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Article

Reactions of a Trinuclear Ruthenium Complex Derived from 3-(2-Pyridyl)indene with Diphenylacetylene and Phenylacetylene: Insertion of Alkynes into the Ru−C bond

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Thermal treatment of the trinuclear ruthenium complex $\{\mu_2\text{-}\eta^5{:}\eta^1\text{-}(C_5H_4N)(C_9H_5)\}Ru_3(CO)_9$ (**1**) with 1 equiv of diphenylacetylene gave the trinuclear complex $\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(PhC{=}CPh)\}Ru_3(CO)_7$ (**2**) via the insertion of an alkyne into the Ru−C(η^1) bond of **1**. Complex **2** could be transformed into the dinuclear and trinuclear complexes $\{\mu_2\text{-}\eta^1{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(PhC{=}CPh)\}Ru_2(CO)_2(\mu_2\text{-}\eta^2{:}\eta^4\text{-}CPh{=}CPhCPh{=}CPh)$ (**3**), $\{\mu_3\text{-}\eta^2{:}\eta^3{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(CPhCPh{=}CPhCPh)\}Ru_3(CO)_6$ (**4**), and $\{\mu_2\text{-}\eta^1{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(PhC{=}CPh)\}Ru_3(CO)_4(\mu_3\text{-}\eta^2\text{-}PhC{=}CPh)_2$ (**5**) in the presence of excess diphenylacetylene. Similarly, reaction of **1** with 1 equiv of phenylacetylene gave the alkyne-inserted product $\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(HC{=}CPh)\}Ru_3(CO)_7$ (**6**), which could also react with excess phenylacetylene to give the complexes $\{\mu_3\text{-}\eta^2{:}\eta^4{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(C{=}CPhCH{=}CPh)\}(\mu_2\text{-}H)Ru_3(CO)_6$ (**7**) and $\{\mu_2\text{-}\eta^2{:}\eta^4\text{-}(C_5H_4N)(C_9H_6)(C{=}CPhCH{=}CPh)\}Ru_2(CO)_4(\mu_2\text{-}CO)$ (**8**). Complex **7** could be transformed slowly into **8** in refluxing toluene. The reactions of 3-(2-pyridyl)indene with internal alkynes catalyzed by $Ru_3(CO)_{12}$ and **1** were also tested, obtaining several C−H/alkyne coupling products, while the reaction with phenylacetylene did not work under the same conditions. The molecular structures of **2**−**8** were determined by X-ray diffraction.

Introduction

As a green and atom-economical method, C−C coupling through C−H bond activation by transition-metal complexes has been developing rapidly in recent years.[1] For example, functional group directed aromatic C−H/alkyne coupling is an effective method not only to introduce olefinic groups to the ortho position of an aromatic ring but also to synthesize various heterocycles.[1a−e,2−5] However, in some cases, terminal alkynes were not suitable, partly because of their oligomerization.[5] We have recently reported the reactions of the trinuclear complex $\{\mu_2\text{-}\eta^5{:}\eta^1\text{-}(C_5H_4N)(C_9H_5)\}Ru_3(CO)_9$ (**1**), derived from 3-(2-pyridyl)indene, with alkenes, giving a series of C−C coupling products via 1,1-insertion of alkenes into the Ru−C(η^1) bond.[6] Here we further report its reactions with diphenylacetylene and phenylacetylene. On the basis of the different reaction results, we wish to get some useful information to understand the different reactivity between internal alkynes and terminal alkynes in chelation-assisted C−H/alkyne coupling reactions.

Results and Discussion

Reaction of 1 with Diphenylacetylene. When the complex $\{\mu_2\text{-}\eta^5{:}\eta^1\text{-}(C_5H_4N)(C_9H_5)\}Ru_3(CO)_9$ (**1**) reacted with 1 equiv of diphenylacetylene in refluxing toluene, the complex $\{\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(PhC{=}CPh)\}Ru_3(CO)_7$ (**2**) was

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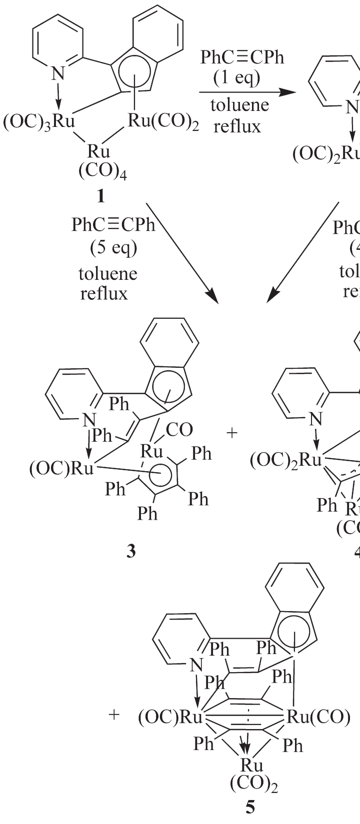
Scheme 1



obtained in 64% yield (Scheme 1). Its ^{1}H NMR spectrum shows five groups of peaks at 8.52−6.70 ppm for the pyridyl and benzo protons and one singlet at 5.01 ppm for the C_5 ring proton of indenyl. Single-crystal X-ray diffraction analysis shows that complex **2** is a triruthenium complex (Figure 1), and the three Ru atoms bond to each other. The Ru(1)−Ru(3) distance (2.6466(6) Å) is much shorter than those of Ru(1)−Ru(2) and Ru(2)−Ru(3) (2.8939(6), 2.8946(6) Å) and the corresponding Ru−Ru distance in complex **1** (2.9393(5) Å). This may be caused by the bridging PhC=CPh ligand. The C(28)−C(29) distance is 1.414(5) Å, longer than the value for a typical C=C double bond (~1.34 Å). The Ru(1)−C(28) and Ru(1)−C(29) distances (2.266(4), 2.282(4) Å) are much longer than the Ru(3)−C(28) distance (2.123(4) Å) but much shorter than the Ru(3)···C(29) distance (3.117 Å), indicating that the PhC=CPh ligand coordinates with Ru(1) in an η^2 mode but with Ru(3) in an η^1 mode.

