

# Synthesis and reactivity of dinuclear rhodium complexes with Rh=C=CHR and Rh=C=C=CRR' units as building blocks

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Dedicated with great admiration to Professor Ernst Otto Fischer on the occasion of his 85th birthday

## Abstract

The reaction of  $[\text{Rh}\{\kappa^2\text{-O}_2\text{S}(\text{O})\text{CF}_3\}(\text{P}^i\text{Pr}_3)_2]$  (**1**) with ethynylferrocene in the presence of KF affords the substituted vinylidene complex  $\text{trans-}[\text{RhF}\{\text{C}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}(\text{P}^i\text{Pr}_3)_2]$  (**2**) which upon treatment with the butadiyne derivative  $\text{Ph}_3\text{SnC}\equiv\text{C}-\text{C}\equiv\text{CSnPh}_3$  produces the chain-like compound  $\text{trans-}[\{\mu\text{-C}\equiv\text{C}-\text{C}\equiv\text{C}\}\{\text{Rh}(\text{C}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5))(\text{P}^i\text{Pr}_3)_2\}_2]$  (**7**). The triflate complex **1** reacts with  $1,4\text{-C}_6\text{H}_4(\text{C}\equiv\text{CH})_2$  to give the dinuclear compound  $\text{trans-}[\{\mu\text{-}1,4\text{-C}_6\text{H}_4(\text{CH}=\text{C}=\text{C})\}_2\{\text{Rh}(\eta^1\text{-OS}(\text{O})_2\text{CF}_3)(\text{P}^i\text{Pr}_3)_2\}_2]$  (**3**) which in the presence of KF undergoes a ligand exchange to give the corresponding difluoro derivative **4**. From **4** and  $\text{RC}\equiv\text{CSnPh}_3$  ( $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ) the complexes **5** and **6**, in which a  $\text{C}_6\text{H}_4$  unit bridges two alkynyl(vinylidene)rhodium(I) fragments, are obtained. Both **6** and **7** react with CO by migratory insertion of the vinylidene units into the alkynyl-metal bonds to afford the dinuclear complexes **8** and **9**, in which an unusual  $\text{C}_8$  or  $\text{C}_4(\text{C}_6\text{H}_4)\text{C}_4$  chain bridges the two rhodium centers. The reactions of  $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2]_2$  (**10**) with the functionalized diynes  $1,1',4,4'\text{-C}_6\text{H}_4(\text{OH})_2(\text{C}\equiv\text{CH})_2$  and  $1,4\text{-C}_6\text{H}_4[\text{C}(\text{Ph})(\text{OH})\text{C}\equiv\text{CH}]_2$  lead, via the corresponding diyne-metal species **11** and **12** as intermediates, to the formation of the bis(vinylidene) complexes **13** and **14**, the latter of which reacts with acidic  $\text{Al}_2\text{O}_3$  by elimination of water to give the novel phenylene-bridged bis(allylidynerhodium) compound  $[\{\mu\text{-}1,4\text{-C}_6\text{H}_4(\text{CPh}=\text{C}=\text{C})\}_2\{\text{RhCl}(\text{P}^i\text{Pr}_3)_2\}_2]$  (**15**) in 80% yield.

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**Keywords:** Alkynyl complexes; Allenylidene complexes; Vinylidene complexes; Triflate complexes; Rhodium

## 1. Introduction

In the context of our studies on the conversion of terminal alkynes  $\text{HC}\equiv\text{CR}$  to the isomeric vinylidenes  $\text{C}=\text{CHR}$  in the coordination sphere of rhodium(I) [1], we have recently shown that also 1,4-bis(ethynyl)benzene and 1,3,5-tris(ethynyl)benzene can be transformed, in the presence of  $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2]_2$  as the template, to the corresponding metal-bonded bis(vinylidenes) and tris(vinylidenes), respectively [2,3]. Moreover, we reported that the reactivity of the rhodium vinylidenes of the type  $\text{trans-}[\text{RhCl}(\text{C}=\text{CHR})(\text{P}^i\text{Pr}_3)_2]$

can be enhanced if the chloro ligand is replaced by fluoride and that the triflate complex  $[\text{Rh}\{\kappa^2\text{-O}_2\text{S}(\text{O})\text{CF}_3\}(\text{P}^i\text{Pr}_3)_2]$  is a suitable starting material for the synthesis of the required fluoro derivatives  $\text{trans-}[\text{RhF}(\text{C}=\text{CHR})(\text{P}^i\text{Pr}_3)_2]$  [4].

