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Isolation and characterization of $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(Ph)CHC(Ph)CHCH_2\}]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$). Reinvestigation of the carbon–carbon bond formation between $\mu\text{-}CH_2$ group and alkynes in $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}$

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Abstract

On reinvestigation of the reaction of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}$ (**1**) with alkynes we have found a much cleaner reaction system than the previous ones which has allowed us to elucidate the reaction mechanism of the intriguing carbon–carbon bond formation of the $\mu\text{-}CH_2$ groups and alkynes and to isolate the pure reaction product of $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(Ph)CHC(Ph)CHCH_2\}]^+$ (**2**). The structure of **2** as the BPh_4^- salt has been determined by an X-ray diffraction study. Similar dirhodium complexes $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(COOMe)CHC(COOMe)CHCH_2\}]^+$ (**3**) and $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(COOMe)CHC(Ph)CHCH_2\}]^+$ (**4**) have been prepared and characterized spectroscopically.

Keywords: Rhodium; μ-Methylene ligand; Alkyne; Insertion reaction; Carbon–carbon bond formation

1. Introduction

The $\mu\text{-}CH_2$ groups in dinuclear rhodium complexes show high reactivity toward sp^2 and sp carbon [1–4]. Ten years ago one of the authors (P.M. M.) studied the reactivity of the $\mu\text{-}CH_2$ groups in the PF_6^- salt of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}$ (**1**) toward monosubstituted alkynes [5]. The alkynes usually gave impure red oily products, but only *p*-chlorophenylacetylene produced a homogeneous solid. From an extensive NMR investigation, it was proposed that carbon–carbon bond formation takes place at three positions of the carbon chain to form a dinuclear structure with a seven-membered metallacycle comprising six carbon atoms and a rhodium of which five carbon atoms are conjugated and coordinated to the other rhodium atom.

In the course of our study on applications of the μ-methylene-bis(pentamethylcyclopentadienylrhodium) complexes [6,7] to organic synthesis or for catalytic oligomerization of unsaturated hydrocarbons [8], we have found a cleaner reaction system than the previous one to investigate the mechanisms of alkyne coupling reactions and allowed us to isolate and characterize a pure reaction product. We report the isolation and the X-ray structure of the coupling product $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(Ph)CHC(Ph)CHCH_2\}]^+$ (**2**) from the reaction system using the BF_4^- or the OTf^- salt of **1**, phenylacetylene, and CH_2Cl_2 as a solvent. We also offer some mechanistic insight on the basis of labeling experiment and NMR monitoring of the reaction.

