Organorhodium Compounds with Novel Bridged Dibenzo[*b*,*e*]fulvalene Ligands†

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A series of novel bisindene derivatives 1,1′-(2,2′-$C_9H_6)_2SiPh_2$, **5**, 1,1′-(2,2′-$C_9H_6)_2Si_2Me_4$, **6**, and 1,1′-(2,2′-$C_9H_6)_2SiMe_2OSiMe_2$, **7**, bearing an intramolecular monosilanylene, disilanylene, or siloxanylene bridge between the 1,1′-positions were synthesized from the reaction of the dianion of dibenzo[*b*,*e*]fulvalene **3** with the corresponding halogen silanes. Introducing a $SiMe_2$ bridge failed because of the less steric demand of the smaller methyl groups. These polycyclic compounds **6** and **7** were deprotonated twice to react with $[(cod)RhCl]_2$, giving the homobimetallic complexes 1,1′-[(η^5-C_9H_5)Rh(cod)]$_2Si_2Me_4$, **11**, and 1,1′-[(η^5-C_9H_5)Rh(cod)]$_2$-$SiMe_2OSiMe_2$, **12**, as an isomeric mixture of the syn- and antifacial species; **2** and both isomers of **12** were characterized by X-ray crystallography. The compound **5** does not give any related metal complex in this reaction due to both phenyl rings blocking the coordination spheres of the indenyl rings.

Introduction

Interest in bimetallic organometallic compounds is based on the expectation that their chemical behavior both in stoichiometric synthesis and in catalysis may differ significantly from that of the analogous mononuclear complexes.[1] A common assumption is that the two metal centers have a cooperative interaction which causes significant increase in the reaction rates or leads to transformations that do not occur when monometallic species are involved. Extensive work has been concentrated on complexes with linked cyclopentadienyl ligands, because the cyclopentadienyl unit is a ligand that binds strongly to a large number of metals in different oxidation states without showing any tendency for dissociation to the mononuclear species. Different linking bridges of alkene and silylene units with various chain lengths have been studied. Fulvalene systems[2,3] occupy a special position based on the direct connection of the two rings and the premise that many bimetallic complexes[4] could mediate electronic communication between the two metal centers through the fulvalene ligand, even in the absence of a direct metal−metal bond.[5] Whereas for fulvalene ligands a large number of homo- and heterobimetallic complexes are known, for the indenyl analogue dibenzofulvalene only a few species for iron and group 6 metals are described in the literature.[6] That seems surprising because the indenyl derivatives are known to show higher reactivity compared with their cyclopentadienyl system. This phenomenon, called the "indenyl effect",[3] is attributed to the ease of slippage from a nominally 18-electron η^5 structure to a 16-electron η^3 structure, assisted by restoration of full aromaticity to the benzene ring. In a few cases η^3-indenyl complexes have been isolated and characterized as stable compounds.[7] Generally in the class of compounds where the five-membered rings are linked by only one bond, the orientation and distance between the two metal groups is not certain due to the noticeable flexibility of the ligand, so that the chemical and physical behavior is often puzzling and cannot be

† Dedicated to Prof. Dr. Jörn Müller on the occasion of his 65th birthday.

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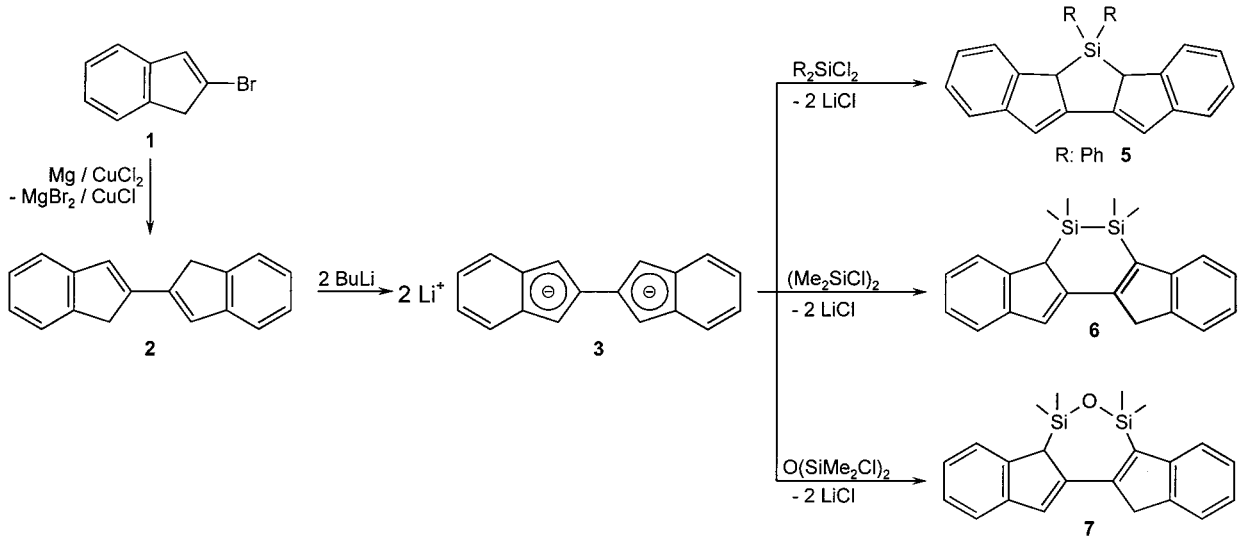
Scheme 1



