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Formation of Dinuclear Ruthenacyclopentenyl Complexes from Reactions of $Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with Terminal Alkynes and Subsequent Ring-Opening Reaction Induced by Bu^tNC To Give Diruthenium μ-Alkenyl Complexes

Masayuki Nishio, Hiroyuki Matsuzaka,† Yasushi Mizobe, and Masanobu Hidai*

Department of Chemistry and Biotechnology, Graduate School of Engineering,
The University of Tokyo, Hongo, Tokyo 113, Japan

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Coordinatively unsaturated complex $Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) reacts with excess $HC{\equiv}CR$ ($R = Tol$, $C{=}CH(CH_2)_3CH_2$; $Tol = 4\text{-}C_6H_4Me$) to form dinuclear ruthenacyclopentenyl complexes $Cp^*Ru(\mu\text{-}SPr^i)[\eta^2{:}\eta^3\text{-}\mu\text{-}CH(Tol)C\{C(Tol){=}CHSPr^i\}CHC(Tol)]RuCp^*$ (**3**) and $Cp^*Ru(\mu\text{-}SPr^i)[\eta^2{:}\eta^3\text{-}\mu\text{-}C\{C(C{=}CH(CH_2)_3CH_2){=}CHSPr^i\}CHC\{(CH_2)_3CH_2\}CH]RuCp^*$ (**4**). These dinuclear metallacycles **3** and **4** are readily converted to μ-σ,π-alkenyl complexes $Cp^*(Bu^tNC)Ru(\mu\text{-}SPr^i)[\eta^1{:}\eta^2\text{-}\mu\text{-}C(Tol){=}CHC\{C(Tol){=}CHSPr^i\}{=}CH(Tol)]RuCp^*$ (**5**) and $Cp^*(Bu^tNC)Ru(\mu\text{-}SPr^i)[\eta^1{:}\eta^2\text{-}\mu\text{-}C\{C(C{=}CH(CH_2)_3CH_2){=}CHSPr^i\}{=}CH\{C{=}CH(CH_2)_3CH_2\}]RuCp^*$ (**6**), respectively, through Bu^tNC-induced ring-opening reactions with retention of the singly bonded diruthenium core bridged by a thiolato ligand. The structures of **3**−**6** have been determined by X-ray crystallography.

Introduction

Recently much interest has been focused on the reactivities of transition metal complexes containing more than one metal, because such compounds have the potential to serve as the catalysts or organometallic reagents for unique transformations of organic substrates by virtue of cooperativity between neighboring metal centers.[1] However, the polynuclear metal complexes often undergo degradative fragmentation under the conditions required for promoting these reactions. Employment of the bridging ligands may work for retaining the multimetallic site intact, and the sulfur-donor ligands have widely been chosen for this purpose due to their ability to make relatively strong bonds with transition metals as well as their high bridging tendency.

Our recent studies on the dinuclear Cp*Ru complexes ($Cp^* = \eta^5\text{-}C_5Me_5$) bridged by thiolato ligands such as $Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*$ (**1**), $Cp^*Ru(\mu\text{-}SPr^i)_3RuCp^*$, and $[Cp^*(Cl)Ru(\mu\text{-}SPr^i)_2RuCp^*][OSO_2CF_3]$ have shown that the diruthenium sites in these complexes can facilitate various stoichiometric or catalytic transformations of substrates such as alkynes, H_2, and alkyl halides in a manner distinct from mononuclear complexes.[2−4] Especially, reactivities of **1** toward terminal alkynes displayed at its well-defined bimetallic site are quite diversified. Thus, oligomerizations of the alkynes readily proceed under ambient conditions at the thiolato-bridged diruthenium center in **1**, where the products sharply depend on the nature of the substituent of the alkyne. In contrast to the oxidative trimerization forming a dinuclear π-alkyne complex for $HC{\equiv}CSiMe_3$,[2a] formation of a dinuclear ruthenacyclopentenyl complex occurred for $HC{\equiv}CCO_2Me$,[2e] in which two alkyne molecules were incorporated at the diruthenium center (Scheme 1). Furthermore, it has also been found that $HC{\equiv}CTol$ ($Tol = 4\text{-}C_6H_4Me$) and $HC{\equiv}CC{=}CH(CH_2)_3CH_2$ undergo trimerization and dimerization, respectively, upon treatment with **1** to give ruthenacyclopentenyl complexes $Cp^*Ru(\mu\text{-}SPr^i)[\eta^2{:}\eta^3\text{-}\mu\text{-}CH(Tol)C\{C(Tol){=}CHSPr^i\}CHC(Tol)]RuCp^*$ (**3**) and $Cp^*Ru(\mu\text{-}SPr^i)[\eta^2{:}\eta^3\text{-}\mu\text{-}C\{C(C{=}CH(CH_2)_3CH_2){=}CHSPr^i\}CHC\{(CH_2)_3CH_2\}CH]RuCp^*$ (**4**).[5] In this paper, we wish to describe the details of the reactions forming **3** and **4** as well as the

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† Present Address: Department of Chemistry, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-03, Japan.

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[5] To our knowledge, insertion of three alkyne molecules into the M−SR bond has not yet been reported. For examples of insertion of alkynes into M−S bonds, see: (a) Agh- Ataby, N. M.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 3531. (b) Petillon, F. Y.; Le Froch-Perennou, F.; Guerchais, J. E.; Sharp, D. W. A. *J. Organomet. Chem.* **1979**, *173*, 89. (c) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2283.

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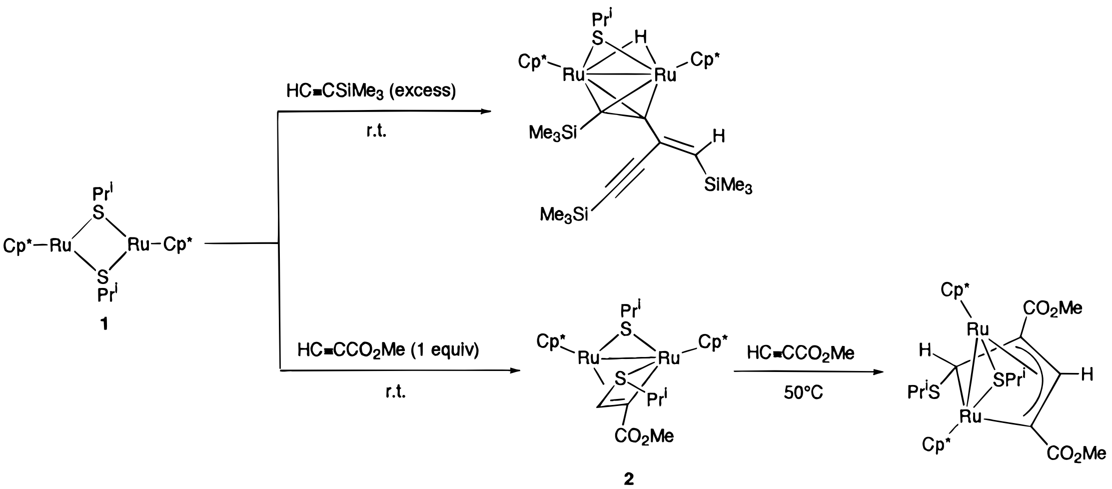
Scheme 1

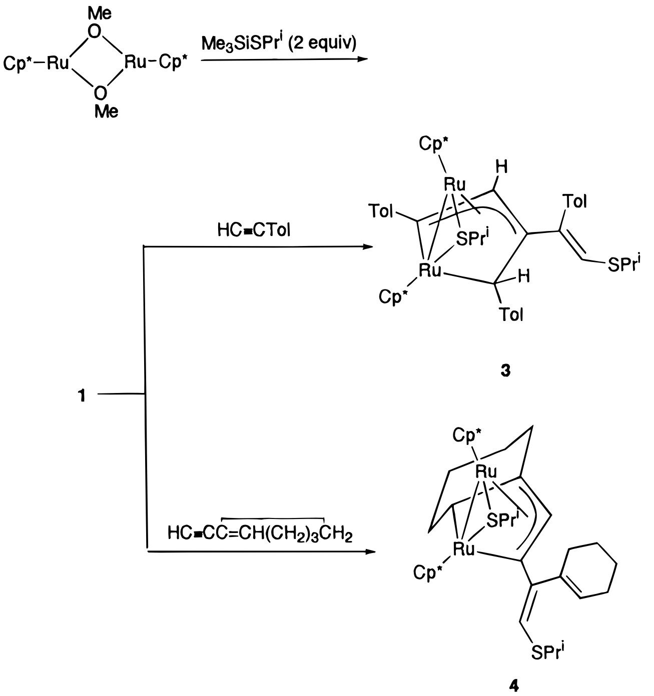


Bu^tNC-induced ring-opening reactions of these ruthenacyclopentenyl complexes affording dinuclear μ-σ,π-alkenyl complexes[5] $Cp^*(Bu^tNC)Ru(\mu\text{-}SPr^i)[\eta^1{:}\eta^2\text{-}\mu\text{-}C(Tol){=}CHC\{C(Tol){=}CHSPr^i\}{=}CH(Tol)]RuCp^*$ (**5**) and $Cp^*(Bu^tNC)Ru(\mu\text{-}SPr^i)[\eta^1{:}\eta^2\text{-}\mu\text{-}C\{C(\overline{C{=}CH(CH_2)_3C}H_2){=}CHSPr^i\}{=}CH\{\overline{C{=}CH(CH_2)_3C}H_2\}]RuCp^*$ (**6**) through dinuclear reductive elimination reactions. Syntheses of **3** and **4** have been reported previously in a preliminary form.[2b]

