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Carbon−Sulfur and Carbon−Phosphorus Bond Cleavage and Subsequent Carbon−Carbon Bond Formation Promoted by an Active Ruthenium(0) Species

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Reaction of $RuH_2(CO)(PPh_3)_3$ (**1**) with thiophene in the presence of styrene gives the novel diruthenium complex $(Ph_3P)(OC)Ru(\mu\text{-}(1Z,3Z)\text{-}PhCH{=}CHCH{=}CHS)(\mu\text{-}PPh_2)Ru(CO)(PPh_3)$ (**2**) with a unique bridging 4-phenyl-1,3-butadienethiolato moiety made up of the 1-thiapenta-2,4-dien-1,5-diyl and phenyl groups, which are derived from the thiophene and triphenylphosphine, respectively. Treatment of **2** on a preparative thin-layer chromatography plate of alumina or silica gel causes *Z*−*E* isomerization of the bridging moiety to give $(Ph_3P)(OC)Ru(\mu\text{-}(1Z,3E)\text{-}PhCH{=}CHCH{=}CHS)(\mu\text{-}PPh_2)Ru(CO)(PPh_3)$ (**5**). The molecular structures of **2** and **5** have been determined by X-ray structure analyses.

Introduction

Activation of thiophenes with transition-metal complexes in solution, modeled on the heterogeneous catalysts in the industrial hydrodesulfurization (HDS) process,[1] has been attracting a number of chemists in the fields of coordination and organometallic chemistry. Coordinatively unsaturated active transition-metal species react with thiophenes generally in two modes:[2] one is α-C−H bond cleavage of thiophenes to afford the corresponding 2-thienyl complexes and the other is insertion of the transition-metal species into the C−S bond of thiophenes to give the corresponding metallathiacyclohexadienes. The latter reaction is often followed by trapping another metal-containing molecule to produce dinuclear complexes with the bridging 1-thiapenta-2,4-diene-1,5-diyl moieties. Such dinuclear complexes formed through the thiophene activation have been reported for various transition metals of groups 6−10.[3−12] Since the most well-known industrial catalysts for heterogeneous HDS are a combination of molybdenum and the other late transition metals,[13] polynuclear (two to four metal centers) systems are expected to be adequate models for the thiophene activation.[14]

In previous reports, hydrogen subtraction from the dihydridoruthenium(II) complex $RuH_2(CO)(PPh_3)_3$ (**1**) with an olefin has been described to give a nascent $Ru^0{-}PPh_3$ species.[15] The $Ru^0{-}PPh_3$ species acts as "$Ru(CO)(PPh_3)_3$" to react with a wide range of organic compounds, including acetophenone, 2-phenylpyridine, and related species.[16] Especially, oxidative addition of the C−H bond in these compounds to the $Ru^0{-}PPh_3$ species is well-known as an important key step in C−H/olefin (Murai) coupling reactions.[16b,17] This highly active char-

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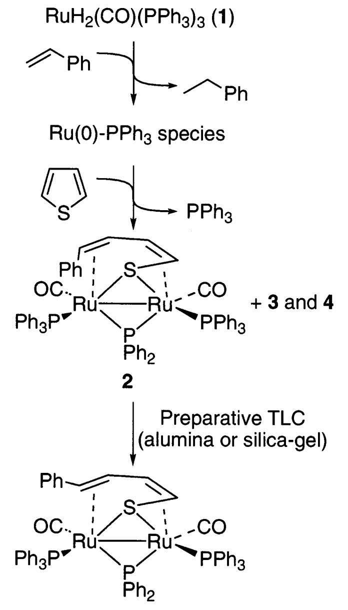
Scheme 1



acter of the Ru^0–PPh_3 species prompts us to examine how the Ru^0–PPh_3 species reacts with thiophenes, whether it be C–H cleavage to give thienyl complexes or metal insertion into the C–S bond to give metallacycles. Herein we report a novel reaction of the Ru^0–PPh_3 species with thiophene, including C–S and C–P bond cleavage and subsequent C–C bond formation, to give unprecedented μ-PPh_2 and μ-4-phenyl-1,3-butadienethiolato moieties. The X-ray crystal structure analyses of the resulting complexes show the formation of the interesting diruthenium complex $(Ph_3P)(OC)Ru(\mu\text{-}(1Z,3Z)\text{-}PhCH{=}CHCH{=}CHS)(\mu\text{-}PPh_2)Ru(CO)(PPh_3)$ (**2**) and its *Z*–*E* isomerization of the bridging thiolato moiety (Scheme 1).

