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A New Heterobimetallic Ru,Rh Complex with a Dianionic Pentalene as Bridging Ligand. Synthesis, Crystal Structure, and Catalytic Activity of [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)]

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The heterobimetallic complex [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)] (**2**) is synthesized and characterized spectroscopically and structurally. The structure of this compound exhibits the two metal centers bonded in an anti disposition to the pentalenyl ligand. The displacement of the coordinated COD by carbon monoxide is studied. The bimetallic complex shows a high activity and selectivity for the dehydrogenative silylation of styrene.

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Introduction

Recently organometallic chemistry of bimetallic systems has become an area of great interest. Many of these complexes have been shown to possess unique properties, such as charge transfer, conductivity, and nonlinear optical behavior.[1] On the other hand, the applications to stoichiometric and catalytic reactions appear very attractive because bimetallic complexes may have higher reaction rates and could lead to transformations that do not occur on mononuclear species.[2]

One of the most interesting types of ligands to study in binuclear organometallic complexes consists of fused aromatic rings. These ligands may connect two or more organometallic centers (which may have different oxidation states) and allow interaction between them.[3] A common assumption is that cooperative interaction between the two metal centers might cause significant increase in the reaction rates. Examples of enhanced reaction rates were reported by Ceccon[4] with complexes of the type [$(CO)_2$Rh(indenyl)Cr$(CO)_3$], where the substitution of CO by COD or NBD (COD = 1,5-cyclooctadiene; NBD = norbonadiene) at the Rh center was shown to be 2000 times faster than in the complex [$(CO)_2$Rh(indenyl)]. This large rate enhancement was ascribed to the simultaneous coordination of the two inorganic units (12e) to the same fused aromatic ligand (10eπ). This sets up an electronic structure where both metals exhibit an overall coordinative unsaturation. It was suggested by the authors that a plausible mechanism involves a rate-determining step addition of the bidentate diolefin to produce a η^1 species from which the loss of two CO's to restore the η^5 coordination occurs in a subsequent fast step. Reports of the enhancement

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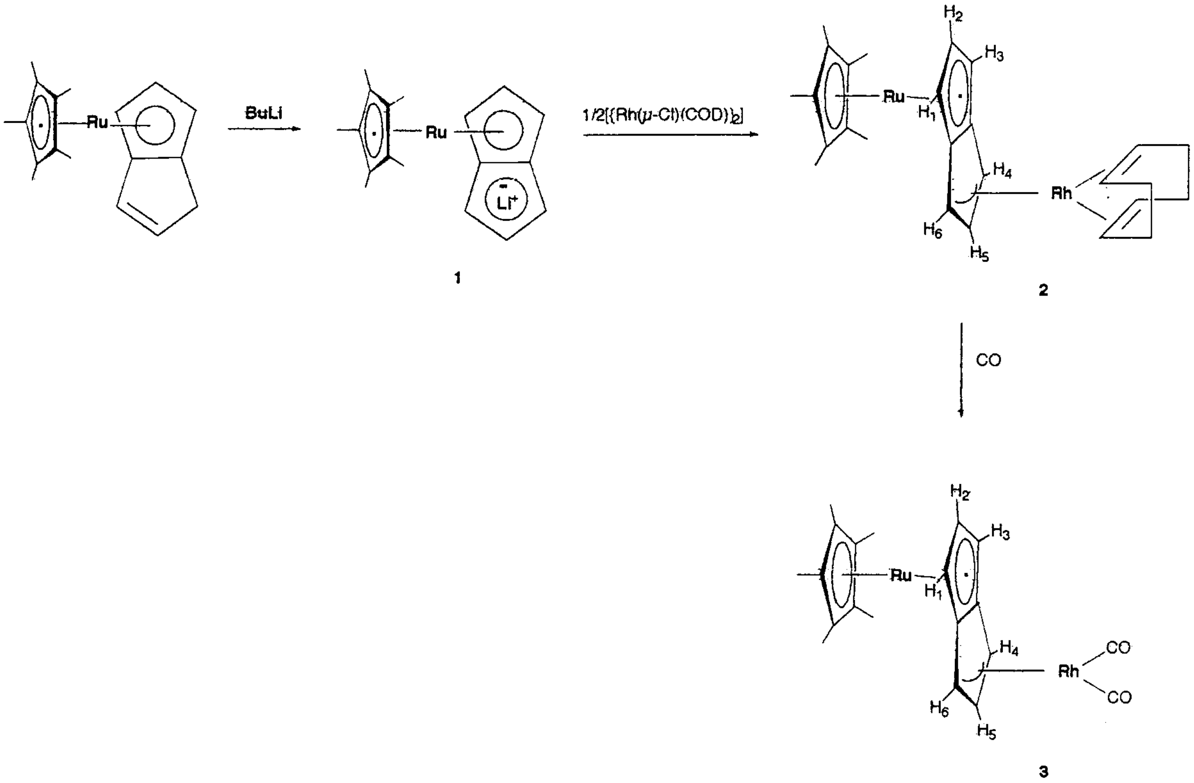
Chart 1