Results and Discussion

Preparation and X-ray Crystal Structures of Dinuclear Ruthenacyclopentenyl Complexes. Starting complex **1** was prepared in situ from the reaction of $Cp^*Ru(\mu\text{-}OMe)_2RuCp^*$ with Me_3SiSPr^i in THF and directly used for subsequent reactions.[2c] When **1** was treated with an excess of HC≡CTol at room temperature, the color of the reaction solution changed immediately from dark blue to dark brown. Subsequent chromatographic workup resulted in the isolation of a dinuclear ruthenacyclopentenyl complex **3** as a dark brown crystalline solid in moderate yield (Scheme 2). The ^1H NMR spectrum suggests that **3** consists of an unsymmetrical diruthenium core resulting from the incorporation of three HC≡CTol molecules into **1**. Thus, the Cp* methyl protons appeared as two singlets at δ 1.36 and 1.29 with the same intensities, while the Pr^i protons were recorded as four doublets and two septets. In addition to these resonances three singlets assignable to the tolyl methyl groups at δ 2.17, 2.20, and 2.29 as well as three singlets with the intensity of 1H each at δ 2.77, 5.35, and 6.49 were observed, apparently arising from three HC≡CTol molecules incorporated. To determine the detailed structure of **3**, an X-ray analysis has been undertaken by using a single crystal of **3**. An ORTEP drawing of **3** is depicted in Figure 1, and relevant crystallographic parameters are listed in Tables 1–3. The notable feature of this reaction is a formal insertion of three HC≡CTol molecules into the Ru–S bond in **1**.[6] These alkynes are linked together in an acyclic and branched manner at the diruthenium site, two of which form a five-membered metallacycle with one Ru atom [Ru(1), C(7), C(8), C(16), and C(17)]. This metallacycle is bound to the other Ru atom at C(7), C(8), and C(16) in a η^3-allyl manner in which the Ru(2)–C(16) bond at 2.378(9) Å is considerably longer than the Ru(2)–C(7) and Ru(2)–C(8) bonds of 2.189(9) and 2.162(8) Å, respectively. This asymmetric interaction of the C(7)–C(8)–C(16) moiety with the metal is reflected in the C–C distance: the C(7)–C(8) distance [1.445(9) Å] is slightly elongated from the C(8)–C(16) distance [1.40(1) Å]. Two Cp*Ru units are further bridged by one SPr^i ligand. A Ru–Ru distance at 2.779(1) Å suggests the presence of a Ru–Ru single bond,[7] which is consistent with the diamagnetic nature of **3** containing two formal Ru(III) centers.

Scheme 2



The reaction of $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ with **1** also results in the formation of the analogous dinuclear

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(6) For reviews of dinuclear complexes with bridging hydrocarbyl ligands, see: (a) Lots, S.; Van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 216. (b) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(7) The Ru–Ru distance in **2** is comparable to those in the related thiolato-bridged diruthenium(III,III) complexes such as $Cp^*(TolC{\equiv}C)Ru(\mu\text{-}SPr^i)_2RuCp^*(C{\equiv}CTol)$ [2.809(3) Å],[3a] $Cp^*(PhCH_2CH_2)Ru(\mu\text{-}SPr^i)_2RuCp^*Br$ [2.844(1) Å],[2c] and $Cp^*(PhCH_2CH_2)Ru(\mu\text{-}SPr^i)_2RuCp^*(CH_2CH_2Ph)$ [2.846(2) Å].[2f]

Table 1. X-ray Crystallographic Data for 3, 4, $5 \cdot {}^1/_2C_7H_8$, and 6

	3	**4**	**$5 \cdot {}^1/_2C_7H_8$**	**6**
(A) Crystal Data				
formula	$C_{53}H_{68}S_2Ru_2$	$C_{42}H_{64}S_2Ru_2$	$C_{61.5}H_{81}NS_2Ru_2$	$C_{47}H_{73}NS_2Ru_2$
mol wt	971.49	835.32	1100.58	918.36
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cryst system	triclinic	triclinic	triclinic	triclinic
cryst color	dark brown	dark brown	green	greenish brown
cryst dimens, mm	0.15 × 0.19 × 0.22	0.14 × 0.22 × 0.21	0.15 × 0.24 × 0.52	0.10 × 0.26 × 0.58
a, Å	13.132(7)	12.235(6)	13.121(1)	11.668(1)
b, Å	16.888(8)	13.925(6)	18.075(3)	17.299(5)
c, Å	12.832(8)	11.904(5)	12.142(2)	11.616(2)
α, deg	99.25(4)	92.73(3)	95.10(1)	95.12(2)
β, deg	119.22(4)	91.48(4)	91.37(1)	100.789(9)
γ, deg	73.12(4)	89.55(4)	93.86(1)	85.73(2)
cell vol, $Å^3$	2382(2)	2025(1)	2860.4(6)	2289.8(8)
Z	2	2	2	2
D_{measd},[a] g cm^{-3}	1.35	1.36	nd[b]	nd[b]
D_{calcd}, g cm^{-3}	1.354	1.37	1.278	1.332
F(000), e	1012	876	1154	964
μ(Mo Kα), cm^{-1}	7.835	8.568	6.38	7.82
(B) Data Collection				
diffractometer	MAC MXC-18	MAC MXC-18	Rigaku AFC7R	Rigaku AFC7R
monochromator	graphite	graphite	graphite	graphite
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)	Mo Kα (0.7107)
temp	room temp	room temp	room temp	room temp
2θ range, deg	$3 < 2\theta < 50$	$3 < 2\theta < 50$	$6 < 2\theta < 55$	$3 < 2\theta < 55$
scan method	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
scan speed, deg min^{-1}	16	16	16	16
reflcns measd	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
no. of unique rflns	7903	6985	13 115	10 505
abs corr	Gaussian integratn	Gaussian integratn	ψ-scan method	ψ-scan method
transm factors			0.88–1.00	0.86–1.00
(C) Solution and Refinement				
no. of rflns used	6597 [$F_o > 3\sigma(F_o)$]	5805 [$F_o > 3\sigma(F_o)$]	4892 [$I > 3\sigma(I)$]	5939 [$I > 3\sigma(I)$]
no. of variables	515	416	577	469
R	0.057	0.072	0.053	0.040
R_w	0.070	0.078	0.029	0.043
max resid density, e $Å^{-3}$	2.2	1.1	1.0	0.72

[a] Flotation. [b] nd = not determined.

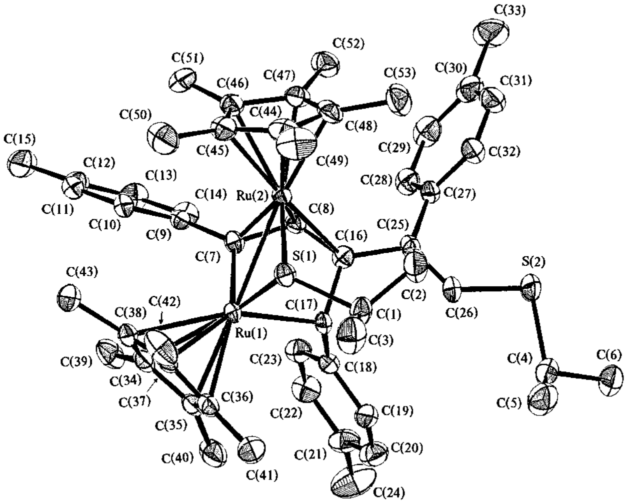

Figure 1. ORTEP drawing of **3** with the atom-labeling scheme.

ruthenacyclic complex **4** in moderate yield (Scheme 2), whose structure has been unambiguously characterized by an X-ray analysis. An ORTEP drawing is shown in Figure 2, and pertinent crystallographic details are given in Tables 1, 4, and 5. It is noteworthy that only two $HC\equiv C\overline{C{=}CH(CH_2)_3C}H_2$ molecules are incorporated into the diruthenium center in this reaction and the ruthenacyclopentenyl core in **4** is derived from the conjugated ene–yne unit in one $HC\equiv C\overline{C{=}CH(CH_2)_3C}H_2$ molecule together with one Ru atom [Ru(1) and C(7)–C(10)]. The C(7)–C(9) atoms in the ruthenacycle in **4** coordinate to the other Ru atom [Ru(2)] in a η^3-allyl manner. It is of interest that bonding of the η^3-allyl moiety in **4** is more symmetrical [C(7)–C(8), 1.44(1); C(8)–C(9), 1.44(1); Ru(2)–C(7), 2.223(8); Ru(2)–C(8), 2.143(8); Ru(2)–C(9), 2.239(8) Å] than that in **3**. The intramolecular distance of 2.796(2) Å between the two Ru atoms is comparable to that in **3**, indicating the presence of a Ru–Ru single bond. In the ^1H NMR spectrum of **4**, three characteristic resonances with the 1H intensity appeared, a sharp singlet at δ 6.17, an unresolvable broad singlet at δ 6.07, and a doublet at δ 4.13 ($^4J_{HH}$ = 1.2 Hz), which may be assigned to the vinyl proton in the $Pr^iSCH{=}$ moiety, the vinyl proton in the cyclohexenyl group, and the methine proton on the central carbon in the η^3-allyl unit [C(8)], respectively. Other NMR data are also consistent with the structure disclosed by the X-ray analysis.