Results and Discussion

The reaction was carried out by heating the benzene solution of **1** and thiophene in the presence of styrene as a hydrogen acceptor at 110 °C. Hydrogen subtraction from **1** gave the Ru^0–PPh_3 species within 30 min, but the subsequent reaction with thiophene took several hours for completion. The ^{31}P NMR spectra of the reaction mixture displayed formation of three product species (**2**–**4**) having one μ-PPh_2 moiety and two PPh_3 ligands in each molecule (see Experimental Section). On the basis of the ^{31}P signal intensities, the formation ratio of **2**–**4** was approximately 9:3:1. In addition, a large quantity of dissociated PPh_3 was also observed but no other significant P-containing byproduct was found.

The major product **2** was isolated in about 40% yield after repeated open-air column chromatographic separations on deactivated alumina. The use of deactivated alumina for the stationary phase was essential for the isolation of **2**. Using silica gel or activated alumina for the stationary phase, the products including **2** were strongly adsorbed on the stationary phase and somewhat converted into the complex **5**. As the spectroscopic characteristics, the complex **2** showed a bridging μ-PPh_2 signal at δ 121.2 and two nonequivalent ^{31}P doublets of the two coordinated PPh_3 ligands at δ 46.2 and 42.5. Four vinylic proton signals at the relatively high field of δ 5.79–3.31 suggested the presence of one thiophene or its derivative moiety. Two strong ν(CO) bands of the carbonyl ligands were observed. These spectroscopic data of **2** were consistent with the structure of $(Ph_3P)(OC)Ru(\mu\text{-}(1Z,3Z)\text{-}PhCH{=}CHCH{=}CHS)(\mu\text{-}PPh_2)Ru(CO)(PPh_3)$, which was disclosed through single-crystal X-ray analysis.

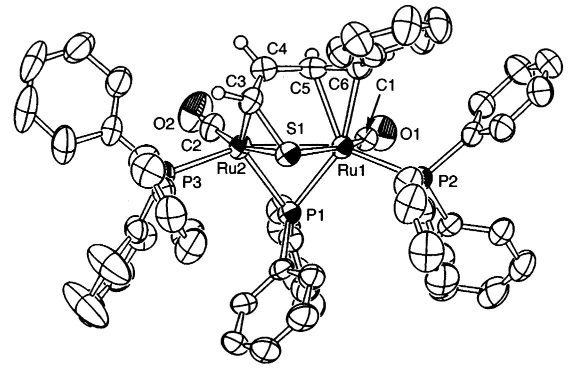


Figure 1. Perspective view of **2** with 30% probability thermal ellipsoids. Hydrogen atoms on the phenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1–Ru2 = 2.7481(7), Ru1–S1 = 2.480(1), Ru2–S1 = 2.407(1), Ru1–P1 = 2.364(1), Ru2–P1 = 2.300(1), Ru1–P2 = 2.355(1), Ru2–P3 = 2.304(1), Ru1–C1 = 1.841(5), Ru2–C2 = 1.833(6), C1–O1 = 1.150(6), C2–O2 = 1.166(7), S1–C3 = 1.768(6), C3–C4 = 1.405(8), C4–C5 = 1.457(8), C5–C6 = 1.413(8); Ru1–S1–Ru2 = 68.42(3), Ru1–P1–Ru2 = 72.20(4), S1–C3–C4 = 118.4(4), C3–C4–C5 = 122.7(5), C4–C5–C6 = 128.3(5), C5–C6–C7 = 130.4(5).