of the rate of exchange have also been found in naphthalene,[5] *s*-indacene, and *as*-indacene bimetallic complexes.[6]

Another particularly interesting type of fused rings system is the dianionic pentalene,[7] a 10 π-electron ligand which has been used to synthesize selectively homo- and heterobinuclear metallocene species. The [Cp*Fe(pentalenyl)FeCp*]$^+$ (Cp* = C_5Me_5) complexes have shown a strong electronic interaction between both metal centers, exhibiting a complete electronic delocalization through the pentalenyl ligand.[3,8,9]

There is a considerable variety of organorhodium(I) compounds in the literature, and most of them have been reported to be active homogeneous catalysts.[10] A search in the chemical literature reveals no binuclear pentalenyl compounds containing rhodium as metal center. However, the synthesis and characterization of the mononuclear complex [Rh(η^4-COD)(η^5-pentalenyl)] has been previously described.[11]

Following our interest in the synthesis and properties of binuclear metallocenes with pentalene, we report the preparation, the reactivity, and the X-ray characterization of the new heterobinuclear complex [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)]. We also describe its behavior as catalyst precursor for the dehydrogenative silylation of styrene.

Results and Discussion

We have recently reported the synthesis of the ruthenium(II) pentalenyl complex [Cp*Ru(η^5-C_8H_7)].[12] This compound reacts, in tetrahydrofuran solution at −80 °C, with a stoichiometric amount of *n*-butyllithium in hexane and leads to the uncharacterized intermediate lithium compound [Cp*Ru(η^5-C_8H_6)Li] (**1**), which in turn reacts with [{Rh(μ-Cl)(η^4-COD)}$_2$] to give the heterobimetallic 34-electron complex [Cp*Ru(μ-C_8H_6)Rh(η^4-COD)] (**2**).Complex **2** is isolated as an orange solid, soluble in pentane, toluene, dichloromethane, and THF and stable to air and moisture. The ^{1}H NMR characterization of the bimetallic complex **2** is proposed from the variations of the spectrum observed on complexing the starting compound [Cp*Ru(η^5-C_8H_7)]. In fact, the spectrum of the mononuclear ruthenium complex exhibits a doublet and a triplet signal for the metal-coordinated ring protons. A similar pattern is observed in compound **2**, showing a doublet resonance at δ 4.25 [$^3J(H_2H_{1,3}) = 2.1$ Hz] and a doublet of triplets at δ 4.12 ppm [$^6J(H_2H_5) = 0.45$ Hz], assigned to equivalents $H_{1,3}$ and H_2, respectively. As expected, upon complexation of the rhodium atom, the protons $H_{4,5,6}$ appear shifted upfield and are observed at δ 4.38 and 5.84 ppm for $H_{4,6}$ and H_5, respectively. The resonance assigned to the H_5 proton appears as a doublet of quartets due to the couplings H_5−$H_{4,6}$ ($^3J = 2.8$ Hz), H_5−H_2 ($^6J = 0.45$ Hz), and ^{103}Rh−H_5 ($^2J = 2.8$ Hz). This pattern of signals is

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[7] (a) Katz, T. J.; Rosenberguer, M. *J. Am. Chem. Soc.* **1962**, *89*, 1105. (b) Katz, T. J.; Rosenberguer, M.; O'Hara, K. *J. Am. Chem. Soc.* **1964**, *86*, 249. (c) Katz. T. J.; Rosenberguer, M. *J. Am. Chem. Soc.* **1963**, *85*, 2031. (d) Oelkers, B.; Chávez, I.; Manriquez, J. M.; Román, E. *Organometallics* **1993**, *12*, 3396. (e) Garland, M. T.; Saillard. I.; Chávez I.; Oëlckers B.; Manriquez J. M. *THEOCHEM* **1997**, *390*, 199.