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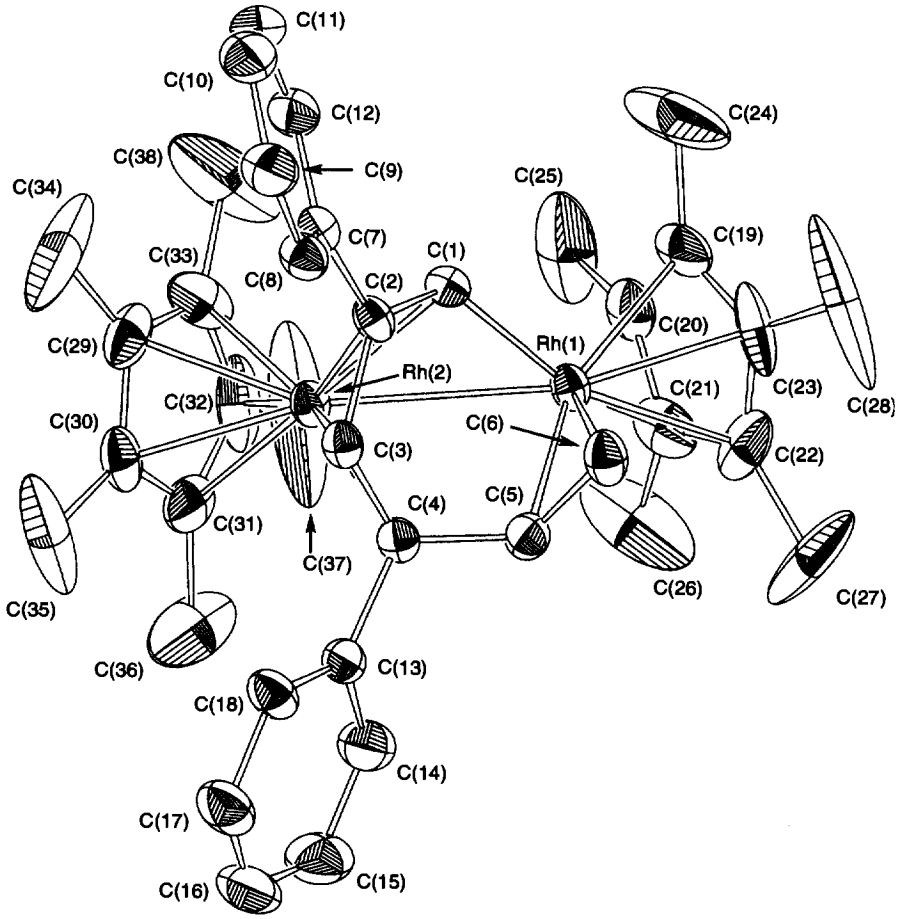
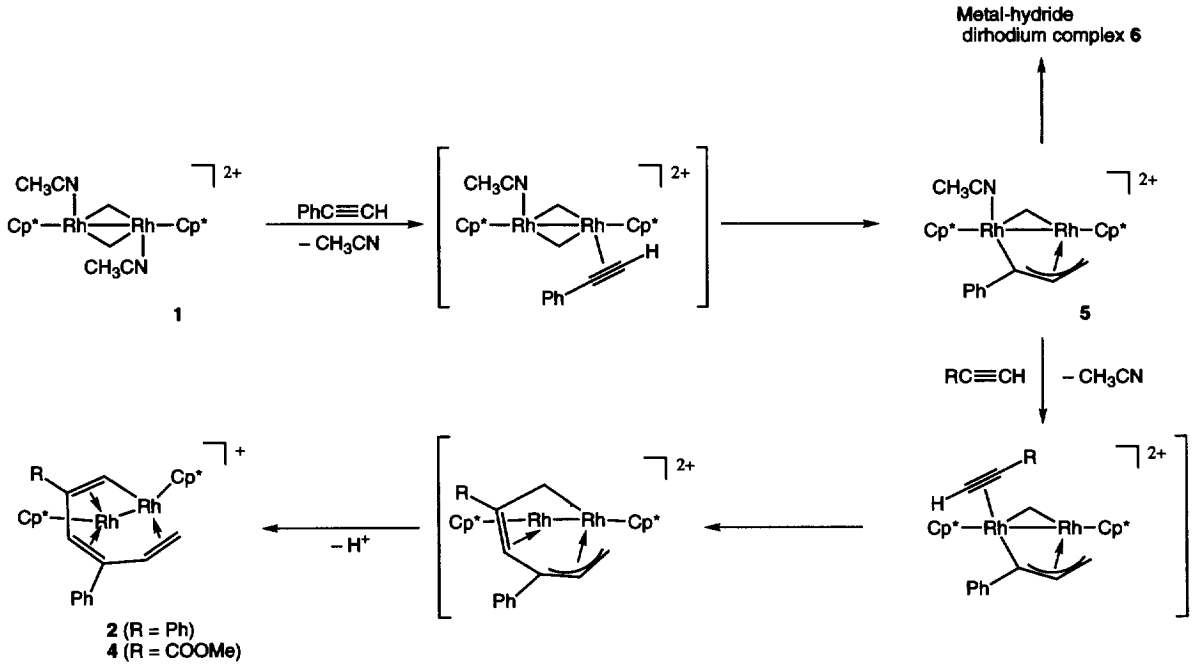


Fig. 1. ORTEP drawing for the cationic part of $2 \cdot BPh_4$. The thermal ellipsoids are drawn at the 30% probability level.

2. Results and discussion

When $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]X_2$ [X = OTf (Tf = trifluoromethanesulfonyl) or BF_4] (**1**) [9] was treated with excess phenylacetylene in CH_2Cl_2 at ambient temperature, the red crystalline product **2** was obtained quantitatively. The ^1H and ^{13}C-NMR spectral patterns of **2** are almost similar to those of *p*-chlorophenylacetylene complex. The assignment, which was established by 2D-NMR measurements, is consistent with that in the previous report [5]. A single crystal X-ray diffraction study was performed of $2 \cdot BPh_4$ obtained from anion exchange of the OTf^- salt. The confirmed structure of $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(Ph)CHC(Ph)CHCH_2\}]^+$ is shown in Fig. 1. The X-ray analysis reveals the presence of a six-membered carbon ligand in complex **2**. The four carbons, C(1) to C(4), in the C_6 chain form a conjugated butadiene unit which is π-bonded to Rh(2) with the Rh–C distances from 2.130(4) to 2.288(4) Å and only the C(1) atom is bound to Rh(1) in a σ-fashion with the shortest Rh–C bond distance of 1.985(5) Å [10]. Both C(5) and C(6) are π-coordinated to Rh(1) with the Rh–C distances of 2.141(4) and 2.140(4) Å, respectively. The Rh(1)–Rh(2) distance of 2.9108(5) Å is much longer than those observed commonly in the di-μ-methylenedirhodium complexes [7].

