Synthesis of [Ru(CO)$_2$(PPh$_3$)(SP)] and [Ru(CO)(PPh$_3$)$_2$(SP)] and their catalytic activities for the hydroamination of phenylacetylene

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Abstract

The reaction of [Ru(CO)$_2$(PPh$_3$)$_3$] (**1**) with *o*-styryldiphenylphophine (SP) (**2**) gave [Ru(CO)$_2$(PPh$_3$)(SP)] (**3**) in 83% yield. This styryl-phosphine ruthenium complex **3** can also be synthesized by the reaction of [Ru(*p*-MeOC$_6$H$_4$NN)(CO)$_2$(PPh$_3$)$_2$]BF$_4$ (**4**) with NaBH$_4$ and **2** in 50% yield. When "Ru(CO)(PPh$_3$)$_3$" generated by the reaction of [RuH$_2$(CO)(PPh$_3$)$_3$] (**8**) with trimethylvinylsilane reacted with **2**, [Ru(CO)(PPh$_3$)$_2$(SP)] (**10**) was produced in moderate yield as an air sensitive solid. The spectral and X-ray data of these complexes revealed that the coordination geometries around the ruthenium center of both complexes corresponded to a distorted trigonal bipyramid with the olefin occupying the equatorial position and the C–C bonding in the olefin moiety in **3** and **10** contained a significant contribution from a ruthenacyclopropane limiting structure. Complexes **3** and **10** showed catalytic activity for the hydroamination of phenylacetylene **11** with aniline **12**. Ruthenium complex **3** in the co-presence of NH$_4$PF$_6$ or H$_3$PW$_{12}$O$_{40}$ proves to be a superior catalyst system for this hydroamination reaction. In the case of the reaction using H$_3$PW$_{12}$O$_{40}$ as an additive, ketimines (**13**) was obtained in 99% yield at a ruthenium-catalyst loading of 0.1 mol%. Some aniline derivatives such as 4-methoxy, 4-trifluoromethyl-, and 4-bromoanilines can also be used in this hydroamination reaction.
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Keywords: Zero-valent ruthenium complexes; *o*-Styrylphosphine; Phenylacetylene; Anilines; Hydroamination

1. Introduction

Transition metal-catalyzed reactions are indispensable synthetic protocols in modern organic synthesis. To date, a large number of reactions have been developed and a variety of compounds have been synthesized. Among these, palladium-catalyzed reactions have been extensively studied [1]. Since the 1990 s, ruthenium-catalyzed reactions have attracted a great deal of interest in organic synthesis [2]. For example, olefin metathesis [3], the oxidation of alcohols and amines [4], asymmetric reduction using hydrogen [5], skeletal rearrangements of enynes [6], cyclization via ruthenacycles [7], cyclopropanations of olefins [8], and nucleophilic additions to acetylenes via vinylidene intermediates [9] have widely been studied. In these cases, ruthenium(II) or higher valent ruthenium complexes usually function as a good catalyst. Recently, ruthenium(0) complexes and their equivalents have also proved to be good catalyst systems for several reactions. For example, in the hydroacylation of olefins with aldehydes and their derivatives, ruthenium(0) complexes such as [Ru(COD)(COT)] (COD: 1,5-cyclooctadiene; COT: 1,3,5-cyclooctatriene) and [Ru$_3$(CO)$_{12}$] showed high catalytic activity [10], and for coupling reactions of arenes with olefins [11,12], acetylenes [13], organoboron reagents [14], the silylation of

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arenes with hydrosilanes [15], and the carbonylation of arenes using olefins and carbon monoxide [16,17], $[Ru(CO)_2(PPh_3)_3]$, $[Ru_3(CO)_{12}]$, and $[RuH_2(CO)(PPh_3)_3]$ [18] are frequently used as catalysts. Thus, ruthenium(0) complexes and their equivalents are highly valuable as well as high-valent ruthenium complexes in organic synthesis. Mitsudo et al. have recently reported that several ruthenium(0) complexes bearing an electron-deficient olefin such as a fumaric acid ester showed unique reactivities [19]. These results suggest that ruthenium(0) complexes function as a catalyst for several reactions. As a result, we initiated a study of the synthesis of novel ruthenium(0) complexes and an examination of their catalytic activities.