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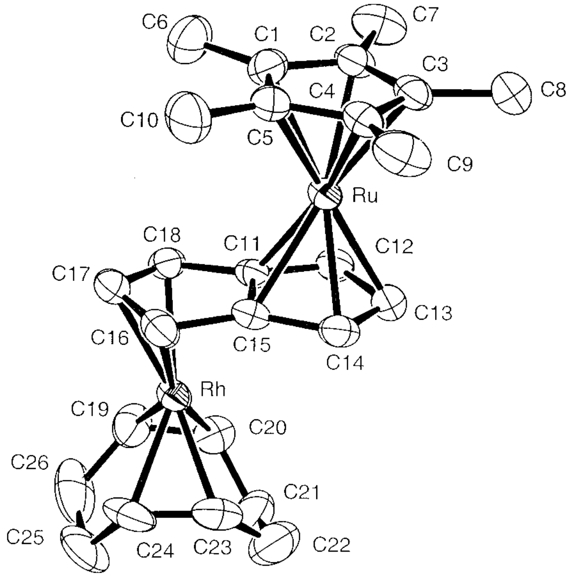

Figure 1. Molecular representation of the bimetallic complex [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)] with the labeling scheme used (H atoms omitted for clarity).

Table 1. Crystal Data and Refinement Parameters for [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)]

empirical formula	$C_{26}H_{33}RhRu$
fw	549.525
temperature (K)	293(2)
wavelength (Å)	Mo Kα (0.71073)
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
a (Å)	14.941(4)
b (Å)	11.193(2)
c (Å)	15.035(3)
β (deg)	117.635(15)
volume (Å^3)	2227.5(8)
Z	4
density(calc) (Mg m^{-3})	1.639
abs coeff (mm^{-1})	1.427
F(000)	1112
index ranges	$-18 \le h \le 21$, $0 \le k \le 15$, $-21 \le l \le 0$
no. of reflns collected	6877
no. of ind reflns	6649 ($R_{int} = 0.0659$)
no. of data/restraints/params	6649/0/258
goodness-of-fit on F^2	0.942
final R indices [$I>2\sigma(I)$]	R1 = 0.0476, wR2 = 0.1134
R indices (all data)	R1 = 0.1013, wR2 = 0.1235
largest diff peak and hole (e Å^{-3})	1.893 and −0.685

Table 2. Selected Bond Distances (Å) for [Cp*Ru(μ-η^5,η^3-C_8H_6)Rh(η^4-COD)]

Ru−C(1)	2.169(4)	Rh−C(18)	2.217(4)
Ru−C(2)	2.169(4)	Rh−C(17)	2.226(4)
Ru−C(3)	2.159(4)	Rh−C(16)	2.200(4)
Ru−C(4)	2.171(4)	Rh−C(19)	2.129(5)
Ru−C(5)	2.166(4)	Rh−C(20)	2.146(5)
Ru−C(11)	2.233(4)	Rh−C(23)	2.137(4)
Ru−C(12)	2.188(5)	Rh−C(24)	2.144(4)
Ru−C(13)	2.194(4)	C(11)−C(18)	1.464(5)
Ru−C(14)	2.183(4)	C(15)−C(16)	1.455(5)
Ru−C(15)	2.237(4)	C(16)−C(17)	1.414(6)
C(11)−C(12)	1.416(5)	C(17)−C(18)	1.417(6)
C(11)−C(15)	1.453(5)	C(12)−C(13)	1.433(6)
C(13)−C(14)	1.419(6)	C(14)−C(15)	1.439(5)
Ru−Cg1[a]	1.7935(4)	Rh−Cg3[b]	1.9305(4)
Ru−Cg2[b]	1.8402(4)		

[a] Cg1 represents the centroid of the pentamethylcyclopentadienyl ring. [b] Cg2 and Cg3 represent the centroid of the C_5 rings of the pentalenyl ligand.

analogous to that shown by the allyl-proton in the complex [Rh(C_2H_4)$_2$indenyl], which appears as a quartet signal.[13] In our complex the quartet corresponding to the resonance of the H_5 proton is further split by the long-distance $^6J(H_5H_2)$ coupling. These results suggest that the rhodium center is coordinated to the fused rings in a η^3-allyl mode. The ^{13}C NMR spectrum shows five resonances for the pentalenyl frame, indicating the lack of its molecular symmetry upon coordination of the two different organometallic fragments.