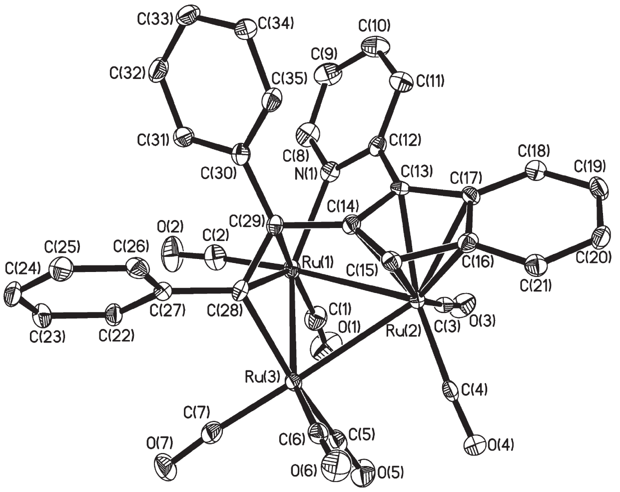


Figure 1. ORTEP diagram of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)−N(1) = 2.190(3), Ru(1)−C(28) = 2.266(4), Ru(1)−C(29) = 2.282(4), Ru(1)−Ru(3) = 2.6466(6), Ru(1)−Ru(2) = 2.8939(6), Ru(2)−Ru(3) = 2.8946(6), Ru(3)−C(28) = 2.123(4), C(28)−C(29) = 1.414(5).

A possible formation mechanism of **2** is shown in Scheme 2. Diphenylacetylene inserts into the Ru−C(η^1) bond first,[7] and then the double bond of the PhC=CPh unit coordinates with a Ru atom to replace a carbonyl. This may promote the formation of the third Ru−Ru bond and release of a carbonyl to give **2a**. **2a** and **2** might be transformed into each other under certain conditions.

Reaction of 2 with Diphenylacetylene. Complex **2** could further react with excess diphenylacetylene to give the dinuclear and trinuclear complexes $\{\mu_2\text{-}\eta^1{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(PhC{=}CPh)\}Ru_2(CO)_2(\mu_2\text{-}\eta^2{:}\eta^4\text{-}CPh{=}CPhCPh{=}CPh)$ (**3**),

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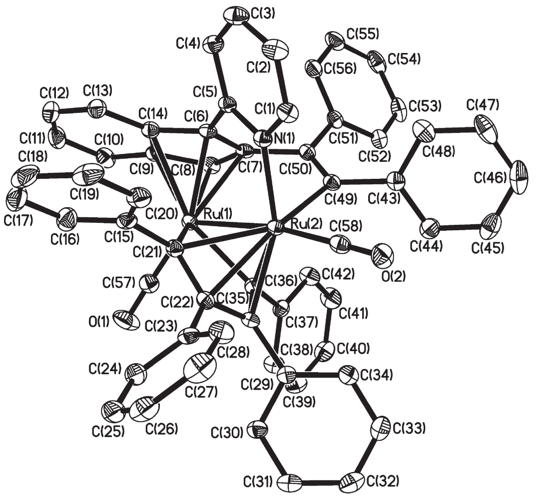


Figure 2. ORTEP diagram of **3**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)−C(21) = 2.063(2), Ru(1)−C(36) = 2.117(2), Ru(1)−Ru(2) = 2.6649(4), Ru(2)−C(49) = 2.107(2), Ru(2)−N(1) = 2.120(2), Ru(2)−C(36) = 2.159(2), Ru(2)−C(35) = 2.206(2), Ru(2)−C(21) = 2.310(2), Ru(2)−C(22) = 2.322(2), C(21)−C(22) = 1.399(3), C(22)−C(35) = 1.462(3), C(35)−C(36) = 1.427(3), C(49)−C(50) = 1.354(3).

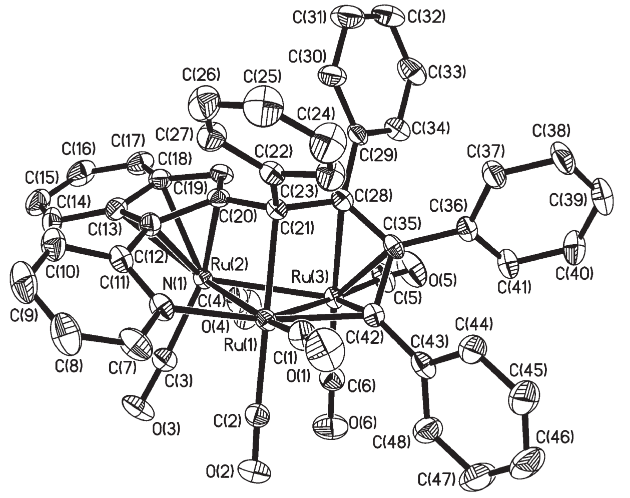
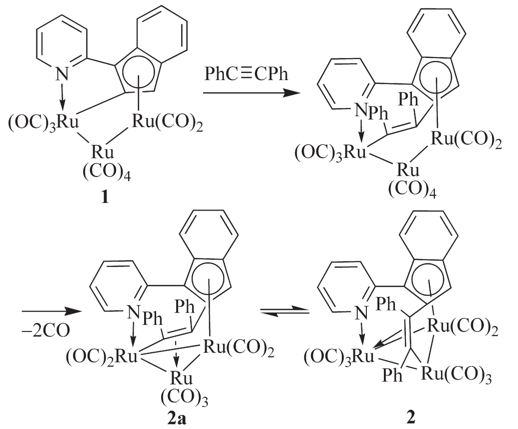


Figure 3. ORTEP diagram of **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)−C(42) = 2.154(6), Ru(1)−N(1) = 2.174(6), Ru(1)−C(21) = 2.175(6), Ru(1)−Ru(3) = 2.684(2), Ru(1)−Ru(2) = 2.860(2), Ru(2)−Ru(3) = 2.754(2), Ru(3)−C(42) = 2.029(6), Ru(3)−C(35) = 2.231(6), Ru(3)−C(28) = 2.431(6), C(21)−C(28) = 1.529(8), C(28)−C(35) = 1.399(9), C(35)−C(42) = 1.438(9).

Scheme 2



{μ_3-η^2:η^3:η^5-(C_5H_4N)(C_9H_5)(CPhCPh=CPhCPh)}$Ru_3(CO)_6$ (**4**), and {μ_2-η^1:η^5-(C_5H_4N)(C_9H_5)(PhC=CPh)}$Ru_3(CO)_4$ (μ_3-η^2-PhC=CPh)$_2$ (**5**) in 66%, 7%, and 12% yields, respectively (Scheme 1). The ^{1}H NMR spectrum of **3** shows eight groups of peaks at 8.89−6.05 ppm for the pyridyl and benzo protons and one singlet at 5.13 ppm for the C_5 ring proton of indenyl. Its IR spectrum only shows two terminal carbonyl absorptions at 1965 and 1922 cm^{-1}. Single-crystal X-ray diffraction analysis revealed that complex **3** is a dinuclear complex incorporating three diphenylacetylene molecules: one is inserted into the Ru−C(η^1) bond, and the others are coupled with a ruthenium atom to from the ruthenacyclopentadiene,[8] which is bonded to another ruthenium atom (Ru(2)) in an η^5 mode (Figure 2). However, the five-membered ring is slightly puckered, with Ru(1) bending away from the C(21)−C(22)−C(35)−C(36) plane (the dihedral angle between the C(21)−C(22)−C(35)−C(36) and C(21)−Ru(1)−C(36) planes is 8.5°). The Ru(1)−Ru(2) distance (2.6649(4) Å) is within the Ru−Ru bond lengths found previously.[8] The C(21)=C(22) and C(35)=C(36) bonds (1.399(3), 1.427 Å) in the π-coordinated bridging PhC(21)=C(22)Ph−PhC(35)=C(36)Ph ligand are much longer than the C(49)=C(50) bond (1.354(3) Å) in the noncoordinated bridging PhC(49)=C(50)Ph ligand.

