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Propargylic Substitution Reaction Catalyzed by Group IV (Ti, Zr, Hf)−Ru Heterobimetallic Complexes

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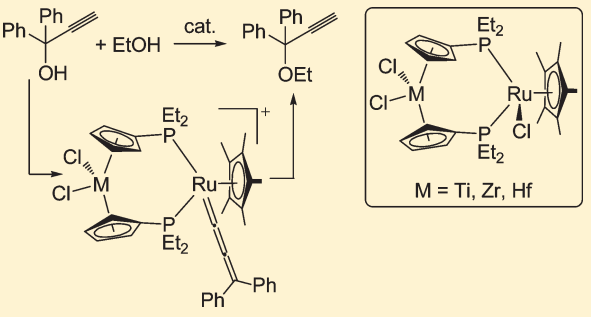
Supporting Information

ABSTRACT: A series of heterobimetallic complexes consisting of group IV metallocenyl diphosphines and Ru were synthesized and structurally characterized. Most of them work as catalysts toward propargylic substitution reaction of 1,1-diphenyl-2-propyn-1-ol (**4**) with EtOH. The stoichiometric reactions of the heterobimetallic complexes $[MCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuClCp^*]$ (M = Zr, Hf) with **4** and $NaBAr^F{}_4$ afforded key reactive intermediate allenylidene complexes $[MCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuCp^*(=C=C=CPh_2)]BAr^F{}_4$, whose molecular structures were confirmed by X-ray analyses. A plausible reaction pathway for the catalytic reaction is proposed where group IV metal chloride and Ru moieties work cooperatively.



INTRODUCTION

Multinuclear transition-metal complexes are expected to supply new reactivity that cannot be accomplished by mononuclear ones, although useful reactions distinctive to multinuclear complexes are limited in number.[1] Meanwhile, we have already reported the synthesis of thiolato-bridged diruthenium complexes and their unique capabilities toward catalytic propargylic substitution reactions of propargylic alcohols with nucleophiles,[2] where the possible electron transfer between two ruthenium atoms plays an important role to promote the reaction.[3] As an extension of our study on the preparation and reactivity of thiolato-bridged diruthenium complexes, we have reported the synthesis of the analogous diruthenium complexes where chloride ligands or bridging thiolato ligands were substituted by other atoms (Br, I,[4] P[5,6]), which demonstrated that the reactivity of diruthenium complexes is significantly affected by halide ligands or bridging ligands coordinated to Ru atoms.

On the other hand, we have quite recently reported the dehydrogenation of amine−boranes catalyzed by Zr−Ru heterobimetallic complexes bearing zirconocenyl diphosphines as auxiliary ligands, where cooperative activation of amine−boranes by both of the metals is the key to facilitate the reaction.[7] In the course of the investigation of other reactivity of the Zr−Ru heterobimetallic complexes, we have envisaged that electron transfer between heterometal atoms can occur when both of the metals are fixed in close proximity because metal−metal bonded Zr−Ru heterobimetallic complexes were indeed isolated.[7] Herein, we wish to report the application of Zr−Ru heterobimetallic complexes and their Hf−Ru and Ti−Ru analogues to the catalytic propargylic substitution reaction.

RESULTS AND DISCUSSION

Preparation and Characterization of Heterobimetallic Complexes. Preparation of a series of heterobimetallic complexes bearing group IV metallocenyl diphosphine moieties is summarized in Scheme 1. The Ti−Ru heterobimetallic complex $[TiCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuClCp^*]$ (**1c**) was prepared by a similar method to the preparation of $[ZrCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuClCp^*]$ (**1a**) and $[HfCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuClCp^*]$ (**1b**), which we previously reported.[7] Introduction of methyl groups to the cyclopentadienylphosphines was also found to be accomplished when the bis(1-diethylphosphino-2,3,4,5-tetramethylcyclopentadienyl) group IV metal dichloride $[MCl_2(\eta^5\text{-}C_5Me_4PEt_2)_2]$ (M = Zr, Hf) was reacted with $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ to afford $[ZrCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5Me_4PEt_2)_2RuClCp^*]$ (**2a**) or $[HfCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5Me_4PEt_2)_2RuClCp^*]$ (**2b**). Furthermore, substitution of the $RuCp^*$ moiety of **1a** with RuCp was feasible by changing the reactant from $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ to $[CpRuCl(PPh_3)_2]$ to obtain $[ZrCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuClCp]$ (**3a**). Formation of these complexes was confirmed by ^1H NMR and ^{31}P NMR spectra, and their detailed structures were confirmed by X-ray analyses (see Supporting Information for details).

