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Carbon−Carbon Bond Formation between Furyl and Triphenylphosphine Ligands in Ruthenium Complexes

Yu-Hao Huang, Wen-Wu Huang, Ying-Chih Lin,* and Shou-Ling Huang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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*Summary: The η^3-allylic complex **8** was obtained from thermolysis of the neutral ruthenium furyl complex **7** with an unsaturated carbon chain on the furyl ligand. Protonation of complex **8c** with HBF_4 generates complex **9c** with an oxygen atom and an olefin group coordinated to the ruthenium metal.*

Metal-mediated processes make possible certain reactions, which are not feasible without the involvement of the metal species. In particular, organometallic ruthenium complexes play important roles in many catalytic reactions, such as asymmetric hydrogenation,[1] olefin metathesis,[2] and polymerization.[3] A better understanding of the mechanism of these reactions revealed the role of the metal and led to wide applications of ruthenium in organic synthesis. To further expand the scope of these applications, it is crucial to explore new reactivity of various complexes of ruthenium. We previously reported the synthesis of a ruthenium cyclopropenyl complex through the deprotonation reaction of a vinylidene complex containing a $-CH_2R$ group at C_β of the vinylidene ligand.[4] The same approach could also be used for the synthesis of a neutral ruthenium furyl complex from the deprotonation of a vinylidene complex containing a $-CH_2CO_2R$ group. Synthesis and reactions of a few furyl complexes of other transition metals have been reported. An iridium σ-furyl complex containing a hydride ligand can be obtained by the reaction of an iridium cyclooctadienyl complex with furan.[5] This iridium furyl complex reacted with *tert*-butylacetylene by insertion of the alkyne into the Ir−C bond to form an iridium vinyl hydride complex.[6] A few tungsten furyl complexes were obtained from the reaction of tungsten propargyl complexes with aldehydes. This furyl ligand is easily dissociated from the metal fragment and further reacts with Grignard reagent.[7] Previously, we reported the formation of oxygen addition products in almost quantitative yield when a simple ruthenium furyl complex was exposed to air.[8] The reaction is proposed to proceed via the formation of an endoperoxide intermediate.[8] In a continuation of our previous effort on exploring new reactions of ruthenium furyl complexes, herein we report our unexpected observation on the thermal reactions of three ruthenium furyl complexes, each with a pendant unsaturated hydrocarbon chain on the furyl ring. Two 5,5-disubstituted propargylic-1,6-enynes, $HCCCH(OH)CH_2CR_2CH{=}CH_2$ (**2a**, R = Ph; **2b**, R = Me), prepared in high yields according to the reported procedures,[9] were used for the synthesis of vinyl−acetylide complexes. Then, three furyl complexes were synthesized by electrophilic alkylations of the acetylide complexes followed by a deprotonation process. Thermolysis of the three furyl complexes all led to unusual coupling products.

As shown in Scheme 1, treatment of [Ru]−Cl ([Ru] = $Cp(PPh_3)_2Ru$) with **2a** in CH_2Cl_2 at room temperature afforded the vinyl−vinylidene complex **3a** exclusively. However, the reaction of [Ru]−Cl with the 1,6-enyne **2b** in the presence of KPF_6 in CH_2Cl_2 yielded a mixture of the vinylidene complex **3b** and the alkenyl−phosphonium complex **4b** in a ratio of ca. 3:2. Separation of **3b** and **4b** was achieved by precipitation of **3b** from a CH_2Cl_2/diethyl ether solution. These reactions proceed via formation of a vinylidene intermediate[10] followed by dehydration. Interestingly,

*To whom correspondence should be addressed. E-mail: yclin@ntu.edu.tw.

