Vinylidene Transition-Metal Complexes, 46[◇]

Di- and Trinuclear Alkyne- and Vinylidenerhodium(I) Complexes Including the X-ray Crystal Structure of a Dendrimer-Like Rh_3 Compound[☆]

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Received April 21, 1998

Keywords: Rhodium / Alkyne complexes / Alkynyl(hydrido) complexes / Vinylidene complexes / Dendrimer-like structure

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The dimer $[RhClL_2]_2$ (**1**; L = P*i*Pr$_3$) reacts with 1,3,5-$C_6H_3(C{\equiv}CH)_3$ to give in the initial step the tris(alkyne)trirhodium compound **2**, which rearranges in toluene at 60 °C to yield the isomeric tris(vinylidene) complex **3**. Treatment of either **2** or **3** with pyridine affords the trinuclear tris(alkynyl)trihydridorhodium(III) complex **4**. The trisilyl derivative 1,3,5-$C_6H_3(C{\equiv}CSiMe_3)_3$ reacts with **1** to form the mononuclear compound **5**, in which only one of the C≡C bonds is coordinated to Rh. The diynes 1,3- and 1,2-$C_6H_4(C{\equiv}CH)_2$ behave analogously to 1,3,5-$C_6H_3(C{\equiv}CH)_3$ and upon treatment with **1** yield initially the bis(alkyne)dirhodium complexes **6** and **7** and subsequently the bis(vinylidene)dirhodium isomers **8** and **9**. The reactions of 1,2-, 1,3-, and 1,4-$C_6H_4(C{\equiv}CSiMe_3)_2$ with **1** take a similar course and give the bis(alkyne) and bis(vinylidene) compounds **10**–**12** and **13**–**15**, respectively. In the same way, the dinuclear bis(alkyne) and bis(vinylidene) complexes **16** and **17** have been prepared from **1** and the naphthalene derivative 1,5-$C_{10}H_6(C{\equiv}CH)_2$. The molecular structures of **17** and of the dendrimer-like Rh_3 compound **3** have been determined by X-ray crystallography.

We have recently shown that terminal alkynes HC≡CR are easily converted to the isomeric vinylidenes :C=CHR in the coordination sphere of rhodium(I).[1][2] This process is thermodynamically preferred,[3] and based on ab initio MO studies its mechanism is quite well understood.[4] Besides acetylene and monosubstituted derivatives HC≡CR with R = alkyl, aryl, vinyl, SiR_3 or CO_2R, also butadiyne[5] and 1,4-bis(ethynyl)benzene[6] have been used as substrates and, in the presence of $[RhCl(PiPr_3)_2]$ as the template, transformed to the isomeric bridge-forming bis(vinylidenes).

The present paper reports that likewise to 1,4-$C_6H_4(C{\equiv}CH)_2$ not only the 1,3- and 1,2-bis(ethynyl)benzene isomers but also the trisubstituted benzene derivative 1,3,5-$C_6H_3(C{\equiv}CH)_3$ forms alkyne- and vinylidenerhodium(I) complexes upon treatment with $[RhClL_2]_2$ (**1**; L = P*i*Pr$_3$). An interesting facet of this work is that while the disilylated compounds 1,3- and 1,2-$C_6H_4(C{\equiv}CSiMe_3)_2$ behave similarly to the parent diynes and yield dinuclear rhodium complexes, the trisilylated triyne 1,3,5-$C_6H_3(C{\equiv}CSiMe_3)_3$ reacts with **1** to give a mononuclear alkynerhodium(I) compound, leaving two of the three triple bonds of 1,3,5-$C_6H_3(C{\equiv}CSiMe_3)_3$ uncoordinated.

Rhodium Complexes from 1,3,5-$C_6H_3(C{\equiv}CH)_3$ and the Trisilylated Derivative

Treatment of a solution of the reactive dimer **1**[7] with 1,3,5-tris(ethynyl)benzene in pentane leads even at −60 °C to a rapid change of colour and, after warming to room temperature and removal of the solvent, gives the triyne complex **2** in ca. 80% yield. The yellow microcrystalline solid is moderately air-sensitive and easily soluble in most organic solvents.

The proposed structure of **2** (see Scheme 1) is fully supported by the spectroscopic data. The IR spectrum displays only one strong C≡C stretch at 1795 cm^{-1} indicating that all three triple bonds are involved in the coordination to the rhodium center. In agreement with this, the ^{1}H-NMR spectrum of **2** shows one signal for the ≡CH protons at δ = 4.02, which due to Rh-H coupling is split into a doublet. For the CH_3 protons of the P*i*Pr$_3$ units a doublet of virtual triplets appears being consistent with the *trans* disposition of the two phosphane ligands at each metal center.[8]

Although **2** is stable both in the solid state and in solution at room temperature, on warming in toluene at 60 °C it slowly rearranges to the tris(vinylidene) complex **3**. In contrast to **2**, the isomer **3** is a dark green solid, the NMR spectra of which indicate a symmetrical structure as shown in Scheme 1. There is only one resonance for the P*i*Pr$_3$ phosphorus atoms in the ^{31}P-NMR and only one set of signals for the phosphanyl CH_3 protons in the ^{1}H-NMR spectrum. The most characteristic feature in the ^{13}C-NMR spectrum of **3** is the position of the signal of the α-C atom of the vinylidene ligands which appears at δ = 292.9 as a doublet of triplets. Both the Rh-C and P-C couplings are significantly larger than those of the resonance for the vinylidene β-C atom at δ = 111.1.

[◇] Part 45: J. Gil-Rubio, M. Laubender, H. Werner, *Organometallics* **1989**, *17*, 1202−1207.

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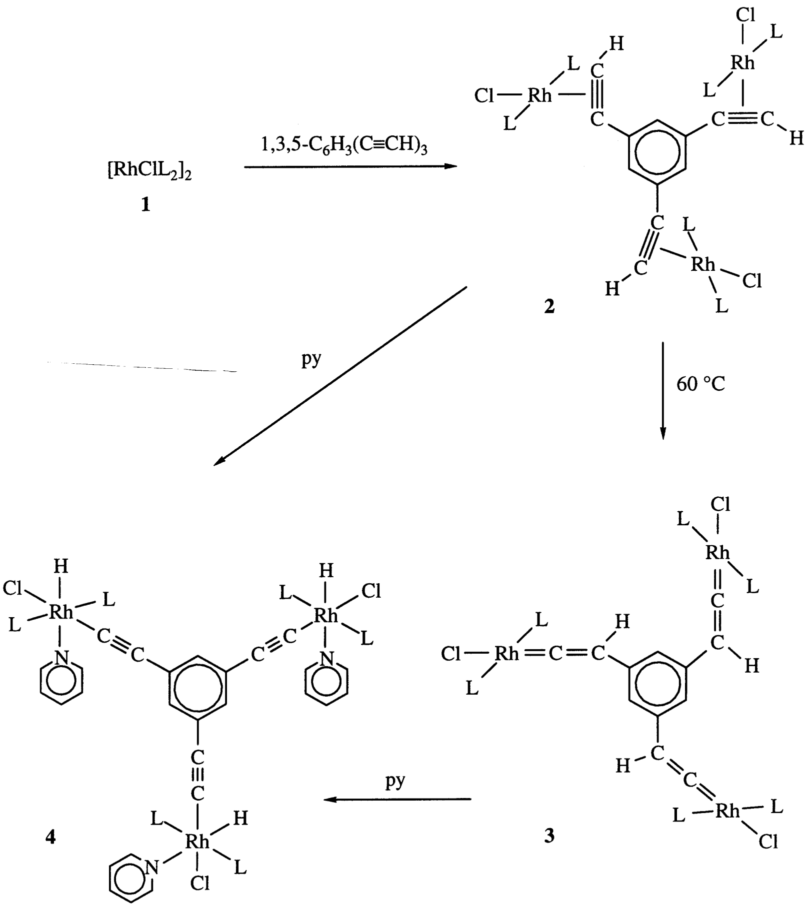
Scheme 1. L = P*i*Pr$_3$