Propargylic Substitution Reaction of Propargylic Alcohol Catalyzed by Heterobimetallic Complexes. We next examined the catalytic activity of these complexes in the propargylic substitution reaction of 1,1-diphenyl-2-propyn-1-ol (**4**) with EtOH. Typical results are shown in Table 1. All the reactions were carried out in the presence of catalytic amounts of catalyst (10 mol %) and $NaBAr^F{}_4$ (10 mol %) ($BAr^F{}_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). The Zr−Ru heterobimetallic complex **1a** as well as Hf−Ru complex **1b** and Ti−Ru complex **1c** showed catalytic activity toward propargylic substitution reaction to afford the corresponding propargylic substituted product (**5**) in moderate yields (Table 1, runs 1−3). Here, **1a** showed almost the same catalytic activity as **1c**, while **1b** showed a slightly higher catalytic activity than **1a** and **1c**. Interestingly, **2a**

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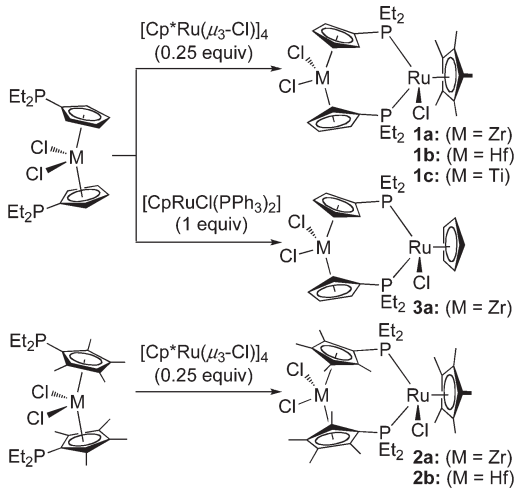
Scheme 1



Scheme 2

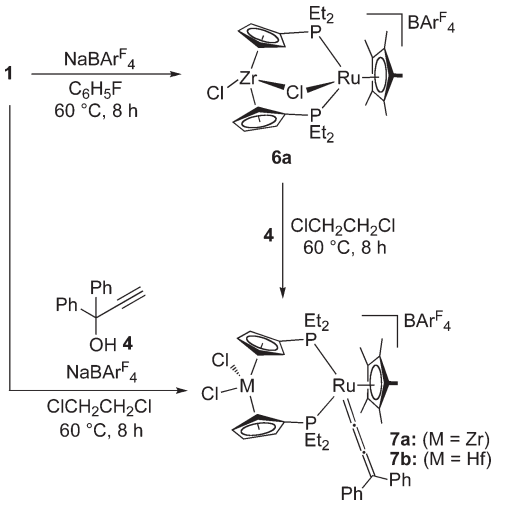
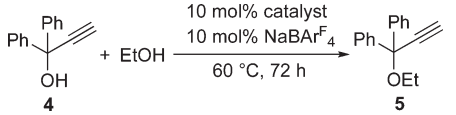


Table 1. Catalytic Propargylic Substitution Reaction of 4 with EtOH[a]



run	catalyst	yield (%)
1	**1a**	57
2	**1b**	71
3	**1c**	56
4	**2a**	4
5	**2b**	18
6	**3a**	55
7	$[(\eta^5\text{-}C_5H_4PEt_2)_2ZrCl_2]$	9
8	[Cp*RuCl(depe)]	0
9[b]	**7a**	53
10[b]	**7b**	71

[a] Reaction of **4** (0.30 mmol) with EtOH (7.5 mL) in the presence of catalyst (0.03 mmol) and $NaBAr^F_4$ (0.03 mmol) at 60 °C for 72 h. [b] Reaction was carried out without $NaBAr^F_4$.

and **2b**, bearing a tetramethyl-substituted metallocenyl diphosphine moiety, showed much less catalytic activity than **1a** and **1b**, respectively (Table 1, runs 4, 5), while **3a**, bearing a cyclopentadienyl (Cp) moiety on Ru, showed almost the same catalytic activity as **1a** (Table 1, run 6). Both mononuclear Zr complex $[(\eta^5C_5H_4PEt_2)_2ZrCl_2]$ (Table 1, run 7) and Ru complex [Cp*RuCl(depe)] (Table 1, run 8) were not catalytically active at all.

The catalytic activity of **1a** is apparently much higher than mononuclear complexes $[(\eta^5\text{-}C_5H_4PEt_2)_2ZrCl_2]$ and [Cp*RuCl(depe)] (depe = 1,2-bis(diethylphosphino)ethane), indicating that both Zr and Ru moieties in **1a** participate in the catalysis. The significant decrease of the catalytic activity of **2a** in comparison with **1a** clarified that substituents of the cyclopentadienyl moiety of the zirconocenyl diphosphine directly affect the catalytic activity. In contrast, **3a** showed almost the same reactivity as **1a**, suggesting that substituents of the cyclopentadienyl moiety of Ru have less influence on the catalytic activity.