unambiguously justified. The organometallic fragments may adopt a mainly transoid conformation due to steric repulsion. Introducing a second bridge in the ligand leads to a more controlled separation between the metal sites, and a minimum of orientational freedom for the five-membered ring metal fragments can be achieved. The interaction between the two metal centers can than be investigated separately for the syn and anti isomers to deduce the conformation influence in the cooperative effect.[8] For that reason, we have developed a new synthetic route to the first dibenzo[*b*,*e*]fulvalene ligands with an additional bridge, preventing the rotation of the indenyl rings against each other. We have introduced cod rhodium moieties to the ligands and studied the syn-/antifacial ratio of the obtained complexes.

Results and Discussion

To synthesize the double-bridged benzofulvene ligands, we converted indene to 2-bromoindene (**1**) by literature methods.[9] **1** reacted with magnesium shavings and anhydrous $CuCl_2$ in THF to give 2,2′-bisindene **2** in good yield.[10] After isolation by column chromatography and crystallization from ether, yellow crystals were obtained, which were analyzed by X-ray diffraction. This study conclusively demonstrates the ideal planar structure of 2,2′-bisindene with a trans configuration of the double bonds. The ^{1}H NMR studies showed only the formation of **2** without the rearangement to the expected 1,1′-bisindene and agreed with those in the literature.[11] With 2 molar equiv of butyllithium the deprotonation from **2** to 2,2′-dilithiobisindenide (**3**) proceeded. The three signals at 6.9, 6.1, and 6.0 ppm in the proton NMR spectrum prove the structure of the white powder as product **3**.

In the following step the second bridge must be introduced in the 1,1′-position. To this end we reacted the halogen silanes Me_2SiCl_2, Ph_2SiCl_2, $Cl_2Si_2Me_4$, and $O(SiMe_2Cl)_2$ with **3** to form the polycyclic systems **4**−**7** (Scheme 1). The size of the central ring varies from five to seven members and has a deciding influence on the stability of the product. For this reason the introduction of the dimethylsilyl bridge failed and led to formation of polymeric siloxane and starting materials instead of **4**. Apparently the methyl groups are too small to sterically shield the silicon atom in the newly formed five-membered ring from attack by reagents. If, instead of the dimethyl adduct, diphenyldichlorosilane is added, **5** may be isolated and reacted with 2 molar equiv of butyllithium to form the dilithio compound **8**. Equally successful was the formation of **6** and **7** as isomeric mixtures in the form of orange oils, whose separation could not be accomplished by either crystallization or column chromatography on silica gel. For this reason not every signal in the ^{1}H NMR spectrum could be definitively assigned. The free ligands reacted in benzene with 2 molar equiv of butyllithium to give the dilithio compounds **9** and **10**, where the products precipitated out of the solution as a white powder. The metathesis reaction of the dilithio compounds **8**−**10** with $[(cod)RhCl]_2$ in THF gave only the corresponding rhodium complexes **11** and **12** of the compounds **9** and **10** (Scheme 2). In the case of **8** the metalation was not complete, probably due to steric blockage by the phenyl rings. The complex **12** was formed as a mixture of the syn and anti isomers in the ratio 1:4; **11** was only obtained as the anti isomer. This fact seems contrary to investigations by Ceccon et al.[8] on metalation of indacene complexes. Bimetallic *as*-indacene complexes have structures similar to our double-bridged bisindenyl compounds **11** and **12** and can thus be structurally compared with these, especially in the case of the $SiMe_2$-$SiMe_2$ bridge. Prior investigations[12] seem to indicate that mononuclear metal reagents give only the anti formation, whereas binuclear reagents favor the syn product. Ceccon et al. showed that the isomer ratio also