We have now applied this methodology to prepare a dinuclear fluororhodium(I) complex with a bridging phenylene group between the two vinylidene-metal units and used this compound for the synthesis of new chain-like organometallic molecules. In the present paper we further illustrate that dinuclear vinylidynerhodium compounds with an extended bridge between the two vinylidene-metal moieties are accessible and that one of them can be transformed to the first complex in which two allenidynerhodium fragments are connected by a  $1,4\text{-C}_6\text{H}_4$  bridge.

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## 2. Results and discussion

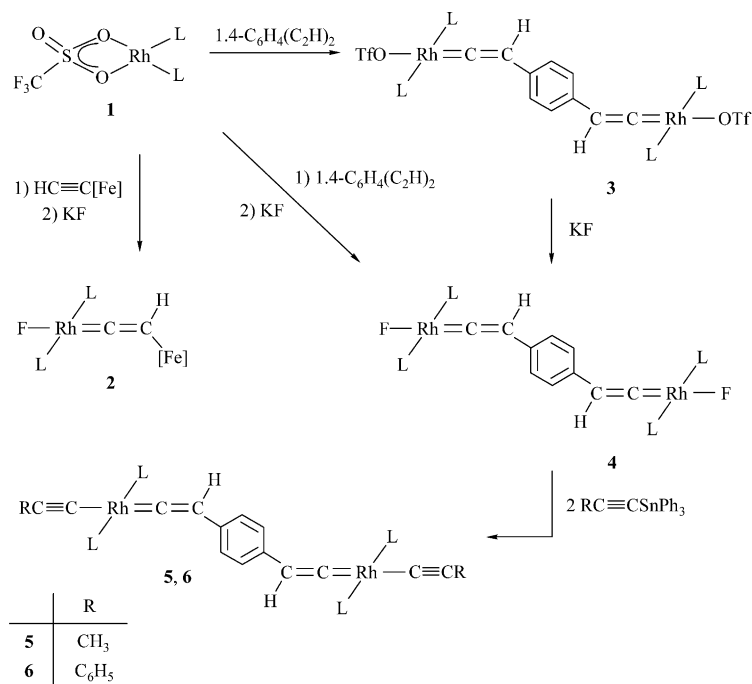
Under rather mild conditions, the triflate compound **1** (recently prepared from  $[(\eta^3\text{-C}_3\text{H}_5)\text{Rh}(\text{P}^i\text{Pr}_3)_2]$  and  $\text{CF}_3\text{SO}_3\text{H}$  [5]) reacts with ethynylferrocene in acetone to give a deeply colored intermediate which we assume is the vinylidene complex *trans*- $[\text{Rh}\{\kappa^1\text{-OS}(\text{O})_2\text{CF}_3\}\{\text{C}=\text{CH}(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}(\text{P}^i\text{Pr}_3)_2]$ . Since this species appeared to be rather labile, it was treated in situ with KF and gave, after recrystallization from pentane, the fluoro derivative **2** in 73% isolated yield (Scheme 1). The violet solid, which gave a correct elemental analysis, is moderately air-sensitive and readily soluble in all common organic solvents. Typical spectroscopic features are the resonance at  $\delta$  45.7 in the  $^{31}\text{P}$ -NMR spectrum, which is split into a doublet of doublets due to  $^{31}\text{P}\text{-}^{19}\text{F}$  and  $^{31}\text{P}\text{-}^{103}\text{Rh}$  couplings, and the signal for the vinylidene proton at  $\delta$  1.18 in the  $^1\text{H}$ -NMR spectrum. The UV-vis spectrum of **2** shows two maxima at  $\lambda$  408 and 553 nm which in agreement with data from the literature are assigned to metal-to-ligand charge transfer bands [6].