Complex **4** is a triruthenium complex incorporating two diphenylacetylene molecules (Figure 3). The two diphenylacetylene molecules are inserted in succession into the Ru−C bond to form a five-membered ring, which is bonded with Ru(3) in a twisted η^3 mode, as shown by the C−C and Ru−C bond lengths (C(21)−C(28) = 1.529(8) Å, C(28)−C(35) = 1.399(9) Å, C(35)−C(42) = 1.438(9) Å; Ru(3)−C(42) = 2.029(6) Å, Ru(3)−C(28) = 2.431(6) Å, Ru(3)−C(35) = 2.231(6) Å). The long distance (3.041 Å) between the Ru(3) and C(21) atoms indicates that they do not bond to each other. The three Ru atoms bond to each other. The Ru(1)−Ru(3) distance (2.684(2) Å) is comparable to the corresponding Ru−Ru distance in **2** (2.6466(6) Å) but is shorter than the Ru(1)−Ru(2) and Ru(2)−Ru(3) distances (2.860(2), 2.754(2) Å). A possible formation mechanism of **4** is shown in Scheme 3. Complex **2** transforms into **2a** first, followed by diphenylacetylene insertion into the Ru−C(Ph) bond, forming the intermediate {μ_3-η^1:η^4:η^5-(C_5H_4N)(C_9H_5)(CPh=CPhCPh=CPh)}$Ru_3(CO)_6$ (**4a**), which then transforms into **4** via the cleavage of a Ru(3)−C bond (from η^4 to η^3) followed by the formation of a new Ru−C σ bond.

Complex **5** is a triruthenium complex incorporating three diphenylacetylene molecules. Its ^{1}H NMR spectrum shows a doublet at 5.41 ppm for two phenyl protons, which is much

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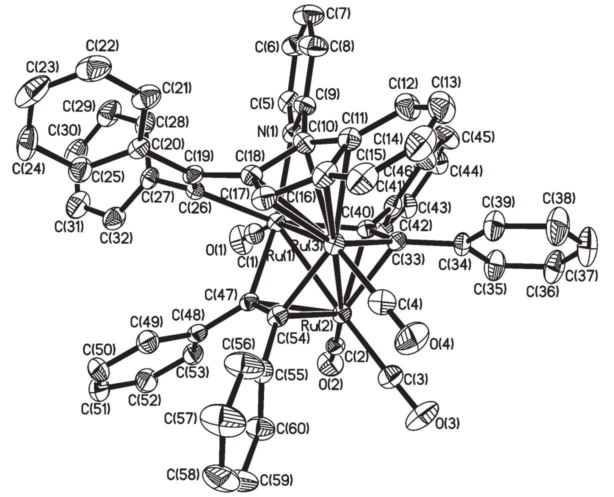
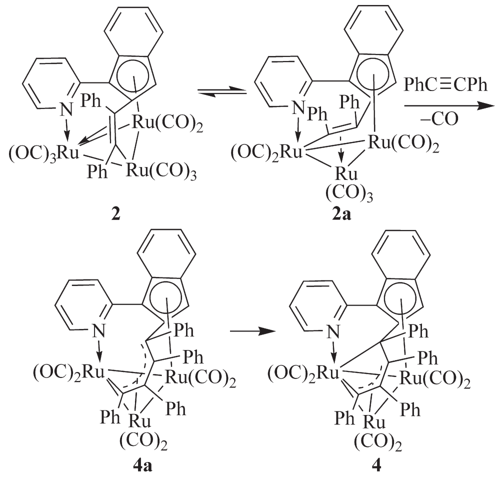


Figure 4. ORTEP diagram of **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths: Ru(1)−C(47) = 2.066(5), Ru(1)−C(26) = 2.098(6), Ru(1)−N(1) = 2.134(5), Ru(1)−C(40) = 2.141(6), Ru(1)−Ru(2) = 2.6298(8), Ru(1)−Ru(3) = 2.8709(10), Ru(2)−C(40) = 2.139(6), Ru(2)−C(54) = 2.146(5), Ru(2)−C(33) = 2.169(6), Ru(2)−C(47) = 2.183(6), Ru(2)−Ru(3) = 2.6938(8), Ru(3)−C(54) = 2.103(6), Ru(3)−C(33) = 2.122(5), C(19)−C(26) = 1.338(7), C(33)−C(40) = 1.412(8), C(47)−C(54) = 1.400(8).

Scheme 3



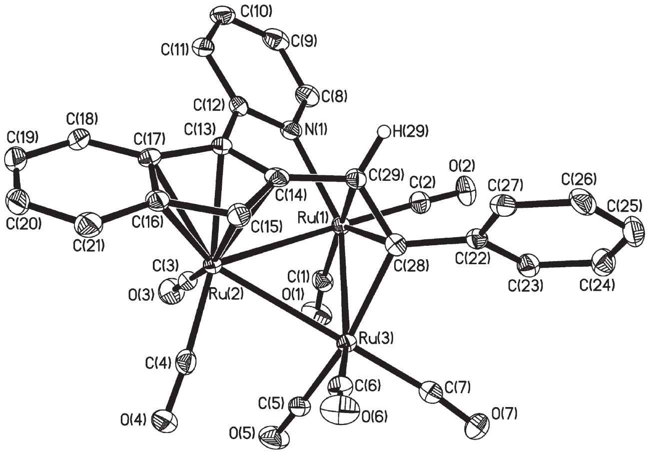
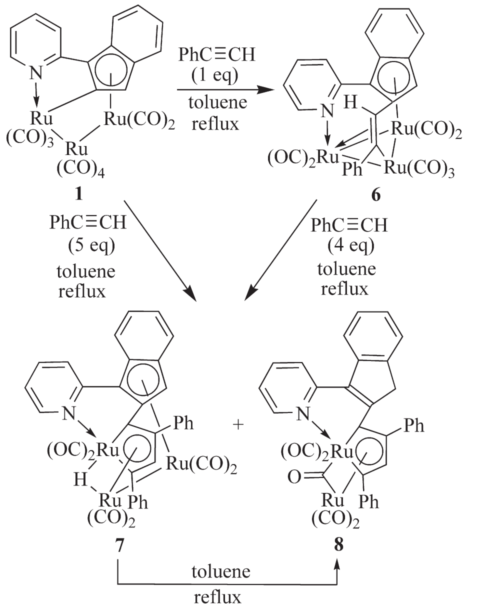


Figure 5. ORTEP diagram of **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity, except for H(29). Selected bond lengths (Å): Ru(1)−N(1) = 2.1715(19), Ru(1)−C(28) = 2.227(2), Ru(1)−C(29) = 2.228(2), Ru(1)−Ru(3) = 2.6449(3), Ru(1)−Ru(2) = 2.9211(5), Ru(2)−Ru(3) = 2.8868(4), Ru(3)−C(28) = 2.090(2), C(28)−C(29) = 1.409(3).