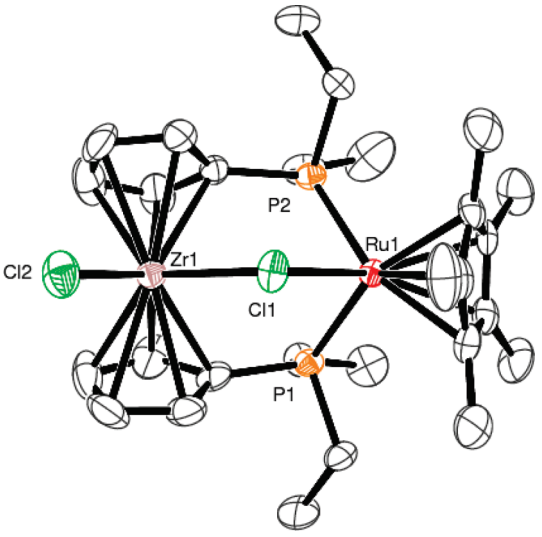


Figure 1. ORTEP drawing of **6a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and BAr^F_4 anion are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Zr(1)···Ru(1), 3.9745(9); Zr(1)−Cl(1), 2.4782(19); Zr(1)−Cl(2), 2.410(3); Ru(1)−Cl(1), 2.4942(17); Ru(1)−P(1), 2.3270(19); Ru(1)−P(2), 2.3511(19); Cl(1)−Zr(1)−Cl(2), 95.55(7); Ru(1)−Cl(1)−Zr(1) 106.13(7); Cl(1)−Ru(1)−P(1), 90.86(7); Cl(1)−Ru(1)−P(2), 88.36(6); P(1)−Ru(1)−P(2), 95.26(7).

Unfortunately, other propargylic alcohols bearing a terminal alkyne moiety such as 1-phenyl-2-propyn-1-ol,[8] 1,1-bis(4-methylphenyl)-2-propyn-1-ol,[9] and propargylic alcohol bearing an internal alkyne moiety such as 1,1-diphenyl-2-propyn-3-phenyl-1-ol[8] were not applicable to this catalytic reaction.

Isolation and Characterization of Heterobimetallic Allenylidene Complexes as Reactive Intermediates. To get some information about the reaction pathway of this catalytic reaction, we investigated stoichiometric reactions of the heterobimetallic complexes **1a** and **1b** with **4**. Treatment of **1a** with $NaBAr^F_4$ afforded $[ZrCl(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2(\mu\text{-}Cl)RuCp^*]BAr^F_4$ (**6a**) in 67% yield, which further reacted with **4** to give the corresponding

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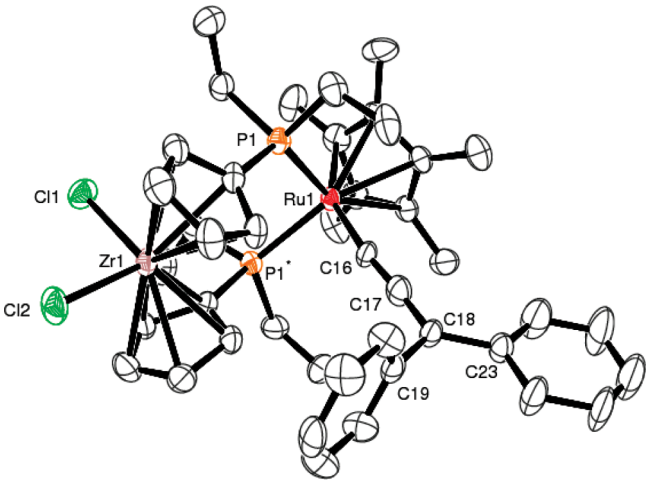


Figure 2. ORTEP drawing of **7a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and BAr^F_4 anion are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Zr(1)···Ru(1), 4.9464(8); Zr(1)−Cl(1), 2.4377(17); Zr(1)−Cl(2), 2.4262(16); Ru(1)−P(1), 2.3175(13); Ru(1)−C(16), 1.901(5); C(16)−C(17), 1.243(8); C(17)−C(18), 1.358(8); Cl(1)−Zr(1)−Cl(2), 97.46(6); P(1)−Ru(1)−C(16), 92.20(12); Ru(1)−C(16)−C(17) 170.9(5); C(16)−C(17)−C(18), 175.1(6); C(17)−C(18)−C(19), 117.6(5); C(17)−C(18)−C(23), 122.9(5); C(19)−C(18)−C(23), 119.5(4); P(1)−Ru(1)−P(1)*, 95.30(4).

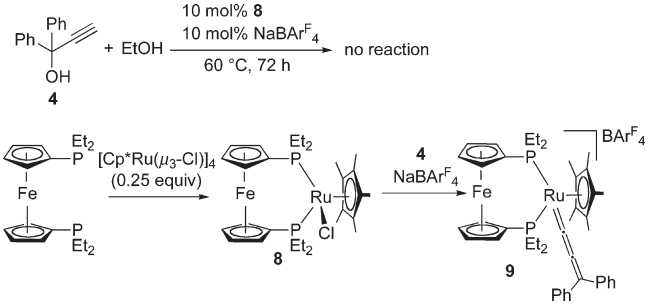
Zr−Ru heterobimetallic allenylidene complex $[ZrCl_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4PEt_2)_2RuCp^*(=C=C=CPh_2)]BAr^F_4$ (**7a**) in 67% yield. Complex **7a** could also be prepared directly by treatment of **1a** with 1.1 equiv of **4** in the presence of 1 equiv of $NaBAr^F_4$ in 57% yield. Similarly, the Hf−Ru heterobimetallic allenylidene complex $[HfCl_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4PEt_2)_2RuCp^*(=C=C=CPh_2)]BAr^F_4$ (**7b**) was obtained in 67% yield (Scheme 2). Thus, formation of the allenylidene complexes **7** should proceed via the formation of the chloride-bridged complexes **6** as intermediates.