The reaction of **1** with 1,4-bis(ethynyl)benzene proceeds similarly to that with ethynylferrocene but in this case we succeeded to isolate the bis(triflate)dirhodium compound **3** as a dark violet solid in 85% yield. Diagnostic for **3** are the signals in the  $^{13}\text{C}$ -NMR spectrum at  $\delta$  304.9 and 112.6 for the  $\alpha$ -C and  $\beta$ -C carbon atoms of the vinylidene ligands and also the resonance at  $\delta$  121.7 for the carbon atom of the  $\text{CF}_3$  group. Treatment of **3** with KF in acetone gives the difluoro derivative **4** by ligand exchange. The direct

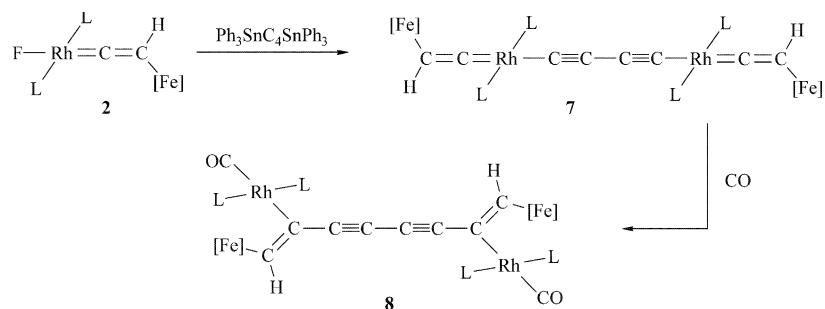
synthesis of **4** via a one-pot reaction of **1** with 1,4- $\text{C}_6\text{H}_4(\text{C}\equiv\text{CH})_2$  and KF is also possible. However, we note that attempts to prepare compound **4** by salt metathesis from the dichloro counterpart *trans*- $[\{\mu\text{-}1,4\text{-C}_6\text{H}_4(\text{CH}=\text{C}=\text{C})_2\}\{\text{RhCl}(\text{P}^i\text{Pr}_3)_2\}_2]$  [2] and KF as the precursors remained unsuccessful.

In agreement with recent studies [7], we found that the Rh–F bond of **4** is rather labile and thus upon treatment of **4** with  $\text{CH}_3\text{C}\equiv\text{CSnPh}_3$  and  $\text{PhC}\equiv\text{CSnPh}_3$  the dinuclear alkynyl(vinylidene) complexes **5** and **6** are formed (see Scheme 1). The ligand displacement is accompanied by a typical change of color from violet to green and affords the products in good to excellent yields. Both **5** and **6** are green, relatively low-melting and air-sensitive solids, which can be stored at  $0^\circ\text{C}$  under argon for days and do not decompose in solution (e.g. in benzene). The coordination of the alkynyl ligand is confirmed by the appearance of two signals in the  $^{13}\text{C}$ -NMR spectra at  $\delta$  131.5 and 109.9 (**5**) and  $\delta$  135.9 and 125.4 (**6**) for the Rh–C $\equiv$ C and Rh–C $\equiv$ C carbon atoms as well as by the strong  $\nu(\text{C}=\text{C})$  stretching mode at  $2073\text{ cm}^{-1}$  in the IR spectrum of **6**. In the UV-vis spectra of **5** and **6**, the maxima are shifted by ca. 50–65 nm to lower frequencies compared with the fluoro derivative **4**, which possibly indicates an increase in delocalization of the  $\pi$ -electrons along the  $\text{RC}\equiv\text{C}\text{-Rh}=\text{C}=\text{CHR}'$  chain.

The reaction of the ferrocenyl-substituted vinylidene complex **2** with half an equivalent of  $\text{Ph}_3\text{SnC}\equiv\text{C}\text{-C}\equiv\text{CSnPh}_3$  affords a green solution together with a white, nearly insoluble solid, which by comparison of the IR and  $^{19}\text{F}$ -NMR spectra was identified as  $\text{Ph}_3\text{SnF}$  [8]. From the green solution, after evaporation of the



Scheme 1. Tf =  $\text{CF}_3\text{SO}_2$ ; L =  $\text{P}^i\text{Pr}_3$ ; [Fe] =  $-\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5$ .

Scheme 2. L =  $\text{P}^i\text{Pr}_3$ ; [Fe] =  $-\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5$ .