The arrangement of the ligand carbons in complex **2** is consistent with that found by the extensive ^1H-NMR measurements [5]. Since the newly formed organic ligand is made up of an aliphatic C_6 chain with two phenyl moieties, the ligand is essentially formed by carbon–carbon bond formation of two phenylacetylene molecules and two μ-CH_2 groups on the dirhodium complex. One proton elimination from the μ-CH_2 or the terminal alkyne is required to produce complex **2**. To discover the origin of the eliminated proton and the position of the incorporated alkynes in the C_6 chain, we carried out the reaction of complex **1** with deuterated phenylacetylene (PhC≡CD). The obtained product includes two deuterium atoms and the arrangement of the C_6 chain is $CHC(Ph)CDC(Ph)CDCH_2$. From this it can be concluded that both terminal carbons of the C_6 chain come from each μ-CH_2 moiety of the starting complex and that one proton was been eliminated from one of the μ-CH_2 moieties. Such the proton elimination from μ-CH_2 moieties is sometimes observed during carbon–carbon bond formations [11]. A perfectly regio-



Scheme 1.

controlled head-to-tail dimerization of phenylacetylene is accompanied by incorporation of the alkynes into two μ-CH_2 ligands of the dirhodium complex.

A similar dirhodium complex $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(COOMe)CH\ C(COOMe)CHCH_2\}]^+$ (**3**) was prepared from complex **1** and excess acetylenecarboxylic acid methyl ester in 40% yield and characterized spectroscopically. Treatment of complex **1** with one equivalent of phenylacetylene followed by the addition of excess acetylenecarboxylic acid methyl ester at -20°C gave $[(RhCp^*)_2\{\eta^1{:}\eta^4{:}\eta^2\text{-}\mu\text{-}CHC(COOMe)CHC(Ph)\ CHCH_2\}]^+$ (**4**) as a mojor product in 35% yield together with **2** and **3** as minor products. The structure of **4** was assumed on the basis of NMR spectra. The positions of the substituent Ph and COOMe groups in the C_6 ligand were assigned by a study of long range C–H couplings. The formation of **4** allows us to predict the order of the alkyne insertion to complex **1**: the CH_2CHCPh– frame is constructed in the first stage and then the –CHC(COOMe)CH– frame is formed to give the whole C_6 chain.

To elucidate the intermediate species in the reaction system at low temperature, a sample of the 1:1 molar ratio of complex **1** and phenylacetylene in CD_2Cl_2 was monitored by ^{1}H-NMR spectroscopy. At -20°C, the reaction proceeded slowly and all of the alkyne was consumed within 30 min. At this time, two dirhodium complexes were formed in a ratio of 3:2 and the minor product of them is complex **2**. The major product, **5**, has a composition of 1:1 ratio of the dirhodium unit and phenylacetylene. The protons of one μ-CH_2 group, which remains intact on the rhodium, resonate at δ 10.58 and 11.44 separately. Appearance of three proton signals at δ 1.79, 3.54 and 5.49 which are coupled with each other suggests formation of a CH_2CH– ligand unit derived from the other μ-CH_2 group. On the basis of the NMR spectra we assumed that the structure of **5** is $[(RhCp^*)_2(\mu\text{-}CH_2)(\eta^1{:}\eta^2\text{-}\mu\text{-}C(Ph)CH\ CH_2)(CH_3CN)]^{2+}$ as shown in Scheme 1. A carbon–carbon bond formation from one μ-CH_2 with phenylacetylene forms the $\eta^1{:}\eta^2$-allyl ligand on the dirhodium. Complex **5** having the $\eta^1{:}\eta^2$-allyl ligand may reasonably lead to the formation of **4** through the further reaction with acetylenecarboxylic acid methyl ester. Complex **5** is also certainly an intermediate for complex **2**.

Upon warming the solution containing the intermediate species **5** to ambient temperature, complex **5** is transformed into a metal–hydride complex **6** having a signal at δ -8.67 with an intensity corresponding to one proton. The metal–hydride complex **6** in situ does not react with the alkynes unlike complex **5**. Unfortunately, we could not isolate complex **6** due to the instability of the complex which decomposed within few hours in the solution at ambient temperature.