Recently, we have reported the formation of an analogous dinuclear ruthenacyclopentenyl complex by the reaction of **1** with $HC\equiv CCO_2Me$, including the isolation of an intermediary four-membered metallacycle $Cp^*Ru(\mu\text{-}SPr^i)\{\mu\text{-}C(CO_2Me){=}CHSPr^i\}RuCp^*$ (**2**) derived from insertion of one $HC\equiv CCO_2Me$ molecule into the Ru–S bond in **1** (Scheme 1).[2e] However, in the present cases, isolation or detection of intermediates was unsuccessful, although many trials were performed. Therefore the reaction pathway to **3** and **4** cannot be

Table 2. Atomic Coordinates and B_{eq} Values for 3[a]

atom	x	y	z	B_{eq}, Å^2
Ru(1)	0.11274(5)	0.24898(4)	0.26908(5)	2.5
Ru(2)	0.29500(5)	0.29909(4)	0.26601(5)	2.7
S(1)	0.1226(2)	0.3818(1)	0.2674(2)	3.3
S(2)	0.5331(2)	0.3445(2)	0.8030(2)	5.2
C(1)	0.1295(9)	0.4541(6)	0.3971(8)	4.3
C(2)	0.245(1)	0.4868(7)	0.460(1)	6.0
C(3)	0.018(1)	0.5246(7)	0.347(1)	6.9
C(4)	0.4460(9)	0.3509(7)	0.8847(9)	5.2
C(5)	0.338(1)	0.4219(8)	0.846(1)	7.3
C(6)	0.533(1)	0.3564(7)	1.0182(9)	5.8
C(7)	0.2728(7)	0.1775(5)	0.2578(7)	2.9
C(8)	0.3797(7)	0.1934(5)	0.3789(7)	2.9
C(9)	0.2844(7)	0.1030(5)	0.2004(7)	2.9
C(10)	0.2128(7)	0.1023(5)	0.0770(7)	3.3
C(11)	0.2210(8)	0.0310(6)	0.0082(8)	4.1
C(12)	0.3027(8)	−0.0438(6)	0.0613(9)	4.2
C(13)	0.3744(9)	−0.0423(6)	0.1850(9)	4.6
C(14)	0.3677(8)	0.0298(5)	0.2548(8)	3.7
C(15)	0.314(1)	−0.1227(7)	−0.011(1)	5.8
C(16)	0.3568(7)	0.2537(5)	0.4582(7)	3.1
C(17)	0.2376(7)	0.2569(5)	0.4555(6)	3.0
C(18)	0.2537(7)	0.1928(5)	0.5334(7)	3.2
C(19)	0.2259(8)	0.2147(6)	0.6276(8)	4.0
C(20)	0.2441(9)	0.1564(7)	0.7040(9)	4.9
C(21)	0.2907(9)	0.0732(6)	0.6896(9)	4.8
C(22)	0.3189(9)	0.0494(6)	0.5962(9)	4.9
C(23)	0.3018(8)	0.1069(6)	0.5191(8)	4.0
C(24)	0.313(1)	0.0097(9)	0.774(1)	8.7
C(25)	0.4546(7)	0.2777(5)	0.5734(7)	3.3
C(26)	0.4285(8)	0.3182(6)	0.6583(7)	3.9
C(27)	0.5822(7)	0.2497(5)	0.5976(7)	3.2
C(28)	0.6387(8)	0.1646(6)	0.6009(8)	4.1
C(29)	0.7581(9)	0.1389(7)	0.6267(9)	5.5
C(30)	0.8260(9)	0.1976(8)	0.6498(9)	5.8
C(31)	0.7730(9)	0.2793(8)	0.6504(9)	5.4
C(32)	0.6520(9)	0.3059(6)	0.6242(9)	4.7
C(33)	0.958(1)	0.170(1)	0.678(1)	8.4
C(34)	0.0020(7)	0.1497(5)	0.1825(8)	3.5
C(35)	−0.0128(8)	0.1890(6)	0.2834(8)	4.0
C(36)	−0.0685(7)	0.2749(6)	0.2592(8)	4.1
C(37)	−0.0889(7)	0.2868(6)	0.1395(8)	3.9
C(38)	−0.0470(7)	0.2105(6)	0.0943(7)	3.7
C(39)	0.043(1)	0.0580(6)	0.169(1)	5.5
C(40)	0.000(1)	0.1435(8)	0.3833(9)	6.0
C(41)	−0.113(1)	0.3367(7)	0.335(1)	6.2
C(42)	−0.1541(8)	0.3652(7)	0.070(1)	6.3
C(43)	−0.0788(9)	0.1948(8)	−0.0383(8)	5.5
C(44)	0.2885(9)	0.3999(6)	0.1646(9)	4.8
C(45)	0.2595(8)	0.3301(7)	0.0853(8)	4.6
C(46)	0.3661(8)	0.2621(6)	0.1312(7)	3.8
C(47)	0.4531(8)	0.2926(6)	0.2404(8)	3.9
C(48)	0.4079(8)	0.3765(6)	0.2619(8)	4.2
C(49)	0.210(1)	0.4872(7)	0.141(1)	7.0
C(50)	0.150(1)	0.3297(9)	−0.032(1)	7.1
C(51)	0.390(1)	0.1854(7)	0.065(1)	5.6
C(52)	0.5837(8)	0.2446(7)	0.3090(9)	5.0
C(53)	0.480(1)	0.4336(7)	0.358(1)	6.2

[a] Numbers in parentheses are estimated standard deviations.

Table 3. Selected Bond Distances and Angles for 3[a]

Distances (Å)			
Ru(1)−Ru(2)	2.779(1)	Ru(1)−S(1)	2.292(2)
Ru(1)−C(7)	2.079(8)	Ru(1)−C(17)	2.154(6)
Ru(1)−C(34)	2.320(9)	Ru(1)−C(35)	2.26(1)
Ru(1)−C(36)	2.24(1)	Ru(1)−C(37)	2.301(7)
Ru(1)−C(38)	2.363(7)	Ru(2)−S(1)	2.312(2)
Ru(2)−C(7)	2.189(9)	Ru(2)−C(8)	2.162(8)
Ru(2)−C(16)	2.378(9)	Ru(2)−C(44)	2.27(1)
Ru(2)−C(45)	2.26(1)	Ru(2)−C(46)	2.27(1)
Ru(2)−C(47)	2.23(1)	Ru(2)−C(48)	2.26(1)
S(1)−C(1)	1.88(1)	S(2)−C(4)	1.87(2)
S(2)−C(26)	1.770(8)	C(7)−C(8)	1.445(9)
C(7)−C(9)	1.48(1)	C(8)−C(16)	1.40(1)
C(16)−C(17)	1.54(1)	C(16)−C(25)	1.50(1)
C(17)−C(18)	1.50(1)	C(25)−C(26)	1.33(1)
C(25)−C(27)	1.49(1)		
Angles (deg)			
Ru(2)−Ru(1)−S(1)	53.21(7)	Ru(2)−Ru(1)−C(7)	51.1(3)
Ru(2)−Ru(1)−C(17)	77.1(3)	S(1)−Ru(1)−C(7)	104.3(3)
S(1)−Ru(1)−C(17)	84.1(2)	C(7)−Ru(1)−C(17)	77.7(3)
Ru(1)−Ru(2)−S(1)	52.55(7)	Ru(1)−Ru(2)−C(7)	47.7(2)
Ru(1)−Ru(2)−C(8)	73.3(3)	Ru(1)−Ru(2)−C(16)	69.2(2)
S(1)−Ru(2)−C(7)	100.2(2)	S(1)−Ru(2)−C(8)	115.4(3)
S(1)−Ru(2)−C(16)	88.8(2)	C(7)−Ru(2)−C(8)	38.8(3)
C(7)−Ru(2)−C(16)	62.8(3)	C(8)−Ru(2)−C(16)	35.6(3)
Ru(1)−S(1)−Ru(2)	72.24(6)	C(4)−S(2)−C(26)	99.6(5)
Ru(1)−C(7)−Ru(2)	81.2(3)	Ru(1)−C(7)−C(8)	114.9(6)
Ru(1)−C(7)−C(9)	125.3(5)	Ru(2)−C(7)−C(8)	69.6(5)
Ru(2)−C(7)−C(9)	128.1(7)	C(8)−C(7)−C(9)	118.4(6)
Ru(2)−C(8)−C(7)	71.6(4)	Ru(2)−C(8)−C(16)	80.6(5)
C(7)−C(8)−C(16)	113.8(7)	Ru(2)−C(16)−C(8)	63.8(5)
Ru(2)−C(16)−C(17)	103.1(4)	Ru(2)−C(16)−C(25)	125.8(7)
C(8)−C(16)−C(17)	112.1(7)	C(8)−C(16)−C(25)	122.8(7)
C(17)−C(16)−C(25)	117.4(8)	Ru(1)−C(17)−C(16)	104.8(6)
Angles (deg)			
Ru(1)−C(17)−C(18)	116.8(5)	C(16)−C(17)−C(18)	110.7(6)
C(16)−C(25)−C(26)	119.7(8)	C(16)−C(25)−C(27)	120.3(8)
C(26)−C(25)−C(27)	119.7(7)	S(2)−C(26)−C(25)	125.9(7)

[a] Numbers in parentheses are estimated standard deviations.

proposed here, but formation of vinylidene species may be involved in these reactions.

Interestingly, the reaction course of terminal alkynes at the thiolato-bridged diruthenium site seems to be affected by the nature of the thiolato ligand. Quite recently, Kölle and his co-workers have reported the reaction of Cp*Ru(μ-SBu^t)$_2$RuCp* with $HC\equiv CCO_2Me$, from which three types of diruthenium complexes containing two, three, or five $HC\equiv CCO_2Me$ molecules incorporated at the diruthenium center have been isolated in addition to a four-membered metallacyclic complex analogous to **2**.[8]

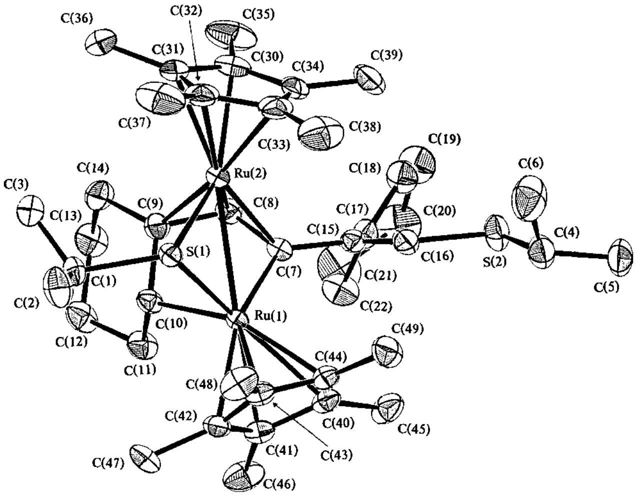

Figure 2. ORTEP drawing of **4** with the atom-labeling scheme.