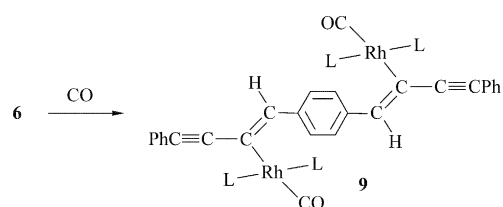
solvent and recrystallization of the residue from acetone, the dinuclear complex **7** was isolated as a green air-sensitive solid in 48% yield (Scheme 2). Characteristic features of **7** are the  $^{13}\text{C}$ -NMR resonances for the  $\alpha$ - and  $\beta$ -carbon atoms of the  $\text{Rh}=\text{C}=\text{C}$  units, which are observed at  $\delta$  309.9 and 108.6 as doublets of triplets due to  $^{13}\text{C}-^{103}\text{Rh}$  and  $^{13}\text{C}-^{31}\text{P}$  couplings. The signal for the two metal-bonded carbons of the  $\text{C}_4$  chain appears at  $\delta$  123.9 also as a doublet of triplets while the resonance of the two central carbon atoms could not be exactly located. It should be mentioned that attempts to prepare compound **7** from **4** and  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  failed.

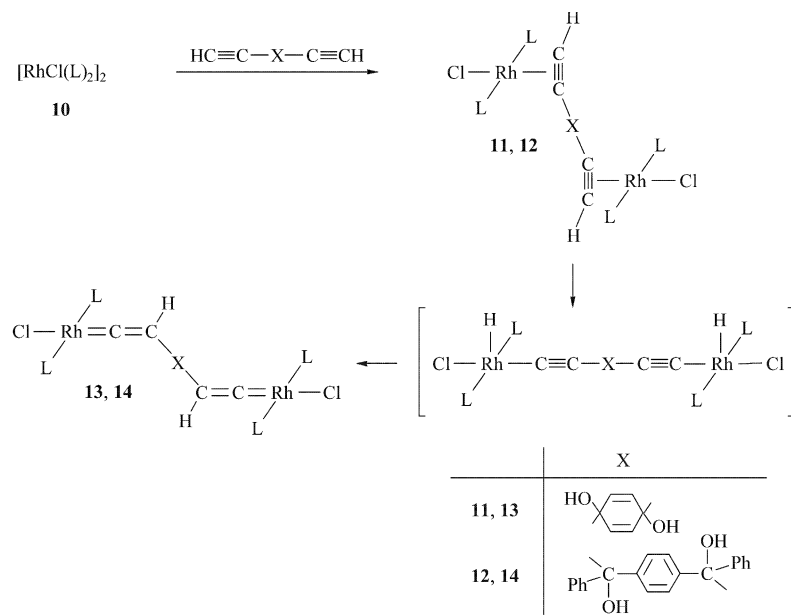
Following the observation that the mononuclear alkynyl complexes  $\text{trans}[\text{Rh}(\text{C}\equiv\text{CR})(=\text{C}=\text{CHR}')(\text{P}^i\text{Pr}_3)_2]$  react with CO to give the butenylnyl compounds  $\text{trans}[\text{Rh}\{\text{C}(\text{C}\equiv\text{CR})=\text{CHR}'\}(\text{CO})(\text{P}^i\text{Pr}_3)_2]$  by migratory insertion of the vinylidene ligand into the  $\text{Rh}-\text{C}$   $\sigma$ -bond [9], we were prompted to study also the analogous reaction of **7** with carbon monoxide. Passing a slow stream of CO through a solution of **7** in pentane at room temperature led to a change of color from green to orange and gave the dinuclear dicarbonyl dirhodium complex **8**, formed by twofold migratory insertion, as an orange air-stable solid in 78% yield. The composition of **8** is supported by the elemental analysis and the mass spectrum. The IR spectrum of **8** displays the  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{CO})$  stretching modes at 2065 and 1939  $\text{cm}^{-1}$ , respectively. The signal of the vinylic  $\text{Rh}-\text{C}=\text{CH}$  protons appears in the  $^1\text{H}$ -NMR spectrum of **8** at  $\delta$  7.55 and thus at nearly the same chemical shift ( $\delta$  7.46) as found for the analogue where instead of a ferrocenyl phenyl unit is linked to each of the terminal carbon atoms of the  $\text{C}_8$  chain [7]. Since in this case the *Z*-configuration at the  $\text{C}=\text{C}$  bond has been confirmed by an X-ray crystal structure analysis [7], we assume that also in **8** the two metal-containing fragments are linked in *cis*-disposition to the carbon-carbon double bond.