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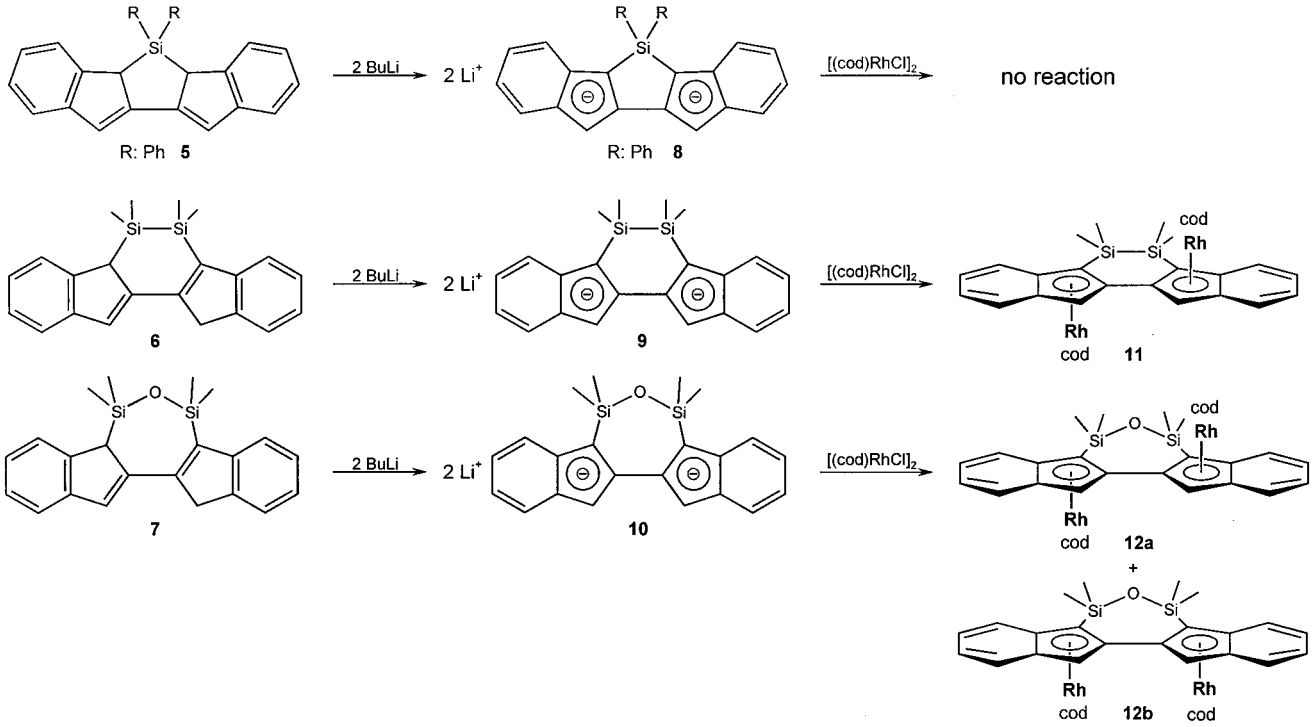
Scheme 2



depends on the steric and electronic properties of the bimetallic reagent. They compared $[(CO)_2RhCl]_2$, $[(ethylene)_2RhCl]_2$, and $[(cod)RhCl]_2$, where the first produced more of the anti isomer and the other two more of the syn product, where the syn/anti ratio is even higher for the more bulky (cod) derivative. Ceccon et al. explained their results as a competition of two different metalation reaction pathways: a one-step reaction with a simultaneous attack of both metal units at one side of the planar ligand resulting in the syn isomer or a two-step mechanism, where a dissociation of the dinuclear reagents is involved. The dissociative two-step pathway is influenced mainly by the electronic effect of the rhodium ligands, solvation by a coordinating solvent, and the structure of the metalation agents, whether it is planar or bent as in $[(cod)_2RhCl]_2$ or $[(ethylene)_2RhCl]_2$ and $[(CO)_2RhCl]_2$, respectively. Less influence was attributed to the conformation of the lithiated ligand and the distance between the two Cp ring centers compared to the metal distance in the reagents. They showed conclusively that the syn isomer is dominant in the metalation of planar ligands with $[(cod)_2RhCl]_2$.

For **11** we observe only the anti isomer and for **12** a 4 times higher ratio for the anti than for the syn isomer, which shows that the steric effect can dominate this mechanistic proposal. We presume that the methyl groups on the silicon atom had a large influence and blocked the concerted attack of the metal agents on the polycyclic ring system. This fact can be deduced from the crystal structure where the methyl groups try to avoid repulsive interactions with the cod ring by bending the silicon atom out of the indenyl plane and slightly distorting the tetrahedral angles. A similar orientation of the methyl groups can be expected in the lithiated ligand, which should be anti like other related compounds.[13] A concerted mechanism is sterically blocked by the methyl group on the opposite side on the five-membered ring of the lithium atom, and only the second reaction pathway is left to form dinuclear species. Another indication for the steric influence of the substituents on the silicon atom is the failure of metalation of **5**, where the phenyl groups block the coordination sphere of the dibenzofulvalene ligand. In contrast, an additional atom in the bridge offers greater flexibility in the ring system to also permit the formation of the syn product for **12**. Additionally, the higher reaction temperature used for the metalation of **11** and **12** (room temperature compared to −30 °C used by Ceccon et al.) might favor the solvent-supported dissociation step of the $[(cod)RhCl]_2$, which is essential for anti formation.

In conclusion, the steric demands of the cod ring with the methyl groups of the silicon atoms and the close proximity of the two five-membered rings of the indenyl systems led to a clear preference for the antifacial species **12a**. The column chromatographic separation of the isomers on silica gel did not give full separation, but the enrichment afforded the possibility of crystallization of single crystals for X-ray diffraction from a mixture of pentane and ether. Discussion of the structures is below.