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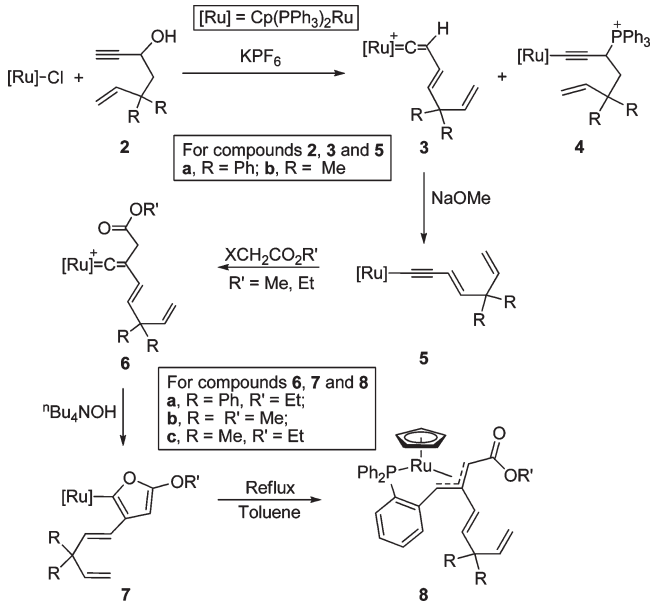
Scheme 1



no allenylidene complex was observed in these reactions. Namely, the dehydration reaction took place at C3−C4, instead of C2−C3, possibly due to the more stable conjugated form of the vinyl−vinylidene ligand. The formation of the minor product **4b**, however, might be attributed to the addition of phosphine to C_γ of the allenylidene ligand.[11] Further deprotonation of complexes **3a**,**b** were carried out with NaOMe to obtain the corresponding acetylide complexes **5a** (R = Ph) and **5b** (R = Me), respectively. Treatment of complexes **5a**,**b** with XCH_2CO_2R' (X = Br, I; R′ = Me, Et) afforded the cationic vinylidene complexes $[Ru]{=}C{=}C(CH_2CO_2R')CH{=}CHCR_2CH{=}CH_2[PF_6]$, (**6a**, R = Ph, R′ = Et; **6b**, R = R′ = Me; **6c**, R = Me, R′ = Et), all in high yield. For example, complex **5b** reacted with ethyl iodoacetate in CH_2Cl_2 to give **6c**, characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectra and analytical data. The ^{31}P NMR spectrum of **6c** displays a singlet resonance at δ 41.48. In the ^{13}C NMR spectrum of **6c**, the resonance assigned to the Ru=C_α carbon atom appears at δ 362.52 as a triplet. In addition, one singlet resonance at δ 27.20 is assigned to the methylene carbon near the ester group of **6c**.

Deprotonation of the vinylidene complex **6a** by *n*-Bu_4NOH in acetone is accompanied by a cyclization reaction, affording the neutral furyl complex **7a**. Under similar conditions, complexes **6b**,**c** also reacted with *n*-Bu_4NOH to give **7b**,**c**, respectively. No three-membered cyclopropenyl complex,[4] supposedly from deprotonation at C_γ followed by a direct intramolecular cyclization, was found. The ^{31}P NMR spectrum of **7c** displays a singlet resonance at δ 50.95. In the ^{13}C NMR spectrum of **7c**, three singlet resonances at δ 164.07, 149.04, and 110.04 are assigned to the carbonyl carbon and two terminal olefinic carbon atoms on the basis of the ^{1}H−^{13}C HMQC and ^{1}H−^{13}C HMBC spectra. The ^{1}H NMR spectrum of **7c** shows a set of coupled doublet resonances at δ 6.86 and 5.90 with $^3J_{HH}$ = 15.9 Hz assigned to the trans protons of the internal olefinic group.