Reaction of Dinuclear Ruthenacyclopentenyl Complexes with Bu^{t}NC. Complex **3** reacted with excess Bu^{t}NC at 80 °C in toluene to afford a diruthenium complex **5**, which was isolated as green crystals in high yield (Scheme 3). On the basis of the spectroscopic data, we previously proposed a dinuclear structure with the metallacyclic framework intact for **5**.[2b] However, more recent X-ray crystallographic study has disclosed that **5** contains a diruthenium core bridged by a σ,π-alkenyl ligand resulting from the Bu^{t}NC-

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(8) Kölle, U.; Rietmann, C.; Tjoe, J.; Wagner, T.; Englert, U. *Organometallics* **1995**, *14*, 703.

Table 4. Atomic Coordinates and B_{eq} Values for 4[a]

atom	x	y	z	B_{eq}, Å^2
Ru(1)	0.22228(7)	0.37900(6)	0.26464(7)	2.5
Ru(2)	0.14257(8)	0.19319(6)	0.21913(8)	2.9
S(1)	0.0475(2)	0.3374(2)	0.2096(2)	3.0
S(2)	0.5583(3)	0.2124(3)	0.0458(3)	5.2
C(1)	−0.067(1)	0.369(1)	0.309(1)	4.0
C(2)	−0.150(1)	0.429(1)	0.239(2)	6.3
C(3)	−0.122(1)	0.282(1)	0.353(2)	6.0
C(4)	0.5464(7)	0.2739(6)	−0.0853(7)	2.5
C(5)	0.6601(7)	0.2666(6)	−0.1371(7)	2.8
C(6)	0.4576(7)	0.2359(7)	−0.1651(7)	3.4
C(7)	0.3068(6)	0.2497(6)	0.2710(6)	1.6
C(8)	0.2651(7)	0.1846(6)	0.3502(7)	2.0
C(9)	0.1684(7)	0.2193(6)	0.4049(7)	1.9
C(10)	0.1723(7)	0.3289(6)	0.4227(7)	1.8
C(11)	0.2418(7)	0.3529(6)	0.5307(7)	2.1
C(12)	0.1973(7)	0.2993(6)	0.6310(7)	2.4
C(13)	0.1934(7)	0.1901(6)	0.6064(7)	2.6
C(14)	0.124(1)	0.163(1)	0.499(1)	4.4
C(15)	0.4130(9)	0.2219(8)	0.219(1)	3.2
C(16)	0.433(1)	0.2411(9)	0.113(1)	3.6
C(17)	0.495(1)	0.1732(9)	0.294(1)	3.8
C(18)	0.537(1)	0.086(1)	0.260(1)	5.0
C(19)	0.618(1)	0.030(1)	0.332(1)	5.7
C(20)	0.662(1)	0.088(1)	0.431(2)	6.7
C(21)	0.588(2)	0.159(1)	0.483(2)	7.2
C(22)	0.530(1)	0.224(1)	0.402(1)	4.8
C(30)	0.140(1)	0.0359(9)	0.183(1)	4.7
C(31)	0.029(1)	0.070(1)	0.186(1)	4.6
C(32)	0.014(1)	0.130(1)	0.097(1)	4.6
C(33)	0.113(1)	0.137(1)	0.0378(1)	4.8
C(34)	0.191(1)	0.076(1)	0.091(1)	4.6
C(35)	0.192(2)	−0.040(1)	0.257(2)	7.3
C(36)	−0.057(2)	0.032(1)	0.263(2)	7.1
C(37)	−0.096(1)	0.172(1)	0.058(2)	7.3
C(38)	0.124(2)	0.197(1)	−0.066(1)	7.7
C(39)	0.301(1)	0.049(1)	0.040(1)	6.4
C(40)	0.370(1)	0.4733(9)	0.223(1)	3.7
C(41)	0.315(1)	0.5106(9)	0.322(1)	3.6
C(42)	0.207(1)	0.5380(8)	0.289(1)	3.3
C(43)	0.196(1)	0.5187(9)	0.168(1)	3.5
C(44)	0.296(1)	0.4781(9)	0.129(1)	3.6
C(45)	0.492(1)	0.453(1)	0.224(1)	5.2
C(46)	0.371(1)	0.539(1)	0.433(1)	6.0
C(47)	0.124(1)	0.591(1)	0.362(1)	5.5
C(48)	0.100(1)	0.544(1)	0.095(1)	5.5
C(49)	0.321(1)	0.461(1)	0.006(1)	5.2

[a] Numbers in parentheses are estimated standard deviations.

induced ring-opening reaction of the metallacycle in **3** (Figure 3). In this reaction, the Ru(III)/Ru(III) pair in **3** is considered to be transformed to a Ru(II)/Ru(II) pair by formal dinuclear reductive elimination (Scheme 3). Since **3** was quantitatively recovered even after heating at 80 °C in toluene for 9 h, this transformation appears to be induced by the interaction of **3** with Bu^{t}NC. The reaction of **4** with Bu^{t}NC proceeded similarly to give a diruthenium complex **6** in high yield, whose structure has also been confirmed by the X-ray crystallography (Figure 4). It is noteworthy that the diruthenium complexes containing only one Bu^{t}NC ligand were selectively obtained, in which the isocyanide binds to the ruthenium atom initially involved in the ruthenacyclopentenyl moiety.

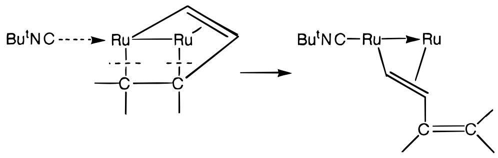
Reactions of the ruthenacyclopentenyl complexes **3** and **4** with CO (1 atm) in place of Bu^{t}NC were also carried out at 80 °C. However, the reaction of **3** resulted in the formation of an intractable Ru species exhibiting the ν(CO) bands at 2006, 1919, and 1779 cm^{-1}, whereas that of **4** afforded Cp*Ru(CO)$_2$SPr^i in 62% yield as the only characterizable product. The fate of the alkyne-derived moieties in both **3** and **4** was uncertain.

Table 5. Selected Bond Distances and Angles for 4[a]

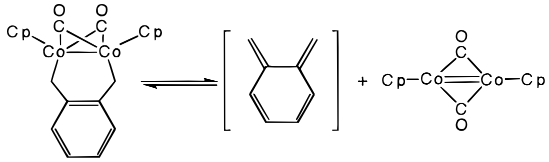
Distances (Å)			
Ru(1)−Ru(2)	2.796(2)	Ru(1)−S(1)	2.291(3)
Ru(1)−C(7)	2.073(8)	Ru(1)−C(10)	2.143(8)
Ru(1)−C(40)	2.32(1)	Ru(1)−C(41)	2.23(1)
Ru(1)−C(42)	2.23(1)	Ru(1)−C(43)	2.32(1)
Ru(1)−C(44)	2.38(1)	Ru(2)−S(1)	2.318(3)
Ru(2)−C(7)	2.223(8)	Ru(2)−C(8)	2.143(8)
Ru(2)−C(9)	2.239(8)	Ru(2)−C(30)	2.21(1)
Ru(2)−C(31)	2.23(1)	Ru(2)−C(32)	2.27(1)
Ru(2)−C(33)	2.28(1)	Ru(2)−C(34)	2.27(1)
S(1)−C(1)	1.89(1)	S(2)−C(4)	1.82(1)
S(2)−C(16)	1.78(1)	C(7)−C(8)	1.44(1)
C(7)−C(15)	1.50(1)	C(8)−C(9)	1.44(1)
C(9)−C(10)	1.53(1)	C(15)−C(16)	1.33(2)
C(15)−C(17)	1.51(2)	C(17)−C(18)	1.37(2)
Angles (deg)			
Ru(2)−Ru(1)−S(1)	53.10(8)	C(7)−Ru(1)−C(9)	65.3(3)
Ru(1)−Ru(2)−S(1)	52.22(8)	C(7)−Ru(2)−C(8)	38.5(3)
C(7)−Ru(2)−C(10)	78.5(3)	C(8)−Ru(2)−C(9)	38.2(2)
Ru(1)−S(1)−Ru(2)	74.7(1)	Ru(1)−C(7)−C(8)	114.4(5)
Ru(1)−C(7)−C(15)	126.6(7)	C(8)−C(7)−C(15)	116.3(8)
C(7)−C(8)−C(9)	113.6(7)	C(8)−C(9)−C(10)	110.2(7)
C(8)−C(9)−C(14)	118.7(8)	C(10)−C(9)−C(14)	117.3(8)
Ru(1)−C(10)−C(9)	104.6(5)	C(7)−C(15)−C(16)	121(1)
C(7)−C(15)−C(17)	116(1)	C(16)−C(15)−C(17)	123(1)
S(2)−C(16)−C(15)	124(1)	C(15)−C(17)−C(18)	119(1)
C(17)−C(18)−C(19)	123(1)		

[a] Numbers in parentheses are estimated standard deviations.