To optimize the reaction, we tested an alternate route, in which the free ligand **7** was reacted with thallium

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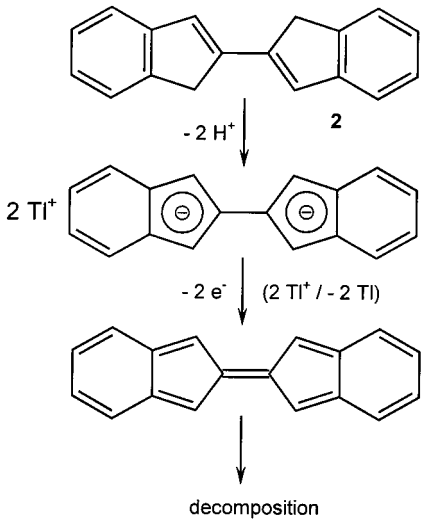
Scheme 3



ethoxide in dioxane to give the thallium compound corresponding to **10**. We hoped this would provide higher yields in the following metalation reaction. Instead this showed only the formation of metallic thallium and a black solution, which contained decomposition products from the ligand. We were able to make the same observation when we reacted **2** in a similar manner and so showed that the siloxane bridge had no influence on this reaction. We attribute the observed results to a spontaneous redox process at the C−C bond between the indenyl rings. A possible intermediate, which we were not able to prove, was the fulvalene type species shown in Scheme 3 from which we would expect no thermal stability by analogy to pentafulvalene and similar compounds[14,6b] Further study of the reaction mixture by MS allowed us to suppose that the indenyl−indenyl bond must have been broken. This is in accordance with literature references describing this bond as labile toward acids and bases.[6b]

X-ray Molecular Structures of 12a,b and 2

The structures of the homobimetallic anti and syn complexes of **12** as determined by X-ray crystallographic analysis are shown in Figures 1 and 2.

Out of a pentane/ether mixture **12a** and **12b** crystallized at 4 °C in the triclinic space group $P\bar{1}$, in which **12a** additionally contains one molecule of *n*-pentane in the asymmetric unit. In both structures the Rh(cod) moieties are η^5-coordinated to the five-membered ring of the polycyclic ligand, but in **12a** an antifacial and in **12b** a synfacial coordination occurs. The cod ring on Rh1 in **12a** is disordered with relative occupation parameters of 43% and 57%, respectively. For this reason these atoms could not be anisotropically refined. The disordered cod rings are tilted against each other with an angle of 7.01(0.47)°. The angles of both olefin planes with respect to the indenyl planes measure 5.83(0.39)° and 7.91(0.32)°, thus lying in the normal range.[15] In the antifacial conformation the indenyl planes are tilted

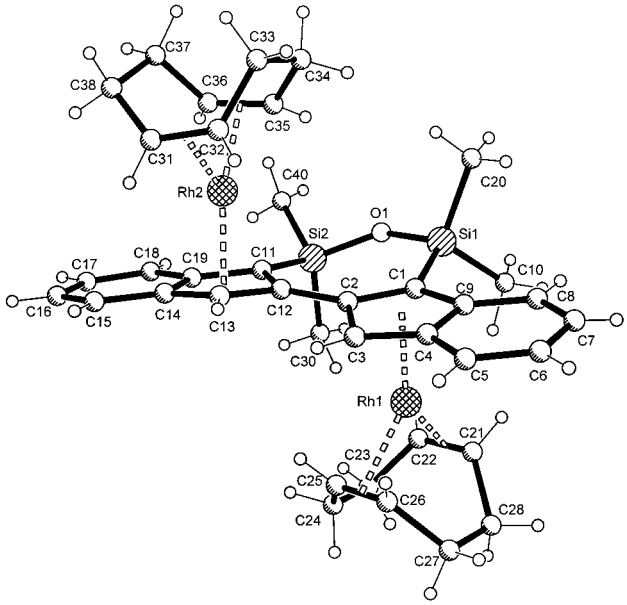


Figure 1. Crystal structure of the antifacial isomer 1,1′-[(η^5-C_9H_5)Rh(cod)]$_2$SiMe$_2$OSiMe$_2$, **12a**.

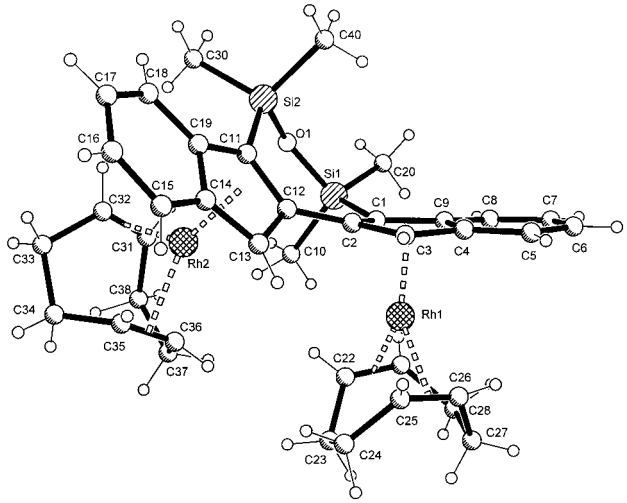


Figure 2. Crystal structure of the synfacial isomer 1,1′-[(η^5-C_9H_5)Rh(cod)]$_2$SiMe$_2$OSiMe$_2$, **12b**.