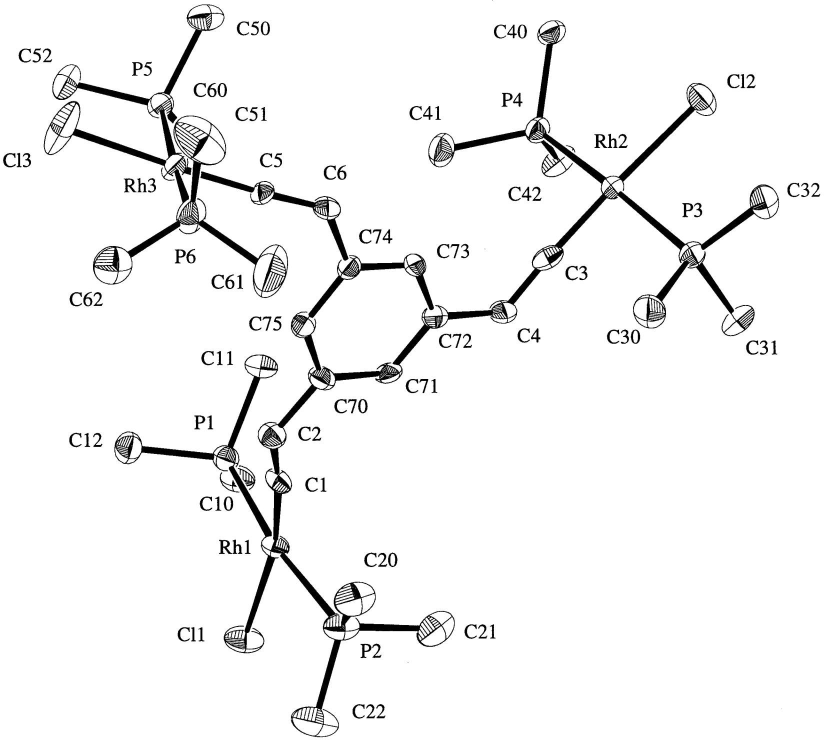


The result of the X-ray crystal structure analysis of **3** is shown in Figure 1. The coordination geometry around the three rhodium centers is square-planar with bond angles (mean values) P−Rh−C of 89.9° and P−Rh−Cl of 90.3°. The axes Cl−Rh−C and P−Rh−P are not exactly linear, the bond angles lying between 166.5° and 177.4° (for Cl−Rh−C) and between 171.09° and 173.61° (for P−Rh−P), respectively. The Rh−C and C−C distances of the vinylidenemetal units are in the expected range, i.e., they are almost identical to the corresponding bond lengths in *trans*-[RhCl(=C=CHMe)(P*i*Pr$_3$)$_2$] and *trans*-[RhCl(=C=CHC(Me)=CH$_2$)(P*i*Pr$_3$)$_2$].[9][10] An unexpected result is that the planes formed by each rhodium center, the α- and β-carbon atoms of the vinylidene ligand and the *ipso*-C atom of the substituted benzene are not coplanar with the central six-membered ring; the respective dihedral angles are between 10° and 15°. The plane of the C$_6$ ring is not exactly perpendicular to the three [Rh,P,P,Cl,α-C] planes, in this case the dihedral angles being 81−89°. The molecule of **3** as a whole can be described as a dendrimer-like species (zero-order dendrimer) with three branched organometallic moieties around the planar C$_6$ core.

The mechanism of the isomerization of **2** to **3** is not clear as yet. Due to theoretical studies[4] it is conceivable that in the initial step an intramolecular oxidative addition occurs and a tris(alkynyl)trishydridotrirhodium complex is generated. In the second step, this intermediate could rearrange to the vinylidene isomer **3**. The assumed stepwise mechanism is supported by the observation that on treatment of **2** with pyridine the trinuclear compound **4** containing three rhodium(III) centers is formed. The same product is also obtained from **3** and excess pyridine. The ^{1}H-NMR spectrum of **4** displays in the high-field region a signal at δ = −17.64 (with the intensity of 3 H) which is consistent with the proposed structure.

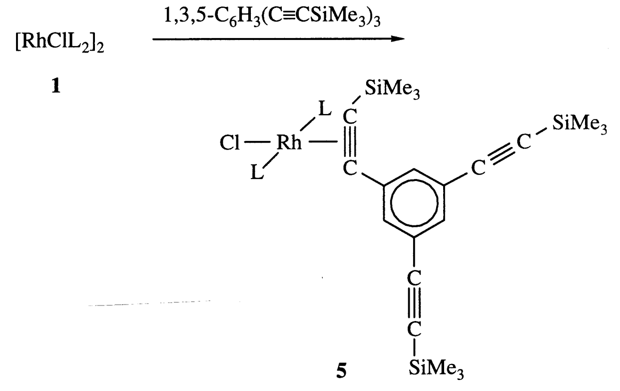
In contrast to 1,3,5-C$_6$H$_3$(C≡CH)$_3$, the trisilylated derivative 1,3,5-C$_6$H$_3$(C≡CSiMe$_3$)$_3$ reacts with **1** to afford the mononuclear alkyne complex **5** (Scheme 2). The IR spectrum of the bright orange solid shows besides the expected band at ca. 1800 cm^{-1} for the C≡C stretching frequency of a metal-bonded alkyne, another absorption at 2140 cm^{-1} which is typical for non-coordinated C≡C bonds. In agreement with this result, the ^{13}C-NMR spectrum of **5** displays two signals at δ = 103.7 and 95.9 for the carbon atoms of the uncoordinated and two signals at δ = 86.4 and 82.2 for those of the coordinated triple bonds. Owing to the Rh-C coupling, the latter resonances are split into doublets with *J*(RhC) of 13.5 Hz.

Figure 1. Molecular structure (ORTEP plot) of 3[a]; the methyl groups of the isopropyl units are omitted for clarity



[a] Selected bond lengths [Å] and angles [°]: Rh1–Cl1 2.381(2), Rh1–P1 2.348(2), Rh1–P2 2.357(2), Rh1–C1 1.790(6), C1–C2 1.319(9), C2–C70 1.471(9), Rh2–Cl2 2.394(2), Rh2–P3 2.345(2), Rh2–P4 2.346(2), Rh2–C3 1.809(6), C3–C4 1.323(9), C4–C72 1.503(9), Rh3–Cl3 2.399(2), Rh3–P5 2.362(2), Rh3–P6 2.357(2), Rh3–C5 1.820(6), C5–C6 1.327(9), C6–C74 1.483(8); P1–Rh1–P2 171.09(7), Cl1–Rh1–C1 166.5(2), P1–Rh1–Cl1 91.10(6), P1–Rh1–C1 89.0(2), P2–Rh1–Cl1 92.15(7), P2–Rh1–C1 89.8(2), Rh1–C1–C2 172.1(6), C1–C2–C70 125.5(6), P3–Rh2–P4 171.97(6), Cl2–Rh2–C3 175.9(2), P3–Rh2–Cl2 90.20(6), P3–Rh2–C3 89.4(2), P4–Rh2–Cl2 90.32(6), P4–Rh2–C3 89.5(2), Rh2–C3–C4 175.8(5), C3–C4–C72 129.2(6), P5–Rh3–P6 173.61(7), Cl3–Rh3–C5 177.4(2), P5–Rh3–Cl3 92.31(7), P5–Rh3–C5 87.9(2), P6–Rh3–Cl3 85.95(7), P6–Rh3–C5 93.6(2), Rh3–C5–C6 176.6(5), C5–C6–C74 128.5(6).