The present reactions converting **3** and **4** into **5** and **6**, respectively, might be represented to be the ligand-induced dinuclear reductive elimination (Scheme 3), as shown in eq 1. Although dinuclear reductive elimination is attracting significant attention as an important step in the transformations of substrates at the multimetallic sites in organometallic chemistry,[9] examples of the *intramolecular* eliminations proceeding with retention of the bimetallic structure are quite limited; Bergman has shown that the dicobaltacyclohexene complex undergoes the retro-dimetalla Diels−Alder reaction which results in the formation of *o*-xylylene and the metal−metal double-bonded cobalt dimer (eq 2).[10]



(1)



(2)

The resulting dicobalt complex is successfully trapped as a phosphine adduct Cp(R$_3$P)Co(μ-CO)$_2$CoCp (Cp = η^5-C$_5$H$_5$) in the reaction with *e.g.* PMe$_2$Ph. On the other hand, for most of the dinuclear eliminations reported to date, eliminations arising from coupling of the hydrocarbyl and hydrido ligands (initially) attached to the adjacent metals are induced by the coordination of

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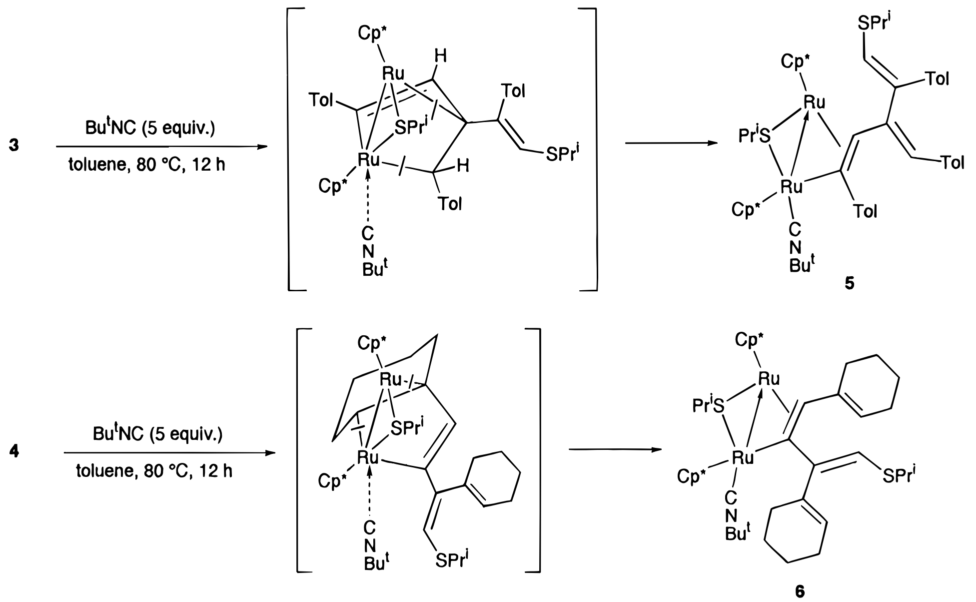
(9) (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Trinquir, G.; Hofmann, R. *Organometallics* **1984**, *3*, 370.

(10) (a) Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834. (b)Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5846.

Scheme 3



certain donor ligands.[11] Included in this category might be the evolution of CH_4 from $[Pd(H)(\mu\text{-}Cl)(\mu\text{-}dppm)_2Pd(CH_3)]Cl$ (dppm = $Ph_2PCH_2PPh_2$) that is presumably initiated by the terminal coordination of the Cl anion[12] and the elimination of ethane from a dimolybdenum precursor $(Me_2N)_2(Et)Mo{\equiv}Mo(Et)(NMe_2)_2$ in the presence of excess CO_2.[13] Reaction of $Cp^*(ArC{\equiv}C)Ru(\mu\text{-}SPr^i)_2RuCp^*(C{\equiv}CAr)$ (Ar = Ph, Tol) with I_2 to give $ArC{\equiv}CC{\equiv}CAr$ together with $Cp^*(I)Ru(\mu\text{-}SPr^i)_2RuCp^*(I)$ may also be interpreted in terms of the I_2-induced dinuclear reductive elimination.[3a] Reactions of this type induced by CO are also known, whereby insertion of CO into the M–C bond takes place prior to eliminations forming aldehydes, ketones, and diketones, as manifested for the dipalladium complex $[Pd(H)(\mu\text{-}Cl)(\mu\text{-}dppm)_2Pd(CH_3)]^+$ cited above,[12] dirhodium complexes $Rh(R)(\mu\text{-}CO)(\mu\text{-}dppm)_2Rh(R)$ (R = CH_3, CH_2Ph),[14] and a dicobalt complex $Co(CH_3)(\mu\text{-}CO)_2(\eta^5{:}\eta^5\text{-}\mu\text{-}C_5H_4CH_2C_5H_4)Co(CH_3)$.[15] However, to the best of our knowledge, isocyanide-induced dinuclear reductive elimination is unprecedented.

X-ray Crystal Structures of 5 and 6. Crystal and data collection parameters are summarized in Table 1, and relevant geometrical parameters for **5** and **6** are given in Tables 6–9. As shown in Figure 3, two singly bonded Cp*Ru units in **5** [Ru–Ru, 2.796(1) Å] are bridged by a SPr^i ligand and a trienyl group, and the remaining site of one Ru atom [Ru(1)] is occupied by a terminal Bu^tNC ligand. The trienyl ligand bridges the two Ru atoms at C(1) and C(2) in the σ, π mode.[6] The Ru(1)–C(1) σ-bonded distance is 2.166(7) Å, while the C(1)–C(2) moiety coordinates to Ru(2) with the Ru(2)–C(1) and Ru(2)–C(2) distances at 2.045(7) and 2.218(7) Å, respectively. Complex **6** has an dinuclear structure analogous to **5**, with a bridging tetraenyl ligand [Ru(1)–C(1), 2.196(4); Ru(2)–C(1), 2.074(4); Ru(2)–C(2), 2.219(5) Å] between two Ru atoms separated by 2.844(1) Å. Around the C(1)–C(2) bond, Ru(1) in both **5** and **6** lies *trans* to C(3) in **5** and C(5) in **6**, respectively. It is to be noted that the Ru atom [Ru(1) in **3** and **4**] and the terminal carbon atom of the η^3-allyl fragment [C(16) in **3** or C(9) in **4**] are originally located on the same side

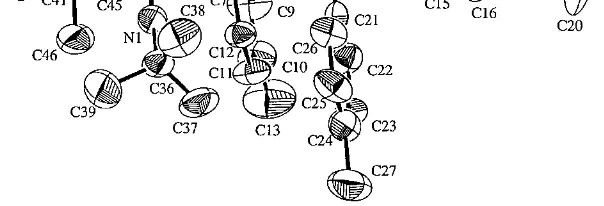


Figure 3. ORTEP drawing of **5** with the atom-labeling scheme.

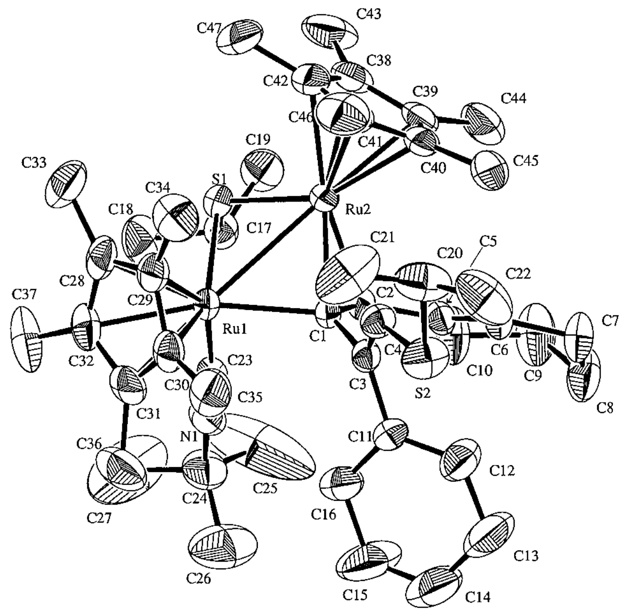


Figure 4. ORTEP drawing of **6** with the atom-labeling scheme.