The complex **2** retained a unique bridging μ-(1*Z*,3*Z*)-4-phenyl-1,3-butadienethiolato moiety, as shown in Figure 1. The μ-PPh_2 moiety also bridged between the two ruthenium centers. Each ruthenium center was coordinated with one PPh_3 and one CO ligand. Both ruthenium centers were considered to be Ru(I), and the Ru–Ru distance of 2.7481(7) Å fell within the range 2.558–2.873 Å for the reported singly bonded Ru(I)–Ru(I) complexes.[18] The C3=C4 and C5=C6 lengths were 1.405(8) and 1.413(8) Å, respectively, being fairly larger than the ordinary C=C bond length. The large C=C bond lengths indicated that these double bonds were π-coordinated to the ruthenium atoms. In contrast, the S1–C3 bond length was 1.768(6) Å, which is almost the same as the S–C bond length in uncomplexed free thiophene (1.78 Å). The 34 total valence electrons corresponded to a coordinatively saturated diruthenium core with one Ru–Ru bond.

The molecular structure of **2** indicated the cleavage of both a C–S bond of thiophene and a C–P bond of PPh_3 by the active Ru^0–PPh_3 species and subsequent

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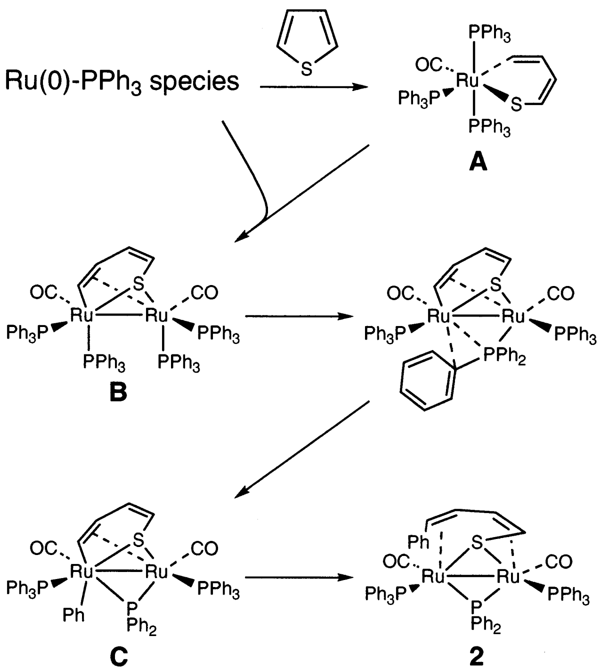
Scheme 2



formation of a new C−C bond between the resulting 1-thiapenta-2,4-diene-1,5-diyl group and the phenyl group to afford the μ-4-phenyl-1,3-butadienethiolato moiety. The following experiments revealed some features of the formation of the dinuclear complex **2**. First, when thiophene was added to a mixture of the active Ru^0-PPh_3 species and **1**, the Ru^0-PPh_3 species was completely converted into a combination of **2**−**4**, while **1** entirely remained. This fact indicates that the dihydride complex **1** did not participate in the formation of **2** and the other dinuclear complexes. Second, when the formation of **2** was carried out in C_6D_6, the ^1H NMR signals in the aromatic region agreed with those of the authentic **2**; no C_6D_5 moiety was incorporated into the μ-4-phenyl-1,3-butadienethiolato moiety. Intramolecular C−P cleavage and C−C bond formation are indicated.