Scheme 4



farther upfield than the other signals, due to the deshielding effect of surrounding groups. From its molecular structure (Figure 4) it is found that one alkyne is inserted into the Ru−C(η^1) bond; the other two coordinate with the Ru_3 core, both in a μ_3-η^2 mode. The C(33)=C(40) and C(47)=C(54) bonds are parallel to the Ru(1)−Ru(3) bond. This type of bonding mode has been observed in a number of clusters.[9] The bridging PhC(19)=C(26)Ph ligand does not coordinate with any Ru atom; therefore, the C(19)=C(26) distance (1.338(7) Å) is much shorter than the C(33)=C(40) and C(47)=C(54) distances (1.412(8), 1.400(8) Å). The Ru(1)−Ru(2) and Ru(2)−Ru(3) distances (2.6298(8), 2.6938(8) Å) are comparable to the corresponding Ru−Ru distances in the complex (μ_3-η^2-PhC=CPh)$_2$Ru$_3$(CO)$_8$ (2.6566(6), 2.6646(7) Å),[9b] but the Ru(1)−Ru(3) distance (2.8709(10) Å) is much longer than the corresponding Ru−Ru distance (2.7264(7) Å).

Complexes **3**−**5** could also be obtained by a one-pot reaction of **1** with excess diphenylacetylene, and the total yield (61%) is slightly higher than that for two steps (54%) (Scheme 1).

Reaction of 1 with Phenylacetylene. Thermal treatment of **1** with 1 equiv of phenylacetylene gave the trinuclear complex {μ_3-η^1:η^2:η^5-(C_5H_4N)(C_9H_5)(HC=CPh)}Ru$_3$(CO)$_7$ (**6**; 24%), in addition to recovered **1** (25%) (Scheme 4).

The ^{1}H NMR spectrum of **6** shows five groups of peaks at 8.72−7.14 ppm for the pyridyl and benzo protons, one singlet at 6.73 ppm for the proton of the bridging CH=CPh

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[9] (a) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J.; Yanez, R.; Mathieu, R. *J. Am. Chem. Soc.* **1989**, *111*, 8959. (b) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1991**, *10*, 2285. (c) Takao, T.; Takemori, T.; Moriya, M.; Suzuki, H. *Organometallics* **2002**, *21*, 5190. (d) Srinivasan, P.; Leong, W. K. *Eur. J. Inorg. Chem.* **2006**, 464.

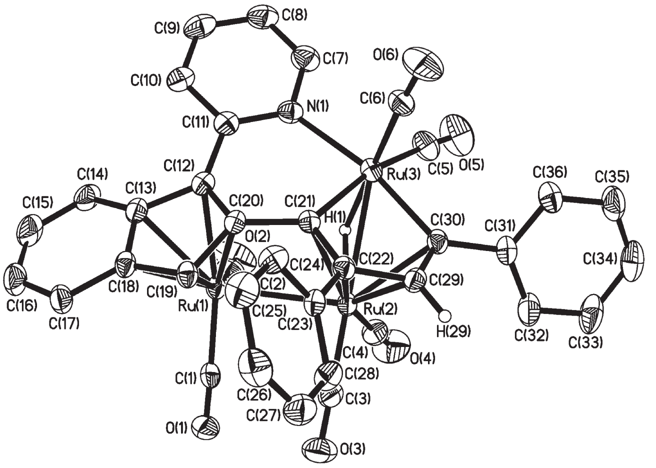

Figure 6. ORTEP diagram of **7**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity, except for H(1) and H(29). Selected bond lengths (Å): Ru(1)−Ru(2) = 2.7878(4), Ru(2)−C(21) = 2.276(3), Ru(2)−C(22) = 2.346(3), Ru(2)−C(29) = 2.300(4), Ru(2)−C(30) = 2.326(3), Ru(2)−Ru(3) = 2.7752(5), Ru(3)−C(21) = 2.106(3), Ru(3)−C(30) = 2.077(4), Ru(3)−N(1) = 2.204(3), C(21)−C(22) = 1.421(5), C(22)−C(29) = 1.458(5), C(29)−C(30) = 1.415(5).

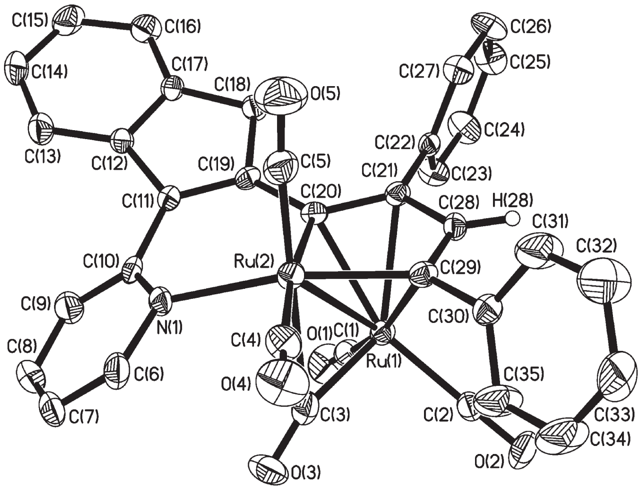

Figure 7. ORTEP diagram of **8**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity, except for H(28). Selected bond lengths (Å): Ru(1)−C(20) = 2.265(5), Ru(1)−C(21) = 2.295(5), Ru(1)−C(28) = 2.267(5), Ru(1)−C(29) = 2.285(5), Ru(1)−Ru(2) = 2.6955(9), Ru(2)−C(20) = 2.113(5), Ru(2)−C(29) = 2.041(5), Ru(2)−N(1) = 2.184(4), C(20)−C(21) = 1.431(6), C(21)−C(28) = 1.427(6), C(28)−C(29) = 1.412(6).

ligand, and one singlet at 4.89 ppm for the C_5 ring proton of indenyl. The structure of **6** is similar to that of **2** (Figure 5). The Ru(1)−Ru(3) and Ru(2)−Ru(3) distances (2.6449(3), 2.8868(4) Å) are comparable to the corresponding Ru−Ru distances in **2** (2.6466(6), 2.8946(6) Å). The Ru(1)−Ru(2) distance (2.9211(5) Å) is slightly longer than the corresponding Ru−Ru distance in **2** (2.8939(6) Å). The CH=CPh ligand coordinates with Ru(1) in an η^2 mode and with Ru(3) in an η^1 mode.