slightly against each other (with an angle of 11.1°); in the synfacial case the twisting, a 54.5° angle, is much stronger due to the steric repulsions of the Rh(cod) units. The distance between the Rh atoms of 4.836 Å lies outside the range of any interaction. This twist has hardly any effect on the central seven-membered ring, because the long siloxane bridge has enough degrees of freedom to relieve the ring strain. Independent of this fact we observe for both complexes **12a** and **12b** an insignificantly longer Rh−C bond to the quartenary C atoms C4 and C9 or C14, C19 of the indenyl ring, which is typical of slight ring slippage to η^3. This effect is common and appears with the characteristic hinge angle,[16] which is in the typical range for indenyl rhodium olefins increasing from 9.1° to 11.16° in both structures. The silicon atoms do not lie in plane of the indenyl groups to which they are bound, but are bent out to the side opposite the metal in order to minimize

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(16) Plane angle between P1(C1, C2, C3) and P2(C3, C4, C9, C1), P3(C11, C12, C13) and P4(C13, C14, C19, C11), respectively.

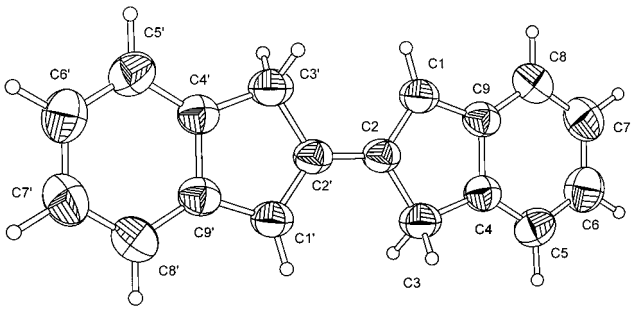

Figure 3. Crystal structure of 2,2′-bisindene, **2.**

the interaction of their bound methyl groups with the Rh(cod) unit.

Bisindene **2** crystallizes with two different molecules in the unit cell. Each molecule is completely flat, and the two molecules in the cell are tilted against each other with an angle of 56.4(0.10)°. The double bonds of the five-membered ring in the molecules form a diene system and lie trans to one another. The structure is shown in Figure 3.

Experimental Section

Reactions were carried out under nitrogen using conventional Schlenk techniques. All solvents were distilled from Na. The NMR spectra were recorded on a Bruker ARX 200 spectrometer in C_6D_6 (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz). [(cod)-RhCl]$_2$[17] was prepared by literature methods. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 311A. For the high-resolution mass spectrometry 18 scans were averaged to compare with the calculated mass for the molecular ion. The X-ray diffraction structural analyses were performed with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 293 K using a Siemens SMART CCD area detector diffractometer. All crystal structures were solved using the direct method (SHELXS86) and subsequently refined by full-matrix least-squares methods (SHELXL93[18]). For the structures of **12a** and **12b** the final adsorption correction was done by SADABS. The positions of all hydrogen atoms could be found for the structure of **3**. The hydrogen atoms that could not be found in the structure of **12a** and **12b** were positioned at calculated coordinates with a fixed thermal parameter. **12a** contains some disordered atoms; these atoms were refined isotropically with a free occupation parameter. The data for structure refinement of **2**, **12a**, and **12b** are listed in Table 1, and selected bond lengths are summarized in Table 2.

Synthesis of 2,2′-Bisindene, 2. To a suspension of 8.4 g (350 mmol) of magnesium and 0.1 mL of methyliodide in 250 mL of THF was dropped slowly 66.7 g (344 mmol) of 2-bromindene in 80 mL of THF at 40 °C. After the Grignard reaction started the solution color changed from pale yellow to red. The mixture was heated to reflux for 2 h until all magnesium reacted. After cooling to 0 °C 49.6 g (370 mmol) of water-free copper chloride was added in a few portions while vigorously stirring. The mixture was then allowed to warm to room temperature and stirred overnight. The suspension was filtered off and washed three times with ether, and the solvent was removed. The dark precipitate was purified by chromatography on neutral alumina eluting with pentane/ether, 1:2. The orange oil was dried in vacuo at 40 °C. Crystallization from ether at 5 °C yielded pale yellow crystals. Yield: 27.9 g (71%). Mp: 231 °C. MS (EI): *m/z* 230 $(M)^+$, 229 $(M - H)^+$, 228 $(M - 2H)^+$, 115 $(M - C_9H_7)^+$, 114 $(M - C_9H_8)^+$, 113 $(M - C_9H_9)^+$. ^{1}H NMR (C_6D_6): δ 7.1−6.9 (m, 8H, arom.), 6.7 (s, 2H, olef.), 3.4 (s, 4H, CH_2). ^{13}H NMR (C_6D_6): δ 145.7, 143.5, 143.3 (quat. C); 127.1, 126.9, 125.2, 123.9, 121.2 (arom., olef.); 39.7 (CH_2). Anal. Calcd for $C_{18}H_{14}$: C, 93.91; H, 6.08. Found: C, 93.89; H, 6.05.