Complexes **6a**, **7a**, and **7b** were characterized by ^1H and ^{31}P NMR spectra as well as X-ray analyses. As shown in Figures 1 and 2, the configuration around the Ru center in both **6a** and **7a** adopts a three-legged piano stool coordination geometry, typical of coordinatively saturated cyclopentadienyl Ru(II) bis(phosphine) complexes.[10] As for **6a**, the interatomic distance between Zr and Ru atoms (3.9745(9) Å) is too long to draw a metal−metal single bond,[11] where the chloride ligand bridges Zr and Ru atoms. The interatomic distance between Zr and Ru (4.9464(8) Å) in **7a** is comparable to that of **1a** (5.0017(4) Å),[7] suggesting that there is also no metal−metal bond. Moreover, the almost linear angles (Ru(1)−C(16)−C(17), 170.9(5)°; C(16)−C(17)−C(18), 175.1(6)°) and the bond distances in the allenylidene moiety (C(16)−C(17), 1.243(8) Å; C(17)−C(18), 1.358(8) Å) in **7a** are comparable to those reported for cationic ruthenium allenylidene complexes.[12] These structural features as well as NMR and IR spectroscopic observations ($\nu_{C=C=C}$ = 1914 cm^{-1}) strongly support the formation of the allenylidene complex **7a**. It should be noted that the complex **7a** offers a rare example of multinuclear allenylidene compounds with only a terminal allenylidene ligand on the heterobimetallic center.[13]

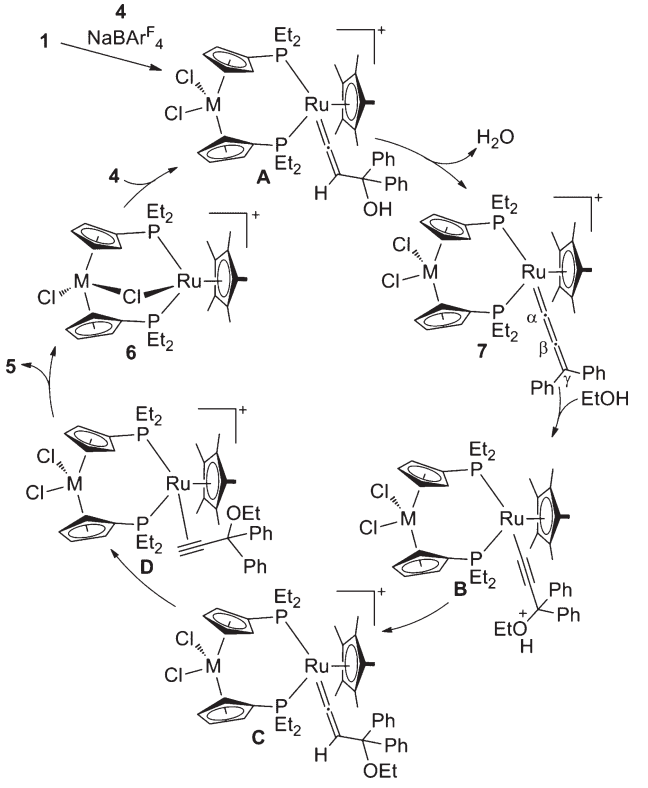
Next, we investigated catalytic reactions of **7a** and **7b**. Treatment of **4** with a catalytic amount of **7a** or **7b** (10 mol %) afforded **5** in 53% and 71% yields, respectively (Table 1, runs 9, 10), demonstrating that **7a** and **7b** show almost the same catalytic activity as the corresponding heterobimetallic complexes **1a** and **1b**.[14] Moreover, propargylic alcohol bearing an internal alkyne moiety is not applicable to this reaction, as shown in the previous section, suggesting that the formation of the Ru allenylidene moiety is necessary for the catalytic reaction to proceed. Meanwhile, we have also investigated the reaction of **2a** with 1.1 equiv of **4** in the presence of 1 equiv of $NaBAr^F_4$ in order to obtain the corresponding allenylidene complex, which resulted in no formation of the desired allenylidene complex. Taking into consideration this result as well as the low catalytic activity of **2** (Table 1, runs 4, 5), it is suggested that the formation of the Ru allenylidene moiety is indeed requisite for the catalytic reaction. Thus, these results strongly support that our catalytic reaction proceeds via the formation of allenylidene complexes **7** as reactive intermediates.

In order to gain more information about our heterobimetallic catalysis, we have newly prepared the Fe−Ru heterobimetallic

Scheme 3



Scheme 4



complex [Cp*RuCl(depf)] (**8**; depf = 1,1′-bis(diethylphosphino)-ferrocene) and investigated the catalytic activity of **8** toward the propargylic substitution reaction of **4** with EtOH, as shown in Scheme 3. Treatment of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with 4 equiv of depf afforded **8** in 73% yield. Next, we investigated the reaction of **4** with catalytic amounts of **8** (10 mol %) and $NaBAr^F{}_4$ (10 mol %). As a result, no formation of **5** was observed in the reaction, while the formation of the corresponding allenylidene complex $[Cp^*Ru(=C=C=CPh_2)(depf)]BAr^F{}_4$ (**9**) was observed *in situ*, confirmed by NMR and IR spectra. Indeed, **9** was successfully isolated by the reaction of **8** with 1 equiv of **4** in the presence of 1 equiv of $NaBAr^F{}_4$ in 77% yield (Scheme 3). These results clearly indicate that group IV metallocenyl diphosphine moieties are essential to the catalytic reaction.