Scheme 2. L = P*i*Pr$_3$



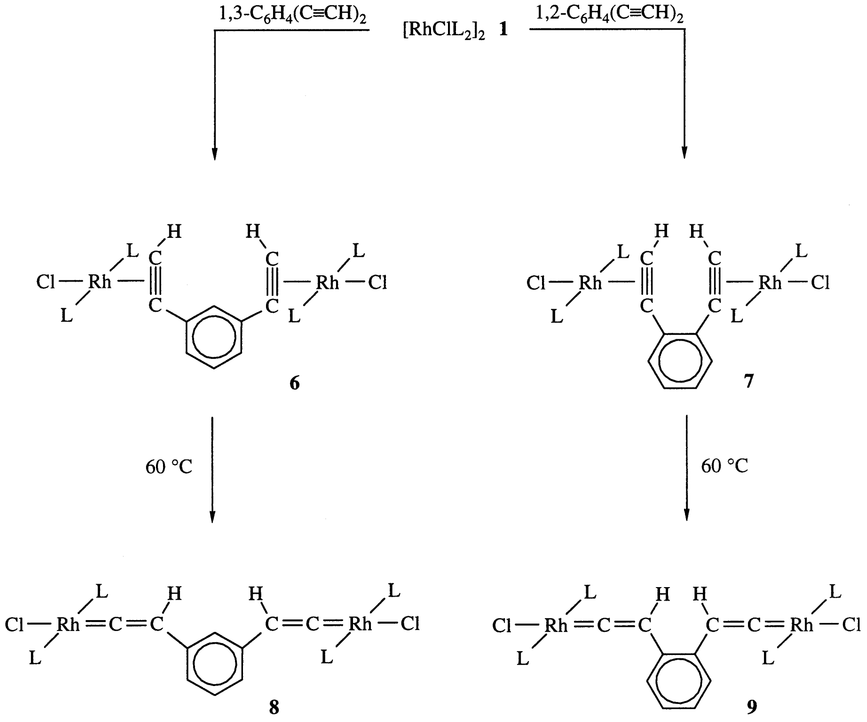
Dinuclear Complexes from Bis(ethynyl)benzene and -naphthalene Derivatives

Likewise to 1,3,5-$C_6H_3(C{\equiv}CH)_3$, the isomers 1,3- and 1,2-$C_6H_4(C{\equiv}CH)_2$ also react with **1** at low temperatures to give the bis(alkyne) complexes **6** and **7** as orange-yellow or yellow microcrystalline solids. The position of the ν(C≡C) stretches in the IR and the chemical shift of the single resonance for the P*i*Pr$_3$ phosphorus nuclei in the ^{31}P-NMR spectra of **6** and **7** are almost identical to those of **2** and thus the proposed structure as shown in Scheme 3 seems to be correct. When heated in toluene, compounds **6** and **7** behave analogously to **2** and afford by an intramolecular rearrangement the isomeric bis(vinylidene) complexes **8** and **9** in excellent yield. Again the spectroscopic data of **8** and **9** are very similar to those of **3** and deserve no further comments.

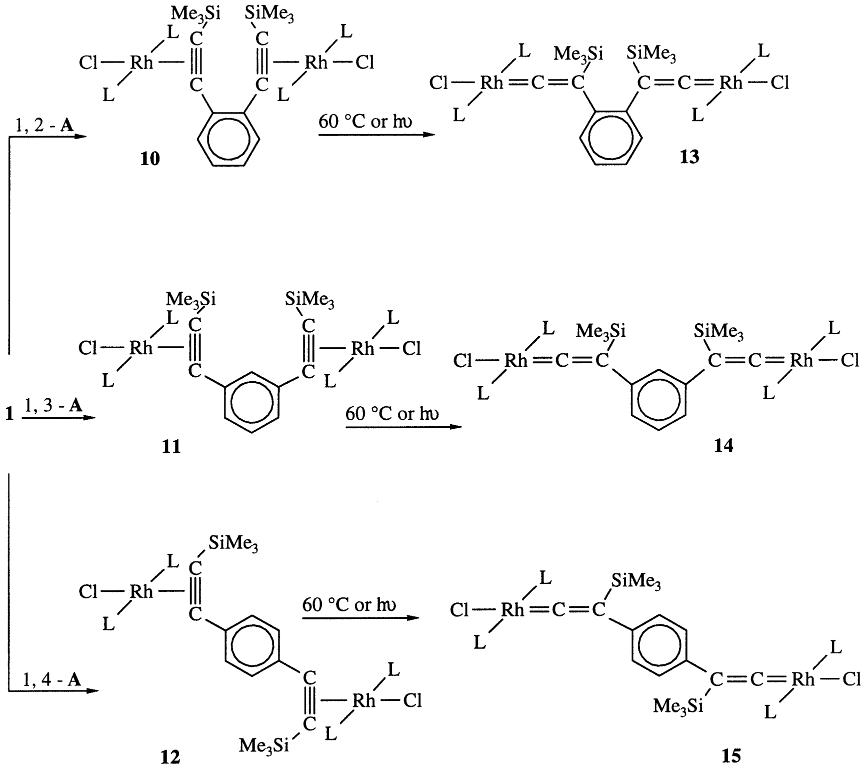
While 1,3,5-$C_6H_3(C{\equiv}CH)_3$ and 1,3,5-$C_6H_3(C{\equiv}CSiMe_3)_3$ behave differently toward the starting material **1**, the disilyl derivatives 1,2-, 1,3-, and 1,4-$C_6H_4(C{\equiv}CSiMe_3)_2$ react in the same way as the parent diynes 1,2-, 1,3-, and 1,4-$C_6H_4(C{\equiv}CH)_2$. In the presence of **1**, they afford the dinuclear dirhodium compounds **10**–**12**, respectively. Since the spectroscopic data of **6**, **7**, and [1,4-$C_6H_4(C{\equiv}CH)_2$\{RhCl(P*i*Pr$_3$)$_2$\}$_2$][6] on one hand and those of **10**–**12** on the other are quite similar, a related structure can be assumed (Scheme 4).

