solution was cooled until crystallization of **3** started (at ~25 °C); yield 0.078 g (90%) of orange-yellow crystals, mp 148 °C dec. ^{1}H NMR (C_6D_6): δ (ppm) 2.34 (s, 6 H, CH_3), 3.54 (d, ^2J(PH) = 16.61 Hz, 4 H, PCH), 6.85–6.98 (complex multiplet, total 12 H, m/p-C_6H_5), 7.38–7.46 (multiplet, ^3J(PH) = 11.60 Hz, 8 H, o-C_6H_5). ^{13}C{^{1}H} NMR (C_6D_6): δ (ppm) 30.61 (t, ^3J(PC) = 16.63 Hz, CH_3), 62.62 (d × d, ^1J(PC) = 110.72 Hz, ^3J(PC) = 5.38 Hz, PCH), 128.10–128.43 (complex multiplet, C_{meta}, AXX′), 128.92–129.95 (pseudotriplet, C_{para}, AXX′), 132.24–132.44 (complex multiplet, C_{ortho}, AXX′), 135.50 (d × m, ^1J(PC) = 89.5 Hz, C_{ipso}, AXX′), 164.15 (t, ^2J(PC) = 6.85 Hz, C-CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) 1.45 (s). MS (m/e, EI): 476 (M$^+$). Anal. Calcd for $C_{32}H_{30}P_2$·0.5Et$_2$O: C, 78.29; H, 6.76; P, 11.87. Found: C, 78.01; H, 6.24; P, 12.09.

Crystallography. A small part of a cubelike crystal of ether-solvated $C_{32}H_{30}P_2$ was mounted in a glass capillary and directly examined on the diffractometer. Geometric and intensity data were collected with an Enraf-Nonius CAD4 diffractometer. Pertinent crystallographic data are given in Table I. Lattice dimensions and Laue symmetry were determined from reflections 20.1 ≤ θ ≤ 21.6°. From systematic absences the space group was uniquely determined as $C2/c$. Intensity data (ω-scan) showed a significant decrease of 13.7% during the first hours (evaporation of Et$_2$O until saturation inside the closed capillary was reached) and were reduced by routine procedures.[17] The two phosphorus

atoms of the formula unit $C_{32}H_{30}P_2$ were located by direct methods (SHELXS-86),[17] and the remaining parts of the molecule in a series of least squares refinements and difference Fourier maps. The atoms of the solvent diethyl ether molecule (a half molecule in the asymmetric unit with a site occupancy 0.5 for the oxygen atom) were found by an alternating sequence of least squares refinements and difference Fourier maps. All hydrogen atoms (except for those on the slightly disordered diethyl ether molecule) could be found, and nearly all of them were refined isotropically. The methyl group at atom C(2) was found to be disordered over two sites and was refined satisfactorily with two sets of three 0.5 H atoms. This resulted in residuals R = 0.0456 and R_w = 0.0376 and an excellent difference Fourier map with all peaks well below 1 e Å^{-3}. The atomic positional parameters for the non-hydrogen atoms are listed in Table II. Supplementary material has been deposited.

(17) Calculations were done by using a Micro-Vaxstation 3100 M76 (Micro VMS V5.3) computer with the programs SHELXS-86 (structure solution), SHELX-76 (structure refinement), DELOS, LEPAGE (cell reduction), and the commerical package SDP/V V3.0.

Synthesis and Molecular Structure of a Dinuclear Ruthenium Dihydride Complex Containing a Perpendicularly Bridging Diphenylacetylene Ligand

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Summary: The reaction of a dinuclear tetrahydridoruthenium complex (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) (1) with 2 equiv of diphenylacetylene results in the formation of the dinuclear ruthenium dihydride complex (η^5-C_5Me_5)Ru(μ-H)$_2$(μ-PhCCPh)Ru(η^5-C_5Me_5) (2), which contains a perpendicularly bridging diphenylacetylene ligand. The complex crystallizes in the triclinic system, in space group $P\bar{1}$, with a = 10.284 (4) Å, b = 15.871 (4) Å, c = 10.286 (3) Å, α = 98.47 (3)°, β = 110.92 (2)°, α = 98.22 (3)°, V = 1515.8 (9) Å^3, and Z = 2. Anisotropic refinement of all atoms except hydrogen atoms converged to the residuals R = 0.0569 and R_w = 0.0539 for 6177 reflections.