Under similar conditions as used for the reaction of **7**, the dirhodium compound **6** also reacts with CO by twofold migratory insertion (see Scheme 3). From pentane solution, the dinuclear complex **9** has been isolated as a yellow solid in 97% yield. In agreement with the spectroscopic data, we assume that each of the

$[\text{Rh}(\text{CO})(\text{P}^i\text{Pr}_3)_2]$  moieties is coordinated to the  $\beta$ -C atom of a butenylnyl unit and that these units are linked together by a  $\text{C}_6\text{H}_4$  bridge. The stereochemistry around each rhodium center is thus quite analogous to that of the mononuclear complex  $\text{trans}[\text{Rh}\{\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh}\}(\text{CO})(\text{P}^i\text{Pr}_3)_2]$  formed from  $\text{trans}[\text{Rh}(\text{C}\equiv\text{CPh})(=\text{C}=\text{CHPh})(\text{P}^i\text{Pr}_3)_2]$  and CO [9].

Besides  $1,4\text{-C}_6\text{H}_4(\text{C}\equiv\text{CH})_2$ , the reactions of the functionalized diynes  $1,1',4,4'\text{-C}_6\text{H}_4(\text{OH})_2(\text{C}\equiv\text{CH})_2$  and  $1,4\text{-C}_6\text{H}_4[\text{C}(\text{Ph})(\text{OH})\text{C}\equiv\text{CH}]_2$  with  $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2]_2$  (**10**) (which in our previous studies was already used as starting material) were also investigated. Treatment of **10** with  $1,1',4,4'\text{-C}_6\text{H}_4(\text{OH})_2(\text{C}\equiv\text{CH})_2$  and  $1,4\text{-C}_6\text{H}_4[\text{C}(\text{Ph})(\text{OH})\text{C}\equiv\text{CH}]_2$  in acetone/ether at  $-20^\circ\text{C}$  led in each case to the precipitation of a yellow solid, the formation of which was supported by the addition of ether. These compounds, supposed to be the diyne complexes **11** and **12** (Scheme 4), can only be handled at low temperatures and, if warmed to ca.  $20^\circ\text{C}$ , rearrange smoothly to the dinuclear bis(vinylidene) isomers **13** and **14** in excellent yields. The conversion, which is accompanied by a characteristic change of color from yellow to deep blue, can be facilitated by the addition of small amounts of  $\text{NEt}_3$ . The IR spectra of the  $\alpha,\omega$ -diyne complexes display two strong absorptions at, respectively, 3585 and 2096  $\text{cm}^{-1}$  (**11**) and 3587 and 2105  $\text{cm}^{-1}$  (**12**), which are assigned to the  $\nu(\text{OH})$  and  $\nu(\text{C}\equiv\text{C})$  stretching modes. In the  $^1\text{H}$ -NMR spectra, a doublet appears at  $\delta$  3.61 (**11**) and  $\delta$  3.83 (**12**) for the  $\text{C}\equiv\text{CH}$  protons and two doublets of virtual triplets at  $\delta$  1.41 and 1.30 (**11**) and  $\delta$  1.13 and 1.05 (**12**) for the  $\text{PCHCH}_3$  protons, the splitting pattern of the latter being diagnostic for the *trans*-position of the  $\text{P}^i\text{Pr}_3$  ligands [10]. In agreement with earlier observations [11], we assume that the conversion of the diyne to the bis(vinylidene) compounds proceeds via the diynyl(hydrido)

Scheme 3. L =  $\text{P}^i\text{Pr}_3$ .