In this report, we describe the synthesis of $[Ru(CO)_2(PPh_3)(SP)]$ and $[Ru(CO)(PPh_3)_2(SP)]$ (SP = o-styryldiphenylphophine), and the characterization of these complexes by NMR, FAB mass, and ESI-TOF mass spectroscopies and X-ray analysis. We also report on the catalytic activities of these complexes in the hydroamination of phenylacetylene with aniline derivatives.
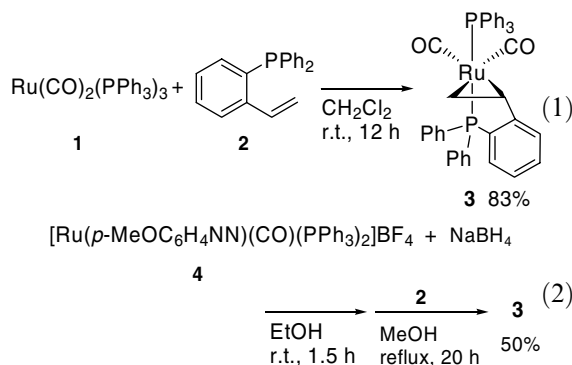
2. Results and discussion

The reaction of $[Ru(CO)_2(PPh_3)_3]$ (**1**) with o-styryldiphenylphosphine (SP) (**2**) [20] gave $[Ru(CO)_2(PPh_3)(SP)]$ (**3**) in 83% yield. The ^1H NMR spectrum of **3** and an X-ray analysis indicated that the olefin moiety of ligand **2** was coordinated to the ruthenium center in a ruthenacyclopropane configuration. The reaction of $[Ru(p-MeOC_6H_4NN)(CO)_2(PPh_3)_2]BF_4$ (**4**) [21] with NaBH_4 and **2** to afforded **3** in moderate yield. In the case of the coordination of **2** to "Ru(CO)(PPh_3)_3" (**9**) which was generated by the hydrogenation of trimethylvinylsilane with $[RuH_2(CO)(PPh_3)_3]$ (**8**), $[Ru(CO)(PPh_3)_2(SP)]$ (**10**) was obtained in moderate yield. The structure of the complex **10** was determined by NMR spectroscopy and X-ray analysis. The coordination mode of the olefin moiety of **2** in **10** was similar to that of **3**. When a hydroamination reaction of phenylacetylene with aniline was carried out in the presence of **3** and $H_3PW_{12}O_{40}$ as a catalyst, ketimine (**13**) was obtained in 99% isolated yield at a 0.1 mol% catalyst loading.

2.1. Preparations and characterizations of $[Ru(CO)_2(PPh_3)(SP)]$ (3) and $[Ru(CO)(PPh_3)_2(SP)]$ (10)

When a reaction of $[Ru(CO)_2(PPh_3)_3]$ (**1**) with o-styryldiphenylphosphine (**2**) (abbreviated to SP) was carried out at room temperature in dichloromethane for 12 h, $[Ru(CO)_2(PPh_3)(SP)]$ (**3**) was obtained as a pale yellow solid in 83% yield (Eq. (1)). As alternative route for synthesis of **3**, a reaction of $[RuH_2(CO)_2(PPh_3)_2]$, which was generated by the reaction of $[Ru(p-MeOC_6H_4NN)(CO)_2(PPh_3)_2]BF_4$ (**4**) with NaBH_4, with **2** afforded **3**. After refluxing for 20 h, **3** was precipitated as a pale yellow solid (50% yield) (Eq. (2)).

$$Ru(CO)_2(PPh_3)_3 + \quad \text{(2)} \quad \xrightarrow[\text{r.t., 12 h}]{CH_2Cl_2} \quad \text{(3) 83%} \quad (1)$$

$$[Ru(p\text{-}MeOC_6H_4NN)(CO)(PPh_3)_2]BF_4 + NaBH_4 \quad (\textbf{4})$$

$$\xrightarrow[\text{r.t., 1.5 h}]{EtOH} \quad \xrightarrow[\text{reflux, 20 h}]{\textbf{2} \quad MeOH} \quad \textbf{3} \quad 50\% \quad (2)$$

Recrystalization of **3** from dichloromethane/hexane afforded pale yellow crystals that were amenable to X-ray analysis [22]. The molecular structure of **3** is shown in Fig. 1. The coordination geometry around the ruthenium center corresponds to a distorted trigonal bipyramid with the olefin occupying an equatorial position.