To confirm the assumed formulation and to determine the detailed geometry, an X-ray structural determination was undertaken. Figure 1 shows a perspective ORTEP view of the complex together with the atom-numbering scheme. The most relevant bond distances are given in Table 1. The complex is heterobinuclear with a ruthenium and a rhodium atom bonded to opposite faces of the dianionic pentalene ligand. The ruthenium atom is symmetrically coordinated to one of the fused cyclopentadienyl rings, and the rhodium atom coordinates to the other ring in a η^3-allyl mode. A η^5-pentamethylcyclopentadienyl and a η^4-cyclooctadiene ligand complete the coordination sphere of the ruthenium and rhodium atoms, respectively.

The Ru−Cp*(centroid) distance is 1.7935(4) Å [individual ruthenium−carbon distances range from 2.159(4) to 2.171(4) Å], which compares well with those found in other pentamethylcyclopentadienyl ruthenium complexes.[14] The ruthenium atom is located at 1.8402(4) Å from the C_5-ring mean plane of pentalene. The Ru atom is more distant from the two carbon atoms of the pentalene bridgehead [Ru−C(11) 2.233(4) and Ru−C(15) 2.237(4) Å] than from the three remote carbon atoms [Ru−C av 2.188(4) Å]. This distortion has been seen in the related iron complex [(Cp*Fe)$_2$(μ-C_8H_6)].[3,8] On the other hand, the rhodium atom is located away from the center of the associated C_5-ring of the bridging pentalene. The "ring slippage" (i.e., the distance between the perpendicular projection of a heavy-atom position on the least-squares plane of the ring and the ring center) is 0 Å for Ru and 0.392 Å for Rh. The Rh−C_5-ring (mean plane) distance is 1.9305(4) Å. The individual Rh−C distances of the nearest carbon atoms of pentalene [Rh−C(16) 2.200(4) Å, Rh−C(17) 2.226(4) Å,and Rh−C(18) 2.217(4) Å] are similar to those shown in the related rhodium(I) complexes [Rh(η^4-COD)(η^5-hydro-*s*-indacenides)].[6]

The conformation of the pentalene group can be rationalized by the angles between the four planar groups: A (C16, C17, C18), B (C11, C15, C16, C18), C (C11, C12, C14, C15), and D (C12, C13 C14). The dihedral angle between B and C is 4.12(0.35)°, in the direction anti from the Figure 1 viewpoint. The dihedral planes A and B form an angle of 11.79(0.48)° in the syn direction, whereas the planes C and D form an angle of 4.15(0.48)° in the anti direction. The pentalene ligand presents a butterfly conformation with dihedral angles of 51.66(0.30)° and 50.70(0.26)°.

When carbon monoxide is bubbled through a toluene solution of the bimetallic complex, the solution becomes

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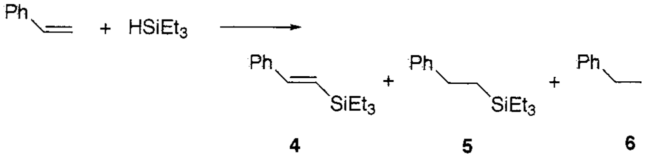
darker. Evaporation of the solution to dryness affords a dark orange solid, very unstable to air and moisture, which is characterized only by IR and NMR spectroscopies. Its IR spectrum exhibits two absorption in the carbonyl region, at 2038 and 1979 cm^{-1}, characteristic of *cis*-dicarbonylrhodium complexes.[15] The ^1H NMR spectrum shows only the signals corresponding to the Cp* and the pentalene protons, displaced to upper field. These results indicate the displacement of the COD ligand to afford the binuclear complex $[Cp^*Ru(\mu\text{-}C_8H_6)\text{-}Rh(CO)_2]$ (**3**).