Transition-metal polyhydride complexes have the potential for creating coordinative unsaturation by thermal induced or photoinduced reductive elimination of dihydrogen.[1] The coordination sites are also generated upon

reaction of polyhydride complexes with olefins. In such reactions, bulky, poorly coordinating, metalation-resistant olefin is used as a hydrogen acceptor. Crabtree et al. reported the dehydrogenation of cyclic alkanes by an Ir(III) complex in the presence of *tert*-butylethylene as a hydrogen acceptor.[2] Similar reactions involving Re(VII) complexes were discovered by Felkin and co-workers.[3] In the preceding communication, we reported that a dinuclear ruthenium tetrahydride-bridged complex, (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5),[4] reacted with ethylene to afford a dinuclear divinyl complex, (η^5-C_5Me_5)Ru(CH=CH$_2$)$_2$(CH$_2$=CH$_2$)Ru(η^5-C_5Me_5), via an activation of the C(sp^2)–H bond of ethylene.[5] In the early stage of this reaction, the ethylene molecule accepted two hydrogen

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atoms from the tetrahydride complex to yield ethane and a coordinatively unsaturated species, which underwent oxidative addition of ethylene leading to the divinyl complex.

We report herein the synthesis and the structure determination of a novel dinuclear ruthenium dihydride complex having a perpendicularly bridged diphenylacetylene ligand.

Results and Discussion

Treatment of the tetrahydride $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru\text{-}(\eta^5\text{-}C_5Me_5)$ (1) with 2 equiv of diphenylacetylene in toluene at room temperature produced a mixture of the 1:1 and 1:2 adducts 2 and 3, together with the hydrogenated products of diphenylacetylene *trans*-stilbene and bibenzyl, which were characterized by means of ^1H NMR spectroscopy and GC-mass spectrometry (eq 1). Formation of *trans*-stilbene and bibenzyl suggests that coordination sites were generated on the bimetallic complex through hydrogen transfer from 1 to diphenylacetylene.
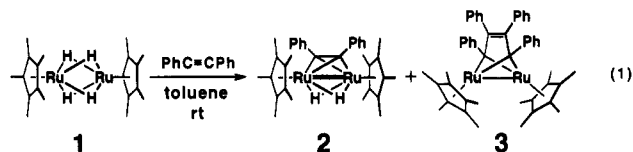
The reaction mixture was separated by column chromatography on neutral alumina with toluene. Crystallization from toluene/pentane afforded analytically pure $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}PhCCPh)Ru(\eta^5\text{-}C_5Me_5)$ (2) in a 35% yield as red needles. The 1:2 adduct 3 was also isolated as a dark brown solid in relatively low yield by chromatographic purification and subsequent crystallization from THF/toluene. The reaction of 1 with an excess amount (10 equiv) of diphenylacetylene resulted in the formation of a complex mixture of several products including 3 and a small amount of 2. From this result it can be concluded that the reaction rate of diphenylacetylene with the 1:1 adduct 2 is comparable to that with 3.

The field-desorption mass spectrum of 3 showed that complex 3 had the composition $C_{48}H_{50}Ru_2$. The intensities of the obtained isotopic peaks agreed well with the calculated values within the experimental error. The ^1H and ^{13}C NMR data for 3 showed two C_5Me_5 ligands to be equivalent. The ^{13}C NMR spectrum revealed eight signals for the phenyl groups and two singlets at δ 155.4 and 101.0 for the C_4 skeleton originated from acetylenic carbons. On the basis of these spectroscopic data, complex 3 could be identified as a dinuclear 1,2,3,4-tetraphenyl-1,3-butadiene complex in which both terminal carbons of diene ligand symmetrically bridged two ruthenium centers. A similar bis(μ-alkylidene) complex $[(C_5H_5)Cr]_2(\mu\text{-}CO)(\mu\text{-}C_4Ph_4)$ was previously reported by Knox et al.,[6] in which carbon-carbon double bond in the bridging C_4 unit was coordinated to one of the chromium centers.