The C(1)–C(2) bond length is 1.480 Å, intermediate between a double bond (1.34 Å) and a single bond (1.54 Å) and the Ru–C(1) and Ru–C(2) bond lengths are 2.174 Å and 2.196 Å, respectively. These bond lengths are consistent with those in complexes that contain a ruthena-
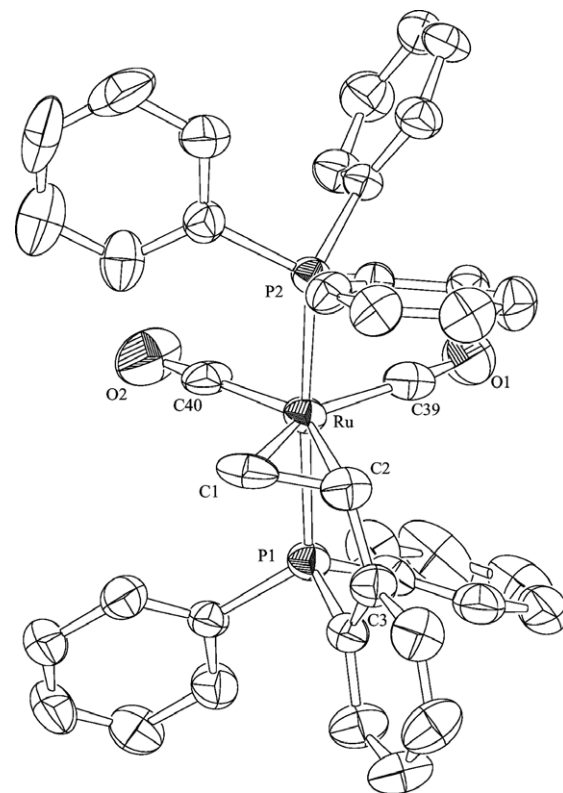
Fig. 1. ORTEP drawing for $[Ru(CO)_2(PPh_3)(SP)]$ (**3**) with ellipsoids drawn at the 50% probability level. All hydrogen atoms are excluded. Selected bond lengths (Å) and angles (deg): Ru–P(1), 2.332(2); Ru–P(2), 2.358(2); Ru–C(1), 2.174(6); Ru–C(2), 2.196(7); Ru–C(39), 1.925(7); Ru–C(40), 1.920(7); C(1)–C(2), 1.480(10); C(39)–O(1), 1.148(7); C(40)–O(2), 1.129(7); P(1)–Ru–P(2), 172.16(6); C(1)–Ru–C(2), 39.6(3); C(39)–Ru–C(40), 102.3(3); P(1)–Ru–C(1), 88.5(2); P(1)–Ru–C(2), 81.0(2).

cyclopropane structure such as Ru(styrene)$_2$(PPh$_3$)$_2$ (**5**) (C–C = 1.40–1.42 Å, Ru–C = 2.169, 2.153, 2.165, and 2.234 Å) [23], Ru(*o*-vinylacetophenone)(CO)(PPh$_3$)$_2$ (**6**) (C–C = 1.43 Å, Ru–C = 2.121 and 2.167 Å) [12f] and Ru(PPh$_3$)$_3$(CO)(C$_2$H$_4$) (**7**) (C–C = 1.451 Å, Ru–C = 2.213 Å and 2.199 Å) [12e]. These results suggest that the C–C bonding in the olefin moiety in **3** contained a significant contribution from a Ru(II) metalacyclopropane limiting structure. Thus, the strong back-donation of electrons to the olefin moiety from the ruthenium stabilizes the electron-rich ruthenium center. The X-ray analysis indicates that the olefin and CO ligands are located in the same plane. The geometry around the ruthenium center corresponds to a distorted trigonal bipyramid and the olefin moiety contained a significant contribution from the ruthenacyclopropane limiting structure. The structural features of **3** in the solid state are similar to [Fe(CO)$_2$(SP)$_2$] where one of two SP ligands is coordinated as a bidentate ligand and the other is coordinated as a monodentate phosphine ligand [24a].

The structure of **3** was maintained in benzene solution as shown by room temperature NMR data. The ^{31}P NMR of **3** showed that two phosphine signals were observed at δ 55.1 (J_{PP} = 257 Hz) and 60.0 (J_{PP} = 257 Hz). These large spin-spin coupling constants indicated that the phosphine ligands are located at the position trans relative to each other. In the ^{1}H NMR spectrum of **3**, the hydrogen signals of the olefin moiety appeared at δ 2.06, 2.13, and 2.98. The high field shifts of these hydrogens in the ^{1}H NMR spectrum suggest that the hybridizations at the olefinic carbons increase toward sp^3, i.e., ruthenacyclopropane. These chemical shifts are consistent with that in [Ru(CO)$_3$(SP)] (δ 2.84, 1.90, 1.90) [24b,25].