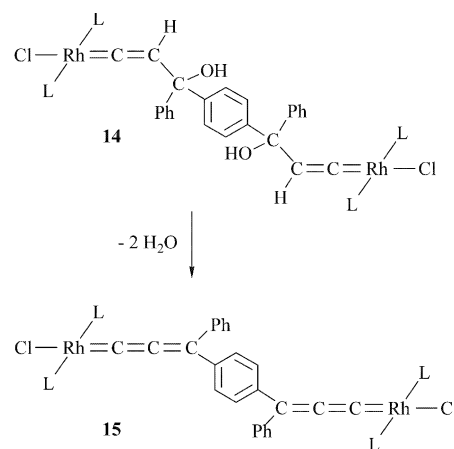
Scheme 4. L = P<sup>i</sup>Pr<sub>3</sub>.

derivatives (shown in Scheme 4) which are generally quite labile and in a few cases have been trapped with pyridine [12].

The bis(vinylidene) complexes **13** and **14** have been isolated as blue or dark blue, relatively air-stable solids and fully characterized by elemental analysis and spectroscopic techniques. They are much less soluble in common organic solvents than the mononuclear counterparts *trans*-[RhCl(=C=CHR)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>], which indicates that in the lattice possibly oligomers are formed via hydrogen bonds. Similarly to **11** and **12**, the IR spectra of **13** and **14** show a strong ν(OH) stretch at 3580 (**13**) and 3568 cm<sup>-1</sup> (**14**) and also a ν(C=C) mode in the expected region. Other typical features are the triplet resonance for the vinylidene protons at δ 0.13 (**13**) and 1.00 (**14**) in the <sup>1</sup>H-NMR spectra and the two low-field signals for the α- and β-carbon atoms of the Rh=C=C units at δ 287.5 and 114.1 (**13**) and 285.3 and 117.2 (**14**) in the <sup>13</sup>C-NMR spectra, respectively. It should be mentioned that in the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra for the protons as well as for the carbon atoms of the bridging C<sub>6</sub>H<sub>4</sub> fragments only a single resonance is observed, being consistent with the proposed structure shown in Scheme 4.

Attempts to convert the bis(vinylidene) into the corresponding bis(allylidyne) complexes were only successful with **14** as the starting material. The appropriate route was to bring a solution of **14** in chloroform in contact with acidic Al<sub>2</sub>O<sub>3</sub> that behaves as a proton source and affords by elimination of water the required product **15** in 80% isolated yield (Scheme 5). Compound **15** is a red-violet solid which, probably due to the absence of OH functionalities, is better soluble in common organic solvents than the precursor **14**. The

ν(C=C=C) stretching mode, characteristic for metal-allylidenes, appears in the IR spectrum at 1875 cm<sup>-1</sup> and thus at a very similar position as found for the mononuclear analogue *trans*-[RhCl(=C=C=CPh<sub>2</sub>)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>] [13]. The <sup>13</sup>C-NMR spectrum of **15** display in the low-field region three signals at δ 250.7, 221.7 and 143.8 which are assigned to the carbon atoms of the two Rh=C=C=C fragments. Since there is only one set of signals for the pairs of these <sup>13</sup>C nuclei and also only one resonance for the phosphorus atoms of the four P<sup>i</sup>Pr<sub>3</sub> ligands, a symmetrical structure of the dinuclear molecule can be assumed. We finally note that, although in recent years an impressive number of organometallic dimers and oligomers in which a conjugated carbon framework is spanned by transition-metal centers has been reported [14], the dinuclear rhodium(I) compound **15** is, to the best of our knowledge, the first species in which two cumulated M=C=C=C

Scheme 5. L = P<sup>i</sup>Pr<sub>3</sub>.

C units are connected by a delocalized arene  $\pi$ -electron system.

### 3. Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1** [5], **10** [15],  $(C_5H_5)Fe(C_5H_4C\equiv CH)$  [16],  $RC\equiv CSnPh_3$  [17],  $Ph_3SnC\equiv C-C\equiv CSnPh_3$  [18],  $1,4-C_6H_4(C\equiv CH)_2$  [19],  $1,1',4,4'-C_6H_4(OH)_2(C\equiv CH)_2$  [20] and  $1,4-C_6H_4[C(Ph)(OH)C\equiv CH]_2$  [20] were prepared as described in the literature. NMR spectra were recorded at room temperature (r.t.) on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a Perkin–Elmer 1420 or an 25 FT-IR infrared spectrometer, and mass spectra on a Finnigan 90 MAT instrument at 70 eV. Melting points were determined by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; vt, virtual triplet; dvt, doublet of virtual triplet; m, multiplet; br, broadened signal;  $N=^3J(P,H)+^5J(P,H)$  or  $^1J(P,C)+^3J(P,C)$ .