Reaction of 6 with Phenylacetylene. Similar to the case for complex **2**, complex **6** could further react with excess phenylacetylene to give the trinuclear and dinuclear complexes $\{\mu_3\text{-}\eta^2{:}\eta^4{:}\eta^5\text{-}(C_5H_4N)(C_9H_5)(C{=}CPhCH{=}CPh)\}(\mu_2\text{-}H)Ru_3(CO)_6$ (**7**) and $\{\mu_2\text{-}\eta^2{:}\eta^4\text{-}(C_5H_4N)(C_9H_6)(C{=}CPhCH{=}CPh)\}Ru_2(CO)_4(\mu_2\text{-}CO)$ (**8**) in 37% and 22% yields, respectively (Scheme 4). The ^1H NMR spectrum of complex **7** shows six groups of peaks at 9.16−7.06 ppm for the pyridyl and benzo protons, one singlet at 7.01 ppm for the proton of the bridging CCPhCHCPh ligand, one singlet at 4.08 ppm for the C_5 ring proton of indenyl, and one singlet at −13.11 ppm for Ru−H, indicating that its structure is different from those of complexes **3**−**5**. Single-crystal X-ray diffraction analysis showed that complex **7** is a trinuclear ruthenacyclopentadiene complex (Figure 6).[8] The Ru(2)−Ru(3) distance (2.7752(5) Å) is longer than the Ru−Ru distance in **3** (2.6649(4) Å). The Ru(1)−Ru(2) distance is 2.7878(4) Å. The long distance (4.058 Å) between Ru(1) and Ru(3) atoms indicates that they do not bond to each other. The Ru(2) and Ru(3) atoms are bridged by a (μ_2-η^2:η^4-C=CPhCH=CPh) fragment and a μ_2-H atom. The C(21)−C(22), C(22)−C(29), and C(29)−C(30) bond lengths are 1.421(5), 1.458(5), and 1.415(5) Å, respectively. The dihedral angle between the C(21)−C(22)−C(29)−C(30) and C(21)−Ru(3)−C(30) planes is 11.5°.

The ^1H NMR spectrum of complex **8** shows four groups of peaks at 9.54−7.01 ppm for the pyridyl and benzo protons, one singlet at 6.54 ppm for the proton of the bridging CCPhCHCPh ligand, and a doublet of doublets at 3.29 ppm for the C_5 ring proton of indenyl. The doublet of doublets for the C_5 ring proton of indenyl indicates that the indenyl group does not coordinate with the Ru atom in an η^5 mode. Its IR spectrum shows four terminal and one bridging carbonyl absorption at 2031, 2000, 1969, 1945, and 1882 cm^{-1}.[8d] Single-crystal X-ray diffraction analysis showed that complex **8** is a dinuclear ruthenacyclopentadiene complex (Figure 7). The Ru(1)−Ru(2) distance (2.6955(9) Å) is slightly longer than the Ru−Ru distance in complex **3** (2.6649(4) Å). The Ru(1) and Ru(2) atoms are bridged by a μ_2-η^2:η^4-C=CPhCH=CPh fragment and a μ_2-CO group. The C(20)−C(21), C(21)−C(28), and C(28)−C(29) bond lengths are 1.431(6), 1.427(6), and 1.412(6) Å, respectively. The dihedral angle between the C(20)−C(21)−C(28)−C(29) and C(20)−Ru(2)−C(29) planes is 7.4°.

On thermal treatment of complex **7** in refluxing toluene for 20 h, complex **8** was obtained in 12% yield, in addition to recovered **7** (60%) (Scheme 4). Similar to the case for complexes **3**−**5**, complexes **7** and **8** could also be obtained by the one-pot reaction of **1** with excess phenylacetylene. The total yield (54%) is much higher than that for two steps (14%) (Scheme 4).

A possible formation mechanism of complexes **7** and **8** is shown in Scheme 5. First, complex **6** transforms to **6a**, and then phenylacetylene inserts into the Ru−C(Ph) bond to form **7a**, followed by the oxidative addition of a C−H bond to the Ru atom to form a five-membered ring, accompanied by the cleavage of a Ru−Ru bond to form complex **7**. Then the μ_2-H atom transfers to the indenyl ring to form complex **8**,[10] accompanied by the cleavage of the η^5-indenyl−Ru bond and a Ru−Ru bond.

Catalytic Reactions of 3-(2-Pyridyl)indene with Alkynes. Alkynes could react with 3-(2-pyridyl)indene to give C−H/alkyne coupling products (**9**−**11**) when using $Ru_3(CO)_{12}$

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[10] Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 311.

Scheme 5

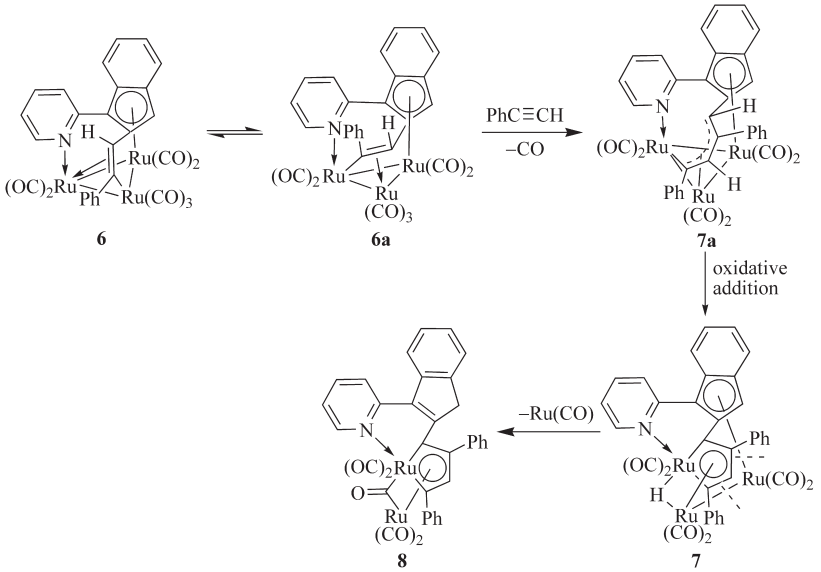
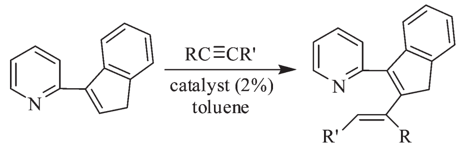