A plausible mechanism for the formation of **2** is shown in Scheme 2 on the basis of the experimental results described above. It is reasonable to assume the intermediary ruthenathiacyclohexadiene species **A**, in consideration of the related examples reported for many transition-metal complexes.[19] The dinucleation between **A** and the Ru^0-PPh_3 species follows to give the diruthenium intermediate **B**, having a frequently reported bridging 1-thiapenta-2,4-diene-1,5-diyl moiety.[3−12] In the formation of **2**, however, the C−P bond of one PPh_3 ligand is successively activated to give the μ-PPh_2 moiety on the diruthenium core, and finally, reductive elimination and a new C−C bond formation on **C** afforded the 4-phenyl-1,3-butadienethiolato moiety. Therefore, the phenyl group is transferred from the PPh_3 ligand to the bridging 1-thiapenta-2,4-dien-1,5-diyl group intramolecularly. Suzuki et al. reported a related reaction sequence for the activation of the C−P bond of PPh_3 and the C−H bond formation to afford C_6H_6 on a diruthenium complex.[20] It is noteworthy that the 1*Z*,3*Z*-configuration of the 1,3-butadienethiolato moiety retained the original cis,cis configuration of the thiophene ring frame, implying that no *Z*−*E* conversion around the C=C bond occurred in the course of the C−S and C−P bond cleavage and subsequent C−C bond formation.

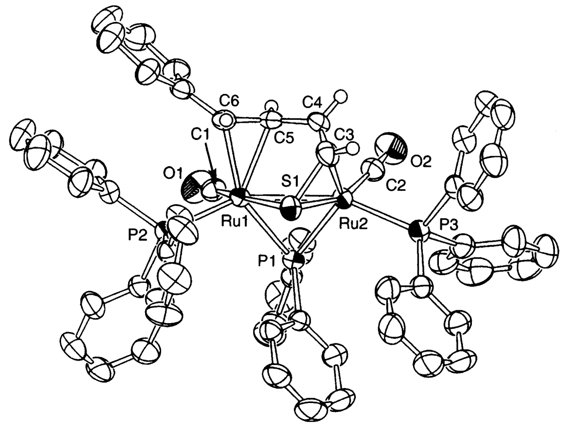


Figure 2. Perspective view of **5** with 30% probability thermal ellipsoids. Hydrogen atoms on the phenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Ru2 = 2.7620(4), Ru1−S1 = 2.456(1), Ru2−S1 = 2.408(1), Ru1−P1 = 2.359(1), Ru2−P1 = 2.299(1), Ru1−P2 = 2.352(1), Ru2−P3 = 2.309(1), Ru1−C1 = 1.837(4), Ru2−C2 = 1.848(4), C1−O1 = 1.153(5), C2−O2 = 1.153(5), S1−C3 = 1.758(4), C3−C4 = 1.358(6), C4−C5 = 1.466(6), C5−C6 = 1.425(6); Ru1−S1−Ru2 = 69.19(3), Ru1−P1−Ru2 = 72.72(3), S1−C3−C4 = 118.5(3), C3−C4−C5 = 123.1(4), C4−C5−C6 = 123.0(4), C5−C6−C7 = 121.9(4).

Unfortunately, all efforts to isolate and purify the minor products **3** and **4** were unsuccessful. Two minor products were not separated from each other, and moreover, a small amount of **2** was not removed completely from the products. Therefore, exact yields for **3** and **4** have not been determined so far. Only NMR spectra of the mixtures of **3** and **4** in various ratios were measured, and their NMR spectroscopic data resembled those of **2** except for upfield shifts of some phenyl protons. These NMR features indicated that **3** and **4** also had the bimetallic structure with the bridging μ-PPh_2 moiety.

The complex **2** in solution was stable in air to heating and UV irradiation. When an excess amount of *p*-toluenesulfonic acid or benzoic acid was added to the solution of **2**, nothing changed. Bubbling H_2 or CO at room temperature into the solution of **2** caused no reaction, and even the alkene part of the 4-phenyl-1,3-butadienethiolato moiety was not hydrogenated. In contrast, when **2** was applied to preparative thin-layer chromatography (preparative TLC) with alumina or silica gel, it was unexpectedly converted into another complex, **5**, whose NMR spectroscopic data were closely similar to those of **2**. The molecular structure of **5** determined by X-ray analysis is shown in Figure 2. The bridging μ-(1*Z*,3*Z*)-4-phenyl-1,3-butadienethiolato moiety was found to be isomerized into the μ-(1*Z*,3*E*)-4-phenyl-1,3-butadienethiolato group. On comparison of these two structures, the isomerization of the *Z* form to the *E* form around the C5=C6 bond reduced the steric repulsion between the phenyl ring of the thiolato moiety and the phosphine bound to the Ru1 atom in **2**. Because