The reaction of complex **1** with disubstituted alkynes, such as diphenylacetylene and acetylenedicarboxylic acid dimethyl ester, did not give the expected product, but complicated mixture. Only a slow formation of a metal–hydride complex analogous to **6** was observed in ^{1}H-NMR spectrum. This metal–hydride complex was also too unstable to isolate. The alkyne insertion reaction into **1** takes place only for the monosubstituted alkynes not for the disubstituted ones. The results from

the labeling experiment which shows no H–D scrambling [12] of deuterated **2** and the low temperature experiment which shows the formation of the η^1:η^2-allyl complex **5** exclude a possibility of an intermediate acetylide formation for the terminal alkyne via an acetylenic C–H bond cleavage. The reaction occurs through the alkyne insertion into the $Rh-CH_2$ bonds and it seems that bulky Cp* ligands prevent the insertion of the disubstituted alkyne into these bonds.

From above results we propose the reaction mechanism as shown in Scheme 1: the species in the brackets are not detected, just only presumed. The reaction starts off by the replacement of the labile acetonitrile ligand with phenylacetylene which is then incorporated into the $Rh-CH_2$ bond to form the η^1:η^2-allyl ligand in complex **5**. After the replacement of the remaining acetonitrile ligand with another alkyne, insertion of the

Table 1
Crystallographic data for $2 \cdot BPh_4$

Crystal data	
Chemical formula	$C_{62}H_{65}BRh_2$
Formula weight	1026.82
Color of crystal	Red
Size of specimen (mm)	$0.30 \times 0.28 \times 0.24$
Crystal system	Triclinic
Space group (number)	$P\bar{1}$ (No. 2)
Lattice constants	
a (Å)	15.698(1)
b (Å)	15.739(7)
c (Å)	11.776(1)
α (°)	104.829(8)
β (°)	109.322(7)
γ (°)	98.508(8)
V (Å^3)	2566.5(5)
Z	2
$D_{calc.}$ (g cm^{-3})	1.329
μ(Mo–K$_\alpha$) (cm^{-1})	6.80
F(000)	1064
Data collection	
Radiation (wave length, λ) (Å)	Mo–K$_\alpha$ (0.71073)
Monochromator	Graphite
Scan method	$\omega-2\theta$
Range of h, k, l	$-20 \le h \le 20$, $-20 \le k \le 0$, $-14 \le l \le 15$
No. of independent reflections	11 774
Data reduction	
Absorption corrections	Empirical Ψ-scan method
Transmission coefficients, A	0.924–1.000
Structure analysis	
Method used in structure solution	Heavy-atom method
No. of parameters refined	585
Cut-off criteria	$\|F_o\| > 3\sigma(\|F_o\|)$
No. independent reflection used for calculation	7420
R	0.042
R_w	0.056
S	1.23
$\Delta\rho$ (e Å^{-3})	1.06, −0.55