Table 1. $Ru_3(CO)_{12}$-Catalyzed C−H/Alkyne Coupling[a]



entry	catalyst	alkyne	product	yield[b] (%)
1	$Ru_3(CO)_{12}$	R = R′ = Ph	R = R′ = Ph (**9**)	67
2	$Ru_3(CO)_{12}$	R = Ph, R′ = Me	R = Ph, R′ = Me (**10**)	38
3	$Ru_3(CO)_{12}$	R = R′ = Et	R = R′ = Et (**11**)	43
4	$Ru_3(CO)_{12}$	R = R′ = CO_2Me	N/A[c]	N/A
5	$Ru_3(CO)_{12}$	R = Ph, R′ = H	N/A[d]	N/A
6	**1**	R = R′ = Ph	R = R′ = Ph (**9**)	20

[a] Reaction conditions: 3-(2-pyridyl)indene (1 mmol), acetylene (5 mmol), catalyst (0.02 mmol), toluene 5 mL, under reflux for 20 h. [b] Isolated yield. [c] The main product is hexacarbomethoxybenzene, determined by GC-mass. [d] Unidentified product.

(2%) as catalyst (Table 1), but the reaction with phenylacetylene did not work under the same conditions (entry 5). Complexes **9**−**11** only exist as *E* isomers, according to their ^{1}H NMR spectra. For entry 2, the formation of two regioisomers is possible, but the C−C bond formation took place in a regiospecific manner. When dimethyl acetylenedicarboxylate was used, only hexacarbomethoxybenzene was formed via trimerization (entry 4). When **1** was used instead of $Ru_3(CO)_{12}$, the reaction could also proceed, but with low yield (entry 6).

Why did phenylacetylene fail to couple with 3-(2-pyridyl)indene in presence of $Ru_3(CO)_{12}$? For the rhodium catalyst system the failure in C−H/alkyne coupling of terminal alkynes was attributed to the oligomerization of terminal alkynes.[5] In our system, according to the reaction results of phenylacetylene with complex **1**, we suppose that two molecules of phenylacetylene could insert into the Ru−C bond of the intermediate **12** to form **13**, followed by oxidative addition of the C−H bond of the PhC=CH fragment and elimination of a hydrogen to form **14** (Scheme 6). The formation of this kind of compound may kill the catalyst.

In conclusion, reactions of the trinuclear ruthenium carbonyl complex $\{\mu_2\text{-}\eta^5{:}\eta^1\text{-}(C_5H_4N)(C_9H_5)\}Ru_3(CO)_9$ (**1**) with diphenylacetylene and phenylacetylene were studied. For phenylacetylene, after the insertion of two molecules of phenylacetylene into the Ru−C bond, the oxidative addition of a C−H bond to the Ru atom can further occur to form a five-membered ring. This difference may be parts of the reason the reactivities of terminal and internal alkynes were quite different in the $Ru_3(CO)_{12}$-catalyzed C−H/alkyne coupling reactions.

Experimental Section

General Considerations. Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. All solvents were distilled from appropriate drying agents under argon before use. ^{1}H NMR spectra were recorded on Bruker AV300 and VARIAN AS-400 spectrometers, while IR spectra were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. $[\mu_2\text{-}\eta^5{:}\eta^1\text{-}(C_5H_4N)(C_9H_5)]Ru_3(CO)_9$ (**1**) was synthesized according to the literature procedure.[8]

Reaction of 1 with Diphenylacetylene. Method A. A solution of 0.20 g (0.27 mmol) of **1** and 0.048 g (0.27 mmol) of diphenylacetylene in 30 mL of toluene was refluxed for 20 h. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed a yellow band, which gave 0.15 g (64%) of **2** as orange crystals. Mp: 145 °C dec. Anal. Calcd for $C_{35}H_{19}NO_7Ru_3$: C, 48.39; H, 2.20; N, 1.61. Found: C, 48.60; H, 2.55; N, 1.66. ^{1}H NMR ($CDCl_3$): δ 8.52 (d, J = 5.2 Hz, 1H, Py H), 7.62 (t, J = 7.4 Hz, 1H, Py H), 7.55−7.48 (m, 2H, Py H), 7.43−7.31 (m, 3H, Ar H), 7.22−6.70 (m, 11H, Ar H), 5.01 (s, 1H, Cp H). IR (ν_{CO}, cm^{-1}): 2053 (s), 2006 (m), 1988 (s), 1981 (s), 1953 (m), 1942 (m), 1913 (m).

Method B. Using a procedure similar to that described above, reaction of **1** (0.20 g, 0.27 mmol) with diphenylacetylene (0.24 g, 1.3 mmol) in 30 mL of toluene under reflux for 20 h gave 0.13 g (48%) of **3** as orange crystals, 0.013 g (5%) of **4** as dark crystals, and 0.025 g (8%) of **5** as red crystals. The following are data for **3**. Mp: 190 °C dec. Anal. Calcd for $C_{58}H_{39}NO_2Ru_2$: C, 70.79; H, 3.99; N, 1.42. Found: C, 70.48; H, 3.60; N, 1.52. ^{1}H NMR($CDCl_3$): δ 8.89 (d, J = 5.5 Hz, 1H, Py H), 7.68−7.61 (m, 3H, Py H), 7.56 (d, J = 8.6 Hz, 1H, Ar H), 7.36 (d, J = 7.5 Hz, 1H, Ar H), 7.29 (t, J = 7.2 Hz, 2H, Ar H), 7.09−6.65 (m, 25H, Ar H), 6.50−6.45 (m, 2H, Ar H), 6.22 (d, J = 8.6 Hz, 1H, Ar H),