Table 6. Atomic Coordinates and B_{eq} Values for $5\cdot{}^1/_2C_7H_8$[a−c]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Ru(1)	0.00683(5)	0.25246(4)	0.39562(6)	3.64(2)
Ru(2)	−0.08675(5)	0.16005(4)	0.21986(6)	3.59(2)
S(1)	−0.0416(1)	0.1258(1)	0.3892(2)	3.83(6)
S(2)	−0.5124(2)	0.0663(1)	0.3593(2)	7.34(9)
N(1)	−0.1472(5)	0.3056(4)	0.5649(5)	4.6(2)
C(1)	−0.1175(5)	0.2653(4)	0.2798(6)	3.4(2)
C(2)	−0.2103(5)	0.2220(4)	0.2984(6)	3.2(2)
C(3)	−0.3099(5)	0.2228(4)	0.2398(6)	3.2(2)
C(4)	−0.3257(5)	0.2465(4)	0.1402(7)	4.1(2)
C(5)	−0.3959(5)	0.1923(4)	0.3056(6)	3.3(2)
C(6)	−0.4155(6)	0.1193(5)	0.3006(7)	5.0(3)
C(7)	−0.1218(5)	0.3372(4)	0.2306(7)	3.6(2)
C(8)	−0.0724(6)	0.3560(4)	0.1358(8)	5.4(3)
C(9)	−0.0821(7)	0.4237(6)	0.0944(7)	6.8(3)
C(10)	−0.1384(8)	0.4781(5)	0.1461(8)	6.3(3)
C(11)	−0.1859(7)	0.4601(5)	0.2404(8)	5.7(3)
C(12)	−0.1796(6)	0.3922(5)	0.2813(6)	4.4(2)
C(13)	−0.1444(8)	0.5540(5)	0.1004(8)	9.7(4)
C(14)	−0.4167(6)	0.2466(5)	0.0687(7)	4.4(3)
C(15)	−0.4131(6)	0.2869(5)	−0.0212(8)	6.8(3)
C(16)	−0.4981(8)	0.2885(6)	−0.0940(7)	8.2(4)
C(17)	−0.5881(7)	0.2526(7)	−0.0779(8)	7.3(4)
C(18)	−0.5908(6)	0.2100(6)	0.0080(8)	7.4(3)
C(19)	−0.5106(7)	0.2086(5)	0.0829(7)	6.1(3)
C(20)	−0.6779(7)	0.2554(7)	−0.1570(8)	11.8(4)
C(21)	−0.4553(5)	0.2464(5)	0.3726(7)	3.7(2)
C(22)	−0.4658(6)	0.3117(5)	0.3410(6)	4.6(3)
C(23)	−0.5202(7)	0.3689(5)	0.4038(8)	5.6(3)
C(24)	−0.5645(6)	0.3510(6)	0.4976(9)	5.7(3)
C(25)	−0.5530(7)	0.2830(6)	0.5308(7)	6.0(3)
C(26)	−0.4998(6)	0.2317(4)	0.4715(7)	5.0(3)
C(27)	−0.6245(6)	0.4085(5)	0.5644(8)	9.1(3)
C(28)	−0.1385(6)	0.1043(4)	0.4902(6)	4.3(2)
C(29)	−0.0867(6)	0.1021(5)	0.6024(7)	6.9(3)
C(30)	−0.1956(6)	0.0310(5)	0.4538(7)	7.2(3)
C(31)	−0.518(1)	−0.0195(6)	0.267(1)	9.0(4)
C(32)	−0.539(2)	−0.015(1)	0.161(2)	10.9(9)
C(33)	−0.610(1)	−0.0673(8)	0.292(1)	15.8(7)
C(34)	−0.442(1)	−0.0658(8)	0.291(1)	11.9(6)
C(35)	−0.0949(6)	0.2818(4)	0.4953(7)	3.9(2)
C(36)	−0.2185(7)	0.3296(5)	0.6495(7)	5.0(3)
C(37)	−0.2865(6)	0.3826(5)	0.5985(7)	7.3(3)
C(38)	−0.2816(7)	0.2605(5)	0.6775(7)	7.6(3)
C(39)	−0.1552(7)	0.3663(5)	0.7483(7)	9.0(4)
C(40)	0.1386(7)	0.3325(6)	0.3533(9)	6.0(3)
C(41)	0.1041(6)	0.3521(5)	0.458(1)	4.9(3)
C(42)	0.1240(6)	0.2929(6)	0.5236(8)	5.4(3)
C(43)	0.1694(7)	0.2392(6)	0.459(1)	6.0(3)
C(44)	0.1817(7)	0.2622(7)	0.354(1)	7.0(4)
C(45)	0.1507(8)	0.3846(7)	0.266(1)	13.8(5)
C(46)	0.0663(6)	0.4258(5)	0.499(1)	11.1(4)
C(47)	0.1123(7)	0.2934(6)	0.6469(9)	10.8(4)
C(48)	0.2077(7)	0.1670(6)	0.492(1)	11.6(4)
C(49)	0.2472(7)	0.2285(7)	0.2645(9)	13.5(5)
C(50)	−0.1032(7)	0.1497(5)	0.0327(7)	4.5(3)
C(51)	−0.1555(6)	0.0890(6)	0.0756(7)	4.9(3)
C(52)	−0.0851(7)	0.0479(5)	0.1280(7)	4.6(3)
C(53)	0.0124(6)	0.0851(6)	0.1235(7)	4.2(3)
C(54)	0.0020(7)	0.1489(5)	0.0642(7)	4.4(3)
C(55)	−0.1450(7)	0.1964(5)	−0.0522(7)	7.8(3)
C(56)	−0.2671(6)	0.0627(5)	0.0480(7)	7.2(3)
C(57)	−0.1063(7)	−0.0256(5)	0.1751(7)	7.5(3)
C(58)	0.1098(6)	0.0538(4)	0.1626(7)	6.9(3)
C(59)	0.0864(6)	0.1947(5)	0.0202(7)	6.9(3)
C(60)*	0.4035	0.4755	0.1217	
C(61)*	0.5137	0.4708	0.1034	
C(62)*	0.5753	0.4921	0.0176	

[a] Numbers in parentheses are estimated standard deviations. [b] The C(32), C(33), and C(34) atoms are related to each other by the disorder of two carbon atoms in the Pr^i group (50%, 75%, and 75% occupancies, respectively) [c] Asterisks denote the ring carbons in the solvato toluene molecule.

Table 7. Selected Bond Distances and Angles for $5\cdot{}^1/_2C_7H_8$[a]

	Distances (Å)		
Ru(1)−Ru(2)	2.796(1)	Ru(1)−S(1)	2.328(2)
Ru(1)−C(1)	2.166(7)	Ru(1)−C(35)	1.894(8)
Ru(1)−C(40)	2.277(9)	Ru(1)−C(41)	2.202(8)
Ru(1)−C(42)	2.201(8)	Ru(1)−C(43)	2.286(9)
Ru(1)−C(44)	2.359(9)	Ru(2)−S(1)	2.276(2)
Ru(2)−C(1)	2.045(7)	Ru(2)−C(2)	2.218(7)
Ru(2)−C(50)	2.267(8)	Ru(2)−C(51)	2.214(8)
Ru(2)−C(52)	2.227(8)	Ru(2)−C(53)	2.219(7)
Ru(2)−C(54)	2.245(8)	S(1)−C(28)	1.834(7)
S(2)−C(6)	1.745(8)	N(1)−C(35)	1.171(8)
C(1)−C(2)	1.435(8)	C(2)−C(3)	1.475(8)
C(3)−C(4)	1.335(9)	C(3)−C(5)	1.502(9)
C(5)−C(6)	1.322(9)		
	Angles (deg)		
Ru(2)−Ru(1)−S(1)	51.77(5)	Ru(2)−Ru(1)−C(1)	46.6(2)
Ru(2)−Ru(1)−C(35)	108.6(2)	S(1)−Ru(1)−C(1)	89.3(2)
S(1)−Ru(1)−C(35)	94.9(2)	C(1)−Ru(1)−C(35)	79.8(3)
Ru(1)−Ru(2)−S(1)	53.46(5)	Ru(1)−Ru(2)−C(1)	50.3(2)
Ru(1)−Ru(2)−C(2)	74.0(2)	S(1)−Ru(2)−C(1)	93.8(2)
S(1)−Ru(2)−C(2)	88.7(2)	C(1)−Ru(2)−C(2)	39.1(2)
Ru(1)−S(1)−Ru(2)	74.77(7)	C(35)−N(1)−C(36)	175.1(9)
Ru(1)−C(1)−Ru(2)	83.1(2)	Ru(1)−C(1)−C(2)	114.4(5)
Ru(1)−C(1)−C(7)	118.4(5)	Ru(2)−C(1)−C(2)	77.0(4)
Ru(2)−C(1)−C(7)	134.2(5)	Ru(2)−C(2)−C(1)	63.9(4)
Ru(2)−C(2)−C(3)	119.8(5)	C(2)−C(1)−C(7)	120.0(6)
C(1)−C(2)−C(3)	127.5(7)	C(2)−C(3)−C(4)	126.2(7)
C(2)−C(3)−C(5)	111.8(7)	C(4)−C(3)−C(5)	122.0(7)
C(3)−C(4)−C(14)	132.9(8)	C(3)−C(5)−C(6)	118.7(7)
C(3)−C(5)−C(21)	117.8(7)	C(6)−C(5)−C(21)	123.6(8)
S(2)−C(6)−C(5)	130.5(7)		

[a] Numbers in parentheses are estimated standard deviations.

with respect to the C(7)−C(8) linkage. These geometrical changes through the reactions with Bu^{t}NC may arise from the steric requirement. The intramolecular distances of the bridging carbon−carbon double bond [C(1)−C(2); 1.435(8) Å in **5** and 1.420(6) Å in **6**] are comparable to those of the bridging vinyl ligands in Cp(CO)Ru(μ-H)(μ-CH=CHMe)Ru(CO)Cp [1.406(5) Å][16] and (Ph$_3$P)(CO)$_2$Ru[μ-O=C(NMe$_2$)](μ-C(Tol)=CHTol)Ru(CO)$_3$ [1.416(9) Å][17] but slightly shorter than those in Cp*Ru(μ-SPr^i)[η^2:η^2-μ-C(CO$_2$Bu^t)=CHSPr^i]RuCp* [1.45(1) Å][2e] and Cp*Ru(μ-H)[μ-C(CO$_2$Me)CHCO$_2$Me][μ-C(CO$_2$Me)=CHCO$_2$Me]RuCp* [1.47(2) Å].[18] The tri- and tetraenyl ligands in **5** and **6** are not planar. In **5** the torsion angles are 20(1) and 83.0(9)° for the C(1)−C(2)−C(3)−C(4) and C(2)−C(3)−C(5)−C(6) linkages, respectively, and in **6** that of the C(2)−C(1)−C(3)−C(4) array is 56.3(5)°.

Experimental Section

General Comments. All manipulations were performed under a nitrogen atmosphere using standard Schlenk tech-

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[11] A diruthenium complex Cp*(H)Ru(μ-SPr^i)$_2$RuCp*(CH$_2$Ph) undergoes dinuclear reductive elimination to give PhCH$_3$ and a coordinatively unsaturated complex Cp*Ru(μ-SPr^i)$_2$RuCp* only by warming to room temperature or 50 °C.[3c] This represents a rare example of the thermal dinuclear reductive elimination, although the detailed reaction mechanism has not yet been clarified.