Table 2
Atom coordinates for $2 \cdot BPh_4$

Atom	x/a	y/b	z/c
Rh(1)	0.58012(2)	0.80045(2)	0.45506(3)
Rh(2)	0.78038(2)	0.81868(2)	0.55981(3)
C(1)	0.6861(3)	0.9043(3)	0.5795(4)
C(2)	0.7576(3)	0.9536(3)	0.5542(4)
C(3)	0.7831(3)	0.9081(3)	0.4518(4)
C(4)	0.7308(3)	0.8242(3)	0.3566(4)
C(5)	0.6286(3)	0.8028(4)	0.3057(4)
C(6)	0.5784(3)	0.8705(4)	0.3210(5)
C(7)	0.8123(3)	1.0465(3)	0.6380(4)
C(8)	0.8422(3)	1.1074(3)	0.5828(5)
C(9)	0.8805(4)	1.1992(4)	0.6522(6)
C(10)	0.8925(4)	1.2299(4)	0.7766(6)
C(11)	0.8672(4)	1.1718(4)	0.8349(5)
C(12)	0.8267(4)	1.0804(4)	0.7676(5)
C(13)	0.7725(3)	0.7754(3)	0.2700(4)
C(14)	0.7413(4)	0.6836(4)	0.2101(5)
C(15)	0.7778(6)	0.6388(5)	0.1263(7)
C(16)	0.8470(6)	0.6890(6)	0.1028(7)
C(17)	0.8780(5)	0.7800(5)	0.1611(6)
C(18)	0.8415(4)	0.8244(4)	0.2439(5)
C(19)	0.4813(4)	0.8035(4)	0.5542(7)
C(20)	0.5077(4)	0.7257(5)	0.5522(6)
C(21)	0.4814(5)	0.6708(4)	0.4288(7)
C(22)	0.4352(4)	0.7156(7)	0.3481(6)
C(23)	0.4370(4)	0.8015(6)	0.430(1)
C(24)	0.4920(8)	0.8798(8)	0.672(1)
C(25)	0.5434(6)	0.699(1)	0.671(1)
C(26)	0.4878(9)	0.5741(6)	0.384(1)
C(27)	0.3885(8)	0.674(1)	0.2051(8)
C(28)	0.3860(7)	0.867(1)	0.383(2)
C(29)	0.9154(4)	0.8463(4)	0.7163(6)
C(30)	0.9192(4)	0.7905(5)	0.6085(6)
C(31)	0.8535(5)	0.7083(4)	0.5658(6)
C(32)	0.8076(4)	0.7139(6)	0.6513(9)
C(33)	0.8458(6)	0.8006(7)	0.7428(6)
C(34)	0.9805(8)	0.9378(7)	0.799(1)
C(35)	0.9882(6)	0.8119(10)	0.549(1)
C(36)	0.8450(9)	0.6283(8)	0.459(1)
C(37)	0.7439(6)	0.632(1)	0.651(2)
C(38)	0.821(1)	0.828(1)	0.858(1)
C(39)*	0.2564(3)	0.8178(3)	0.8273(4)
C(40)*	0.2709(5)	0.8678(4)	0.9517(5)
C(41)*	0.2861(6)	0.9620(4)	0.9942(6)
C(42)*	0.2875(5)	1.0101(4)	0.9122(7)
C(43)*	0.2742(5)	0.9647(4)	0.7915(6)
C(44)*	0.2584(4)	0.8705(4)	0.7484(5)
C(45)*	0.2047(3)	0.6608(3)	0.6289(4)
C(46)*	0.2657(3)	0.6709(4)	0.5664(5)
C(47)*	0.2382(4)	0.6323(4)	0.4354(5)
C(48)*	0.1496(4)	0.5830(3)	0.3624(5)
C(49)*	0.0857(3)	0.5715(3)	0.4185(5)
C(50)*	0.1146(3)	0.6096(3)	0.5497(4)
C(51)*	0.1657(3)	0.6662(3)	0.8388(4)
C(52)*	0.0813(3)	0.6893(3)	0.8138(4)
C(53)*	0.0134(3)	0.6543(4)	0.8529(5)
C(54)*	0.0286(4)	0.5965(3)	0.9217(5)
C(55)*	0.1121(4)	0.5741(4)	0.9515(5)
C(56)*	0.1795(3)	0.6081(3)	0.9108(5)
C(57)*	0.3432(3)	0.6838(4)	0.8457(4)
C(58)*	0.3487(4)	0.5929(4)	0.8161(5)
C(59)*	0.4318(5)	0.5686(5)	0.8628(7)
C(60)*	0.5127(5)	0.6331(7)	0.9399(7)
C(61)*	0.5108(4)	0.7219(6)	0.9684(5)
C(62)*	0.4283(4)	0.7476(4)	0.9253(5)
B	0.2421(3)	0.7070(4)	0.7845(5)

* Carbons of BPh_4 part

second alkyne molecule and the subsequent proton elimination from one of the CH_2 moieties in the C_6 ligand take place to give **2** or **4**. It is important that the dirhodium complex **2** or **4** maintains a saturated 34-electron state ([4]e). Intermediate unsaturated complexes resulted from the second carbon–carbon bond formation should be readily transformed into the electronically saturated complexes **2** and **4** by the proton elimination. The driving force of the intriguing proton elimination can be attributed to the formation of the thermodynamically stable dirhodium complex [11]. In the absence of the alkyne, complex **5** is transformed into the metal–hydride complex **6** at ambient temperature. This transformation must be slower than the second insertion of alkynes producing **2** or **4**.

We have elucidated the reaction of the μ-CH_2 ligands in complex **1** with the monosubstituted alkynes in this paper. The reactions are controlled by the elimination of acetonitrile, the coordination of the alkyne and the stability of the resulting products. To form the electronically saturated complexes the proton elimination from the μ-CH_2 takes place. The results of the carbon–carbon bond formation of the μ-CH_2 ligand with the unsaturated organic compounds should be an important indication of how to construct new organometallic compounds using this system.