Thermolysis of three complexes **7a**−**c** by heating their toluene solutions to reflux for up to 2 days afforded the corresponding η^3-allylic complexes **8a**−**c** in high yield.[12] The new coupling reaction between the furyl ligand and one phenyl group of the phosphine ligand, giving **8**, is accompanied by dissociation of a PPh_3 ligand. Characterization of complexes **8a**−**c** relies on their ^{1}H, ^{13}C, ^{31}P, and 2-D NMR spectra. For example, the ^{31}P NMR spectrum of **8c** displays a singlet peak at δ 84.27. Resonances of the OCH_2 group split into two multiplets at δ 4.28 and 4.05 in the ^{1}H NMR spectrum because of the presence of the stereogenic metal center generated in the formation of **8c**. In addition, two doublet resonances at δ 8.09 and 6.51 with $^3J_{HH}$ = 15.8 Hz are assigned to the trans protons of the internal olefinic group. In addition, the ^{1}H NMR spectrum of **8c** also displays one doublet resonance at δ 1.27 with $^3J_{PH}$ = 14.0 Hz and one singlet resonance at δ 5.86 assigned to two allylic protons. The ^{13}C NMR spectrum of **8c** shows a singlet resonance at δ 35.84 assigned to the center carbon of the allylic ligand and two resonances at δ 81.82 and 55.86 assigned to other two allylic carbon atoms.[13]

The structure of **8c** was further confirmed by a solid-state single-crystal X-ray diffraction analysis. Yellow single crystals suitable for X-ray diffraction were grown via slow evaporation of a methanol solution of **8c**. An ORTEP drawing is shown in Figure 1. It is apparent that C−C bond formation between a phenyl group of the coordinated phosphine ligand and the furyl ligand has occurred. In addition, opening of the furyl ligand causes C_α and two other ring carbon atoms to be bound to the ruthenium center in a η^3-allylic bonding mode. The bond lengths C(19)−C(20) and C(20)−C(28) of the allylic ligand are 1.420(13) and 1.455(13) Å, respectively. Both stay within the range between double- and single-bond lengths, suggesting π electron delocalization within the allylic unit. The Ru(1)−C(19), Ru(1)−C(20), and Ru(1)−C(28) bond distances of 2.164(10), 2.098(9), and 2.192 (8) Å, respectively, are normal for a η^3-allylic bonding mode. The bond lengths are comparable to those of the ruthenium allylic complex reported by Green et al.[14] The bond angle C(19)−C(20)−C(28) of 114.8(8)° is slightly smaller than that of the reported allylic complex.[15] This can be explained by the steric effect between the ethyl acetate group in a syn position and the long unsaturated carbon chain bound to the central carbon of the allylic ligand.

Formation of complex **8** can be accounted for by the possible processes depicted in Scheme 2. Dissociation of a

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(12) Thermolysis of **7c** (0.10 g, 0.11 mmol) was carried out in toluene under nitrogen by heating the solution to reflux for 2 days. The solvent was then removed under vacuum, and the crude product was purified by neutral Al_2O_3 column chromatography with 1/10 Et_2O/hexanes as eluent to yield **8c** (0.05 g, yield 75%). Slow evaporation of a methanol solution of **8c** generated yellow single crystals suitable for X-ray diffraction. Selected spectroscopic data for **8c**: ^{1}H NMR (C_6D_6) δ 8.05 (d, 1H, $^3J_{HH}$ = 15.8 Hz, C*H*=), 6.51 (d, 1H, $^3J_{HH}$ = 15.8 Hz, C*H*=), 6.15 (dd, 1H, $^3J_{HH}$ = 17.3 Hz, $^2J_{HH}$ = 10.5 Hz, 1H, C*H*=), 5.86 (s, 1H, allylic C*H*), 5.26 (dd, 1H, $^3J_{HH}$ = 17.3 Hz, $^2J_{HH}$ = 1.1 Hz, CH_2=), 5.14 (dd, 1H, $^3J_{HH}$ = 10.5 Hz, $^2J_{HH}$ = 1.1 Hz, CH_2=), 4.58 (s, 5H, Cp), 1.27 (d, 1H, $^3J_{PH}$ = 14.0 Hz, allylic C*H*); ^{31}P NMR (C_6D_6) δ 84.27; ^{13}C NMR (C_6D_6) δ 176.23 (*C*=O), 148.28 (*C*H=), 134.22 (*C*H=), 131.02 (*C*H=), 110.62 (*C*H_2=), 83.27 (Cp), 81.82 (allylic *C*H), 55.86 (allylic *C*H), 35.84 (central *C*). Anal. Calcd for $C_{36}H_{37}O_2PRu$: C, 68.23; H, 5.89. Found: C, 68.47; H, 6.05. Complete spectroscopic data are given in the Supporting Information.