The structure of complex 2 was also assigned on the basis of ^1H and ^{13}C NMR spectrometry, infrared spectroscopy, and elemental analysis. The ^1H resonance signals for the hydride and $\eta^5\text{-}C_5Me_5$ ligands were observed at δ -14.0 and 1.62, respectively, in a 1:15 intensity ratio. Characteristic resonances for the bridging acetylenic carbons were equivalently observed at δ 109.0 in the ^{13}C NMR spectrum, and the value was comparable with those reported for $Co_2(PhCCPh)(CO)_6$ (δ 89.2)[7] and Co_2-
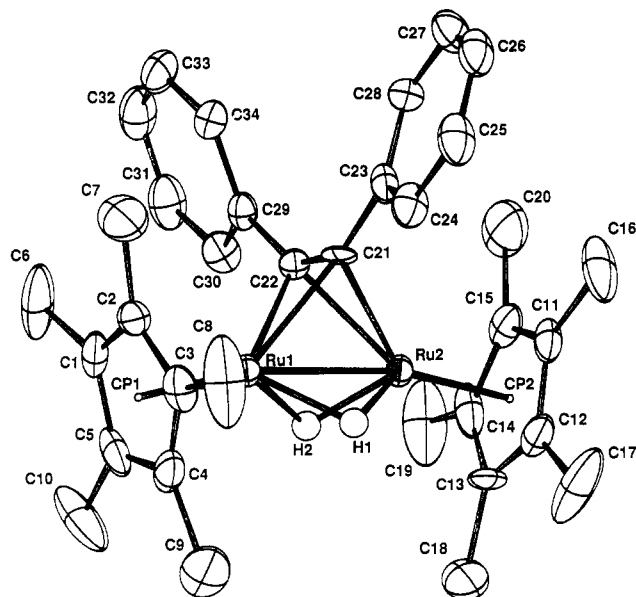

Figure 1. ORTEP view of complex 2 with the atomic labeling scheme.

Table I. Crystallographic Data for Complex 2

(A) Crystal Data	
formula	$Ru_2C_{34}H_{42}$
temp, °C	25
space group	$P\bar{1}$
a, Å	10.284 (4)
b, Å	15.871 (4)
c, Å	10.286 (3)
α, deg	98.47 (2)
β, deg	110.92 (2)
γ, deg	98.22 (3)
V, Å³	1515.8 (9)
mol wt	652.85
Z	2
ρ_{calc}, g/cm³	1.429

(B) Measurement of Intensity Data	
radiation (λ, Å)	Mo Kα (0.710 68)
monochromator	graphite
reflcns measd	$+h,+k,+l$
2θ scan range, deg	2-60
ω-scan width (A + 0.14 tan J) A	1.3
ω-scan rate, deg/min	6
no. of reflcns collcd	9333
no. of independent reflcns	8856
no. of data used ($F > 3\sigma F$)	6177
abs corr	none
abs coeff, cm^{-1}	9.98
P factor	0.01
final residuals	
R	0.0569
R_w	0.0539

$(PhCCPh)(CO)_6(PBu^n{}_3)$ (δ 89.6 and 91.7)[7] but more shielded than $(C_5H_5)_2Ru_2(PhCCPh)(CO)$ (δ 144.8).[8] Electron density at the bridging acetylenic carbons in 2 would increase due to the high donating ability of the C_5Me_5 group in comparison with those in $(C_5H_5)_2Ru_2\text{-}(PhCCPh)(CO)$. In contrast, the strong π-accepting CO ligand in the latter complex depresses the electron density at the acetylenic carbons.