3. Experimental details

Phenylacetylene and acetylenecarboxylic acid methyl ester were obtained from Tokyo Kasei Kogyo and they were degassed with Ar before using. Solvents were dried over P_2O_5 (dichloromethane) or Mg (methanol) and distilled immediately prior to use. $[(RhCp^*)_2(\mu\text{-}CH_2)_2(CH_3CN)_2]^{2+}$ (**1**) was prepared according to the literature procedure [9]. All reactions of complex **1** and alkynes were carried out under Ar atmosphere. Column chromatography was performed by using 70–230 mesh silica-gel.

Table 3
Selected bond distances (Å) and bond angles (°) for **2**·BPh_4

Bond distances			
Rh(1)–Rh(2)	2.9108(5)	Rh(1)–C(1)	1.985(5)
Rh(1)–C(5)	2.141(4)	Rh(1)–C(6)	2.140(4)
Rh(2)–C(1)	2.171(4)	Rh(2)–C(2)	2.218(4)
Rh(2)–C(3)	2.130(4)	Rh(2)–C(4)	2.288(4)
C(1)–C(2)	1.425(6)	C(2)–C(3)	1.445(6)
C(3)–C(4)	1.410(6)	C(4)–C(5)	1.465(6)
C(5)–C(6)	1.425(7)		
Bond angles			
Rh(2)–Rh(1)–C(1)	48.2(1)	Rh(2)–Rh(1)–C(5)	73.0(1)
Rh(2)–Rh(1)–C(6)	97.4(1)	Rh(1)–Rh(2)–C(1)	43.0(1)
Rh(1)–Rh(2)–C(2)	71.8(1)	Rh(1)–Rh(2)–C(3)	83.2(1)
Rh(1)–Rh(2)–C(4)	68.6(1)	Rh(1)–C(1)–Rh(2)	88.8(2)
Rh(1)–C(1)–C(2)	126.7(3)	Rh(2)–C(1)–C(2)	72.8(2)
Rh(2)–C(2)–C(1)	69.3(2)	Rh(2)–C(2)–C(3)	67.3(2)
C(1)–C(2)–C(3)	119.0(4)	Rh(2)–C(3)–C(2)	73.9(2)
Rh(2)–C(3)–C(4)	77.6(2)	C(2)–C(3)–C(4)	124.9(4)
Rh(2)–C(4)–C(3)	65.4(2)	Rh(2)–C(4)–C(5)	107.7(3)
C(3)–C(4)–C(5)	119.7(4)	Rh(1)–C(5)–C(4)	109.8(3)
Rh(1)–C(5)–C(6)	70.5(3)	C(4)–C(5)–C(6)	122.7(4)
Rh(1)–C(6)–C(5)	70.6(3)		