The preparation of [Ru(CO)(PPh$_3$)$_2$(SP)] (**10**) was achieved via a two-step pathway. In the first step, [RuH$_2$-(CO)(PPh$_3$)$_3$] (**8**) was converted to "Ru(CO)(PPh$_3$)$_3$" (**9**) by the hydrogenation of trimethylvinylsilane at 90 °C [26]. Styrylphosphine **2** was then added to a solution of **9** at room temperature, and the resulting mixture was stirred at room temperature for 22 h. [Ru(CO)(PPh$_3$)$_2$(SP)] (**10**) was isolated as a lemon yellow air sensitive solid (Eq. (3)). After recrystalization from benzene, lemon yellow colored crystals were obtained. The molecular structure of **10** was determined by X-ray analysis (Fig. 2) [22]. The coordination geometry around the ruthenium center corresponds to a distorted trigonal bipyramid. The three phosphine ligands are coordinated with a meridional geometry. The phosphorus atom of styrylphosphine **2** is coordinated at a trans position to the triphenylphosphine and the olefin moiety of **2** is coordinated at a cis position to these three phosphine ligands. The C(1)–C(2) bond length is 1.46 Å, almost the same as that of **3**. The bond length of Ru–C(2) is 2.23 Å, slightly longer than that of Ru–C(1). We attribute this to steric repulsion between the C(2) and the triphenylphosphine. The bond length between the ruthenium and the carbon of the CO ligand, i.e., Ru–C(57), is

slightly (≈0.06 Å) shorter than that of **3** but the bond length of C(57)–O(1) is slightly longer. These results indicate that the CO ligand in **10** is more strongly bound to the ruthenium than in **3**. Thus, back donation from the ruthenium strengthens the Ru–C(57) bond but weakens the C(57)–O(1) bond.
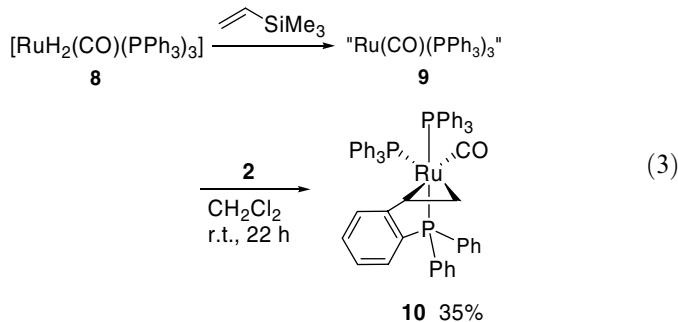
In the IR spectrum of **10**, CO stretching was observed at 1937 cm^{-1}. This value is 28 cm^{-1} smaller than that for **3** (1965 cm^{-1}). This low wave-number shift of CO stretching indicates that back donation from the ruthenium to the CO ligand in **10** becomes larger than that of **3**. This would be expected, because the two PPh$_3$ ligands in **10** should increase the electron density on the ruthenium. The bond lengths of Ru–P(1), Ru–P(2), and Ru–P(3) in **10** are 2.325, 2.358, and 2.450 Å, respectively. These results indicate that the triphenylphosphine ligand (P(3)) in the equatorial plane is weakly coordinated to the ruthenium due to the steric repulsion among these phosphine ligands.

The solution ^{1}H and ^{31}P NMR spectral data are consistent with the structure in the solid state. Thus, in these complexes, π-backbonding from the ruthenium(0) center to the olefin moiety caused the hybridization at the olefinic carbons to approach sp^3.

2.2. Attempts to hydroaminate phenylacetylene with aniline using ruthenium complexes 3 and 10 as catalysts

To explore applications of ruthenium complexes **3** and **10** as catalysts, we employed these complexes in the ruthenium-catalyzed hydroamination of phenylacetylene (**11**) with anilines, to give ketimines. In 1999, Wakatsuki et al. reported this type of hydroamination [28]. In their case, a combination of [Ru$_3$(CO)$_{12}$] and NH$_4$PF$_6$ proved to be highly effective as a catalyst. We used complexes **3** and **10**, instead of [Ru$_3$(CO)$_{12}$] as a catalyst for the hydroamination of **11** with aniline (**12**). When a reaction of **11** with **12** was carried out with **3** or **10** as a catalyst, a small amount of ketimine (**13**) was obtained in each case. They reported that the addition of NH$_4$PF$_6$ dramatically increased the yield of the hydroamination product [28]. We also carried out the hydroamination of **11** with **3** using NH$_4$PF$_6$ as an additive. The use of this ammonium salt increased the yield of **13** to 72% (run 1 in Eq. (4)). When similar ruthenium–phosphine complexes, such as **1**, [Ru(CO)$_3$(PPh$_3$)$_2$], **8**, and **10** were used as catalysts, **13** was formed in 16%,