Plausible Reaction Pathway. A plausible reaction pathway is shown in Scheme 4. First, **1** reacts with **4** in the presence of $NaBAr^F{}_4$ to form a vinylidene complex (**A**). Subsequent dehydration of **A** leads to the formation of allenylidene complex **7**. Next, nucleophilic attack of EtOH to the C_γ atom of the allenylidene ligand results in the formation of an alkynyl complex (**B**), then the hydrogen atom shifts into the C_β atom on the ligand to give another vinylidene complex (**C**). Complex **C** is then transformed into the η^2-coordinated propargylic ether tautomer (**D**), which liberates **5** with the formation of the chloride-bridged heterobimetallic complex **6**. Finally, **6** reacts with another **4** to regenerate the vinylidene complex **A**. In the previously reported propargylic substitution reactions catalyzed by thiolato-bridged diruthenium complexes, it was revealed that the electron transfer between two ruthenium atoms is the key step to facilitate catalysis.[3] In contrast, the distances between heterometals in the present catalysts such as complexes **1** and **7** are too long to interact with, as shown in Figure 2. At present, we consider that the formation of the chloride-bridged complex **6** is the key step that promotes the dissociation of **5** from **D**. However, the difference of catalytic activity between **1a** (or **1c**) and **1b** may suggest that the electronic nature of the group IV metal may affect the catalytic activity; that is, the possibility that electronic transfer between heterometals facilitates catalysis cannot be ruled out. The significant decrease of the catalytic activity of **2a** compared to those of **1a**, **3a**, and **5a** is probably due to the steric repulsion between methyl substituents of the zirconocene moiety and the pentamethylcyclopentadienyl ligand on Ru, which prevents not only the facile transformation of **D** into **6** but also subsequent formation of the allenylidene complex **7**.

In summary, novel heterobimetallic complexes **1c**, **2a**, **2b**, **3a**, and **6a** consisting of group IV metallocenyl diphosphines and Ru were synthesized and structurally characterized. It was demonstrated that complexes **1** and **3a** work as catalysts toward the propargylic substitution reaction of **4** with EtOH to obtain **5** in moderate yields, whereas complex **2**, bearing tetramethyl-substituted metallocenyl diphosphine as an auxiliary ligand, did not work as a catalyst at all. Treatment of the heterobimetallic complexes **1a** and **1b** with **4** in the presence of $NaBAr^F{}_4$ afforded the corresponding heterobimetallic allenylidene complexes **7a** and **7b**, respectively, as reactive intermediates, and their molecular structures were confirmed by X-ray analyses. Studies on the reaction pathway revealed that both group IV metallocenyl diphosphine dichloride moieties and the Ru allenylidene moiety work cooperatively in the catalytic reaction. Further work is currently in progress to develop other useful and intriguing reactions distinctive to our heterobimetallic system.

EXPERIMENTAL SECTION

General Procedures. ^1H NMR (270 MHz) and ^{31}P NMR (109 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvents. ^{31}P NMR chemical shifts were quoted relative to an external standard of 85% H_3PO_4. Elemental analyses were performed at the Microanalytical Laboratory of The University of Tokyo or on an Exeter Analytical CE-440 elemental analyzer. IR spectra were recorded on a JASCO FT/IR 4100 Fourier transform infrared spectrophotometer. All reactions were carried out under a dry nitrogen atmosphere or in an argon-filled glovebox. Solvents were dried by general methods and degassed before use. $[Cp^*Ru(\mu_3\text{-}Cl)]_4$,[15] $[CpRuCl(PPh_3)_2]$,[16] $[Cp^*RuCl(depe)]$,[17] $NaBAr^F{}_4$,[18] depf,[19] $Na[C_5H_4PEt_2]$, $[(\eta^5\text{-}C_5H_4PEt_2)_2ZrCl_2]$, **1a**, and **1b**[7] were prepared according to the literature procedures. $Na[C_5Me_4PEt_2]$ was synthesized according to the slightly modified procedure of the preparation of $Na[C_5H_4PEt_2]$, using LiC_5Me_4H instead of CpLi. Other reagents were purchased commercially and used as received.