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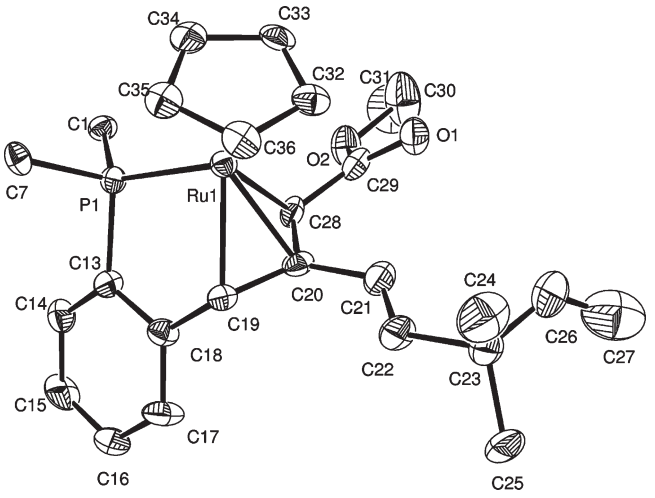
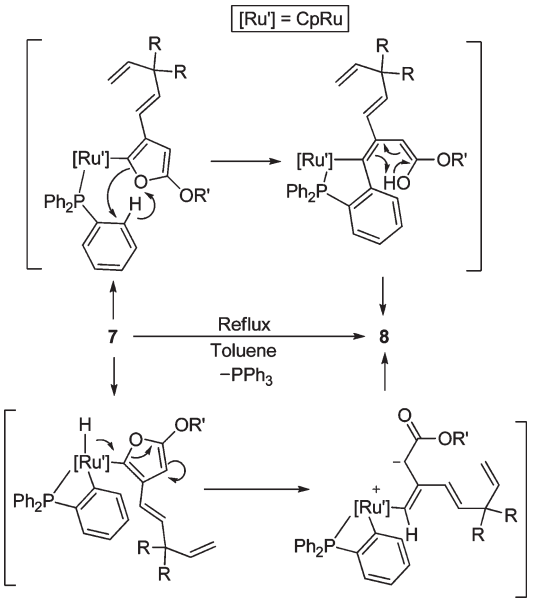


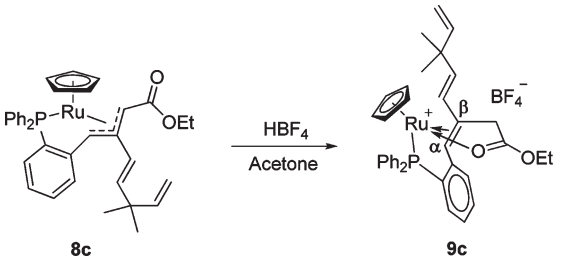
Figure 1. ORTEP drawing of **8c**, with the phenyl groups of the phosphine ligands (except the ipso carbons and the phenyl group with C−C bond formation) and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−C(19), 2.164(10); Ru(1)−C(20), 2.098(9); Ru(1)−C(28), 2.192(8); C(18)−C(19), 1.501(13); C(19)−C(20), 1.420(13); C(20)−C(21), 1.517(13); C(21)−C(22), 1.300(14); C(20)−C(28), 1.455(13); C(28)−C(29), 1.450(14); C(29)−O(1), 1.251(11); C(18)−C(19)−C(20), 123.6(8); C(19)−C(20)−C(28), 114.8(8); C(29)−C(28)−C(20), 122.6(8); C(28)−C(20)−C(21), 121.7(8); C(21)−C(20)−C(19), 123.4(9).