Synthesis of 2,2′-Dilithiobis(indenide), 3. To a solution of 7.66 g (33.3 mmol) 2,2′-bisindenyl in 250 mL of benzene was dropped slowly 28.8 mL (2.5 M in hexane) of *n*-BuLi at room temperature. After 2 days the solid was separated using a D4-frit and washed with hexane. The white powder was dried in vacuo and stored under nitrogen. Yield: 7.65 g (95%). ^{1}H NMR (DMSO-d_6): δ 6.9 (m, 4H), 6.1 (m, 4H), 6.0 (s, 4H).

Synthesis of 1,1′-(2,2′-C_9H_6)$_2$SiPh$_2$, 5. To a solution of 3.91 g (16.2 mmol) of 2,2′-dilithiobis(indenide) in 150 mL of THF was added via syringe 4.11 mL (20 mmol) of dichlorodiphenylsilane at −40 °C. The resulting solution was stirred at −40 °C for 30 min and allowed to warm to room temperature overnight. The solution was evaporated, and the solid redissolved in ether and chromatographed on silica gel eluting with ether. The solvent was evaporated and recrystallized from ether/pentane. The ligand **5** was obtained as an orange oil. Yield: 4.8 g (73%). MS (EI): *m/z* 410 $(M)^+$, 332 $(M - C_6H_5)^+$, 219 $(M - C_{15}H_9)^+$, 217 $(M - C_{15}H_{11})^+$. High-resolution MS: *m/z* calcd 410.1491, found 410.1502. ^{1}H NMR (acetone-d_6): δ 7.7−6.8 (m, 20 H), 4.14 (s, br, 2H).

Synthesis of 1,1′-(2,2′-C_9H_6)$_2$(SiMe$_2$)$_2$, 6. The same procedure as for the synthesis of **5** was used except that 1.5 mL (8 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldilsilane was used instead of 1,3-dichloro-1,1,3,3-tetramethyldilsiloxane. Yield: 1.99 g (80%). MS (EI): *m/z* 344 $(M)^+$, 285 $(M - SiMe_2)^+$, 172 $(M - SiMe_2 - C_9H_4)^+$, 170 $(M - SiMe_2 - C_9H_6)^+$. High-resolution MS: *m/z* calcd 344.1416, found 344.1410. ^{1}H NMR (DMSO-d_6): δ 7.55−7.1 (m, 8H, arom.), 7.04 (s, 1H, olef.), 3.60 (s, 1H, CHSi), 3.38 (s, 2H, CH_2), 0.17 (s, 6H, $SiMe_2$), 0.08 (s, 6H, $SiMe_2$).

Synthesis of 1,1′-(2,2′-C_9H_6)$_2$ SiMe$_2$OSiMe$_2$, 7. A 3.13 g (13 mmol) sample of 2,2′-dilithiobis(indenide) was dissolved in 120 mL of THF and treated with 3 mL (15 mmol) of 1,3-dichloro-1,1,3,3-tetramethyldilsiloxane at −40 °C via syringe. The resulting solution was stirred at −40 °C for 30 min and allowed to warm to room temperature overnight. The solution was evaporated, and the solid redissolved in 20 mL of hexane and chromatographed on silica gel eluting with hexane/ether (10:1). A yellow−orange mixture of isomers **7** was obtained. Yield: 3.44 g (74%). MS (EI): *m/z* 360 $(M)^+$, 345 $(M - CH_3)^+$, 228 $(M - SiMe_2OSiMe_2)^+$, 227 $(M - H - SiMe_2OSiMe_2)^+$. High-resolution MS: *m/z* calcd 360.1365, found 360.1368. ^{1}H NMR (DMSO-d_6): δ 7.15 (d, 2H, arom.), 6.96 (d, 2H, arom.), 6.2 (m, 4H, arom.), 5.96 (s, 1H, olef.), 3.22 (s, 2H, CH_2), 3.41 (s, 1H, CHSi), 0.15 (s, 12H, $SiMe_2$).

Synthesis of [(cod)Rh(η^5-$C_9H_5SiMe_2$)]$_2$, 11. To a stirring solution of 0.2 g (0.6 mmol) of 1,1′-(2,2′-C_9H_6)$_2$($SiMe_2$)$_2$ in 10 mL of THF at −78 °C was added 0.48 mL of *n*-BuLi (2.5 M in hexane solution) via syringe. After 2 h at room temperature the suspension was treated with 0.28 g (0.57 mmol) of [codRhCl]$_2$ and stirred overnight. The solvent was evaporated, and the residue redissolved in 10 mL pentane and 3 mL ether and chromatographed on silica gel eluting with pentane/ether (10:1). The first yellow fraction contained the product. It seems to form only the anti isomer. Yield: 223 mg (56%). MS (EI): *m/z* 764 $(M)^+$, 656 $(M - cod)^+$, 654 $(M - cod - 2H)^+$, 596 $(M - cod - SiMe_2)^+$, 594 $(M - cod - 2H - SiMe_2)^+$, 484 $(M - 2cod - 2H - SiMe_2)^+$, 326 $(M - Rh - cod - SiMe_2)^+$. High-resolution MS: *m/z* calcd 764.1248, found 764.1246. ^{1}H NMR (C_6D_6): δ 7.4, 7.1−7.0 (m, 8H, arom.), 5.05 (s, 2H, olef.), 4.3 (m, 4H, olef., cod), 3.9 (m, 4H, olef., cod); 1.6 (m, 12H, CH_2, cod), 1.4 (m, 4H, CH_2, cod), 0.59 (s, 6H, $SiMe_2$), 0.48 (s, 6H, $SiMe_2$). ^{13}C NMR (C_6D_6): δ 123.5, 122.7, 119.93, 119.91 (arom.), 119.6 ($J_{Rh-C} = 2.1$ Hz, C4 or C9), 115.8 ($J_{Rh-C} = 2.0$ Hz, C4 or