Fig. 2. ORTEP drawing of [Ru(CO)(PPh$_3$)$_2$(SP)] (10) with ellipsoids drawn at the 50% probability level. All hydrogen atoms are excluded. Selected bond lengths (Å) and angles (deg): Ru–P(1), 2.325(3); Ru–P(2), 2.358(3); Ru–P(3), 2.450(3); C(1)–C(2), 1.46(2); Ru–C(1), 2.17(1); Ru–C(2), 2.23(1); Ru–C(57), 1.86(1); C(57)–O(1), 1.17(1); P(1)–Ru–P(2), 165.95(10); P(1)–Ru–P(3), 95.9(1); P(1)–Ru–C(1), 83.9(4); P(1)–Ru–C(2), 80.3(3); P(1)–Ru–C(57), 89.2(4); P(2)–Ru–P(3), 97.8(1); P(3)–Ru–C(2), 101.7(3); C(1)–Ru–C(2), 38.8(4); C(1)–Ru–C(57), 112.9(5).

49%, 8%, and 10% yields, respectively (runs 2–5 in Eq. (4)). These results suggested that Ru(CO)$_2$(SP) moiety is important for attaining high reactivity.

$$Ph\text{—}\!\!\equiv\!\!\text{—}H + PhNH_2 \xrightarrow[\substack{0.6 \text{ mol% } NH_4PF_6 \\ 100\ ^\circ C,\ 6\ h}]{0.3 \text{ mol% catalyst}} \underset{13}{Ph}\overset{N^{\diagup Ph}}{\underset{}{\diagdown}}$$

11   12

run	catalyst	yield	
1	[Ru(CO)$_2$(PPh$_3$)(SP)] (3)	72%	(4)
2	[Ru(CO)$_2$(PPh$_3$)$_3$] (1)	16%	
3	[Ru(CO)$_3$(PPh$_3$)$_2$]	49%	
4	[RuH$_2$(CO)(PPh$_3$)$_3$] (8)	8%	
5	[Ru(CO)(PPh$_3$)$_2$(SP)] (10)	10%	

In the case of the hydroamination of acetylenes with amines using Au(I)-catalyst, H$_3$PW$_{12}$O$_{40}$ (14) was found to function as an effective additive [29]. In place of NH$_4$PF$_6$, 14 was employed as an additive in the present hydroamination reaction. Ketimine 13 was obtained in 99% isolated yield in the presence of 0.1 mol% of 3 (run 1 in Eq. (5)). When 0.2 mol% of NH$_4$PF$_6$ was used for reac-

tion 5 in place of 14, the yield of 13 was 43%. These results indicate that the combination of ruthenium complex 3 and NH$_4$PF$_6$ or 14 functions as a good to excellent catalyst system for the hydroamination of phenylacetylene. Although Wakatsuki et al. claimed that the presence of a phosphine ligand had a retarding effect on catalytic activity, a combination of 3 having phosphine ligands and 14 was found to be a superior catalytic system for the hydroamination of phenylacetylene. The hydroamination reaction of 11 was examined using some other amines. In the case of the reaction with 4-methoxyaniline, the corresponding ketimines was isolated in 50% yield (run 2 in Eq. (5)). Aromatic amines having CF$_3$ and Br groups can also be used in this reaction, but the yields of the products were seriously decreased to 16% and 19%, respectively (runs 3 and 4 in Eq. (5), respectively). It is interesting that although the aryl carbon-bromine bond is prone to be cleaved by low-valent transition metal complexes, the bromo-substituent remained in the product. Unfortunately, the hydroamination reactions using 1,1,3,3-tetramethylbutylamine and phenylhydrazine did not proceed.

$$Ph\text{---}\equiv\text{---}H + R\text{-}NH_2 \xrightarrow[\substack{0.2\ mol\%\ H_3PW_{12}O_{40}\ (\mathbf{14}) \\ 100\ °C,\ 48\ h}]{\substack{0.1\ mol\% \\ Ru(CO)_2(PPh_3)(SP)\ (\mathbf{3})}} \underset{Ph}{\overset{N^{\cdot R}}{\bigg|\bigg|}} \tag{5}$$

	11		**13** 99%
run 1	**12**	R = C₆H₅	99%
run 2		R = 4-MeOC₆H₄	50%
run 3		R = 4-CF₃C₆H₄	16%
run 4		R = 4-BrC₆H₄	19%