Scheme 2



phosphine ligand on **7** occurred when a toluene solution of **7** was heated to reflux. One pathway presumably involves ortho metalation of a phenyl group of the remaining PPh_3 on complex **7**, resulting in formation of a Ru(IV)[16] hydride intermediate with a four-membered ring.[17] Afterward, a hydride shift to C_α of the furyl ligand is followed by opening of the furyl ring to form a zwitterionic intermediate. Then, as shown in the lower part of Scheme 2, a subsequent reductive elimination of the furyl and the phenyl groups with concomitant coordination of the double bond to the ruthenium center forms **8**. Alternatively, the direct cleavage of the PPh_3 ortho C−H bond by the Ru−C_1−O bond of the furyl group with formation of C_1−C_{ortho} and O−H bonds leading to compound **9** is also depicted in the upper part of Scheme 2. The feasibility of the cleavage of ortho agostic C−H bonds by deprotonation assisted by both metal and ligand has been demonstrated by DFT calculations.[18] Previously we reported dioxygen addition to a furyl ligand with no hydrocarbon chain to give an endoperoxide intermediate.[8] However, complexes **7a**−**c** are stable in air, most likely because of the presence of the pendant unsaturated hydrocarbon chain. The ring-opening reaction of a furyl ring system in organometallic lanthanide complexes has been reported. A CH_2SiMe_3 group has been used as a proton sponge for the furyl ligand, resulting in opening of the five-membered ring.[19] Also, a rare example of ortho metalation with concomitant C−C bond formation has been reported in the UV irradiation of an iron thiocarbonyl phosphite complex, affording the thioaldehyde complex by insertion of the thiocarbonyl C atom into an ortho C−H bond of an axially bound $P(OPh)_3$ phenyl group.[20] In our complexes, the intramolecular coupling reaction involves the furyl ligand with a long unsaturated hydrocarbon chain, resulting in connecting this chain to the phosphine ligand, and the furyl ligand serves as a hydride acceptor for the opening of the five-membered ring. To our knowledge, this intramolecular coupling reaction to bring a long hydrocarbon chain to a phosphine ligand is the first example of this type.

Scheme 3



The protonation reaction of **8c** was also explored by using HBF_4. Treatment of **8c** in acetone with HBF_4 afforded the cationic complex **9c** (Scheme 3) by direct addition of a proton to one of the terminal carbon of the η^3-allyl ligand having the ester group. The structure of complex **9c** is supported by

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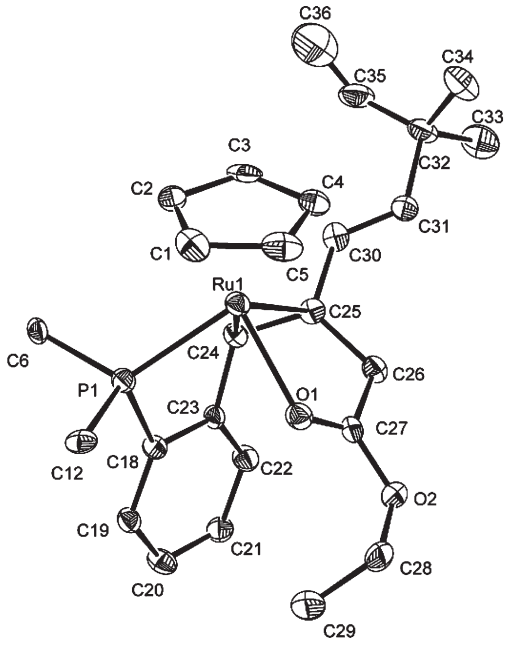

Figure 2. ORTEP drawing of **9c** with the phenyl groups on the phosphine ligand (except the ipso carbon and the phenyl group with formation of a C−C bond) and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−C(24), 2.196(8); Ru(1)−C(25), 2.260(8); Ru(1)−O(1), 2.144(6); Ru(1)−P(1), 2.325(2); C(23)−C(24), 1.515(11); C(24)−C(25), 1.433(11); C(25)−C(26), 1.509(11); C(26)−C(27), 1.494(11); C(27)−O(1), 1.236(10); C(27)−O(2), 1.320(10); C(30)−C(31), 1.323(11); Ru(1)−C(24)−C(25), 73.7(5); C(24)−C(25)−C(26), 120.7(8); C(25)−C(26)−C(27), 112.1(7); C(24)−C(25)−C(30), 118.1(7); C(26)−C(25)−C(30), 117.3(7).