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(18) (a) SHELXS-86: Sheldrick, G. M. *Acta Chrystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL-93*, University of Göttingen: Germany, 1993.

Table 1. Crystal Data for 2, 12a and 12b

	12a	12b	2
Crystal Parameters			
chemical formula	$C_{38}H_{46}ORh_2Si_2 \times C_5H_{12}$	$C_{38}H_{46}ORh_2Si_2$	$C_{18}H_{14}$
fw (g mol^{-1})	852.90	780.75	230.29
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	11.4098(2)	8.41010(10)	5.9212(2)
b (Å)	13.0305(2)	11.98760(10)	7.8380(3)
c (Å)	14.4861(2)	18.0669(2)	13.95520(10)
α (deg)	100.7820(10)	76.7930(10)	103.5260(10)
β (deg)	95.4660(10)	85.1040(10)	98.303(2)
γ (deg)	111.0380(10)	73.3390(10)	92.6330(10)
volume (Å^3)	1943.45(5)	1698.44(3)	620.96(3)
Z	2	2	2
D(calcd) (g cm^{-3})	1.457	1.558	1.232
μ(Mo Kα) (cm^{-1})	0.943	1.075	0.069
Data Collection			
cryst size (mm^{-3})	0.42 × 0.21 × 0.1	0.38 × 0.33 × 0.08	0.38 × 0.24 × 0.14
θ range	$2.9 \le 2\theta \le 55.0$	$2.32 \le 2\theta \le 61.2$	$3.04 \le 2\theta \le 50$
index range (h, k, l)	−16→14, −18→18, −20→20	−12→8, −17→17, −25→25	−8→7, −11→11, −15→19
transmn max./min.	0.94498/0.72648	0.92261/0.74326	
data	15 016	15 998	3896
ind obsd reflns (R_{int})	8847 [$R_{(int)} = 0.0539$]	10209 [$R_{(int)} = 0.0561$]	2160 [$R_{(int)} = 0.0951$]
no. of ind reflns	8847	10 206	2093
no. of params	546	510	220
Refinement			
$\Delta(\rho)$ (e·Å^{-3})	0.819 and −0.726	0.993 and −1.253	0.209 and −0.192
GOF	0.729	0.948	1.194
R^a	0.0387 (0.0718)^b	0.0516(0.0945)	0.0743 (0.1470)
$wR_2{}^a$	0.0848 (0.1020)^b	0.0824 (0.0963)	0.1139 (0.1828)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]^{1/2}\sum[w(F_o^2)]]^{1/2}$, $[F_o > 4\sigma(F_o)]$. [b] Based on all data.

Table 2. Selected Bond Lengths (Å) and Torsion Angles (deg) from the Crystal Structures of 2, 12a, and 12b

bond	2	12a	12b	bond	2	12a	12b
Rh(1)−C(3)		2.190(4)	2.218(4)	Rh(2)−C(13)		2.194(4)	2.207(3)
Rh(1)−C(1)		2.276(4)	2.234(4)	Rh(2)−C(11)		2.244(4)	2.240(4)
Rh(1)−C(2)		2.299(4)	2.272(4)	Rh(2)−C(12)		2.281(4)	2.288(3)
Rh(1)−C(4)		2.341(4)	2.340(4)	Rh(2)−C(14)		2.353(4)	2.342(4)
Rh(1)−C(9)		2.352(4)	2.324(4)	Rh(2)−C(19)		2.377(4)	2.335(4)
Si(1)−O(1)		1.624(4)	1.630(3)	Si(2)−O(1)		1.627(4)	1.632(3)
Si(1)−C(1)		1.875(4)	1.881(3)	Si(2)−C(11)		1.866(4)	1.859(4)
C(1)−C(2)	1.378(4)	1.450(5)	1.447(5)	C(11)−C(12)	1.382(4)	1.452(6)	1.436(5)
C(1)−C(9)	1.460(4)	1.462(6)	1.475(5)	C(11)−C(19)	1.461(4)	1.469(6)	1.471(5)
C(2)−C(3)	1.482(4)	1.439(6)	1.417(5)	C(12)−C(13)	1.478(4)	1.432(5)	1.429(5)
C(3)−C(4)	1.479(4)	1.429(6)	1.442(5)	C(13)−C(14)	1.486(4)	1.438(6)	1.453(5)
C(4)−C(5)	1.379(4)	1.413(6)	1.410(5)	C(14)−C(15)	1.386(4)	1.425(6)	1.408(5)
C(4)−C(9)	1.416(4)	1.430(6)	1.424(5)	C(14)−C(19)	1.406(4)	1.431(6)	1.426(5)
C(5)−C(6)	1.381(5)	1.369(7)	1.372(5)	C(15)−C(16)	1.382(5)	1.376(7)	1.374(6)
C(6)−C(7)	1.391(5)	1.401(8)	1.399(6)	C(16)−C(17)	1.387(5)	1.407(8)	1.401(6)
C(7)−C(8)	1.390(5)	1.366(8)	1.372(6)	C(17)−C(18)	1.381(5)	1.377(7)	1.365(6)
C(8)−C(9)	1.372(4)	1.423(6)	1.413(5)	C(18)−C(19)	1.375(4)	1.413(6)	1.417(5)
C(2)−C(12)		1.474(5)	1.479(4)	C(12)−C(12)^b	1.436(6)		
C(2)−C(2)^a	1.437(6)						
C(1)−C(2)−C(12)−C(11)		11.2(7)	−46.34(0.65)				