3.1. Preparation of 2

To a solution of **1**·$(BF_4)_2$ (190 mg, 0.25 mmol) in dichloromethane (30 ml) was added a solution of phenylacetylene in dichloromethane (1 M solution, 2.5 ml, 2.5 mmol). The color of the reaction mixture immediately changed from yellow to red within a few minutes. After the solvent and the remaining alkyne were evaporated under reduced pressure, the resulting crude product was purified by column chromatography (3% methanol in dichloromethane was used as an eluent) to give pure **2**·BF_4 (178 mg, 90% yield). Further purification was performed by recrystallization from dichloromethane/diethyl ether. Characterization of **2**·BF_4; ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.51 (dd, J_{H-H} = 1.5 Hz, J_{Rh-H} = 3.3 Hz, 1H, C*H*C(Ph)CHC(Ph)CHCH$_2$), 7.53–7.29 (m, 10H, Ph), 5.41 (br dd, J_{H-H} = 1.5, 1.5 Hz, 1H, CHC(Ph)C*H*C(Ph)CHCH$_2$), 3.84 (dddd, J_{H-H} = 10.7, 7.6, 1.5 Hz, J_{Rh-H} = 1.5 Hz, 1H, C*H*CH$_2$), 2.03 (s, 15H, Cp*), 1.89 (dd, J_{H-H} = 7.6, J_{Rh-H} = 2.3 Hz, 1H, one of CH_2), 1.39 (s, 15H, Cp*), 0.50 (dd, J_{H-H} = 10.7, J_{Rh-H} = 1.6 Hz, 1H, one of CH_2). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 154.1 (dd, J_{Rh-C} = 36, 16 Hz, *C*HC(Ph)CHC(Ph)CHCH$_2$), 139.3 (s, Ph), 133.1 (s, Ph), 129.7 (s, Ph), 129.4 (s, Ph), 129.3 (s, Ph), 127.7 (s, Ph), 126.6 (s, Ph), 125.7 (s, Ph), 108.5 (d, J_{Rh-C} = 6 Hz, *C*Ph), 101.7 (d, J_{Rh-C} = 6 Hz, C_5Me_5), 101.1 (d, J_{Rh-C} = 6 Hz, C_5Me_5), 83.2 (d, J_{Rh-C} = 7 Hz, *C*Ph), 76.4 (d, J_{Rh-C} = 6 Hz, CHC(Ph)*C*HC(Ph)CHCH$_2$), 55.1 (d, J_{Rh-C} = 7 Hz, *C*HCH$_2$), 43.8 (d, J_{Rh-C} = 15 Hz, CH*C*H$_2$), 10.3 (s, C_5Me_5), 9.3 (s, C_5Me_5). Deuterated **2**·BF_4 was prepared from **1**·BF_4 and PhC≡CD according to the same procedure mentioned above. ^{1}H-NMR of deuterated **2**·BF_4; (270 Hz, $CDCl_3$): δ 8.52 (d, J_{Rh-H} = 3.3 Hz, C*H*C(Ph)CDC(Ph)CDCH$_2$), 7.53–7.29 (m, 10H, Ph), 2.03 (s, 15H, Cp*), 1.89 (d, J_{Rh-H} = 2.3 Hz, one of CH_2), 1.39 (s, 15H, Cp*), 0.50 (d, J_{Rh-H} = 1.3 Hz, one CH_2). Complex **2**·OTf was prepared from **1**·$(OTf)_2$ and phenylacetylene in 92% yield. Complex **2**·BPh_4 was prepared by a quantitative replacement of the OTf^- of **2** with $NaBPh_4$ in methanol. The single crystal of the BPh_4^- salt for X-ray diffraction study was obtained after recrystallization from ethyl acetate/di-

ethyl ether. Characterization of **2**·BPh_4; ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.36 (d, $J=3.0$ Hz, 1H, C*H*C(Ph)CHC(Ph)CHCH$_2$), 7.47–7.29 (m, 18H, Ph protons except for metha and para protons of BPh_4), 7.02 (t, $J=7.3$ Hz, 8H, metha protons of BPh_4), 6.86 (t, $J=7.3$ Hz, 4H, para protons of BPh_4), 5.28 (br s, 1H, CHC(Ph)C*H*C(Ph)CHCH$_2$), 3.79 (ddt, $J=10.5$, 7.3, 2.3 Hz, 1H, C*H*CH$_2$), 1.95 (s, 15H, Cp*), 1.88 (dd, $J=7.3$, 2.0 Hz, 1H, one of CH$_2$), 1.26 (s, 15H, Cp*), 0.50 (dd, $J=10.9$, 1.6 Hz, 1H, one of CH$_2$). FAB mass spectrum: m/z (%) 707 (100) $C_{38}H_{45}Rh_2$ $(M-BPh_4)^+$. Anal. Found: C, 72.35; H, 6.41. $C_{62}H_{65}BRh_2$ calc.: C, 72.52; H, 6.38.

3.2. Preparation of 3

Complex **3** was prepared from complex **1** and excess acetylenecarboxylic acid methyl ester according to the same procedure mentioned above (40% yield). Characterization of **3**·BPh_4; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, $J=3.4$, 1.7 Hz, 1H), 7.41–7.39 (m, 8H), 7.01 (t, $J=7.3$ Hz, 8H), 6.86 (t, $J=7.1$ Hz, 4H), 5.80 (brs, 1H), 4.03 (ddt, $J=11.7$, 9.1, 1.4 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 1.92 (dd, $J=7.6$, 2.4, Hz, 1H), 1.84 (s, 15H), 1.63 (s, 15H), 0.10 (dd, $J=11.5$, 1.7 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.8, 167.7, 164.2 (q, $J_{B-C}=49$ Hz), 164.0 (dd, $J_{Rh-C}=36$, 15 Hz), 136.3, 125.4, 121.5, 103.0 (d, $J_{Rh-C}=6$ Hz), 102.1 (d, $J_{Rh-C}=7$ Hz), 97.6 (d, $J_{Rh-C}=5$ Hz), 87.9 (d, $J_{Rh-C}=5$ Hz), 65.9 (d, $J_{Rh-C}=9$ Hz), 53.1, 52.9, 51.1 (d, $J_{Rh-C}=7$ Hz), 44.1 (d, $J_{Rh-C}=14$ Hz), 10.2, 9.4.