Metal complexes containing bridging alkyne are abundant for most elements of the transition series, in which

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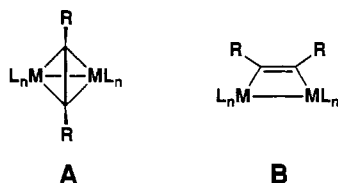
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Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Complex 2

atom	x	y	z	B(eq), Å²
CP(1)	1.01040 (0)	0.66133 (0)	0.90022 (0)	
CP(2)	0.60246 (0)	0.83918 (0)	0.48908 (0)	
Ru(1)	0.86918 (5)	0.71426 (2)	0.80354 (5)	2.75 (1)
Ru(2)	0.69643 (5)	0.78576 (2)	0.63089 (5)	2.77 (1)
C(1)	0.9233 (8)	0.6013 (5)	0.8977 (9)	4.6 (3)
C(2)	0.9842 (8)	0.6778 (6)	1.0037 (8)	4.9 (3)
C(3)	1.0789 (7)	0.7318 (5)	0.9673 (9)	4.4 (2)
C(4)	1.0807 (9)	0.6890 (6)	0.8391 (11)	6.5 (3)
C(5)	0.9850 (10)	0.6067 (6)	0.7934 (9)	5.4 (3)
C(6)	0.8158 (11)	0.5241 (7)	0.8954 (16)	10.3 (5)
C(7)	0.9552 (15)	0.6959 (9)	1.1387 (11)	10.6 (6)
C(8)	1.1804 (12)	0.8176 (7)	1.0614 (15)	10.1 (5)
C(9)	1.1799 (12)	0.7225 (10)	0.7601 (17)	13.2 (7)
C(10)	0.9555 (15)	0.5355 (8)	0.6658 (12)	10.5 (5)
C(11)	0.6036 (9)	0.8991 (5)	0.5766 (7)	4.4 (2)
C(12)	0.7054 (8)	0.8930 (5)	0.5163 (9)	4.7 (3)
C(13)	0.6667 (8)	0.8122 (6)	0.4192 (8)	5.1 (3)
C(14)	0.5383 (11)	0.7695 (6)	0.4187 (8)	5.4 (3)
C(15)	0.4984 (7)	0.8221 (6)	0.5147 (9)	5.1 (3)
C(16)	0.6028 (15)	0.9760 (6)	0.6827 (10)	9.5 (5)
C(17)	0.8343 (12)	0.9633 (9)	0.5427 (15)	11.4 (6)
C(18)	0.7384 (17)	0.7802 (10)	0.3246 (13)	13.9 (7)
C(19)	0.4390 (15)	0.6821 (7)	0.3191 (12)	9.8 (5)
C(20)	0.3589 (12)	0.8030 (9)	0.5471 (15)	10.9 (6)
C(21)	0.7266 (6)	0.7889 (4)	0.8496 (6)	2.8 (2)
C(22)	0.6501 (7)	0.7116 (4)	0.7751 (6)	3.1 (2)
C(23)	0.7291 (8)	0.8610 (4)	0.9593 (7)	3.6 (2)
C(24)	0.8526 (9)	0.9269 (5)	1.0293 (8)	4.4 (2)
C(25)	0.8537 (11)	0.9978 (5)	1.1289 (9)	5.8 (3)
C(26)	0.7330 (13)	1.0018 (6)	1.1597 (9)	6.8 (4)
C(27)	0.6100 (11)	0.9359 (6)	1.0900 (10)	6.1 (3)
C(28)	0.6045 (8)	0.8656 (5)	0.9893 (8)	4.4 (2)
C(29)	0.5412 (7)	0.6393 (4)	0.7708 (7)	3.2 (2)
C(30)	0.4711 (7)	0.5740 (5)	0.6476 (9)	4.3 (2)
C(31)	0.3707 (9)	0.5026 (5)	0.6467 (11)	5.7 (3)
C(32)	0.3407 (9)	0.4987 (6)	0.7675 (13)	6.7 (4)
C(33)	0.4102 (10)	0.5642 (6)	0.8910 (11)	6.2 (3)
C(34)	0.5094 (8)	0.6336 (5)	0.8933 (8)	4.6 (2)
H(1)	0.876 (7)	0.796 (5)	0.711 (7)	2.28
H(2)	0.763 (7)	0.704 (5)	0.614 (7)	2.28