[a] Symmetric transformation used to generate this atom: $-x+1, -y, -z+1$ [b] Symmetric transformation used to generate this atom: $-x+2, -y+1, -z+1$

C9), 114.1 ($J_{Rh-C} = 5.2$ Hz, C2), 76.1 ($J_{Rh-C} = 4.3$ Hz, C1); 75.1 ($J_{Rh-C} = 4.6$ Hz, C3); 70.4 ($J_{Rh-C} = 13.5$ Hz, olef., cod), 67.9 ($J_{Rh-C} = 13.7$ Hz, olef., cod); 32.5, 30.4 (CH_2, cod); −0.9, −4.4 ($SiMe_2$).

Synthesis of [(cod)Rh(η^5-$C_9H_5SiMe_2$)]$_2$O, 12. To 0.28 g (0.76 mmol) of **7** in 20 mL of THF was added 0.68 mL of *n*-BuLi (2.5 M in hexane solution) at −78 °C via syringe. The solution was stirred for 2 h at room temperature and then treated with 0.39 g (0.82 mmol) of [codRhCl]$_2$. After stirring overnight, the solvent was evaporated and the precipitate redissolved in 10 mL of pentane and 2 mL of ether. The dark suspension was chromatographed on silica gel eluting with pentane/ether (10:1). The first yellow fraction was identified as isomere **12a**; the second orange oil was characterized as 1:1 mixture of **12a** and **12b**. Both products were recrystallized from ether. Yield: 501 mg (84%). MS (EI): m/z 780 (M)$^+$, 672 (M − cod)$^+$, 670 (M − cod − 2H)$^+$, 570 (M − Rh − cod)$^+$, 568 (M − Rh − cod − 2H)$^+$, 438 (M − Rh − cod − 2H − $SiMe_2OSiMe_2$)$^+$. High-resolution MS: m/z calcd 780.1197, found 780.1201. **12a**: ^{1}H NMR (C_6D_6): δ 7.3−7.2 (m, 4H, arom.), 7.1−7.05 (m, 4H, arom.), 5.13 (s, 2H, olef.), 4.3 (m, 4H, olef., cod), 3.9 (m, 4H, olef., cod); 1.6 (m, 12H, CH_2, cod), 1.4 (m, 4H, CH_2, cod), 0.64 (s, 6H, $SiMe_2$), 0.54 (s, 6H, $SiMe_2$). ^{13}C NMR (C_6D_6): δ 123.8, 122.6, 119.8, 119.5 (arom.), 119.1 ($J_{Rh-C} = 2.1$ Hz, C4 or C9), 115.3 ($J_{Rh-C} = 2.1$ Hz, C4 or C9), 114.5 ($J_{Rh-C} = 5.2$ Hz, C2), 78.8 ($J_{Rh-C} = 4.1$ Hz, C1); 77.0 ($J_{Rh-C} = 4.7$ Hz, C3); 71.0 ($J_{Rh-C} = 13.6$ Hz, olef., cod), 68.2 ($J_{Rh-C} = 13.9$ Hz, olef., cod); 33.1, 29.8

(CH_2, cod); 3.35, 2.67 ($SiMe_2$). **12b**: ^{1}H NMR (C_6D_6): δ 7.3−7.2 (m, 4H, arom.), 7.1−7.05 (m, 4H, arom.), 5.19 (s, 2H, olef.), 4.3 (m, 4H, olef., cod), 3.9 (m, 4H, olef., cod); 1.6 (m, 12H, CH_2, cod), 1.4 (m, 4H, CH_2, cod), 0.56 (s, 6H, $SiMe_2$), 0.33 (s, 6H, $SiMe_2$).

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 168464−168466 for the compounds **2**, **12a**, and **12b**, respectively.

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Supporting Information Available: Full crystallographic tables of the three X-ray structures **12a**, **12b**, and **2** including ORTEP and cell drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

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