To obtain information with respect to the role of $H_3PW_{12}O_{40}$ (**14**), we investigated the following three catalytic reactions (runs 1–3 in Eq. (6)) and two NMR studies. When the hydroamination reaction of **11** with **12** was carried out in the presence of $PhNH_3Cl$ in place of **14**, a trace amount of product was detected by GC analysis (run 1 in Eq. (6)). When $Na_3PW_{12}O_{40}$ was used as an additive, **13** was obtained in 35% isolated yield (run 2 in Eq. (6)). This result suggests that the proton in $H_3PW_{12}O_{40}$ is not essential for accomplish this hydroamination reaction. In the case of the reaction using both $Na_3PW_{12}O_{40}$ and $PhNH_3Cl$ as additives, the yield of **13** was slightly decreased to 28%. This result indicates that the presence of $PhNH_3Cl$ slightly retards the activity of the catalyst. In the case of the reaction of **14** with 200 equivalents of **12** in benzene-d_6, the chemical shift of the ortho hydrogens of **12** was slightly (0.05 ppm) shifted to lower field. When a large excess amount (200 equivalents) of **12** was used for the reaction with $Na_3PW_{12}O_{40}$, the ortho hydrogen in **12** was observed at slightly (0.02 ppm) lower field.

$$Ph\text{---}\equiv\text{---}H + PhNH_2 \xrightarrow[\substack{additive,\ 100\ °C,\ 48\ h}]{\substack{0.1\ mol\% \\ [Ru(CO)_2(PPh_3)(SP)]\ (\mathbf{3})}} \underset{Ph}{\overset{N^{\cdot Ph}}{\bigg|\bigg|}} \tag{6}$$

	additive	**13**
		11 **12**
run 1	0.2 mol% PhNH₃Cl	trace
run 2	0.2 mol% Na₃PW₁₂O₄₀	35%
run 3	0.2 mol% Na₃PW₁₂O₄₀/ 0.2 mol%PhNH₃Cl	28%
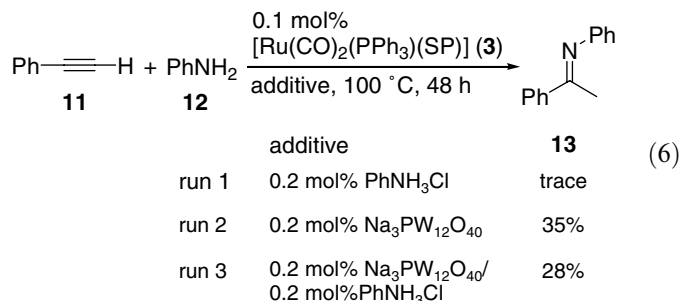
These results described above suggest that $H_3PW_{12}O_{40}$ (**14**) does not function as a proton source to generate anilinium species, protons in **14** are unnecessary to accomplish this hydroamination reaction, and a large anion moiety, i.e., $PW_{12}O_{40}^{3-}$, seems to be important for this reaction. Unfortunately, however, the effect of **14** as an additive could not be clarified at present. Elucidation of the certain role of **14** must await further studies.

3. Conclusion

In this paper, we have reported on the synthesis of two new ruthenium(0)–phosphine complexes bearing *o*-styryldiphenylphosphine (**2**) as a bidentate ligand and the application of these complexes to hydroamination of phenylacetylene with aniline. The X-ray analyses and ¹H NMR spectra of these complexes **3** and **10** show that the olefin moiety of ligand **2** is coordinated to the ruthenium center in a ruthenacyclopropane fashion. Thus, the back

donation of electrons from the ruthenium center to the olefin moiety is significant. The degree of back donation in **10** appears to be larger than that in **3** because **3** contains two CO ligands, which function as a good π-acceptor of electrons from the ruthenium. In both cases, the phosphorous atom of **2** is coordinated to the ruthenium at a trans position relative to the triphenylphosphine.

Ruthenium complex **3** in the co-presence of NH_4PF_6 or $H_3PW_{12}O_{40}$ proves to be good to superior catalyst systems for hydroamination of **11** with **12**. When $H_3PW_4O_{12}$ is employed as an additive, ketimines **13** was formed in 99% yield even at a ruthenium-catalyst loading of 0.1 mol%. Some aniline derivatives such as 4-methoxy-, 4-trifluoromethyl-, and 4-bromoanilines can also be used in this reaction.