NMR spectra and solid-state structure determination using X-ray diffraction analysis. The ^{1}H NMR spectrum of complex **9c** displays two doublet resonances at δ 3.95 and 2.70 with $^2J_{HH}$ = 19.0 Hz assignable to the methylene protons near the ester group, showing correlations to the ^{13}C resonance at δ 39.33 in the ^{1}H−^{13}C HSQC spectrum. The ^{1}H signal at δ 6.13 is assigned to the proton at C_α (see Scheme 3 for the α-labeling), showing correlation with the ^{13}C resonance at δ 77.98. Two doublet resonances attributable to the internal olefinic trans protons appear at δ 6.25 and 5.98 with $^3J_{HH}$ = 16.0 Hz. The ^{13}C NMR spectrum of **9c** displays a distinctive resonance at δ 187.95 assigned to the carbonyl carbon, which shifts more downfield than that of complex **8c** due to the coordination of the oxygen atom to the ruthenium center. The ESI mass spectrum of complex **9c** exhibits a signal at m/z 635.16, corresponding to the parent ion.

Slow diffusion of pentane into a solution of **9c** in CH_2Cl_2 allowed isolation of single crystals suitable for an X-ray diffraction study. An ORTEP drawing of **9c** is shown in Figure 2. For **9c**, the shorter lengths of Ru(1)−C(24) (2.196(8) Å) and Ru(1)−C(25) (2.260(8) Å) and the longer length of C(24)−C(25) (1.433(11) Å) compared to those in complex **8c** reveal that the degree of π-back-donation in complex **9c** might be stronger than that in **8c**. The C(25)−C(26) and C(26)−C(27) bond distances of 1.509(11) and 1.494(11) Å, respectively, are normal for a C−C single bond. The C(27)−O(1) bond length is 1.236(10) Å, which is comparable with that in **8c** (1.251(11) Å), possibly indicating weak σ-donation from O(1) to Ru(1).

Notably, complex **9c** represents a rare example of an Ru complex featuring a tridentate ligand donating six electrons to the ruthenium metal via phosphine, an oxygen atom, and an olefin group. In the literature, a bimetallic ruthenium complex of biquinone, also with an olefinic and an oxygen binding, was synthesized from a ruthenium cyclooctatriene complex and *p*-biquinone.[21] In another case, a ruthenium hydrido acyl complex was reacted with diphenylacetylene to afford a ruthenium complex with the α,β-unsaturated ketone moiety bound to the metal in an η^4 coordination mode, involving both a classical η^2 coordination of the olefinic bond and a rather uncommon side-on coordination of the CO bond.[22] Here we demonstrated the transformation of an allylic ligand with an ester substituent to a β,γ-unsaturated ester group by protonation.

In conclusion, we have synthesized propargylic enyne compounds **2a**,**b**, from which the three neutral ruthenium complexes **7a**−**c** were obtained, each containing a furyl ligand with an unsaturated hydrocarbon chain in high yield. Unexpectedly, upon heating the toluene solution of **7** to reflux, the furyl complexes **7a**−**c** transformed into complexes **8a**−**c**, respectively, each with an allylic ligand binding to the ruthenium center in a η^3 coordinating mode. Obviously the long chain on the furyl ligand plays a key role in changing the reactivity of these complexes. Further reactivity of these furyl and allylic complexes is currently under investigation.

Acknowledgment. We thank the National Science Council, Taiwan, Republic of China, for financial support. We are grateful for a reviewer suggesting the alternative mechanism for the formation of **8** from **7**.

Supporting Information Available: Text, figures, CIF files, and a table giving synthetic and spectroscopic data of the compounds and complete crystallographic data for **8c** and **9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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