Scheme 6

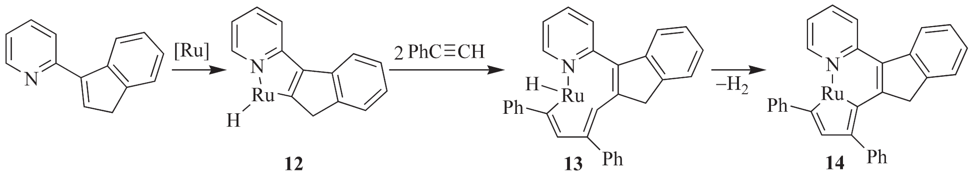


Table 2. Crystal Data and Summary of X-ray Data Collection

	2·$0.5CH_2Cl_2$	**3**·CH_2Cl_2	**4**·CH_2Cl_2·$0.75H_2O$	**5**·CH_2Cl_2	**6**	**7**	**8**
formula	$C_{35.50}H_{20}$-$ClNO_7Ru_3$	$C_{59}H_{41}Cl_2$-NO_2Ru_2	$C_{49}H_{32.5}Cl_2$-$NO_{6.75}Ru_3$	$C_{61}H_{41}Cl_2$-NO_4Ru_3	$C_{29}H_{15}$-NO_7Ru_3	$C_{36}H_{21}$-NO_6Ru_3	$C_{35}H_{21}$-NO_5Ru_2
fw	911.19	1068.97	1117.37	1226.06	792.63	866.75	737.67
T, K	113(2)	113(2)	294(2)	294(2)	113(2)	294(2)	294(2)
λ, Å	0.71070	0.71070	0.71073	0.71073	0.71070	0.71073	0.71073
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P\overline{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	11.884(2)	11.7745(17)	16.572(14)	20.532(5)	9.7376(15)	10.0956(11)	10.591(3)
b, Å	17.465(3)	12.896(2)	10.185(9)	13.568(3)	15.292(2)	15.8247(18)	17.577(5)
c, Å	30.543(6)	15.508(2)	27.55(2)	18.234(4)	17.301(3)	19.840(2)	16.021(4)
α, deg	90	100.362(3)	90	90	90	90	90
β, deg	90	91.551(3)	98.248(15)	102.230(4)	91.758(2)	92.212(2)	97.542(5)
γ, deg	90	90.523(3)	90	90	90	90	90
V, $Å^3$	6339(2)	2315.3(6)	4602(7)	4964(2)	2574.9(7)	3167.3(6)	2956.8(14)
Z	8	2	4	4	4	4	4
D_{calcd}, g cm^{-3}	1.909	1.533	1.613	1.640	2.045	1.818	1.657
μ, mm^{-1}	1.548	0.814	1.138	1.060	1.788	1.460	1.066
F(000)	3560	1080	2214	2448	1536	1696	1464
cryst size, mm	0.20 × 0.20 × 0.20	0.16 × 0.14 × 0.10	0.24 × 0.20 × 0.16	0.18 × 0.16 × 0.12	0.20 × 0.18 × 0.14	0.20 × 0.18 × 0.12	0.28 × 0.14 × 0.14
θ range, deg	2.17−27.89	1.73−27.86	1.24−25.02	1.01−26.43	2.09−27.87	1.65−26.44	1.73−25.02
no. of rflns collected	55 570	29 194	23 119	27 950	31 814	17 802	12 588
no. of indep rflns/R_{int}	7563/0.0652	10 951/0.0308	8108/0.0423	10 145/0.0769	6143/0.0427	6487/0.0306	5165/0.0657
no. of params	470	614	622	650	362	419	388
goodness of fit on F^2	1.204	1.034	1.154	0.988	1.038	1.049	1.024
R1, wR2 ($I > 2\sigma(I)$)	0.0466/0.0852	0.0350/0.0795	0.0506/0.1200	0.0469/0.0949	0.0244, 0.0536	0.0297, 0.0685	0.0402, 0.0717
R1, wR2 (all data)	0.0507/0.0868	0.0405/0.0829	0.0767/0.1338	0.1172/0.1221	0.0304, 0.0562	0.0481, 0.0782	0.0845, 0.0847
largest diff peak, hole (e $Å^{-3}$)	0.763, −0.725	0.608, −0.750	0.986, −1.270	0.723, −0.676	0.429, −0.682	1.057, −0.699	0.689, −0.742

6.05 (d, *J* = 7.0 Hz, 2H, Ar H), 5.13 (s, 1H, Cp H). IR (ν_{CO}, cm^{-1}): 1965 (s), 1922 (s). The following are data for **4**. Mp: 130−131 °C. Anal. Calcd for $C_{48}H_{29}NO_6Ru_3$: C, 56.58; H, 2.87; N, 1.37. Found: C, 56.20; H, 3.01; N, 1.21. ^1H NMR ($CDCl_3$): δ 8.24 (d, *J* = 8.6 Hz, 1H, Py H), 7.92 (d, *J* = 5.4 Hz, 1H, Ar H), 7.75−7.64 (m, 3H, Py H), 7.54 (d, *J* = 8.0 Hz, 1H, Ar H), 7.46−6.68 (m, 22H, Ar H), 5.27 (s, 1H, Cp H). IR (ν_{CO}, cm^{-1}): 2028 (s), 1995 (s), 1969 (s), 1925 (m), 1919 (m), 1911 (m). The following are data for **5**. Mp: 130−131 °C. Anal. Calcd for $C_{60}H_{39}NO_4Ru_3$: C, 63.15; H, 3.44; N, 1.23. Found: C, 63.00; H, 3.80; N, 1.28. ^1H NMR ($CDCl_3$): δ 8.03 (d, *J* = 8.6 Hz, 1H, Py H) (7.71 (m, 2H), 7.58 (m, 2H), 7.50−6.53 (m, 29H)) (Py H and Ar H), 6.19 (d, *J* = 7.4 Hz, 2H, Ar H), 5.68 (s, 1H, Cp H), 5.41 (d, *J* = 7.4 Hz, 2H, Ar H). IR (ν_{CO}, cm^{-1}): 2005 (s), 1976 (s), 1933 (s).

Reaction of 2 with Diphenylacetylene. Using a procedure similar to that described above, reaction of **2** (0.10 g, 0.12 mmol) with diphenylacetylene (0.082 g, 0.46 mmol) in 30 mL of refluxing toluene for 20 h gave **3** (0.075 g, 66%), **4** (0.008 g, 7%), and **5** (0.016 g, 12%).

Reaction of 1 with Phenylacetylene. Method A. Using a procedure similar to that described above, reaction of **1** (0.20 g, 0.27 mmol) with phenylacetylene (0.027 g, 0.27 mmol) in 30 mL of refluxing toluene for 20 h gave **6** (0.050 g, 24%) as orange crystals, in addition to unreacted **1** (0.050 g, 25%). Mp: 175 °C dec. Anal. Calcd for $C_{29}H_{15}NO_7Ru_3$: C, 43.94; H, 1.91; N, 1.77. Found: C, 43.94; H, 2.31; N, 1.82. ^1H NMR ($CDCl_3$): δ 8.72 (d, *J* = 5.4 Hz, 1H, Py H), 7.89 (t, *J* = 7.8 Hz, 1H, Py H), 7.59 (d, *J* = 7.8 Hz, 1H, Py H), 7.53 (m, 1H, Py H), 7.42−7.14 (m, 11H, Ar H), 6.73 (s, 1H, =CH), 4.89 (s, 1H, Cp H). IR (ν_{CO}, cm^{-1}): 2053 (s), 2002 (s), 1992 (s), 1970 (s), 1947 (m), 1916 (s).