In contrast to compound **5**, which is rather inert, the dinuclear complexes **10**–**12** smoothly rearrange to the vinylidenerhodium compounds **13**–**15** (Scheme 4). The isomerization can be performed either thermally (in toluene at 60 °C) or photochemically and leads to the dark-red moisture-sensitive solids in 60–70% yield. Compounds **13**–**15** were identified by IR, NMR, and UV/Vis spectroscopy as well as by satisfactory microanalyses. In analogy to the re-

Scheme 3. L = P*i*Pr$_3$

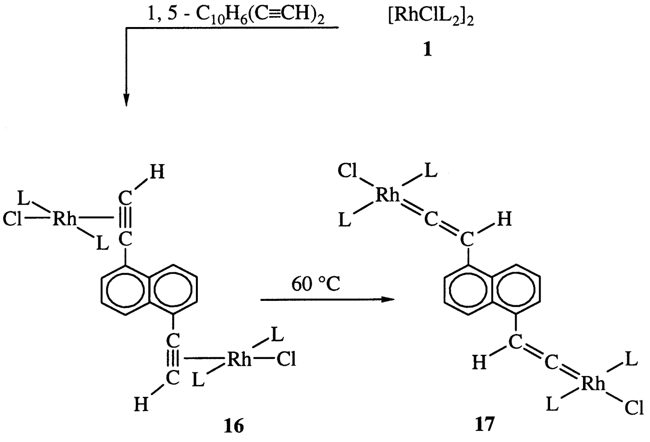


Scheme 4. A = C$_6$H$_4$(C≡CSiMe$_3$)$_2$; L = P*i*Pr$_3$



arrangement of the mononuclear complexes *trans*-[RhCl(RC≡CSiR'$_3$)(P*i*Pr$_3$)$_2$] to *trans*-[RhCl{=C=C(SiR'$_3$)R}(P*i*Pr$_3$)$_2$],[11] there is no evidence that the isomerization of **10**−**12** to **13**−**15** occurs stepwise and thus a concerted mechanism is most likely.[4][12] Although there might be some steric hinderance between the two bulky RhCl(alkyne)(P*i*Pr$_3$)$_2$ units, particularly in compounds **10** and **11**, the reaction of the bis(alkyne) to the bis(vinylidene) complexes proceeds very cleanly and is not accompanied by the formation of oligomeric or polymeric by-products.

Scheme 5. L = P*i*Pr$_3$



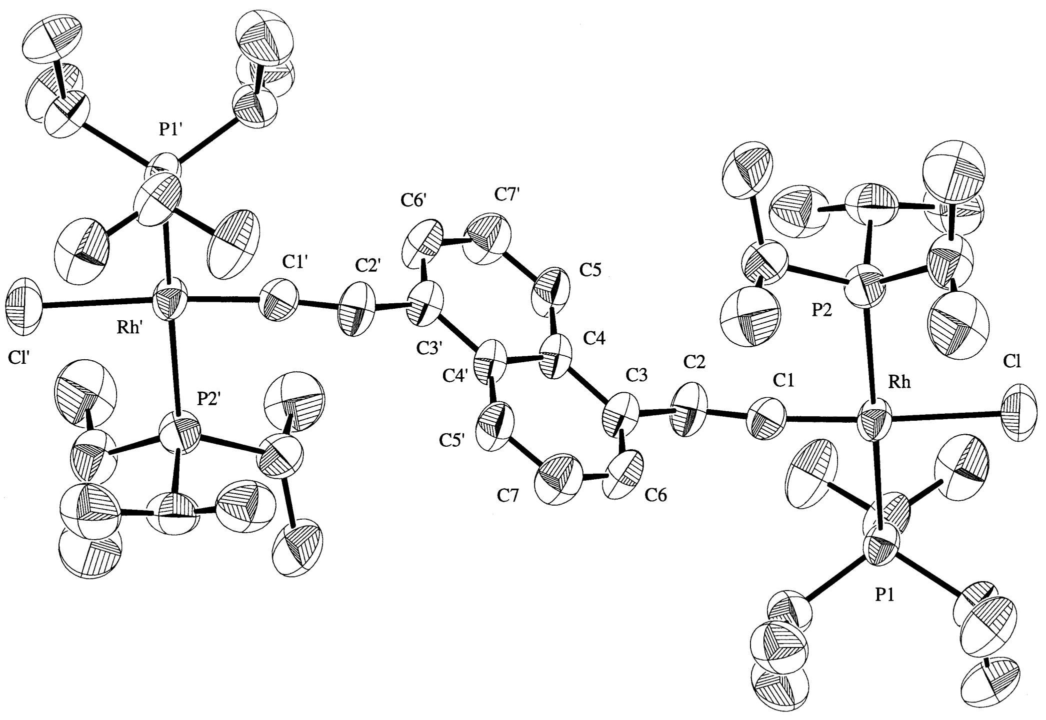
Not only 1,2-, 1,3-, and 1,4-bis(ethynyl)benzene but also 1,5-bis(ethynyl)naphthalene reacts with the starting material **1** in a stepwise manner to give initially the bis(alkyne) and then the bis(vinylidene) compounds **16** and **17**, respectively (Scheme 5). Both have been isolated as red-violet or violet solids in good yield. Single crystals of **17** could be grown from toluene and the molecular structure was determined by X-ray crystallography. As is shown in Figure 2, the dinuclear complex contains a center of inversion which is the midpoint of the C4−C4′ bond. Both rhodium atoms possess a square-planar coordination sphere with axes P1−Rh−P2 and Cl−Rh−C1 that deviate slightly from linearity. The distances Rh−C1 and C1−C2 are almost the same as in the tris(vinylidene) complex **3** and agree with the cumulene-like arrangement. A characteristic structural feature of **17** in the crystal is that the dihedral angle between the planes [Rh,P1,P2,Cl] and [C3,C4,C5,C6,C7] is 78.8(3)° and the torsional angle C1−C2−C3−C4 is 137(1)°. In order to explain these unexpected values, we assume that the non-perpendicular arrangement between the coordination planes [ClRhP$_2$C] and the naphthalene minimizes the steric repulsion between the two space-filling [RhCl(P*i*Pr$_3$)$_2$] units.

This work was supported by the *Deutsche Forschungsgemeinschaft* (SFB 347) and the *Fonds der Chemischen Industrie.* We are grateful to Dr. *B. Stempfle* and Dr. *C. Grünwald* for NMR spectra, to Mrs. *R. Schedl* and Mr. *C. P. Kneis* for performing the elemental analyses and DTA measurements, and to the *Degussa AG* for the gifts of chemicals.

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1**,[7a] the diynes 1,2-$C_6H_4(C{\equiv}CH)_2$, 1,3-$C_6H_4(C{\equiv}CH)_2$, and 1,5-$C_{10}H_6(C{\equiv}CH)_2$, the triyne 1,3,5-$C_6H_3(C{\equiv}CH)_3$, and the trimethylsilyl derivatives 1,2-$C_6H_4(C{\equiv}CSiMe_3)_2$ and 1,3,5-$C_6H_3(C{\equiv}CSiMe_3)_3$ were prepared analogously as described in the literature.[13] 1,3- and 1,4-$C_6H_4(C{\equiv}CSiMe_3)_2$ were commercial products from ABCR. − IR: Perkin-Elmer 1420. − UV/Vis: Hewlett Packard 8452 A. − NMR: Bruker AC 200 and AMX 400 [dvt = doublet of virtual triplets; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^2J(PC) + {}^4J(PC)$, respectively]. − Melting points determined by DTA.

Figure 2. Molecular structure (ORTEP plot) of **17**[a]



[a] Selected bond lengths [Å] and angles [°]: Rh−Cl 2.374(2), Rh−P1 2.360(2), Rh−P2 2.359(2), Rh−C1 1.780(8), C1−C2 1.30(1), C2−C3 1.48(1), C3−C4 1.42(1), C4−C5 1.42(1), C6−C7 1.41(1), C4−C4′ 1.42(1); P1−Rh−P2 172.30(8), Cl−Rh−C1 174.2(3), P1−Rh−Cl 90.96(8), P1−Rh−C1 89.3(2), P2−Rh−Cl 90.28(8), P2−Rh−C1 88.7(2), Rh−C1−C2 173.1(7), C1−C2−C3 126.9(8).