4. Experimental

4.1. General Information

All manipulations of air and/or water sensitive materials were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. NMR spectra were obtained using Varian UNITY INOVA 600 and JEOL JNM-EX 270 spectrometers. ¹H NMR signals are quoted relative to internal $CHCl_3$ ($\delta = 7.26$) or tetramethylsilane. $^{31}C\{^1H\}$ NMR signals are quoted relative to internal $CDCl_3$ ($\delta = 77.0$) or tetramethylsilane. $^{31}P\{^1H\}$ NMR signals are quoted relative to external H_3PO_4. ¹H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (Hz), relative intensity. ^{31}C NMR data are reported as follows: chemical shift in ppm (δ), multiplicity, and coupling constant (Hz). IR spectra were measured on a Hitachi 270-50 infrared spectrometer. ESI-TOF mass spectra were obtained using JEOL JMS-T100LC. FAB mass spectra were obtained using JEOL JMS-700.

4.2. GC analysis

Conditions for GC analyses were as follows: Shimadzu GC-14 A (equipped with CBP-20, 25 m × 0.2 mm); initial temperature, 70 °C or 120 °C; final temperature, 250 °C; rate, 10 °C/min; injection temperature, 250 °C; detector temperature, 250 °C

4.3. Solvents and materials

Benzene and toluene were distilled from sodium/benzophenone ketyl prior to use. Benzene-d_6 was distilled from sodium/benzophenone ketyl and degassed by freeze–pump–thaw cycles. $[RuH_2(CO)(PPh_3)_3]$ (**8**) [11b] and $[Ru(CO)_2(p\text{-}MeOC_6H_4NN)(PPh_3)_2]BF_4$ (**4**) [21] were prepared by previously described methods. *o*-Styryldiphenylphosphine (**2**) was prepared by according to the literature from the Grignard reagent of *o*-bromostyrene in THF and chlorodiphenylphosphine [20].

4.4. Synthesis of dicarbonyl(o-styryldiphenylphosphine)(triphenylphosphine)ruthenium(0), [Ru(CO)$_2$(PPh$_3$)(SP)] (3): procedure A

A mixture of [Ru(CO)$_2$(PPh$_3$)$_3$] (1) (3.09 g, 3.27 mmol) and *o*-styryldiphenylphosphine (2) (1.05 g, 3.67 mmol) in dichloromethane (35 mL) was stirred at room temperature for 12 h under a nitrogen atmosphere. The yellow solution was concentrated under reduced pressure until a pale yellow deposit was observed. The deposit was washed with hexane (20 mL × 1), methanol (20 mL × 3), hexane (20 mL × 2), and dried *in vacuo*. The pale yellow powder was isolated in 83% yield (1.92 g).

4.5. Synthesis of 3: procedure B

In a two-necked flask equipped with a reflux condenser were placed [Ru(CO)$_2$ (*p*-MeOC$_6$H$_4$NN)(PPh$_3$)$_2$]BF$_4$ [21] (4), NaBH$_4$, and dry ethanol and stirred at room temperature for 1.5 h to afford [RuH$_2$(CO)$_2$(PPh$_3$)$_2$]. The solvent was decanted and obtained cream white product was dried *in vacuo*. An amount of *o*-styryldiphenylphosphine (2) equivalent to the ruthenium complex and methanol were then added, and the heterogeneous solution was refluxed for 20 h to afford a pale-yellow precipitate. The product, isolated by filtration, was washed with methanol and hexane and dried under reduced pressure (50% yield). ^{1}H NMR(600 MHz, C$_6$D$_6$) δ = 2.06 (ddd, *J* = 14.4, 7.8, 3.6, 1H, CH=C*H*H), 2.13 (ddd, *J* = 13.8, 7.8, 3.0, 1H, CH=CH*H*), 2.98 (ddd, *J* = 12.0, 7.8, 3.6, 1H, C*H*=CH$_2$), 6.72 (t, *J* = 7.2, 1H, ArH), 7.88-6.92 (m, 26H, ArH), 8.23 (dd, *J* = 9.0, 7.2, 2H, ArH); ^{31}C{^{1}H} NMR(151 MHz, C$_6$D$_6$) δ = 37.82 (t, J_{CP} = 4.45, CH=CH$_2$), 55.28 (brs, *CH*=CH$_2$), 124.58 (d, J_{CP} = 5.9, SP), 127.09 (d, J_{CP} = 14.4, SP), 128.35 (d, J_{CP} = 9.6, P(C$_6$H$_5$)$_3$), 128.53 (d, J_{CP} = 6.6, SP), 128.59 (d, J_{CP} = 6.45, SP), 129.45 (d, J_{CP} = 1.8, SP), 129.87 (d, J_{CP} = 1.8, P(C$_6$H$_5$)$_3$), 129.9 (brs, SP), 130.33 (d, J_{CP} = 2.4, SP), 131.24 (d, J_{CP} = 43.8, SP), 131.82 (d, J_{CP} = 10.1, SP), 132.32 (d, J_{CP} = 2.0, SP), 134.16 (d, J_{CP} = 12.6, SP), 134.39 (d, J_{CP} = 11.4, P(C$_6$H$_5$)$_3$), 134.76 (d, J_{CP} = 40.8, SP), 134.8 (d, J_{CP} = 40.8, P(C$_6$H$_5$)$_3$), 139.2 (d, J_{CP} = 49, SP), 163.45 (dd, J_{CP} = 28, 2.5, SP), 206.64 (dd, J_{CP} = 13, 11.7, CO), 209.75 (t, J_{CP} = 13, CO); ^{31}P{^{1}H} NMR (243 MHz, C$_6$D$_6$): δ = 55.1 (d, J_{PP} = 257), 60.0 (d, J_{PP} = 257); IR (KBr, cm^{-1}) 1960 (v_{Ru-CO}), 1894 (v_{Ru-CO}); IR (CDCl$_3$, cm^{-1}) 1965 (v_{Ru-CO}), 1899 (v_{Ru-CO}). HRMS (FAB) Calcd for C$_{40}$H$_{32}$O$_2$P$_2$Ru: 708.0921, found 708.0918.

