal of the solvent, the residue was purified by alumina column chromatography using dichloromethane as eluent to give a pale yellow solid in quantitative yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.68−6.80 (m, 29H, Ar), 4.98 (s, 5H, Cp), 4.10 (ddt, 1H, J = 14.2, 10.7, 1.7 Hz, olefin), 3.73 (ddd, 1H, J = 23.4, 10.7, 2.2 Hz, olefin), 1.71 (ddt, 1H, J = 16.4, 10.5, 2.2 Hz, olefin). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 145.2 (d, J = 6 Hz), 145.0 (d, J = 6 Hz), 133.6, 133.3 (d, J = 11 Hz), 133.1, 132.9 (d, J = 5 Hz), 132.5 (d, J = 10 Hz), 131.9 (d, J = 11 Hz), 129.9 (d, J = 10 Hz), 129.4 (d, J = 11 Hz), 129.2, 128.7, 128.5 (d, J = 7 Hz), 128.3 (d, J = 5 Hz), 123.7 (d, J = 11 Hz), 41.5, 32.9 (d, J = 78 Hz). ^{31}P NMR (CDCl$_3$, 160 MHz): δ 56.7 (d, J = 4 Hz), 39.7 (d, J = 4 Hz). IR (cm^{-1}, KBr): 840 (ν_{P-F}). Anal. Calcd for $C_{43}H_{37}F_6P_3Ru$: C, 59.93; H, 4.33. Found: C, 59.82; H, 4.58.

Synthesis of [Cp*Ru(PPh$_3$)(C$_6$H$_4$PPh$_2$CH=CH$_2$)][PF$_6$] (2b). The title complex was prepared by a method similar to that for complex **2a** in 83% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.76−6.66 (m, 29H, Ar), 2.73 (dd, 1H, J = 23.0, 8.1 Hz, olefin), 2.59−2.50 (m, 2H, olefin), 1.32 (s, 15H, CH$_3$). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 133.6 (d, J = 11 Hz), 132.9 (d, J = 11 Hz), 132.7, 132.4 (d, J = 15 Hz), 132.0 (d, J = 15 Hz), 130.0−129.3 (m), 128.3 (d, J = 15 Hz), 127.6 (d, J = 14 Hz), 127.4 (d, J = 14 Hz), 127.4−127.2 (m), 45.7, 40.9 (d, J = 106 Hz). ^{31}P NMR (CDCl$_3$, 160 MHz): δ 56.5 (d, J = 4 Hz), 41.1 (d, J = 4 Hz). IR (cm^{-1}, KBr): 842 (ν_{P-F}). Anal. Calcd for $C_{48}H_{47}F_6P_3Ru$: C, 61.87; H, 5.08. Found: C, 62.03; H, 5.36.

Table 1. Crystallographic Data for Complex 2b

empirical formula	$C_{48}H_{47}F_6P_3Ru$
fw	931.88
cryst dimens	0.33 × 0.13 × 0.05 mm
cryst system	monoclinic
lattice params	a = 12.366(6) Å
	b = 30.378(5) Å
	c = 11.245(5) Å
	β = 93.51(3)°
	V = 4216(2) Å^3
space proup	$P2_1/c$ (No. 14)
Z	4
D_{calcd}	1.468 g cm^{-3}
F(000)	1912
μ(Mo Kα)	5.47 cm^{-1}
no. of rflns measd	
total	10 373
unique	10 174 (R_{int} = 0.153)
no. of observns	4168 ($I > 2.0\sigma(I)$)
no. of params	570
residuals: R; R_w	0.069; 0.080
goodness of fit indicator	1.18

X-ray Diffraction Analysis. A crystal of complex **2b** suitable for X-ray diffraction was mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC7R automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at −50 °C in the range of $6° < 2\theta < 55°$ with a scan rate of 8° min^{-1}. Intensities were measured by the ω-scan method. Three standard reflections were monitored every 150 measurements as a check of the stability of the crystals, and no damage was observed in all of the measurements. Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques. All non-hydrogen atoms were refined by full-matrix least squares using anisotropic thermal parameters, and all hydrogen atoms were refined using the riding model. A summary of the crystallographic data is given in Table 1.

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Supporting Information Available: Crystallographic data of complex **2b** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] (a) Bruce, M. I.; Koutsantonis, G. A. *Aust. J. Chem.* **1991**, *44*, 207. (b) Kawata, Y.; Sato, M. *Organometallics* **1997**, *16*, 1093.