1. Preparation of [1,3,5-$C_6H_3(C{\equiv}CH)_3\{RhCl(PiPr_3)_2\}_3$] (**2**): A solution of 126 mg (0.14 mmol) of **1** in 20 ml of pentane was treated dropwise at −60°C with a solution of 14 mg (0.09 mmol) of 1,3,5-$C_6H_3(C{\equiv}CH)_3$ in 3 ml of pentane. A fairly rapid change of colour from dark red to orange occurred. After the solution was warmed to room temperature, it was stirred for 10 min and then the solvent was removed in vacuo. The yellow microcrystalline residue was repeatedly washed with small portions (1−2 ml) of pentane (0°C) and dried; yield 106 mg (77%); m. p. 125°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (≡CH), 1795 (C≡C). − ^1H NMR (200 MHz, C_6D_6): δ = 8.70 (s, 3 H, C_6H_3), 4.02 [d, J(RhH) = 2.4 Hz, 3 H, ≡CH], 2.36 (m, 18 H, PCHCH$_3$), 1.27 [dvt, N = 12.8, J(HH) = 6.1 Hz, 54 H, PCHCH_3], 0.98 [dvt, N = 13.9, J(HH) = 7.0 Hz, 54 H, PCHCH_3]. − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.3 [d, J(RhP) = 117.0 Hz]. − $C_{66}H_{132}Cl_3P_6Rh_3$ (1526.7): calcd. C 51.92, H 8.71; found C 51.80, H 8.91.

2. Preparation of [1,3,5-$C_6H_3\{CH{=}C{=}RhCl(PiPr_3)_2\}_3$] (**3**): A solution of 106 mg (0.07 mmol) of **2** in 10 ml of toluene was stirred for 2 h at 60°C, which led to a change of colour from orange-yellow to dark green. After cooling to room temperature, the solvent was removed in vacuo. The residue was dissolved in ca. 2 ml of toluene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 6 cm). With toluene, a blue-green fraction was eluted which was brought to dryness in vacuo. The remaining green solid was washed twice with 2-ml portions of pentane (0°C) and dried; yield 78 mg (73%); m. p. 159°C (dec.). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). − UV (hexane): λ_{max} = 580, 438, 294, 242, 224 nm. − ^1H NMR (200 MHz, C_6D_6): δ = 6.77 (s, 3 H, C_6H_3), 2.74 (m, 18 H, PCHCH$_3$), 1.31 [dvt, N = 13.4, J(HH) = 7.0 Hz, PCHCH_3), signal of =CH protons partially covered by signal of PCHCH_3 protons. − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 292.9 [dt, J(RhC) = 59.8, J(PC) = 15.8 Hz, Rh=C], 133.2, 129.7 (both s, C_6H_3), 111.1 [dt, J(RhC) = 15.2, J(PC) = 6.3 Hz, Rh=C=C], 23.8 (vt, N = 20.2 Hz, PCHCH$_3$), 20.2 (s, PCHCH$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.1 [d, J(RhP) = 135.1 Hz]. − $C_{66}H_{132}Cl_3P_6Rh_3$ (1526.7): calcd. C 51.92, H 8.71; found C 51.25, H 8.79.

3. Reaction of Compounds **2** *and* **3** *with Pyridine: a)* A mixture of 115 mg (0.08 mmol) of **2** and 0.1 ml (1.22 mmol) of pyridine was heated for 10 min at ca. 100°C, which led to a change of colour from yellow to off-white. After the reaction mixture was cooled to room temperature, 2 ml of pentane was added, and the solution was stored for 12 h at −78°C. A white solid precipitated which was separated from the mother liquor, washed twice with 2-ml portions of pentane (0°C) and dried; yield 82 mg (58%). Although the ^1H- and ^{31}P-NMR spectra confirmed that the isolated sample was pure, no reliable elemental analysis of **4** could be obtained. − *b)* Analogously as described for a), by using 102 mg (0.07 mmol) of **3** and 0.1 ml (1.22 mmol) of pyridine as the starting materials. White solid; yield 99 mg (80%). − IR (KBr): $\tilde{\nu}$ = 2150 cm^{-1} (RhH), 2080 (C≡C). − ^1H NMR (200 MHz, $CDCl_3$): δ = 9.51, 7.68−6.50 (both m, 18 H, C_6H_3 and NC_5H_5), 2.71 (m, 18 H, PCHCH$_3$), 1.26 [dvt, N = 13.0, J(HH) = 6.2 Hz, 54 H, PCHCH_3], 1.11 [dvt, N = 13.2, J(HH) = 6.3 Hz, 54 H, PCHCH_3], −17.64 [dt, J(RhH) = 13.8, J(PH) = 13.7 Hz, 3 H, RhH]. − ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 37.7 [d, J(RhP) = 97.4 Hz].

4. Preparation of trans-[$RhCl\{\eta^2$-$Me_3SiC{\equiv}CC_6H_3$-3,5-$(C{\equiv}CSiMe_3)_2\}(PiPr_3)_2$] (**5**): A solution of 200 mg (0.22 mmol) of **1** in 20 ml of pentane was treated dropwise at −60°C with a solution of 144 mg (0.44 mmol) of 1,3,5-$C_6H_3(C{\equiv}CSiMe_3)_3$ in 3 ml of pentane. After the solution was worked up as described for **2** a bright orange solid was obtained; yield 222 mg (61%); m. p. 66°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2140 cm^{-1} $(C{\equiv}C)_{uncoord}$, 1795 $(C{\equiv}C)_{coord}$. − ^1H NMR (200 MHz, C_6D_6): δ = 7.68−7.38 (m, 3 H, C_6H_3), 2.28 (m, 6 H, PCHCH$_3$), 1.29 [dvt, N = 13.5, J(HH) = 6.7 Hz, 18 H, PCHCH_3], 1.01 [dvt, N = 12.8, J(HH) = 6.3 Hz, 18 H, PCHCH_3], 0.27 (s, 9 H, $SiMe_3$), 0.17 (s, 18 H, $SiMe_3$). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 135.3, 134.8, 125.6, 124.3 (all s, C_6H_3), 103.7, 95.9 (both s, $C{\equiv}C_{uncoord}$), 86.4, 82.2 [both d, J(RhC) = 13.5 Hz, $C{\equiv}C_{coord}$], 22.6 (vt, N = 17.1 Hz, PCHCH$_3$), 21.0, 19.5, (both s, PCHCH$_3$], 1.0, 0.5 (both s, $SiMe_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.1 [d, J(RhP) = 116.3 Hz].