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of this steric repulsion, the Ru1−C5 and Ru1−C6 lengths of **2** (2.261(5) and 2.309(5) Å, respectively) were larger than those of **5** (2.232(4) and 2.252(4) Å, respectively), and the C4−C5−C6 and C5−C6−C7 angles of **2** (128.3(5) and 130.4(5)°) were far larger than the ideal value, 120°. After the isomerization, the corresponding angles became closer to 120° (123.0(4) and 121.9(4)°, respectively). Except for the steric hindrance around the Ru1 atom due to the configuration of the μ-4-phenyl-1,3-butadienethiolato moiety, there was no significant difference between the $[Ru_2(\mu\text{-}PPh_2)(CO)_2(PPh_3)_2]$ cores of **2** and **5**.[21]

Table 1. Crystallographic Data for 2 and 5

	2·$0.5C_6H_6$	**5**
chem formula	$C_{60}H_{49}O_2P_3Ru_2S \cdot 0.5C_6H_6$	$C_{60}H_{49}O_2P_3Ru_2S$
fw	1168.22	1129.17
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	14.174(2)	12.879(2)
b/Å	18.277(2)	19.454(4)
c/Å	11.229(1)	11.121(1)
α/deg	98.509(9)	97.72(1)
β/deg	112.161(9)	104.757(10)
γ/deg	92.57(1)	103.20(2)
V/Å^3	2648.1(6)	2567.7(7)
Z	2	2
D_{calcd}/g cm^{-3}	1.465	1.460
F(000)	1190.00	1148.00
μ(Mo Kα)/cm^{-1}	7.45	7.66
no. of data collected	12 679	12 311
no. of unique data	12 185	11 787
R_{int}	0.026	0.039
transmissn range	0.8112−0.8616	0.9121−0.9991
no. of params	649	619
R1[a]	0.044 for 7579 obsd ($I > 2\sigma(I)$)	0.037 for 7618 obsd ($I > 2\sigma(I)$)
R[b]	0.089 for all data	0.073 for all data
wR2[c]	0.157 for all data	0.107 for all data
goodness of fit[d]	1.20	1.01

[a] $\sum||F_o| - |F_c||/\sum|F_o|$. [b] $\sum(F_o^2 - F_c^2)/\sum F_o^2$. [c] $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [d] $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

Experimental Section

General Comments. Reactions were generally carried out in sealed glass tubes under reduced pressures. Most manipulations were performed under a dry, oxygen-free atmosphere using Schlenk-type flasks or in a glovebox. The starting dihydride complex $[RuH_2(CO)(PPh_3)_3]$ (**1**) was prepared by procedures slightly modified from those in the literature.[16,22] Styrene was distilled under reduced pressure prior to use to remove the inhibitor. Deactivated alumina for column chromatography was prepared by mixing appropriate amounts of water and Merck aluminum oxide 90 (activity I); the final water content was adjusted to about 10−15% w/w (Brockmann's activity IV−V). Alumina and silica gel preparative TLC plates (20 cm × 20 cm, 2 mm thickness) were used as purchased from Merck. All other reagents are commercially available and were used without further purification. Solvents were dried and purified in the usual manner and stored under an atmosphere of nitrogen. Infrared spectra were recorded on a JASCO FT-IR 420 spectrometer using KBr disks. All NMR spectra were recorded on a JEOL GX-400 spectrometer.