Table III. Selected Bond Distances (Å) and Angles (deg) for Complex 2

CP(1)ᵃ-Ru(1)	1.835	CP(2)-Ru(2)	1.836
Ru(1)-Ru(2)	2.552 (1)	Ru(2)-C(21)	2.150 (7)
Ru(1)-C(21)	2.146 (7)	Ru(2)-C(22)	2.162 (7)
Ru(1)-C(22)	2.159 (7)	Ru(2)-C(11)	2.205 (8)
Ru(1)-C(1)	2.207 (8)	Ru(2)-C(12)	2.217 (9)
Ru(1)-C(2)	2.186 (8)	Ru(2)-C(13)	2.200 (9)
Ru(1)-C(3)	2.159 (7)	Ru(2)-C(14)	2.158 (7)
Ru(1)-C(4)	2.179 (10)	Ru(2)-C(15)	2.171 (8)
Ru(1)-C(5)	2.227 (10)	Ru(2)-H(1)	1.70 (7)
Ru(1)-H(1)	1.73 (8)	Ru(2)-H(2)	1.57 (8)
Ru(1)-H(2)	1.83 (7)	C(21)-C(22)	1.315 (8)
H(1)-H(2)	1.65 (9)		
CP(1)-Ru(1)-Ru(2)	168.07 (3)	CP(2)-Ru(2)-Ru(1)	167.11 (3)
Ru(1)-C(21)-Ru(2)	72.9 (2)	Ru(1)-C(22)-Ru(2)	72.4 (2)
Ru(1)-H(1)-Ru(2)	96 (4)	Ru(1)-H(2)-Ru(2)	97 (4)
C(21)-Ru(1)-C(22)	35.6 (2)	C(21)-Ru(2)-C(22)	35.3 (2)
Ru(1)-C(21)-C(23)	139.3 (4)	Ru(2)-C(21)-C(23)	129.6 (5)
Ru(1)-C(22)-C(29)	129.3 (5)	Ru(2)-C(22)-C(29)	138.6 (4)
Ru(1)-C(21)-C(22)	72.8 (5)	Ru(2)-C(21)-C(22)	72.7 (4)
Ru(1)-C(22)-C(21)	71.7 (4)	Ru(2)-C(22)-C(21)	71.8 (4)
C(21)-C(22)-C(29)	143.0 (7)	C(22)-C(21)-C(23)	140.6 (7)

ᵃ CP(x) is the centroid of the C_5Me_5 ligand.

C_{2v} symmetry. The Ru–Ru distance of 2.552 (1) Å is shorter than that for a Ru–Ru single bond and is close to the value of 2.505 (1) Å found in the molecule $(\eta^5\text{-}C_5H_5)$-$Ru(\mu\text{-CO})(\mu\text{-PhCCPh})Ru(\eta^5\text{-}C_5H_5)$.[8] The metal–metal bond distance cannot be a rigid criterion for determining the metal–metal bond order, but we tentatively adopted a structure having Ru–Ru double bond for the complex 2, as the 18-electron rule applied to the complex 2 required a metal–metal double bond between ruthenium centers. The C(21)–C(22) distance of 1.315 (8) Å was normal for alkynes that lie perpendicular to metal–metal bond in dinuclear complexes, in which typical C–C distances range from 1.3 to 1.4 Å.[8] The H(1)–H(2) distance of 1.65 (9) Å shows that there is no bonding interaction between the hydride ligands. The average Ru–C bond distance of 2.154 Å between acetylenic carbons and ruthenium atoms is consistent with those for π-bonded carbon–metal bonds. The C(21)–C(22)–C(29) and C(22)–C(21)–C(23) angles are 143.0 (7) and 140.6 (7)°, respectively, and the two phenyl groups on the acetylenic carbons are bent away from the ruthenium centers.

While the bridging alkyne ligand in $\{(C_3H_7{}^iO)_3P\}_2Rh(\mu\text{-}H)_2(\mu\text{-PhCCPh})Rh\{P(OC_3H_7{}^i)_3\}_2$ readily inserted into a Rh–H bond to result in the formation of a $\mu\text{-}\sigma,\pi$-vinylic complex,[10] such an alkyne insertion reaction did not occur even when complex 2 was heated in toluene at 40 °C for 2 h.

the alkyne lies either perpendicular to or parallel to the metal–metal axis (structure A or B).[8,9] The X-ray diffraction study of 2 confirmed the structure with the perpendicularly bridged alkyne ligand. Single crystals of 2 were grown from the mixed solvent of toluene and pentane. The results of the single-crystal X-ray diffraction study are displayed in Figure 1. Experimental parameters are given in Table I, and positional and thermal parameters, in Table II. Tables III lists some of the relevant bond distances and angles.