5. Preparation of [1,3-$C_6H_4(C{\equiv}CH)_2\{RhCl(PiPr_3)_2\}_2$] (**6**): Analogously as described for **2**, by using 147 mg (0.16 mmol) of **1** and 20 mg (0.16 mmol) of 1,3-$C_6H_4(C{\equiv}CH)_2$ as starting materials. Orange-yellow solid; yield 128 mg (77%); m. p. 118°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (≡CH), 1790 (C≡C). − ^1H NMR (200 MHz, C_6D_6): δ = 7.08−6.42 (m, 4 H, C_6H_4), 3.73 [d, J(RhH) = 2.8 Hz, 2 H, ≡CH], 2.06 (m, 12 H, PCHCH$_3$), 1.03 [dvt, N = 13.8, J(HH) = 7.3 Hz, 36 H, PCHCH_3], 0.87 [dvt, N = 13.1, J(HH) = 7.3 Hz, 36 H, PCHCH_3]. − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.8 [d, J(RhP) = 116.3 Hz]. − $C_{46}H_{90}Cl_2P_4Rh_2$ (1043.8): calcd. C 52.93, H 8.69; found C 53.02, H 8.94.

6. Preparation of [1,2-$C_6H_4(C{\equiv}CH)_2\{RhCl(PiPr_3)_2\}_2$] (**7**): Analogously as described for **2**, by using 117 mg (0.13 mmol) of **1** and 16 mg (0.13 mmol) of 1,2-$C_6H_4(C{\equiv}CH)_2$ as starting materials. Yellow solid; yield 88 mg (65%); m. p. 135°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (≡CH), 1790 (C≡C). − ^1H NMR (200 MHz, C_6D_6): δ = 8.73−7.29 (m, 4 H, C_6H_4), 4.53 [d, J(RhH) = 2.2 Hz, 2 H, ≡CH], 2.25 (m, 12 H, PCHCH$_3$), 1.21 [dvt, N = 13.1, J(HH) = 6.9 Hz, 36 H, PCHCH_3], 1.07 [dvt, N = 12.6, J(HH) = 6.4 Hz, 36 H, PCHCH_3]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 131.8, 127.4, 127.0 (all s, C_6H_4), 88.3, 85.2 [both d, J(RhC) = 17.8 Hz, C≡C], 22.9 (vt, N = 17.6 Hz, PCHCH$_3$), 20.5, 20.3 (both s, PCHCH$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 34.0 [d, J(RhP) = 116.3 Hz]. − $C_{46}H_{90}Cl_2P_4Rh_2$ (1043.8): calcd. C 52.93, H 8.69; found C 53.13, H 8.63.

7. Preparation of [1,3-$C_6H_4\{CH{=}C{=}RhCl(PiPr_3)_2\}_2$] (**8**): Analogously as described for **3**, by using 134 mg (0.13 mmol) of **6** as starting material. Blue-green solid; yield 102 mg (75%), m. p. 82°C (dec.). − IR (pentane): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). − UV (hexane): λ_{max} = 580, 446, 282, 240, 224, 210 nm. − ^1H NMR (200 MHz, C_6D_6): δ = 7.29−6.54 (m, 4 H, C_6H_4), 2.63 (m, 12 H, PCHCH$_3$), 1.16 [dvt, N = 13.7, J(HH) = 6.7 Hz, PCHCH_3], signal of =CH protons partially covered by signal of PCHCH_3 protons. − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 293.1 [dt, J(RhC) = 60.0, J(PC) = 15.9 Hz, Rh=C], 135.7, 132.2, 125.6, 122.5 (all s, C_6H_4), 111.3 [dt, J(RhC) = 15.3, J(PC) = 6.4 Hz, Rh=C=C], 23.7 (vt, N = 20.3 Hz, PCHCH$_3$), 20.1 (s, PCHCH$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.2 [d, J(RhP) = 133.9 Hz]. − $C_{46}H_{90}Cl_2P_4Rh_2$ (1043.8): calcd. C 52.93, H 8.69; found C 53.29, H 9.08.

8. Preparation of [1,2-$C_6H_4\{CH{=}C{=}RhCl(PiPr_3)_2\}_2$] (**9**): Analogously as described for **3**, by using 121 mg (0.12 mmol) of **7** as starting material. Bright green solid; yield 84 mg (67%); m. p. 128°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). − UV (hexane): λ_{max} = 574, 436, 280, 240, 222 nm. − ^1H NMR (200 MHz, C_6D_6): δ = 7.80−6.48 (m, 4 H, C_6H_4), 2.70 (m, 12 H, PCHCH$_3$), 2.25 [dt, J(PH) = 3.1, J(RhH) = 1.0 Hz, 2 H, =CH], 1.29 [dvt, N = 13.0, J(HH) = 6.2 Hz, 72 H, PCHCH_3]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 292.2 [dt, J(RhC) = 59.6, J(PC) = 15.3 Hz, Rh=C], 132.9, 128.9, 127.1 (all s, C_6H_4), 110.3 [dt, J(RhC) = 15.5, J(PC) = 5.7 Hz, Rh=C=C], 24.0 (vt, N = 20.2 Hz, PCHCH$_3$), 20.3 (s, PCHCH$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.6 [d, J(RhP) =

133.7 Hz]. − $C_{46}H_{90}Cl_2P_4Rh_2$ (1043.8): calcd. C 52.93, H 8.69; found C 52.72, H 8.29.

9. Preparation of $[1,2\text{-}C_6H_4(C{\equiv}CSiMe_3)_2\{RhCl(PiPr_3)_2\}_2]$ (**10**): Analogously as described for **2**, by using 157 mg (0.17 mmol) of **1** and 46 mg (0.17 mmol) of $1,2\text{-}C_6H_4(C{\equiv}CSiMe_3)_2$ as starting materials. Light orange solid; yield 156 mg (77%); m. p. 112°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1810 cm^{-1} (C≡C). − ^{1}H NMR (400 MHz, C_6D_6): δ = 9.93−6.64 (m, 4 H, C_6H_4), 2.98 (m, 12 H, PC*H*CH$_3$), 1.33 [dvt, *N* = 13.9, *J*(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$], 1.08 [dvt, *N* = 11.7, *J*(HH) = 6.1 Hz, 36 H, PCHC*H*$_3$], 0.6 (s, 18 H, SiMe$_3$). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 138.2, 132.2, 126.5 (all s, C_6H_4), 109.2 [d, *J*(RhC) = 18.8 Hz, *C*≡C], 85.1 [d, *J*(RhC) = 12.5 Hz, C≡*C*], 22.9 (vt, *N* = 15.6 Hz, P*C*HCH$_3$), 21.3, 19.6 (both s, PCH*C*H$_3$], 0.7 (s, SiMe$_3$). − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 29.5 [d, *J*(RhP) = 117.7 Hz]. − $C_{52}H_{106}Cl_2P_4Rh_2Si_2$ (1188.2): calcd. C 52.56, H 8.99; found C 52.84, H 9.02.

10. Preparation of $[1,3\text{-}C_6H_4(C{\equiv}CSiMe_3)_2\{RhCl(PiPr_3)_2\}_2]$ (**11**): Analogously as described for **2**, using 121 mg (0.13 mmol) of **1** and 36 mg (0.13 mmol) of $1,3\text{-}C_6H_4(C{\equiv}CSiMe_3)_2$ as starting materials. Light orange solid; yield 114 mg (74%); m. p. 106°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1800 cm^{-1} (C≡C). − ^{1}H NMR (200 MHz, C_6D_6): δ = 7.54−6.75 (m, 4 H, C_6H_4), 2.40 (m, 12 H, PC*H*CH$_3$), 1.37 [dvt, *N* = 13.5, *J*(HH) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.10 [dvt, *N* = 12.4, *J*(HH) = 6.2 Hz, 36 H, PCHC*H*$_3$], 0.46 (s, 18 H, SiMe$_3$). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 134.2, 130.8, 126.3, 125.8 (all s, C_6H_4), 105.8 [d, *J*(RhC) = 19.8 Hz, *C*≡C], 80.6 [d, *J*(RhC) = 16.8 Hz, C≡*C*], 22.5 (vt, *N* = 16.0 Hz, P*C*HCH$_3$), 21.3, 19.5 (both s, PCH*C*H$_3$), 0.9 (s, SiMe$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.2 [d, *J*(RhP) = 117.9 Hz]. − $C_{52}H_{106}Cl_2P_4Rh_2Si_2$ (1188.2): calcd. C 52.56, H 8.99; found C 52.75, H 8.93.