Method B. Using a procedure similar to that described above, reaction of **1** (0.20 g, 0.27 mmol) with phenylacetylene (0.14 g, 1.4 mmol) in 30 mL of refluxing toluene for 20 h gave **7** (0.090 g, 39%) and **8** (0.030 g, 15%), both as orange crystals. The following are data for **7**. Mp: 150 °C dec. Anal. Calcd for $C_{36}H_{21}NO_6Ru_3$: C, 49.88; H, 2.44; N, 1.62. Found: C, 49.53; H, 2.80; N, 1.63. ^1H NMR ($CDCl_3$): δ 9.16 (d, *J* = 5.3 Hz, 1H, Py H) (8.00 (d, *J* = 7.8 Hz, 1H), 7.93−7.75 (m, 4H), 7.46 (m, 3H), 7.35−7.11 (m, 8H)) (Py H and Ar H), 7.06 (d, *J* = 7.7 Hz, 1H, Ar H), 7.01 (s, 1H, PhC=CH), 4.08 (s, 1H, Cp H), −13.11 (s, 1H, Ru−H). IR (ν_{CO}, cm^{-1}): 2025 (s), 2004 (s), 1973 (s), 1954 (s), 1926 (s). The following are data for **8**. Mp: 180 °C dec. Anal. Calcd for $C_{35}H_{21}NO_5Ru_2$: C, 56.99; H, 2.87; N, 1.90. Found: C, 56.65; H, 3.01; N, 1.98. ^1H NMR ($CDCl_3$): δ 9.54 (d, *J* = 5.6 Hz, 1H, Py H), 7.94 (d, *J* = 7.7 Hz, 1H, Py H), 7.87 (t, *J* = 6.9 Hz, 2H, Py H), 7.60−7.01 (m, 14H, Ar H), 6.54 (s, 1H, PhC=CH), 3.29 (dd, *J* = 23.4, 9.7 Hz, 2H, Cp H). IR (ν_{CO}, cm^{-1}): 2031 (s), 2000 (s), 1969 (s), 1945 (s), 1882 (s).

Reaction of 6 with Phenylacetylene. Using a procedure similar to that described above, reaction of **6** (0.050 g, 0.063 mmol) with phenylacetylene (0.026 g, 0.25 mmol) in 30 mL of refluxing toluene for 20 h gave **7** (0.020 g, 37%) and **8** (0.010 g, 22%).

Thermal Reaction of 7. Using a procedure similar to that described above, thermal treatment of **7** (0.050 g, 0.058 mmol) in 30 mL of refluxing toluene for 20 h gave **8** (0.005 g, 12%), in addition to unreacted **7** (0.030 g, 60%).

Catalytic Reaction of 3-(2-Pyridyl)indene with Alkynes. A solution of 1.0 mmol of 3-(2-pyridyl)indene, 5.0 mmol of an alkyne, and 0.013 g (0.02 mmol) of $Ru_3(CO)_{12}$ in 5 mL of toluene was refluxed for 20 h. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed the product.

Complex **9**: pale yellow solid, yield 0.25 g (67%). Mp: 53−54 °C. Anal. Calcd for $C_{28}H_{21}N$: C, 90.53; H, 5.70; N, 3.77. Found: C, 90.23; H, 6.08; N, 3.50. ^{1}H NMR ($CDCl_3$): δ 8.53 (d, J = 4.8 Hz, 1H, Py H), 7.85 (t, J = 7.6 Hz, 1H, Py H), 7.50−7.00 (m, 16H, Py H and Ar H), 6.97 (s, 1H, =CH), 3.69 (s, 2H, Cp H). ^{13}C NMR ($CDCl_3$): δ 149.2, 143.4, 141.8, 137.9, 137.5, 135.9, 130.3, 128.8, 128.6, 127.8, 127.4, 127.1, 126.8, 125.4, 123.9, 123.8, 122.3, 121.9, 41.9. MS (ESI): m/z 371 ([M^+]).

Complex **10**: pale yellow solid, yield 0.116 g (38%). Mp 48−50 °C. Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.43; H, 6.21; N, 4.54. ^{1}H NMR($CDCl_3$): δ 8.76 (d, J = 4.4 Hz, 1H, Py H), 7.88 (d, J = 7.6 Hz, 1H, Py H), 7.74 (d, J = 8.7 Hz, 1H, Py H), 7.65−7.16 (m, 10H, Py H and Ar H), 6.05 (m, 1H, =C−H), 3.58 (s, 2H, Cp H), 1.44 (d, J = 7.0 Hz, 3H, Me-H). ^{13}C NMR ($CDCl_3$): δ 143.1, 141.3, 137.2, 136.3, 129.4, 128.5, 127.6, 127.1, 126.6, 126.5, 125.8, 125.0, 123.6, 123.4, 121.8, 121.7, 120.0, 118.2, 42.0, 15.6. MS (ESI) m/z: 310([M^+]).

Complex **11**: pale yellow oil, yield 0.118 g (43%). Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.52; H, 7.61; N, 5.13. ^{1}H NMR ($CDCl_3$): δ 8.75 (d, J = 4.4 Hz, 1H, Py H), 7.75 (d, J = 7.6 Hz, 1H, Py H), 7.66 (t, J = 7.6 Hz, 1H, Py H), 7.46 (d, J = 7.6 Hz, 2H, Ar H), 7.30 (t, J = 7.6 Hz, 1H, Py H), 7.20 (t, J = 7.2 Hz, 2H, Ar H), 5.30 (t, J = 7.3 Hz, 1H, =CH), 3.60 (s, 2H, Cp H), 2.26 (m, 2H, Et H) = 1.71 (m, 2H, Et H), 1.05 (t, J = 7.5 Hz, 3H, Et H), 0.65 (t, J = 7.5 Hz, 3H, Et H). ^{13}C NMR ($CDCl_3$): δ 149.2, 144.7, 142.6, 136.5, 129.8, 126.4, 124.6, 124.0, 123.3, 121.6, 121.3, 42.3, 30.8, 22.6, 13.8, 13.2. MS (ESI): m/z 276([M^+]).

Catalytic Reaction of 3-(2-Pyridyl)indene with Phenylacetylene. Using a procedure similar to that described above, on thermal treatment of 0.19 g (1.0 mmol) of 3-(2-pyridyl)indene, 0.51 g (5.0 mmol) of phenylacetylene, and 0.013 g (0.02 mmol) of $Ru_3(CO)_{12}$ in 5 mL of refluxing toluene for 24 h, only unreacted 3-(2-pyridyl)indene (0.15 g, 78%) was recovered.

Crystallographic Studies. Single crystals of complexes **2**−**8** suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2 solution. Data collection was performed on a Bruker Smart 1000 (for **4**, **5**, **7**, and **8**) or a Rigaku MM-OO7/Saturn 70 (for **2**, **3**, and **6**) diffractometer, using graphite-monochromated Mo Kα radiation ($\omega-2\theta$ scans). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were carried out with the SHELXL-97 program system. The crystal data and summary of X-ray data collection are given in Table 2.

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Supporting Information Available: CIF files giving crystallographic details for **2**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.