The diruthenium unit in complex 2 was bridged transversely by a diphenylacetylene ligand and also by two hydrides so that the central $Ru_2C_2H_2$ core had approximate

Experimental Section

Materials and Methods. All manipulations were carried out under an argon atmosphere with use of standard Schlenk techniques. Toluene and pentane were purified and distilled under argon prior to use according to established procedure.[11] Benzene-d_6 was dried over 4A molecular sieves under an atmosphere of argon and was vacuum-transferred into a storage vessel. Diphenylacetylene was purchased from commerical sources and used without further purification. Celite and the neutral alumina (Merck Art. 1097) used for column chromatography were deox-

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ygenated under vacuum prior to use.

Infrared spectra were recorded on a Hitachi 260-50 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a JEOL GX-270 instrument. Field-desorption mass spectra were measured on a Hitachi GC-MS M80 high-resolution mass spectrometer.

Elemental analysis was performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology.

$(\eta^5$-$C_5Me_5)Ru(\mu$-H$)_4Ru(\eta^5$-$C_5Me_5)$ was prepared according to the previously published method.[4]

Crystallographic Data Collection and Structure Refinement. A crystal was mounted on a glass fiber. Unit cell constants were determined from 25 machine-centered reflections. Data were collected with graphite-monochromated Mo $K\alpha$ radiation at ambient temperature with a Rigaku AFC-5 diffractometer. Data in the range of $2° < 2\theta < 60°$ were collected. Data processing was performed on a FACOM A-70 computer using the R-CRYSTAN structure solving program library obtained from the Rigaku Corp. The crystal of **2** belongs to the triclinic crystal system. The positions of the metal atoms were determined by heavy-atom methods. All non-hydrogen atoms and two bridging hydrogen atoms were located by subsequent difference Fourier synthesis. Ru and C atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were refined isotropically.

Reaction of $(\eta^5$-$C_5Me_5)Ru(\mu$-H$)_4Ru(\eta^5$-$C_5Me_5)$ (1) with Diphenylacetylene. Preparation of $(\eta^5$-$C_5Me_5)Ru(\mu$-H$)_2(\mu$-PhCCPh)Ru$(\eta^5$-$C_5Me_5)$ (2) and $(\eta^5$-$C_5Me_5)Ru($\mu$-PhCPhCCPhCPh)Ru$(\eta^5$-$C_5Me_5)$ (3). To a solution of $(\eta^5$-$C_5Me_5)Ru(\mu$-H$)_4Ru(\eta^5$-$C_5Me_5)$ (1) (0.405 g, 0.85 mmol) in toluene (5 mL) was added diphenylacetylene (0.303 g, 1.70 mmol) at room temperature. After being stirred for 12 h, the resulting reaction mixture was passed through a short column packed with Celite. Solvent was removed from the filtrate under reduced pressure to leave a dark brown solid. The ¹H NMR (60 MHz) spectrum of the residual solid in C_6D_6 showed the formation of complexes **2** and **3** in a 1.3:1 ratio, which was determined on the basis of the intensities of two singlet peaks at δ 1.62 and 1.54 ascribed to the