Recently, dehydrogenative silylation reactions of organic compounds with silanes have emerged as a viable alternative for the synthesis of vinylsilanes.[16] These compounds are versatile intermediates in organic reactions, and their synthesis is catalyzed by transition metal complexes.[17] Considering that rhodium complexes have been reported to be effective catalysts,[18] this prompted us to test the activity of the bimetallic complex **2** in dehydrogenative silylation of styrene. Thus, the reaction of 1 equiv of triethylsilane (1.5 mmol) with 3 equiv of styrene (4.5 mmol) in the presence of a catalytic amount of complex **2** (0.015 mmol) at 80 °C gave a mixture of (*E*)-1-phenyl-2-(triethylsilyl)ethene (**4**, dehydrogenative silylation product) and 1-phenyl-2-(triethylsilyl)ethane (**5**, hydrosilylation product) with a product distribution of 87:13 for the silicon compounds (i.e., 1.31 and 0.29 mmol for **4** and **5**, respectively).



Along with these products, ethylbenzene (**6**) is obtained in an equal amount to that of **4**, and this result clearly shows that styrene acted also as hydrogen acceptor. A 100% conversion of silane (turnover number 100) was observed after 1 h of reaction time. Interestingly, the catalyst activity and selectivity are found to be similar to that of the cationic rhodium complex $[Rh(COD)_2]BF_4/PPh_3$, which is to our knowledge one of the most active rhodium catalysts reported to date for dehydrogenative silylation.[16] Further catalytic studies on related binuclear complexes are currently underway.

Experimental Section

General Data. All manipulations were carried out under pure dinitrogen atmosphere using a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri-Train purifier or a vacuum line using standard Schlenk-tube techniques. Reagent-grade solvents were distilled under dinitrogen from sodium/benzophenone ketyl (tetrahydrofuran, toluene, petroleum ether). The starting compounds $[Cp^*Ru(\eta^5\text{-}C_8H_7)]$[12] ($Cp^* = \eta^5\text{-}C_5Me_5$), $[\{Rh(\mu\text{-}Cl)(\eta^4\text{-}COD)\}_2]$[19] (COD = 1,5-cyclooctadiene), and dihydropentalene[20] (C_8H_8) were prepared according to published methods. Styrene and triethylsilane were purchased from Aldrich and were degassed before use. Elemental analyses (C and H) were made with a Fisons EA 1108 microanalyzer. FTIR were measured on a Bruker Vector-22 spectrophotometer using Nujol mulls between KBr disks. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC-200P and Bruker AC 80 spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane. GC and GC−MS spectra (EI, 70 eV) were recorded on HP 5890 series II and HP 5889 A spectrometers.

Synthesis of $[Cp^*Ru(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_6)Rh(\eta^4\text{-}COD)]$ (2). A solution of complex $[Cp^*Ru(\eta^5\text{-}C_8H_7)]$ (0.5 g, 1.4 mmol) in tetrahydrofuran (20 mL) was cooled to −80 °C. A hexane solution of *n*-butyllithium (1.6 mol L^{-1}; 0.9 mL; 1.4 mmol) was then added. The reaction mixture was allowed to warm to room temperature and then stirred for 30 min. The mixture was cooled to −80 °C, and the binuclear complex $[\{Rh(\mu\text{-}Cl)(\eta^4\text{-}COD)\}_2]$ (0.37 g; 0.7 mmol) in tetrahydrofuran solution (20 mL) was slowly added via syringe. After stirring the mixture for 1 h, the solution was evaporated to dryness. The solid residue was extracted with petroleum ether to eliminate the solid lithium chloride formed. The evaporation of the solution gives an orange solid, which was crystallized from toluene. Yield: 0.37 g (46%). Anal. Calcd for $C_{26}H_{33}RhRu$: C, 56.83; H, 6.05. Found: C, 56.75; H, 6.13. ^1H NMR (C_6D_6, 200 MHz): δ 1.76 (s, 15 H, Me, C_5Me_5), 1.84−2.07 (m, 8 H, CH_2, COD), 4.12 [dt, $^3J(H_1H_2)$ = 2.1 Hz, $^6J(H_2H_5)$ = 0.45 Hz, 1 H, H_2], 4.25 [d, $^3J(H_2H_{1,3})$ = 2.1 Hz, 2H, H_1H_3], 4.2−4.3 (m, CH, 4 H, COD), 4.38 [d, $^3J(H_3H_{4,6})$ = 2.8 Hz, 2 H, H_4H_6], and 5.84 [dq, $^3J(H_4H_5)$ = $^3J(H_5H_6)$ = $^2J(RhH_5)$ = 2.8 Hz, $^6J(H_2H_5)$ = 0.45 Hz, 1 H, H_5]. $^{13}C\{^1H\}$ NMR (C_6D_6, 50 MHz): δ 12.35 (s, C_5*Me*$_5$), 33.13 (s, CH_2, COD), 61.43 (s, C_8H_6), 70.30 (s, C_8H_6), 70.43 (s, COD), 70.79 (s, C_8H_6), 78.92 (s, C_8H_6), 83 99 (s, *C*$_5$Me$_5$), 99.01 (s, C_8H_6).