Preparation of $[TiCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4PEt_2)_2RuClCp^*]$ (1c). To a slurry of $Na[C_5H_4PEt_2]$ (367 mg, 2.08 mmol) in toluene (25 mL) and a trace amount of THF (0.1 mL) was added $[TiCl_4(thf)_2]$ (332 mg, 0.994 mmol), and the mixture was stirred at room temperature for 4 h. Then, $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (272 mg, 0.250 mmol) was added to the reaction mixture and stirred for a further 12 h. The resulting reaction mixture was filtered through a pad of Celite, and solvent was removed from the filtrate in vacuo. The resulting brown residue was washed with hexane (7 mL × 3) and Et_2O (7 mL × 2), then recrystallized from benzene−hexane to afford **1c**·1.5C_6H_6 as brown blocks. Crystals of **1c**·1.5C_6H_6 are effluorescent and gave off benzene to afford a brown powder of **1c** (242 mg, 0.347 mmol, 35% isolated yield) after drying in vacuo. ^1H NMR (C_6D_6): δ 7.84 (br, 2H, C_5H_4), 7.03 (br, 2H, C_5H_4), 5.50 (br, 2H, C_5H_4), 2.35 (br, 2H, PCH_2), 1.81 (br, 6H, PCH_2), 1.43 (s, 15H, Cp*), 1.08 (br t, $^3J_{HH}$ = 7.6 Hz, 6H, CH_2Me), 0.61 (br t, $^3J_{HH}$ = 7.8 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 37.7 (s). Anal. Calcd for $C_{28}H_{43}Cl_3P_2TiRu$: C, 48.26; H, 6.22. Found: C, 47.97; H, 6.03.

Preparation of $[ZrCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5Me_4PEt_2)_2RuClCp^*]$ (2a). To a slurry of $Na[C_5Me_4PEt_2]$ (1.03 g, 4.43 mmol) in toluene (50 mL) and a trace amount of THF (0.2 mL) was added $[ZrCl_4(thf)_2]$ (773 mg, 2.05 mmol), and the mixture was stirred at room temperature for 3 h. Then, $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (557 mg, 0.512 mmol) was added to the reaction mixture, and the mixture was stirred for a further 6 h. The resulting reaction mixture was filtered through a pad of Celite, and solvent was removed from the filtrate in vacuo. The resulting orange residue was washed with hexane (10 mL × 4) to afford **2a** as an orange solid (1.09 g, 1.28 mmol, 62% isolated yield). Orange plates of **2a**·1.5C_6H_6 suitable for X-ray crystallography were obtained by layering hexane onto a benzene solution of **2a**. ^1H NMR (C_6D_6): δ 2.62−2.51 (m, 2H, PCH_2), 2.09−1.97 (m, 30H, C_5Me_4 and PCH_2), 1.53 (s, 15H, Cp*), 1.03 (dt, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, CH_2Me), 0.63 (dt, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 40.3 (s). Anal. Calcd for $C_{36}H_{59}Cl_3P_2RuZr$: C, 50.72; H, 6.98. Found: C, 51.01; H, 7.27.

Preparation of $[HfCl_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5Me_4PEt_2)_2RuClCp^*]$ (2b). To a slurry of $Na[C_5Me_4PEt_2]$ (100 mg, 0.431 mmol) in toluene (10 mL) and a trace amount of THF (0.1 mL) was added $[HfCl_4(thf)_2]$ (95.1 mg, 0.205 mmol), and the mixture was stirred at room temperature for 3 h. Then, $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (55.7 mg, 0.0512 mmol) was added to the reaction mixture, and the mixture was stirred for a further 6 h. The resulting reaction mixture was filtered through a pad of Celite; then solvent was removed from the filtrate in vacuo. The resulting orange residue was washed with hexane (3 mL × 3) to afford **2b** as an orange solid (80.5 mg, 0.0857 mmol, 42% isolated yield). Red blocks of **2b** suitable for X-ray crystallography were obtained by layering hexane onto a benzene solution of **2b**, which was then kept cooled at 0 °C. ^1H NMR (C_6D_6): δ 2.71 (br, 2H, PCH_2), 2.16−1.99 (m, 30H, C_5Me_4 and PCH_2), 1.54 (s, 15H, Cp*), 1.15 (dt, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, CH_2Me), 0.61 (dt, $^3J_{HP}$ = 12.7 Hz,

$^3J_{HH}$ = 7.0 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 41.2 (s). Anal. Calcd for $C_{36}H_{59}Cl_3HfP_2Ru$: C, 46.01; H, 6.33. Found: C, 45.96; H, 6.33.

Preparation of [ZrCl$_2$(μ-η^5:η^1-C$_5$H$_4$PEt$_2$)$_2$RuClCp] (3a). To a slurry of [CpRuCl(PPh$_3$)$_2$] (1.41 g, 1.94 mmol) in toluene (25 mL) was added [(η^5-C$_5$H$_4$PEt$_2$)$_2$ZrCl$_2$] (1.00 g, 2.13 mmol), and the mixture was refluxed overnight. Then, solvent was removed in vacuo, and the resulting orange residue was washed with Et$_2$O (10 mL × 4) to afford **3a** as an orange solid (904 mg, 1.35 mmol, 69% isolated yield). Red needles of **3a** suitable for X-ray crystallography were obtained by layering hexane onto a toluene solution of **3a**. ^1H NMR (C_6D_6): δ 7.99 (br, 2H, C_5H_4), 6.69 (br, 2H, C_5H_4), 6.61−6.59 (m, 2H, C_5H_4), 5.74 (br, 2H, C_5H_4), 4.40 (s, 5H, Cp), 2.26−2.11 (m, 2H, PCH_2), 1.90−1.79 (m, 4H, PCH_2), 1.71−1.52 (m, 2H, PCH_2), 0.78−0.62 (m, 12H, CH_2Me). Anal. Calcd for $C_{23}H_{33}Cl_3P_2RuZr$: C, 41.22; H, 4.96. Found: C, 41.09; H, 4.91.