[(Ph$_3$P)(OC)Ru(μ-(1*Z*,3*Z*)-PhCH═CHCH═CHS)(μ-PPh$_2$)-Ru(CO)(PPh$_3$)] (2). In a reaction tube complex **1** (600 mg, 0.65 mmol), styrene (411 mg, 3.95 mmol), and thiophene (340 mg, 4.04 mmol) were sealed with benzene (15 mL) under vacuum. The mixture was allowed to react at 110 °C for 3 h. After the reaction mixture was transferred to a Schlenk tube, benzene was removed under reduced pressure at room temperature. The NMR spectra of the residual solid showed the signal sets of three products (**2**−**4**). On the basis of the ^{31}P signal intensities, the formation ratio of the products **2**−**4** was approximately 9:3:1, respectively.

Selected NMR data for **3** are as follows. ^1H NMR (C_6D_6): δ 6.13 (t, phenyl H), 5.91 (t, phenyl H), 5.50 (m, vinyl H), 4.84 (m, overlapped, phenyl H and vinyl H), 4.68 (m, vinyl H), 2.97 (m, vinyl H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 138.5 (s, μ-PPh$_2$), 60.2 (d, $^3J_{PP} = 29$ Hz, PPh$_3$), 46.7 (d, $^3J_{PP} = 29$ Hz, PPh$_3$). Selected NMR data for **4** are as follows. ^1H NMR (C_6D_6): δ 6.02 (t, phenyl H), 5.30 (m, overlapped, phenyl H and vinyl H), 4.88 (m, vinyl H), 3.63 (m, vinyl H), 2.66 (m, vinyl H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 153.6 (s, μ-PPh$_2$), 53.2 (d, $^3J_{PP} = 29$ Hz, PPh$_3$), 51.7 (d, $^3J_{PP} = 29$ Hz, PPh$_3$). The other phenyl proton signals were overlapped in the aromatic region of δ 8.5−6.5.

The red residual solid was applied to open-air column chromatography on deactivated alumina (activity IV−V; eluent benzene/hexane (1:1)). After repeated purification by column chromatography, the major product **2** was isolated (146 mg, 39% yield based on Ru) as an orange-red solid.

IR (KBr): 1926 (s, ν(C≡O)), 1902 cm^{-1} (s, ν(C≡O)). ^1H NMR (C_6D_6): δ 8.2−6.5 (m, overlapped, phenyl H), 5.79 (m, vinyl H), 5.56 (m, vinyl H), 4.43 (m, vinyl H), 3.31(m, vinyl H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 121.2 (s, μ-PPh$_2$), 46.2 (d, $^3J_{PP} = 19$ Hz, PPh$_3$), 42.5 (d, $^3J_{PP} = 19$ Hz, PPh$_3$). FAB-MS: m/z 1129 $[M - 1]^+$. Anal. Calcd for $C_{60}H_{49}O_2P_3Ru_2S \cdot 0.5C_6H_6$: C, 64.77; H, 4.49; S, 2.74. Found: C, 64.72; H, 4.69; S, 2.67.

[(Ph$_3$P)(OC)Ru(μ-(1*Z*,3*E*)-PhCH═CHCH═CHS)(μ-PPh$_2$)-Ru(CO)(PPh$_3$)] (5). In a reaction tube the complex **1** (201 mg, 0.22 mmol), styrene (138 mg, 1.33 mmol), and thiophene (104 mg, 1.24 mmol) were sealed with benzene (5 mL) under vacuum. The mixture was allowed to react at 110 °C for 3 h. After the reaction mixture was transferred to a Schlenk tube, benzene was removed under reduced pressure at room temperature. The red residue was dissolved in benzene and the solution passed through a column of deactivated alumina (the activity IV−V; eluent CH_2Cl_2/hexane (1:3)). A red fraction was collected to afford 174 mg of a ruthenium-containing dark red solid. The solid was applied to a silica gel preparative TLC plate and was developed three times by dipping the bottom end of the plate in the eluent of benzene/hexane (1:2). After the third development, a yellow band appeared slightly above the starting point, while a reddish brown band remained at the starting point. The yellow band was extracted with CH_2Cl_2/MeOH (10:1) three times. The removal of the solvents under reduced pressure gave 43 mg of **5** as a yellow solid (yield 35%). The reddish brown band was so strongly adsorbed on the plate that any single compound could not be collected.