#### 3.1. Preparation of *trans*-[RhF{C=CH(C<sub>5</sub>H<sub>4</sub>)Fe(C<sub>5</sub>H<sub>5</sub>)}(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>] (2)

A solution of 423 mg (0.74 mmol) of **1** in 15 ml of acetone was cooled at  $-78^\circ C$  and treated with 155 mg (0.74 mmol) of ethynylferrocene. The reaction mixture was slowly warmed to r.t. and stirred for 12 h. It was then treated with 86 mg (1.50 mmol) of KF and stirred for 3 h at r.t. A gradual change of color from black to dark violet occurred. The solvent was evaporated in vacuo and the residue was extracted with 20 ml of pentane. The extract was concentrated to ca. 2 ml in vacuo and then stored for 12 h at  $-60^\circ C$ . Violet crystals precipitated which were separated from the mother liquor, washed three times with 2 ml of pentane ( $0^\circ C$ ) each and dried; yield 351 mg (73%), m.p. (dec.)  $64^\circ C$ . Anal. Found: C, 55.14; H, 8.03. Calc. for  $C_{30}H_{52}FFeP_2Rh$ : C, 55.23; H 8.03%. IR (Nujol):  $\nu(C=C)$  1645,  $\nu(RhF)$  468  $cm^{-1}$ . UV–vis (hexane):  $\lambda_{max}$  408, 553 nm.  $^1H$ -NMR ( $C_6D_6$ , 400 MHz):  $\delta$  4.02 (s, 5H,  $C_5H_5$ ), 3.99, 3.97 (both m, 2H each,  $C_5H_4$ ), 2.55 (m, 6H, PCHCH<sub>3</sub>), 1.34 (dvt,  $N=13.3$ ,  $J(H,H)=7.0$  Hz, 36H, PCHCH<sub>3</sub>), 1.18 (m, 1H, =CHC<sub>5</sub>H<sub>4</sub>).  $^{13}C$ -NMR ( $C_6D_6$ , 100.6 MHz):  $\delta$  104.9 (m, Rh=C=C), 73.1 (s, *ipso*-C of  $C_5H_4$ ), 69.3 (s,  $C_5H_5$ ), 67.3, 66.0 (both s,  $C_5H_4$ ), 23.5 (vt,  $N=18.2$  Hz, PCHCH<sub>3</sub>), 20.5 (s, PCHCH<sub>3</sub>); signal for the Rh=C=C carbon atom not exactly located.  $^{19}F$ -NMR ( $C_6D_6$ , 376.6 MHz):  $\delta$   $-218.1$  (br s).  $^{31}P$ -NMR ( $C_6D_6$ , 162.0 MHz):  $\delta$  45.7 [dd,  $J(Rh,P)=144.1$ ,  $J(F,P)=18.1$  Hz].

#### 3.2. Preparation of *trans*-[ $\mu$ -1,4- $C_6H_4$ (CH=C=)<sub>2</sub>]{Rh( $\eta^1$ -OS(O)<sub>2</sub>CF<sub>3</sub>)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (3)