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Table 8. Atomic Coordinates and B_{eq} Values for 6[a]

atom	x	y	z	B_{eq}, Å^2
Ru(1)	−0.03984(3)	−0.27021(2)	0.17396(4)	2.58(1)
Ru(2)	−0.21756(3)	−0.14947(2)	0.13378(4)	2.63(1)
S(1)	−0.0224(1)	−0.13607(8)	0.1827(1)	2.97(3)
S(2)	−0.4765(1)	−0.3902(1)	0.0526(1)	4.65(4)
N(1)	0.0598(4)	−0.2720(3)	0.4408(4)	4.0(1)
C(1)	−0.2149(4)	−0.2481(3)	0.2235(4)	2.4(1)
C(2)	−0.2187(4)	−0.1860(3)	0.3118(4)	2.5(1)
C(3)	−0.3012(4)	−0.3105(3)	0.2027(4)	2.7(1)
C(4)	−0.3658(4)	−0.3239(3)	0.0956(4)	3.1(1)
C(5)	−0.3151(4)	−0.1629(3)	0.3758(4)	2.7(1)
C(6)	−0.4267(4)	−0.1787(3)	0.3400(4)	3.3(1)
C(7)	−0.5222(4)	−0.1585(4)	0.4094(5)	4.5(1)
C(8)	−0.4753(5)	−0.1370(5)	0.5359(6)	5.8(2)
C(9)	−0.3785(6)	−0.0827(4)	0.5492(6)	5.9(2)
C(10)	−0.2778(5)	−0.1199(4)	0.4943(5)	4.9(2)
C(11)	−0.3129(4)	−0.3540(3)	0.3045(5)	3.3(1)
C(12)	−0.4208(5)	−0.3696(4)	0.3263(5)	4.9(2)
C(13)	−0.4338(7)	−0.4046(5)	0.4337(7)	7.3(2)
C(14)	−0.3299(8)	−0.4405(7)	0.4982(9)	10.8(4)
C(15)	−0.2225(8)	−0.4179(6)	0.4878(8)	10.1(3)
C(16)	−0.2084(5)	−0.3776(4)	0.3842(6)	5.1(2)
C(17)	0.0415(4)	−0.0927(3)	0.3301(5)	3.5(1)
C(18)	0.1741(5)	−0.1038(4)	0.3449(6)	5.3(2)
C(19)	0.0012(5)	−0.0074(3)	0.3396(5)	4.6(2)
C(20)	-0.5291(6)	−0.3770(4)	−0.1014(6)	5.8(2)
C(21)	−0.4482(8)	−0.4185(5)	−0.1795(7)	8.3(3)
C(22)	−0.6485(6)	−0.4095(5)	−0.1330(7)	7.3(2)
C(23)	0.0148(4)	−0.2681(3)	0.3434(5)	3.0(1)
C(24)	0.1130(6)	−0.2723(4)	0.5656(5)	5.0(2)
C(25)	0.066(2)	−0.2055(7)	0.6267(8)	19.4(5)
C(26)	0.0824(8)	−0.3441(6)	0.6119(7)	8.8(3)
C(27)	0.2410(9)	−0.275(1)	0.573(1)	16.9(5)
C(28)	0.0671(5)	−0.2976(3)	0.0351(5)	4.0(1)
C(29)	−0.0414(5)	−0.3337(3)	−0.0043(5)	3.6(1)
C(30)	−0.0504(5)	−0.3895(3)	0.0758(5)	3.6(1)
C(31)	0.0506(5)	−0.3879(3)	0.1641(5)	4.2(1)
C(32)	0.1238(5)	−0.3309(4)	0.1390(5)	4.1(1)
C(33)	0.1156(6)	−0.2395(4)	−0.0265(6)	5.8(2)
C(34)	−0.1209(6)	−0.3247(4)	−0.1197(5)	5.4(2)
C(35)	−0.1405(6)	−0.4481(4)	0.0585(6)	5.5(2)
C(36)	0.0830(7)	−0.4448(4)	0.2583(6)	6.6(2)
C(37)	0.2475(5)	−0.3170(5)	0.2017(7)	6.8(2)
C(38)	−0.2613(5)	−0.0334(3)	0.0592(6)	4.3(1)
C(39)	−0.3573(4)	−0.0531(3)	0.1087(5)	3.8(1)
C(40)	−0.4035(4)	−0.1196(3)	0.0420(5)	3.4(1)
C(41)	−0.3355(5)	−0.1426(3)	−0.0462(5)	4.0(1)
C(42)	−0.2451(5)	−0.0896(4)	−0.0332(5)	4.3(1)
C(43)	−0.1943(6)	0.0390(4)	0.0891(7)	6.8(2)
C(44)	−0.4101(6)	−0.0064(4)	0.2008(6)	5.7(2)
C(45)	−0.5202(5)	−0.1504(4)	0.0439(6)	4.8(2)
C(46)	−0.3724(6)	−0.1967(4)	−0.1535(5)	5.9(2)
C(47)	−0.1601(6)	−0.0855(5)	−0.1150(6)	6.6(2)

[a] Numbers in parentheses are estimated standard deviations.

niques. Solvents were dried and distilled before use. ^1H NMR spectra were obtained on a JEOL GX-400 or EX-270 spectrometer, and IR spectra were recorded on a Shimadzu 8100M spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400II CHN analyzer or at the Elemental Analysis Laboratory, Department of Chemistry, The University of Tokyo.

Complex **1** was prepared in situ by treatment of $Cp^*Ru(\mu\text{-}OMe)_2RuCp^*$ [19] with Me_3SiSPr^i (2 equiv) and used directly for the subsequent reactions with alkynes. Yields of **3** and **4** were given on the basis of the amount of $Cp^*Ru(\mu\text{-}OMe)_2RuCp^*$. The reagents HC≡CTol, $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$, and Bu^tNC were commercially obtained and degassed prior to use.

Reaction of $Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*$ (1) with HC≡CTol To Form Dinuclear Metallacycle 3. To a THF (30 mL) solution of **1** prepared in situ from $Cp^*Ru(\mu\text{-}OMe)_2RuCp^*$ (1.07 g, 2.00 mmol) and Me_3SiSPr^i (644 mg, 4.35 mmol) was added HC≡CTol (732 mg, 6.32 mmol), and the mixture was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure, the resulting dark brown residue was dissolved in hexane and purified by chromatography through silica gel eluting with benzene/hexane (2/1). The solvent was evaporated from a single dark brown band to give **3** (470 mg, 24%). Single crystals suitable for the X-ray structural analysis were obtained by recrystallization from toluene−acetonitrile. ^1H NMR (C_6D_6, 400 MHz): δ 7.74, 7.15 (d, 2H each, J = 7.7 Hz, aryl), 7.32, 7.05 (d, 2H each, J = 7.8 Hz, aryl), 6.94, 6.86 (d, 2H each, J = 7.5 Hz, aryl), 6.49, 5.35 (s, 1H each, $\eta^2{:}\eta^3\text{-}\mu\text{-}CH_a(Tol)C\{C(Tol){=}C\mathit{H}_bSPr^i\}CH_cC(Tol)$ and H_c), 3.53, 2.78 (sep, 1H each, J = 6.7 Hz, $SC\mathit{H}Me_2$), 2.77 (s, 1H, H_a), 2.29, 2.20, 2.17 (s, 3H each, $C_6H_4\mathit{Me}$), 1.86, 1.68, 1.08, 0.99 (d, 3H each, J = 6.7 Hz, $SCH\mathit{Me}_2$), 1.36, 1.29 (s, 15H each, $C_5\mathit{Me}_5$). Anal. Calcd for $C_{53}H_{68}S_2Ru_2$: C, 65.53; H, 7.06; S, 6.60. Found: C, 65.27; H, 7.23; S, 5.81.

Table 9. Selected Bond Distances and Angles for 6[a]

Distances (Å)			
Ru(1)−Ru(2)	2.844(1)	Ru(1)−S(1)	2.341(1)
Ru(1)−C(1)	2.196(4)	Ru(1)−C(23)	1.891(5)
Ru(1)−C(28)	2.267(5)	Ru(1)−C(29)	2.307(5)
Ru(1)−C(30)	2.292(5)	Ru(1)−C(31)	2.230(5)
Ru(1)−C(32)	2.217(5)	Ru(2)−S(1)	2.266(1)
Ru(2)−C(1)	2.074(4)	Ru(2)−C(2)	2.219(5)
Ru(2)−C(38)	2.245(5)	Ru(2)−C(39)	2.242(5)
Ru(2)−C(40)	2.275(5)	Ru(2)−C(41)	2.285(5)
Ru(2)−C(42)	2.240(5)	S(1)−C(17)	1.850(5)
S(2)−C(20)	1.808(7)	N(1)−C(23)	1.160(6)
C(1)−C(2)	1.420(6)	C(1)−C(3)	1.504(6)
C(3)−C(4)	1.339(7)	C(5)−C(6)	1.332(6)
C(11)−C(12)	1.380(7)		
Angles (deg)			
Ru(2)−Ru(1)−S(1)	50.70(3)	Ru(2)−Ru(1)−C(1)	46.4(1)
Ru(2)−Ru(1)−C(23)	108.6(1)	S(1)−Ru(1)−C(1)	89.7(1)
S(1)−Ru(1)−C(23)	91.0(2)	C(1)−Ru(1)−C(23)	85.8(2)
Ru(1)−Ru(2)−S(1)	53.08(3)	Ru(1)−Ru(2)−C(1)	50.1(1)
Ru(1)−Ru(2)−C(2)	72.4(1)	S(1)−Ru(2)−C(1)	94.9(1)
S(1)−Ru(2)−C(2)	90.0(1)	C(1)−Ru(2)−C(2)	38.5(2)
Ru(1)−S(1)−Ru(2)	76.22(4)	C(23)−N(1)−C(24)	176.5(5)
Ru(1)−C(1)−Ru(2)	83.5(2)	Ru(1)−C(1)−C(2)	112.1(3)
Ru(1)−C(1)−C(3)	121.4(3)	Ru(2)−C(1)−C(2)	76.3(3)
Ru(2)−C(1)−C(3)	128.6(3)	Ru(2)−C(2)−C(1)	65.2(3)
Ru(2)−C(2)−C(5)	122.5(3)	C(2)−C(1)−C(3)	121.7(4)
C(1)−C(2)−C(5)	127.2(4)	C(1)−C(3)−C(4)	119.6(4)
C(1)−C(3)−C(11)	117.9(4)	C(4)−C(3)−C(11)	122.5(4)

[a] Numbers in parentheses are estimated standard deviations.