11. Preparation of $[1,4\text{-}C_6H_4(C{\equiv}CSiMe_3)_2\{RhCl(PiPr_3)_2\}_2]$ (**12**): Analogously as described for **2**, by using 139 mg (0.15 mmol) of **1** and 41 mg (0.15 mmol) of $1,4\text{-}C_6H_4(C{\equiv}CSiMe_3)_2$ as starting materials. Yellow solid; yield 128 mg (72%); m. p. 108°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1790 cm^{-1} (C≡C). − ^{1}H NMR (200 MHz, C_6D_6): δ = 8.65−6.51 (m, 4 H, C_6H_4), 2.40 (m, 12 H, PC*H*CH$_3$), 1.38 [dvt, *N* = 13.6, *J*(HH) = 6.9 Hz, 36 H, PCHC*H*$_3$], 1.08 [dvt, *N* = 12.8, *J*(HH) = 6.2 Hz, 36 H, PCHC*H*$_3$], 0.37 (s, 18 H, SiMe$_3$). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 132.1, 122.3 (both s, C_6H_4), 106.4 [d, *J*(RhC) = 18.7 Hz, *C*≡C], 80.6 [d, *J*(RhC) = 14.4 Hz, C≡*C*], 22.4 (vt, *N* = 17.1 Hz, P*C*HCH$_3$), 21.0, 19.4 (both s, PCH*C*H$_3$), 0.8 (s, SiMe$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.1 [d, *J*(RhP) = 116.9 Hz]. − $C_{52}H_{106}Cl_2P_4Rh_2Si_2$ (1188.2): calcd. C 52.56, H 8.99; found C 52.14, H 8.68.

12. Preparation of $[1,2\text{-}C_6H_4\{C(SiMe_3){=}C{=}RhCl(PiPr_3)_2\}_2]$ (**13**): *a)* A solution of 134 mg (0.11 mmol) of **10** in 10 ml of toluene was stirred for 1.5 h at 60°C. A change of colour from orange-red to dark brown occurred. After the solution was cooled to room temperature, it was concentrated to ca. 2 ml in vacuo and then 5 ml of pentane was added. A redbrown solid precipitated which was filtered, washed twice with 2-ml portions of pentane and dried; yield 81 mg (62%). − *b)* A solution of 106 mg (0.09 mmol) of **10** in 10 ml of benzene was irradiated for 2 h at room temperature with a UV lamp (500-W mercury arc). After the solvent was removed, the remaining residue was recrystallized from pentane (20°C to −60°C). Dark red crystals; yield 69 mg (65%); m. p. 109°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1610 cm^{-1} (C=C). − UV (hexane): λ_{max} = 568, 440, 280, 240, 222, 206 nm. − ^{1}H NMR (400 MHz, C_6D_6): δ = 7.82−6.48 (m, 4 H, C_6H_4), 2.71 (m, 12 H, PC*H*CH$_3$), 1.27 [dvt, *N* = 13.6, *J*(HH) = 6.9 Hz, 36 H, PCHC*H*$_3$], 0.87 [dvt, *N* = 13.5, *J*(HH) = 6.8 Hz, 36 H, PCHC*H*$_3$], 0.25 (s, 18 H, SiMe$_3$). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 286.4 [dt, *J*(RhC) = 60.3, *J*(PC) = 15.9 Hz, Rh=C], 131.6, 126.7, 124.7 (all s, C_6H_4), 110.7 [dt, *J*(RhC) = 10.5, *J*(PC) = 3.8 Hz, Rh=C=*C*], 22.6 (vt, *N* = 20.1 Hz, P*C*HCH$_3$), 21.3 (s, PCH*C*H$_3$), 0.7 (s, SiMe$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.6 [d, *J*(RhP) = 133.7 Hz]. − $C_{52}H_{106}Cl_2P_4Rh_2Si_2$ (1188.2): calcd. C 52.56, H 8.99; found C 52.11, H 8.96.

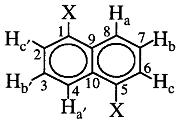
13. Preparation of $[1,3\text{-}C_6H_4\{C(SiMe_3){=}C{=}RhCl(PiPr_3)_2\}_2]$ (**14**): *a)* A solution of 132 mg (0.11 mmol) of **11** in 10 ml of toluene was stirred for 2.5 h at 60°C. A change of colour from orange-red to dark brown occurred. After the solution was worked up as described for **13**, a dark red solid was obtained; yield 85 mg (65%). − *b)* A solution of 118 mg (0.10 mmol) of **11** in 10 ml of benzene was irradiated for 2 h at room temperature with a UV lamp (500-W mercury arc). The work-up procedure was the same as for **13**. Dark red crystals; yield 72 mg (61%); m. p. 81°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). − UV (hexane): λ_{max} = 502, 358, 240, 222, 204 nm. − ^{1}H NMR (200 MHz, C_6D_6): δ = 7.67−6.72 (m, 4 H, C_6H_4), 2.71 (m, 12 H, PC*H*CH$_3$), 1.33 [dvt, *N* = 13.4, *J*(HH) = 6.4 Hz, 36 H, PCHC*H*$_3$], 0.86 [dvt, *N* = 13.2, *J*(HH) = 6.2 Hz, 36 H, PCHC*H*$_3$], 0.27 (s, 18 H, SiMe$_3$). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 291.3 [dt, *J*(RhC) = 60.2, *J*(PC) = 15.8 Hz, Rh=C], 133.4, 130.2, 126.5, 125.0 (all s, C_6H_4), 110.2 [dt, *J*(RhC) = 9.8, *J*(PC) = 3.7 Hz, Rh=C=*C*], 22.1 (vt, *N* = 19.9 Hz, P*C*HCH$_3$), 21.1 (s, PCH*C*H$_3$), 0.9 (s, SiMe$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 42.5 [d, *J*(RhP) = 135.2 Hz]. − $C_{52}H_{106}Cl_2P_4Rh_2Si_2$ (1188.2): calcd. C 52.56, H 8.99, Rh 17.32; found C 52.09, H 8.94, Rh 17.15.