Preparation of [ZrCl(μ-η^5:η^1-C$_5$H$_4$PEt$_2$)$_2$(μ-Cl)RuCp*]BAr$^F_4$ (6a). To a solution of **1a** (92.7 mg, 0.125 mmol) in C_6H_5F (5 mL) was added NaBAr$^F_4$ (111 mg, 0.125 mmol), and the mixture was heated at 60 °C and stirred for 8 h. The resulting reaction mixture was filtered, and hexane was layered onto the filtrate to afford **6a** as red plates (132 mg, 0.0842 mmol, 67% isolated yield). ^1H NMR (CD_2Cl_2): δ 7.66 (br, 8H, BAr$^F_4$), 7.50 (br, 4H, BAr$^F_4$), 7.07 (br, 2H, C_5H_4), 6.54 (br, 2H, C_5H_4), 6.22 (br, 2H, C_5H_4), 6.12 (br, 2H, C_5H_4), 2.49−2.06 (m, 6H, PCH_2), 1.96−1.84 (m, 2H, PCH_2), 1.64 (s, 15H, Cp*), 1.10 (dt, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.6 Hz, 6H, CH_2Me), 0.91 (dt, $^3J_{HP}$ = 14.3 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.7 (s). Anal. Calcd for $C_{60}H_{55}Cl_3BCl_2F_{24}P_2RuZr$: C, 45.96; H, 3.54. Found: C, 45.76; H, 3.64.

Preparation of [ZrCl$_2$(μ-η^5:η^1-C$_5$H$_4$PEt$_2$)$_2$RuCp*(=C=C=CPh$_2$)]BAr$^F_4$ (7a). Method A. To a solution of **1a** (110.3 mg, 0.149 mmol) in $ClCH_2CH_2Cl$ (3 mL) was added NaBAr$^F_4$ (133 mg, 0.150 mmol) and **4** (34.5 mg, 0.166 mmol), and the mixture was heated and stirred at 60 °C for 8 h. The resulting reaction mixture was filtered, and all the volatiles were removed in vacuo. The resulting reddish-purple residue was recrystallized from CH_2Cl_2−hexane and kept cooled at −35 °C to afford **7a** as dark orange plates (150 mg, 0.0853 mmol, 57% isolated yield). **Method B.** To a solution of **6a** (108.5 mg, 0.0692 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was added **4** (14.4 mg, 0.0691 mmol); then the mixture was heated at 60 °C and stirred for 8 h. The resulting reaction mixture was filtered, and all the volatiles were removed in vacuo. The resulting reddish-purple residue was recrystallized from CH_2Cl_2−hexane and kept cooled at −35 °C to afford **7a** as dark orange plates (81.0 mg, 0.0461 mmol, 67% isolated yield). ^1H NMR (CD_2Cl_2): δ 7.68−7.67 (m, 14H, BAr$^F_4$ and CPh), 7.66 (br, 4H, BAr$^F_4$), 7.65−7.40 (m. 4H, CPh), 6.89 (br, 2H, C_5H_4), 6.75 (br, 4H, C_5H_4), 5.79 (br, 2H, C_5H_4), 2.27−2.18 (m, 2H, PCH_2), 2.03−1.95 (m, 2H, PCH_2), 1.86 (s, 15H, Cp*), 1.77−1.67 (m, 2H, PCH_2), 1.61−1.54 (m, 2H, PCH_2), 1.25 (dt, $^3J_{HP}$ = 15.7 Hz, $^3J_{HH}$ = 7.8 Hz, 6H, CH_2Me), 0.61 (dt, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.4 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.0 (s). IR (KBr, cm^{-1}): 1914 (s, $\nu_{C=C=C}$). Anal. Calcd for $C_{75}H_{65}BCl_2F_{24}P_2RuZr$: C, 51.23; H, 3.73. Found: C, 50.76; H, 3.92.