Reaction of $Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*$ (1) with $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ To Form Dinuclear Metallacycle 4. To a THF (30 mL) solution of **1** prepared in situ from $Cp^*Ru(\mu\text{-}OMe)_2RuCp^*$ (1.07 g, 2.00 mmol) and Me_3SiSPr^i (628 mg, 4.24 mmol) was added $HC{\equiv}C\overline{C{=}CH(CH_2)_3C}H_2$ (450 mg, 4.25 mmol), and the mixture was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure, the resulting dark brown residue was dissolved in hexane and purified by chromatography through silica gel eluting with benzene/hexane (2/1). The solvent was evaporated from a single dark brown band to give **4** (419 mg, 25%). Single crystals for X-ray structural analysis were obtained by recrystallization from benzene−acetonitrile. ^1H NMR (C_6D_6, 400 MHz, methylene protons in the cyclohexenyl groups omitted): δ 6.17 (s, 1H, $\eta^2{:}\eta^3\text{-}\mu\text{-}C\{C(\overline{C{=}CH_a(CH_2)_3C}H_2){=}C\mathit{H}_bSPr^i\}CH_cC\text{-}\{(CH_2)_3\overline{CH_2)\}C}H)$, 6.07 (br s, 1H, H_a), 4.13 (d, 1H, J = 1.2 Hz, H_c), 3.44, 3.23 (sep 1H each, J = 6.7 Hz, $SC\mathit{H}Me_2$), 1.79, 1.67 (s, 15H each, $C_5\mathit{Me}_5$), 1.78, 1.71, 1.42, 1.31 (d, 3H each, J = 6.7 Hz, $SCH\mathit{Me}_2$). Anal. Calcd for $C_{42}H_{64}S_2Ru_2$: C, 60.40; H, 7.72; S, 7.68. Found: C, 60.48; H, 7.62; S, 7.19.

Reaction of Dinuclear Metallacycle 3 with Bu^tNC To Form Diruthenium Complex 5. To a toluene (7 mL)

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solution of **3** (126 mg, 0.130 mmol) was added Bu^{t}NC (74 μL, 0.65 mmol), and the mixture was stirred at 80 °C for 12 h. The volatile materials were removed in vacuo, and the resulting solid was crystallized from toluene−MeOH to give **5**·$^1/_2$C$_7$H$_8$ as green crystals (115 mg, 80%). IR (KBr): ν(CN) 2062 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 8.02, 6.81 (d, 2H $J = 7.9$ Hz, aryl), 7.50, 7.46, 7.37, 7.35, (d, 1H each, $J = 7.9$ Hz, aryl), 7.11 (m, 4H, aryl), 6.46, 5.57, 2.30 (s, 1H each, η^1:η^2-μ-C(Tol)=CH_aC{C(Tol)=CH$_b$SPr^i}=CH$_c$Tol, H$_b$, and H$_c$), 2.99, 2.55 (br s, 1H each, SCHMe$_2$), 2.47, 2.11, 1.96 (s, 3H each, C$_6$H$_4$$Me$), 1.97, 1.54 (s, 15H each, C$_5$$Me_5$), 1.32, 1.28, 1.15, 1.00 (d, 3H each, $J = 6.7$ Hz, SCHMe_2), 1.09 (s, 9H, Bu^t). Anal. Calcd for C$_{61.5}$H$_{81}$NS$_2$Ru$_2$: C, 67.12; H, 7.42; N, 1.27. Found: C, 66.47; H, 7.53; N, 1.31.

Reaction of Dinuclear Metallacycle 4 with Bu^{t}NC To Form Diruthenium Complex 6. To a toluene (7 mL) solution of **4** (162 mg, 0.194 mmol) was added Bu^{t}NC (110 μL, 0.973 mmol), and the mixture was stirred at 80 °C for 12 h. The volatile materials were removed in vacuo, and the resulting solid was crystallized from toluene−MeOH to give **6** as greenish brown crystals (125 mg, 70%). IR (KBr): ν(CN) 2058 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz, methylene protons in the cyclohexenyl groups are omitted): δ 6.34 (s, 1H, η^1:η^2-μ-C{C(C=CH$_a$(CH$_2$)$_3$CH$_2$)=CH_bSPr^i}=CH{C=CH$_c$(CH$_2$)$_3$CH$_2$}), 6.30, 5.56 (br s, 1H each, H$_a$ and H$_c$), 3.33, 2.88 (sep, 1H each, $J = 6.7$ Hz, SCHMe$_2$), 1.95, 1.52 (s, 15H each, C$_5$$Me_5$), 1.76, 1.54, 1.45, 1.39 (d, 3H each, $J = 6.7$ Hz, SCHMe_2), 1.09 (s, 9H, Bu^t). The signal for the vinyl proton attached to the coordinated carbon−carbon double bond could not be assigned, which is presumably overlapping with the signals due to methylene protons. Anal. Calcd for C$_{47}$H$_{73}$NS$_2$Ru$_2$: C, 61.47; H, 8.01; N, 1.53. Found: C, 60.85; H, 8.11; N, 1.57.

Reaction of Dinuclear Metallacycle 4 with CO. Through a solution of **4** (181 mg, 0.217 mmol) in toluene (10 mL) was bubbled CO gas for 30 min at room temperature, and the solution was stirred at 80 °C under CO atmosphere for 6 h. During this period the color of the solution changed from dark brown to reddish orange. After removal of the solvent under reduced pressure, the resulting solid was dissolved in hexane and loaded on an activated alumina column. Elution with benzene/hexane (1/9) gave the uncharacterizable orange oily material (38 mg). A yellow band was successively obtained upon elution with THF/hexane (1/2), from which Cp*Ru(CO)$_2$SPr^i was isolated as yellow crystals (49 mg, 62%) after removal of the solvent followed by crystallization of the residue from hexane at −78 °C. IR (KBr): ν(CO) 2006, 1948 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 270 MHz): δ 3.10 (sep, 1H, $J = 6.6$ Hz, SCHMe$_2$), 1.61 (d, 6H, $J = 6.6$ Hz, SCHMe_2), 1.54 (s, 15H, C$_5$$Me_5$). Anal. Calcd for C$_{15}H_{22}O_2$SRu: C, 49.03; H, 6.03. Found: C, 49.46; H, 6.16.

X-ray Crystallographic Studies. Crystals suitable for the X-ray analysis were sealed in glass capillaries under Ar and mounted on a four-circle diffractometer equipped with a graphite monochromator. The data collection was performed at room temperature. Intensity data were corrected for the Lorentz−polarization effect and for absorption. Details of the X-ray crystallography for **3**, **4**, **5**·$^1/_2$C$_7$H$_8$, and **6** are summarized in Table 1. In all cases, structure solution and refinements by assuming space group $P1$ instead of $P\bar{1}$ were unsuccessful.

3 and 4. The orientation matrices and unit cell parameters were derived from a least-squares fit of 25 machine-centered reflections with 2θ values between 20 and 25°. Three check reflections measured every 100 reflections showed no significant decay during data collection. All calculations were performed by using the UNIX-III program package at the computer center of The University of Tokyo.[20] The Ru atoms were found by the direct-methods programs MULTAN (for **3**) or SHELXS-86[21] (for **4**). Subsequent cycles of block-diagonal least-squares refinements and difference Fourier maps revealed all non-hydrogen atoms, which were refined anisotropically. Hydrogen atoms were not included in the structure factor calculations of **3** and **4**.

5·$^1/_2$C$_7$H$_8$ and 6. Cell constants and orientation matrices for data collection were obtained from a least-squares fit of 25 machine centered reflections in the range $27 < 2\theta < 33°$ for **5**·$^1/_2$C$_7$H$_8$ or $39 < 2\theta < 40°$ for **6**. The intensities of three representative reflections were measured every 150 reflections, for which no significant decay was observed during data collection. Structure solution and refinements were performed by using the TEXSAN crystallographic software package.[22] The structures were solved by a combination of Patterson methods and Fourier techniques and refined by the use of full-matrix least-squares techniques. Hydrogen atoms were placed at the calculated positions and included in the refinements with fixed parameters. In the structure refinements of **5**·$^1/_2$C$_7$H$_8$, two methyl carbon atoms attached to C(31) in the SPr^i group were placed at the three disordered positions and refined as C(32), C(33), and C(34) with 75%, 75%, and 50% occupancies, respectively. In the final stages of the structure solution of **5**·$^1/_2$C$_7$H$_8$, three peaks were found in a difference Fourier map, which were assignable to the three independent ring carbon atoms in the toluene molecule packed at the crystallographic inversion center. However, isotropic refinements attempted for these three carbon atoms resulted in the increased distortion of the benzene core. Therefore these were not refined and included in the structure refinements as fixed contributors. The benzylic carbon atom in this toluene molecule could not be placed due to the high degree of disorder. Hydrogen atoms in the solvating toluene and that attached to C(31) in the disordered Pr^i group were not included in the refinements of the structure for **5**·$^1/_2$C$_7$H$_8$.

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Supporting Information Available: Tables of thermal parameters and complete bond distances and angles for **3**, **4**, **5**·$^1/_2$C$_7$H$_8$, and **6** and tables of hydrogen atom coordinates for **5**·$^1/_2$C$_7$H$_8$ and **6** (34 pages). Ordering information is given on any current masthead page.

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