3.3. Preparation of 4

To a cooled solution (−20°C) of **1**·$(BF_4)_2$ (100 mg, 0.25 mmol) in dichloromethane (30 ml) was added slowly a solution of phenylacetylene in dichloromethane (1 M solution, 0.13 ml, 0.13 mmol). After stirring for 3 h acetylenecarboxylic acid methyl ester (44 mg, 0.52 mmol) was added to the solution. Then the reaction mixture was warmed to ambient temperature and stirred further for 5 h. The solvent and the remaining alkyne were evaporated under reduced pressure. The residue was purified by column chromatography (1% methanol in dichloromethane was used as an eluent) to give pure **4**·BF_4 (36 mg, 35% yield). The by-products, **2**·BF_4 and **3**·BF_4 were also obtained in 28 and 9% yields, respectively. Characterization of **4**·BF_4; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, $J=3.0$, 1.5 Hz, 1H), 7.49 (dd, $J=7.3$, 7.1 Hz, 2H), 7.38 (d, $J=7.1$ Hz, 2H), 7.32 (t, $J=7.3$ Hz, 1H), 5.67 (brs, 1H), 3.90–3.84 (m, 1H), 3.87 (s, 3H), 2.01 (s, 15H), 1.97 (dd, $J=6.8$, 2.0 Hz, 1H), 1.53 (s, 15H), 0.38 (dd, $J=11.2$, 1.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.3, 161.7 (dd, $J_{Rh-C}=35$, 20 Hz), 188.4, 129.6, 128.1, 125.6, 102.3 (d, $J_{Rh-C}=6$ Hz), 101.7 (d, $J_{Rh-C}=7$ Hz), 94.4 (d, $J_{Rh-C}=6$ Hz), 85.1 (d, $J_{Rh-C}=7$ Hz), 81.4 (d, $J_{Rh-C}=6$ Hz), 55.0 (d, $J_{Rh-C}=8$ Hz), 53.0, 44.2 (d, $J_{Rh-C}=15$ Hz), 10.3, 9.2.

3.4. NMR monitoring study

A reaction of **1**·$(OTf)_2$ (10 mg, 11 μmol) and phenylacetylene (1.2 mg, 11 μmol) in CD_2Cl_2 (0.5 ml) was monitored by ^{1}H-NMR (400 MHz) at −20°C. All of phenylacetylene in the reaction mixture was consumed within 30 min. At this time the reaction mixture consisted of **2**·OTf (29%), **5**·$(OTf)_2$ (43%) and the remaining starting complex **1**·$(OTf)_2$ (28%). The yields are estimated by the intensity of the methyl proton signals of the Cp* groups. Spectrum of **5**·$(OTf)_2$; δ 7.70–7.30 (m, 5H, Ph), 5.49 (dd, $J=10.3$, 6.8 Hz, 1H, C*H*CH$_2$), 3.54 (d, $J=6.8$ Hz, 1H, one of CHC*H*$_2$), 1.79 (d, $J=10.3$ Hz, 1H, one of CHC*H*$_2$), 1.61 (s, 15H, Cp*), 1.40 (s, 15H, Cp*). Upon warming the reaction mixture to ambient temperature, **5** was immediately transformed into the metal–hydride complex **6**. Spectrum of **6**; δ 7.50–7.20 (m, 5H), 5.50 (m, 1H), 5.42 (m, 1H), 4.22 (m, 1H), 1.89 (s, 15H), 1.72 (s, 15H), −8.67 (m, 1H).

3.5. Crystal structure determination of 2·BPh4

The X-ray diffraction experiment was performed at 23°C on a Rigaku automated four-circle diffractometer AFC7S with graphite monochromated Mo–K_α radiation. The lattice constants were determined by least-squares treatment using setting angles of 25 reflections in the $29.5 < 2\theta < 30°$ range. The diffraction data were collected by the $\omega - 2\theta$ scan technique at a scan rate of 8° min^{-1} in θ and a scan width of $1.68 + 0.30 \tan\theta/°$. A total of 11774 independent reflections with $2\theta \leq 55°$ were measured. Three standard reflections were monitored at every 150 measurements and showed no detectable decay of the crystal during the data collection. The intensities were corrected for Lorentz-polarization factors and empirical absorption corrections with a set of ψ scan data were applied. Crystallographic data are summarized in Table 1. The structure solution was carried out using the teXsan software [13]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Atom coordinates and selected bond angles and lengths are summarized in Tables 2 and 3, respectively.

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