Preparation of [HfCl$_2$(μ-η^5:η^1-C$_5$H$_4$PEt$_2$)$_2$RuCp*(=C=C=CPh$_2$)]BAr$^F_4$ (7b). To a solution of **1b** (124 mg, 0.150 mmol) in $ClCH_2CH_2Cl$ (3 mL) was added NaBAr$^F_4$ (133 mg, 0.150 mmol) and **4** (34.6 mg, 0.166 mmol), and the mixture was heated at 60 °C and stirred for 8 h. The resulting reaction mixture was filtered, and all the volatiles were removed in vacuo. The resulting reddish-purple residue was recrystallized from CH_2Cl_2−hexane and kept cooled at −35 °C to afford **7b** as red needles (185 mg, 0.100 mmol, 67% isolated yield). ^1H NMR (CD_2Cl_2): δ 7.67−7.65 (m, 14H, BAr$^F_4$ and CPh), 7.63 (br, 4H, BAr$^F_4$), 7.50−7.40 (m. 4H, CPh), 6.79 (br, 2H, C_5H_4), 6.67 (br, 2H, C_5H_4), 6.63 (br, 2H, C_5H_4), 5.68 (br, 2H, C_5H_4), 2.31−2.14 (m, 2H, PCH_2), 2.04−1.93 (m, 2H, PCH_2), 1.86 (s, 15H, Cp*), 1.78−1.70 (m, 2H, PCH_2), 1.69−1.54 (m, 2H, PCH_2), 1.25 (dt, $^3J_{HP}$ = 15.7 Hz, $^3J_{HH}$ = 7.8 Hz, 6H, CH_2Me), 0.58 (dt, $^3J_{HP}$ = 18.1 Hz, $^3J_{HH}$ = 7.4 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 40.6 (s). IR (KBr, cm^{-1}): 1914 (s, $\nu_{C=C=C}$). Anal. Calcd for $C_{75}H_{65}BCl_2F_{24}HfP_2Ru$: C, 48.81; H, 3.55. Found: C, 48.38; H, 3.70.

Preparation of [Cp*RuCl(depf)] (8). To a slurry of [Cp*Ru(μ_3-Cl)]$_4$ (227 mg, 0.209 mmol) in THF (7.5 mL) was added depf (303 mg, 0.837 mmol), and the mixture was stirred at room temperature for 18 h. Then, solvent was removed in vacuo, and the resulting orange residue was extracted with CH_2Cl_2 and filtered through a pad of Celite. After solvent was removed from the filtrate, the resulting orange-yellow residue was washed with hexane (5 mL × 4) to afford **8** as a yellow solid (389 mg, 0.614 mmol, 73% isolated yield). ^1H NMR (C_6D_6): δ 5.31 (br, 2H, C_5H_4), 4.04 (br, 2H, C_5H_4), 4.01 (br, 2H, C_5H_4), 3.91 (br, 2H, C_5H_4), 2.45 (br, 2H, PCH_2), 1.90 (br, 4H, PCH_2), 1.90 (br, 2H, PCH_2), 1.57 (s, 15H, Cp*), 1.13−0.97 (m, 12H, CH_2Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 34.2 (s). Anal. Calcd for $C_{28}H_{43}ClFeP_2Ru$: C, 53.05; H, 6.84. Found: C, 52.49; H, 6.82.

Preparation of [Cp*Ru(=C=C=CPh$_2$)(depf)]BAr$^F_4$ (9). To a solution of **8** (127 mg, 0.200 mmol) in $ClCH_2CH_2Cl$ (4 mL) were added NaBAr$^F_4$ (177 mg, 0.200 mmol) and **4** (43.6 mg, 0.209 mmol), and the mixture was heated at 60 °C and stirred for 24 h. The resulting reaction mixture was filtered, and all the volatiles were removed in vacuo. The resulting reddish-purple residue was then recrystallized from CH_2Cl_2−hexane and kept cooled at −35 °C to afford **9** as red blocks (252 mg, 0.153 mmol, 77% isolated yield). ^1H NMR (CD_2Cl_2): δ 7.73−7.58 (m, 14H, BAr$^F_4$ and CPh), 7.50 (br, 4H, BAr$^F_4$), 7.44−7.38 (m. 4H, CPh), 4.36 (br, 4H, C_5H_4), 4.13 (br, 2H, C_5H_4), 4.03 (br, 2H, C_5H_4), 2.18−2.05 (m, 2H, PCH_2), 1.90 (br, 2H, PCH_2), 1.81 (s, 15H, Cp*), 1.73−1.63 (m, 2H, PCH_2), 1.48 (br, 2H, PCH_2), 1.17 (dt, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, CH_2Me), 0.77 (dt, $^3J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.6 Hz, 6H, CH_2Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.7 (s). IR (KBr, cm^{-1}): 1911 (s, $\nu_{C=C=C}$). Anal. Calcd for $C_{75}H_{65}BF_{24}FeP_2Ru$: C, 54.53; H, 3.97. Found: C, 54.33; H, 4.07.

Catalytic Propargylic Substitution Reaction of 4 with EtOH. A typical experimental procedure for the reaction of **4** with EtOH catalyzed by **1a** is described as follows. Compounds **1a** (22.2 mg, 0.030 mmol), NaBAr$^F_4$ (26.6 mg, 0.030 mmol), and **4** (62.5 mg, 0.30 mmol) were placed in a 20 mL flask. Anhydrous EtOH (7.5 mL) was added, and then the mixture was stirred at 60 °C for 72 h. After the solvent was removed in vacuo, the resulting reddish-purple residue was extracted with hexane (1 mL × 3) and purified by column chromatography (SiO_2) with EtOAc−*n*-hexane (1/9) to give **5** as a pale yellow oil.

■ ASSOCIATED CONTENT

Supporting Information. CIF file with X-ray crystallographic data for **1c**·1.5C$_6$H$_6$, **2a**·1.5C$_6$H$_6$, **2b**, **3a**, **7b**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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