C_5Me_5 ligands. Purification of the dark brown residual solid by column chromatography on neutral alumina with toluene afforded **2** and **3** as maroon and dark brown solids, respectively. Crystallization from the mixed solvent of toluene and pentane gave **2** (0.193 g, 35%) as maroon needles. **2**: mp 196 °C; IR (KBr) 3063, 2959, 2887, 1694, 1587, 1488, 1379 cm⁻¹; ¹H NMR (C_6D_6, TMS) δ 7.75–7.23 (m, 10 H, *Ph*), 1.62 (s, 30 H, C₅*Me₅*), −13.98 (s, 2 H, Ru-*H*-Ru); ¹³C NMR (C_6D_6, TMS) δ 141.4 (s, *Ph-ipso*), 130.0 (d, J_{CH} = 159.0 Hz, *Ph*), 128.3 (d, J_{CH} = 157.3 Hz, *Ph*), 125.1 (d, J_{CH} = 159.0 Hz, *Ph*), 109.0 (s, *acetylenic*), 89.9 (s, C₅Me₅), 11.7 (q, J_{CH} = 125.4 Hz, C₅*Me₅*). Anal. Calcd for $C_{34}H_{42}Ru_2$: C, 62.55; H, 6.48. Found: C, 62.64; H, 6.75. Complex **3** obtained by means of column chromatography was inevitably contaminated by a small amount of **2**. Crystallization from the mixed solvent of tetrahydrofuran and toluene afforded **3** (0.099 g, 14%) as dark brown powder. **3**: ¹H NMR (C_6D_6, TMS) δ 7.64–6.71 (m, 20 H, *Ph*), 1.54 (s, 30 H, C₅*Me₅*); ¹³C NMR (C_6D_6, TMS) δ 155.4 (s, Ru-*C*-(Ph)-C(Ph)-), 147.6 (s, *Ph-ipso*), 138.5 (s, *Ph-ipso*), 131.4 (d, J_{CH} = 157.6 Hz, *Ph*), 131.3 (d, J_{CH} = 157.6 Hz, *Ph*), 127.5 (d, J_{CH} = 161.6 Hz, *Ph*), 127.1 (d, J_{CH} = 163.8 Hz, *Ph*), 126.0 (d, J_{CH} = 160.7 Hz, *Ph*), 124.8 (d, J_{CH} = 159.7 Hz, *Ph*), 101.0 (s, Ru-*C*(Ph)-*C*-(Ph)-), 88.1 (s, C₅Me₅), 11.2 (q, J_{CH} = 125.4 Hz, C₅*Me₅*). Anal. Calcd for $C_{48}H_{50}Ru_2$: C, 69.56; H, 6.04. Found: C, 69.23; H, 6.34. In the field-desorption mass spectrum of **3**, intensities of the obtained isotopic peaks for $C_{48}H_{50}Ru_2$ agreed with the calculated values within the experimental error.

Acetylene Insertion Reactions of the C,S and η^4 Isomers of Cp*Ir(2,5-dimethylthiophene) with MeSC≡CSMe and MeSC≡CMe. Formation of Novel Chelated Bicyclocarbene Complexes

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Summary: The reactions of Cp*Ir(C,S-2,5-Me₂T) (**2**) with the acetylenes MeSC≡CSMe and MeSC≡CMe give the bicyclocarbene insertion products **3** and **4**. The same

2   **3** (Y = SMe), **4** (Y = Me)
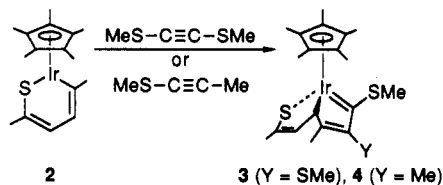
products are obtained from the reactions of these acetylenes with Cp*Ir(η^4-2,5-Me₂T) (**1**). The carbene–diene structure of **3** was established by an X-ray crystallographic study.

As part of our interest in the mechanism of thiophene hydrodesulfurization on heterogeneous catalysts,[2,3] we have

examined various modes of thiophene coordination and reactivity in model transition-metal complexes. In one of these studies, we observed[4,5] that Cp*Ir(η^5-2,5-Me₂T)²⁺, where Cp* = η^5-C₅Me₅ and 2,5-Me₂T = 2,5-dimethylthiophene, undergoes a 2-electron reduction to the neutral complex Cp*Ir(2,5-Me₂T) which has been isolated in two isomeric forms (eq 1); isomer 1, Cp*Ir(η^4-2,5-Me₂T), rearranges in the presence of bases to the more thermodynamically stable **2**, Cp*Ir(C,S-2,5-Me₂T). The sulfur in

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