4.6. Synthesis of carbonyl(o-styryldiphenylphosphine)bis-(triphenylphosphine)ruthenium(0), [Ru(CO)(PPh$_3$)$_2$-(SP)] (10)

A mixture of [RuH$_2$(CO)(PPh$_3$)$_3$] (8) and trimethylvinylsilane (15) (1.6 mL, 10.9 mmol) in benzene (15 mL) was stirred at 90 °C for 1.5H under a nitrogen atmosphere. After cooling to room temperature, *o*-styryldiphenylphos-

phine (2) (0.33 g, 1.05 mmol) was added to the wine red solution and stirred at room temperature for 22 h. The red-orange solution evaporated under reduced pressure and the residue was washed with hexane (10 mL × 3). Addition of 30 mL of hexane to a toluene (3 mL) solution of the solid gave yellow solid. This solid was washed with hexane (3 mL × 2), and then dried *in vacuo*. The resulting lemon yellow powder was obtained in 35 % yield (0.35 g). Recrystallization from a minimum volume of benzene gave yellow crystals of [Ru(CO)(PPh$_3$)$_2$(SP)] (10). ^{1}H NMR(600 MHz, C$_6$D$_6$) δ = 2.15 (brm, 1H, CH=C*H*H), 2.26 (brm, 1H, CH=C*H*H), 2.73 (ddd, *J* = 15.7, 7.9, 4.2, 1H, C*H*=CH$_2$), 7.3-6.6 (m, 42H, ArH), 8.13 (t, *J* = 8.5, 2H, ArH). ^{31}C{^{1}H} NMR(105.9 MHz, C$_6$D$_6$) δ = 43.3 (br, CH=CH$_2$), 51.4 (br, *CH*=CH$_2$), 164.68 (d, J_{CP} = 20.2, SP), 213.62 (t, J_{CP} = 13, CO). ^{31}P{^{1}H} NMR(109 MHz, C$_6$D$_6$): δ = 43.3 (br), 51.8 (dd, J_{PP} = 233, 16.8), 60.4 (dd, J_{PP} = 233, 21.4); IR (C$_6$D$_6$, cm^{-1}) 1937 (v_{CO}); FAB-MS 679 (M$^+$−PPh$_3$), 654 (M$^+$+1-SP), 652 (M$^+$+1-CO-PPh$_3$), 625 (M$^+$+1-CO-PPh$_3$), 389 (M$^+$+1-CO-2PPh$_3$); ESI-TOF-MS (ESI$^+$) 913 (M$^+$-CO). HRMS (FAB-MS) Calcd for C$_{57}$H$_{47}$OP$_3$Ru: 942.1833, found 942.1906.

4.7. Typical procedure for the catalytic reaction of phenylacetylene (11) with aniline (12)

A mixture of [Ru(CO)$_2$(PPh$_3$)(SP)] (3) (3.5 mg, 0.005 mmol), 11 (0.51 g, 5 mmol), 12 (0.465 g, 5 mmol), and H$_3$PW$_{12}$O$_{40}$ (28.8 mg, 0.01 mmol) was stirred at 100 °C for 48 h under a nitrogen atmosphere. The product was isolated from the reaction mixture by distillation under reduced pressure.

Appendix A. Supplementary data

CCDC 602700 and 602701 contains the supplementary crystallographic data for 3 and 10. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.015.

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