14. Preparation of $[1,4\text{-}C_6H_4\{C(SiMe_3){=}C{=}RhCl(PiPr_3)_2\}_2]$ (**15**): *a)* A solution of 137 mg (0.12 mmol) of **12** in 10 ml of toluene was stirred for 3 h at 60°C. A change of colour from orange-red to dark brown occurred. After the solution was worked up as described for **13**, a dark brown solid was obtained; yield 91 mg (64%). − *b)* A solution of 121 mg (0.10 mmol) of **12** in 10 ml of benzene was irradiated for 2 h at room temperature with a UV lamp (500-W mercury arc). After the solvent was removed, the remaining residue was recrystallized from pentane (20°C to −60°C). Dark red crystals; yield 75 mg (63%); m. p. 60°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). − UV (hexane): λ_{max} = 536, 346, 248, 222, 202 nm. − ^{1}H NMR (400 MHz, C_6D_6): δ = 7.62−6.95 (m, 4 H, C_6H_4), 2.75 (m, 12 H, PC*H*CH$_3$), 1.31 [dvt, *N* = 13.0, *J*(HH) = 6.5 Hz, 36 H, PCHC*H*$_3$], 0.85 [dvt, *N* = 13.4, *J*(HH) = 6.6 Hz, 36 H, PCHC*H*$_3$], 0.28 (s, 18 H, SiMe$_3$). − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.2 [d, *J*(RhP) = 135.1 Hz]. − $C_{52}H_{106}Cl_2P_4Rh_2Si_2$ (1188.2): calcd. C 52.56, H 8.99; found C 52.14, H 9.23.

15. Preparation of $[1,5\text{-}C_{10}H_6(C{\equiv}CH)_2\{RhCl(PiPr_3)_2\}_2]$ (**16**): Analogously as described for **2**, by using 123 mg (0.13 mmol) of **1** and 23 mg (0.13 mmol) of $1,5\text{-}C_{10}H_6(C{\equiv}CH)_2$ as starting materials. Red-violet solid; yield 95 mg (67%); m. p. 122°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (≡CH), 1795 (C≡C). − ^{1}H NMR (400 MHz, C_6D_6): δ = 9.17 [d, *J*(H_cH_b) = 6.8 Hz, 2 H, H_c and $H_{c'}$], 8.44 [d, *J*(H_aH_b) = 8.4 Hz, 2 H, H_a and $H_{a'}$], 7.61 {dd, *J*(H_bH_a) = *J*(H_bH_c) = 1/2 [*J*(H_bH_a) + *J*(H_bH_c)] = 7.6 Hz, 2 H, H_b and $H_{b'}$}, 4.37 [d, *J*(RhH) = 2.4 Hz, 2 H, ≡CH], 2.34 (m, 12 H, PC*H*CH$_3$), 1.29 [dvt, *N* = 13.2, *J*(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$], 1.28 [dvt, *N* = 13.4, *J*(HH) = 6.8 Hz, 36 H, PCHC*H*$_3$]. − ^{31}P NMR (81.0 MHz, C_6D_6): δ = 33.9 [d, *J*(RhP) = 117.7 Hz]. − $C_{50}H_{92}Cl_2P_4Rh_2$ (1093.9): calcd. C 54.90, H 8.48, Rh 18.82; found C 54.73, H 8.88, Rh 18.48.

16. Preparation of $[1,5\text{-}C_{10}H_6\{CH{=}C{=}RhCl(PiPr_3)_2\}_2]$ (**17**): Analogously as described for **3**, by using 132 mg (0.12 mmol) of **16** as starting material. Violet solid; yield 96 mg (73%); m. p. 196°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=C). − ^{1}H NMR (400 MHz, C_6D_6): δ = 7.82 [dd, *J*(H_bH_a) = *J*(H_bH_c) = 7.6 Hz, 2 H, H_b and

Figure 3. Numbering scheme in **16** and **17** for NMR assignments



X = (C≡CH){RhCl(P*i*Pr$_3$)$_2$}

or (CH=C){RhCl(P*i*Pr$_3$)$_2$}

H$_{b'}$], 7.11 [d, J(HH$_b$) = 7.6 Hz, 2 H, H$_a$ or H$_c$], 7.01 [d, J(HH$_b$) = 7.6 Hz, 2 H, H$_a$ or H$_c$], 2.72 (m, 12 H, PC*H*CH$_3$), 2.27 [t, J(PH) = 3.2 Hz, 2 H, =CH], 1.28 [dvt, N = 13.6, J(HH) = 6.9 Hz, 72 H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 137.8 (s, C^1 and C^5), 130.3 (s, C^9 and C^{10}), 129.3, 128.5, 125.6 (all s, C^2 and C^6, C^3 and C^7, C^4 and C^8), 107.6 [dt, J(RhC) = 15.3, J(PC) = 5.8 Hz, Rh=C=*C*], 24.1 (dvt, N = 20.0 Hz, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$), signal of Rh=C could not be observed. – ^{31}P NMR (81.0 MHz, C$_6$D$_6$): δ = 43.4 [d, J(RhP) = 135.1 Hz]. – $C_{50}H_{92}Cl_2P_4Rh_2$ (1093.9): calcd. C 54.90, H 8.48, Rh 18.82; found C 54.51, H 8.30, Rh 19.17.

17. Determination of the X-ray Crystal Structure of **3**[14]: Single crystals were grown upon cooling of a saturated solution of **3** in acetone from 50°C to 25°C. Crystal data (from 25 reflections, 10° < Θ < 15°): monoclinic; space group $P\,2_1/c$ (No. 14); a = 29.729(5), b = 11.2733(9), c = 26.579(5) Å, β = 114.406(8)°; V = 8112(2) Å^3, Z = 4; $d_{\text{calcd.}}$ = 1.250 gcm^{-3}; μ(Mo-K_α) = 0.853 mm^{-1}; crystal size 0.72 × 0.44 × 0.40 mm; Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator, zirconium filter (factor 16.4); T = 173(2) K; ω-2θ scan, max. 2θ = 48°; 13712 reflections measured, 12400 independent (R$_{\text{int.}}$ = 0.0395), 8211 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ scan method) was applied (min. transmission 82.49%). The structure was solved by direct methods (SHELXS-86)[15]. Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93)[16]. The positions of all hydrogen atoms except H(2), H(4), H(6), H(71), H(73), and H(75) were calculated according to ideal geometry and were refined by using the riding method. The positions of H(2), H(4), H(6), H(71), H(73), and H(75) could be located in a final difference Fourier synthesis and refined without restrictions. Conventional R = 0.0505 [for 8211 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.1218 for all 12400 located reflections; reflection/parameter ratio 16.2; residual electron density +0.869/−0.842 eÅ^{-3}.

18. Determination of the X-ray Crystal Structure of **17**[14]: Single crystals were grown upon cooling of a saturated solution of **17** in toluene from 80°C to 25°C. Crystal data (from 25 reflections, 10° < Θ < 15°): triclinic; space group $P\bar{1}$ (No. 2); a = 8.843(2), b = 12.093(3), c = 15.496(3) Å, α = 107.45(1), β = 96.65(1), γ = 94.51(1)°; V = 1559.1(6) Å^3, Z = 2; $d_{\text{calcd.}}$ = 1.267 gcm^{-3}; μ(Mo-K_α) = 0.744 mm^{-1}; crystal size 0.2 × 0.3 × 0.45 mm; Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation (λ = 0.7093 Å), graphite monochromator, zirconium filter (factor 15.4); T = 293(2) K; ω-θ scan, max. 2θ = 60°; 6930 reflections measured, 6500 independent (R$_{\text{int.}}$ = 0.0243), 4675 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86)[15]. Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93)[16]. The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by using the riding method. One half of multi-disordered toluene is present in the asymmetric unit. Though two alternative positions were found and refined anisotropically (with occupation factor of 0.5 each), bond lengths and angles within this molecule could not be refined properly. Conventional R = 0.0775 [for 4675 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.4229 for all 6500 located reflections; reflection/parameter ratio 16.2; residual electron density +1.473/−0.860 eÅ^{-3}.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101424. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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