Although only unsatisfactory elemental analysis data for **5** have been obtained, the MS data for **5** and the results of the *Z*−*E* isomerization and the X-ray structure analysis (vide infra) confirmed the composition of **5**.

IR (KBr): 1925 (s, ν(C≡O)), 1906 cm^{-1} (s, ν(C≡O)). ^1H NMR (C_6D_6): δ 8.3−6.5 (m, overlapped, phenyl H), 5.86 (m, vinyl H), 4.95 (m, vinyl H), 4.48 (m, vinyl H), 2.40 (m, vinyl H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 103.8 (s, μ-PPh$_2$), 46.6 (d, $^3J_{PP} = 29$ Hz, PPh$_3$), 42.4 (d, $^3J_{PP} = 29$ Hz, PPh$_3$). FAB-MS: m/z 1129 $[M - 1]^+$.

***Z*−*E* Isomerization of 2 into 5.** A solution of complex **2** (6.9 mg, 0.22 mmol) in a solvent mixture (5 mL) of benzene and hexane (1:2) was applied to a silica gel preparative TLC plate. After the second development using a benzene/hexane (1:2) eluent, the yellow band of **5** appeared and the rest of **2** was adsorbed at the starting point on the TLC plate. The yellow band was extracted with CH_2Cl_2/MeOH (10:1) three times. The removal of the solvents under reduced pressure gave 5.3 mg of a yellow solid of **5** (yield 77%). The NMR spectra

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[21] Interestingly, in the $^{31}P\{^1H\}$ NMR spectra of all dimeric complexes **2**−**5** the terminal PPh$_3$ resonances appear as doublets with $^3J_{PP} > 19$ Hz, while the μ-PPh$_2$ signals appear as slightly broad singlets with negligible $^2J_{PP}$ values. We have no reasonable explanation for this strange spin interaction between the two terminal P nuclei through the P−Ru−Ru−P structure.

[22] Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

of the solid showed the *Z*−*E* isomerization from **2** to **5**. Use of an alumina plate in place of silica gel gave similar results.

Structural Determination of 2 and 5. Crystallographic data and details of the diffraction measurement are summarized in Table 1. Recrystallization of **2** and **5** from benzene/hexane gave single crystals suitable for X-ray structural analyses, respectively, and the crystals of **2** were obtained as a benzene hemisolvate (**2**·$0.5C_6H_6$). Crystals used for the measurements were glued on a glass fiber. Data collection was carried out at 296 K. Cell constants were obtained from the least-squares refinement of the setting angles of 25 reflections in the range $26.08° \leq 2\theta \leq 31.07°$ for **2**·$0.5C_6H_6$, while the range was $25.79° \leq 2\theta \leq 29.58°$ for **5**. An empirical absorption correction was applied for each of the reflection data for **2**·$0.5C_6H_6$ and **5** based on the azimuthal scans of several reflections. All data were corrected for Lorentz and polarization effects.

The crystal structures were solved by direct methods[23,24] and expanded using Fourier techniques.[25] A full-matrix least-squares refinement on F^2 was used. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms H(2)−H(4) for **2** and H(1)−H(4) for **5** were located on the basis of the difference Fourier maps, and their positions were refined, but their isotropic thermal parameters were fixed. The other hydrogen atoms were included but not refined. The benzene molecule in the crystal **2**·$0.5C_6H_6$ was located on a center of inversion of the lattice, and only the three carbon atoms C(61), C(62), and C(63) were refined for a half of the benzene under the restraint on the structure of the idealized geometry.

Neutral atom scattering factors, corrected for anomalous dispersion, were taken from the literature.[26] All calculations were performed on a Rigaku RASA-7 automatic structure analysis system using the teXsan crystallographic software package.[27]

Supporting Information Available: Complete crystallographic data for **2**·$0.5C_6H_6$ and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. The same data as CIF files have also been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 177819 and 177820, which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk). Tables of structure factors are available from the authors upon request.

OM020127S

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