Synthesis of $[Cp^*Ru(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_6)Rh(CO)_2]$ (3). A solution of complex **2** (20 mg, 0.04 mmol) in toluene (20 mL) was exposed under a carbon monoxide atmosphere for 4 h with stirring. The resulting solution was evaporated to dryness. The complex is obtained as a dark orange solid, in quantitative yield (by NMR). IR (Nujol): ν(CO), 2038 and 1979 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 1.61 (s,15 H, Me, C_5Me_5), 3.85 (t, 1H), 3.98 (dd, 2H), 4.94 (dd, 2H), and 5.47 (t, 1H).

Dehydrogenative Silylation Reaction. In a typical catalytic test, a two-necked flask equipped with a magnetic bar was charged with $[Cp^*Ru(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_6)Rh(\eta^4\text{-}COD)]$ (8.0 mg; 0.015 mmol). The reactor was evacuated and filled with nitrogen. Styrene (0.5 mL; 4.5 mmol) and toluene (3 mL) were added to the flask. The mixture was stirred for 5 min, and Et_3SiH (0.23 mL; 1.5 mmol) was added. After 5 min, the reaction flask was immersed in an 80 °C bath and kept at this temperature. The progress of the reaction was monitored by GLC. The products were identified by ^1H NMR, by GC−MS, and by comparison with literature data.[16] GC−MS analyses of the products are given in the following format: *m*/*z* (relative intensity).

(*E*)-PhCH=CHSiEt$_3$. ^1H NMR ($CDCl_3$, 80 MHz): δ 7.46−7.29 (m, 5H, Ph), 6.99 (d, $^3J(HH)$ = 19.3 Hz, 1 H, PhCH=), 6.50 (d, $^3J(HH)$ = 19.3 Hz, 1 H, Et_3SiCH=), 1.03 (t, $^3J(HH)$ = 7.9 Hz, 9 H, C*H*$_3$CH$_2$Si), 0.70 (q, $^3J(HH)$ = 7.9 Hz, 6H, CH$_3$*CH*$_2$-Si). GC−MS, 218 ($M^+ - C_2H_5$, 100) 161 (67), 133 (36), 131 (64), 105 (47), 59 (54), and 57 (35).

Crystal Structure Determination of $[Cp^*Ru(\mu\text{-}\eta^5,\eta^3\text{-}C_8H_6)Rh(\eta^4\text{-}COD)]$ (2). Suitable crystals for X-ray diffraction were obtained from a toluene solution. A single crystal of approximate dimensions 0.65 × 0.40 × 0.04 was used for the cell determination and data collection. Lattice constants were

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determined by least-squares fitting of the setting angles of 25 reflections. Data were recorded using the $\omega-2\theta$ scan mode up to a 2θ of 60.82°. A significant monotonic decay of the standards of about 19% was observed, so a polynomial correction was applied. All intensities were corrected for Lorentz polarization and absorption effects (empirical ψ scan, max. and min. transmission were 0.6153 and 0.5676, respectively). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 over the complete set of data using SHELXL-97.[21] Anisotropic thermal parameters were refined for the non-hydrogen atoms, and the hydrogen atoms were introduced in calculated positions. Crystal data and data collection and refinement details are given in Table 1. All X-ray diffraction data are collected at 293(2) K.

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Supporting Information Available: Full tables of crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic displacement coefficients, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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