A solution of 245 mg (0.43 mmol) of **1** in 10 ml of acetone was cooled at  $-78^\circ C$  and treated with 27 mg (0.21 mmol) of  $1,4-C_6H_4(C\equiv CH)_2$ . The reaction mixture was slowly warmed to r.t. and stirred for 12 h. The solvent was evaporated in vacuo, the residue was dissolved in 3 ml of pentane and the solution stored at  $-78^\circ C$  for 6 h. A dark violet solid precipitated which was separated from the mother liquor, washed twice with 2 ml of pentane ( $-20^\circ C$ ) and dried; yield 464 mg (85%). Anal. Found: C, 44.95; H, 7.34; S, 4.80. Calc. for  $C_{48}F_6H_{90}O_6P_4Rh_2S_2$ : C, 45.37; H, 7.14; S, 5.03%. IR (Nujol):  $\nu(C=C)$  1621  $cm^{-1}$ .  $^1H$ -NMR (acetone-*d*<sub>6</sub>, 400 MHz):  $\delta$  7.05 (s, 4H,  $C_6H_4$ ), 2.52 (m, 12H, PCHCH<sub>3</sub>), 1.38 [dvt,  $N=13.5$ ,  $J(H,H)=6.8$  Hz, 72H, PCHCH<sub>3</sub>]; signal for the Rh=C=CH proton not exactly located.  $^{13}C$ -NMR (acetone-*d*<sub>6</sub>, 100.6 MHz):  $\delta$  304.9 [d,  $J(Rh,C)=64.5$  Hz, Rh=C], 126.5 (s,  $C_6H_4$ ), 121.7 [q,  $J(F,C)=322.0$  Hz, CF<sub>3</sub>], 121.5 (s, *ipso*-C of  $C_6H_4$ ), 112.6 [dt,  $J(Rh,C)=17.6$ ,  $J(P,C)=4.0$  Hz, Rh=C=C], 24.3 (vt,  $N=20.4$  Hz, PCHCH<sub>3</sub>), 20.0 (s, PCHCH<sub>3</sub>).  $^{19}F$ -NMR (acetone-*d*<sub>6</sub>, 376.6 MHz):  $\delta$   $-78.6$  (s).  $^{31}P$ -NMR (acetone-*d*<sub>6</sub>, 162.0 MHz):  $\delta$  42.8 [d,  $J(Rh,P)=134.6$  Hz].

#### 3.3. Preparation of *trans*-[ $\mu$ -1,4- $C_6H_4$ (CH=C=)<sub>2</sub>]{RhF(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (4)

A solution of 109 mg (0.08 mmol) of **3** in 10 ml of acetone was treated with 23 mg (0.34 mmol) of KF and stirred for 3 h at r.t. A gradual change of color from black to dark violet occurred. The solvent was evaporated in vacuo and the residue was extracted twice with 40 ml of pentane each. The extract was concentrated to ca. 2 ml in vacuo and then stored for 16 h at  $-78^\circ C$ . A violet solid precipitated which were separated from the mother liquor at low temperature, washed twice with 2 ml of pentane ( $-20^\circ C$ ) each and dried; yield 51 mg (58%), m.p. (dec.)  $60^\circ C$ . Anal. Found: C, 54.38; H, 9.24. Calc. for  $C_{46}F_2H_{90}P_4Rh_2$ : C, 54.65; H, 8.97%. MS (FAB):  $m/z$  1011 [ $M^+$ ], 814 [ $M^+-2F-2P^iPr_3$ ]. IR (Nujol):  $\nu(C=C)$  1619  $cm^{-1}$ . UV–vis (hexane):  $\lambda_{max}$  398, 554 nm.  $^1H$ -NMR ( $C_6D_6$ , 400 MHz):  $\delta$  7.13 (s, 4H,  $C_6H_4$ ), 2.48 (m, 12H, PCHCH<sub>3</sub>), 1.70 (br s, 2H, Rh=C=CH), 1.30 [dvt,  $N=13.5$ ,  $J(H,H)=6.8$  Hz, 72H, PCHCH<sub>3</sub>].  $^{13}C$ -NMR ( $C_6D_6$ , 100.6 MHz):  $\delta$  124.9 (s,  $C_6H_4$ ), 121.9 (s, *ipso*-C of  $C_6H_4$ ), 112.2 (br s, Rh=C=C), 23.3 (vt,  $N=18.6$  Hz, PCHCH<sub>3</sub>), 20.2 (s, PCHCH<sub>3</sub>); signal for the Rh=C=C carbon atom not exactly located.  $^{19}F$ -NMR ( $C_6D_6$ , 376.6 MHz):  $\delta$   $-215.5$  (br s).  $^{31}P$ -NMR ( $C_6D_6$ , 162.0 MHz):  $\delta$  45.5 [dd,  $J(Rh,P)=144.1$ ,  $J(F,P)=11.9$  Hz].

### 3.4. Preparation of *trans*-[ $\{\mu$ -1,4- $C_6H_4(CH=C=)$ ] $\}_2\{Rh(C\equiv CCH_3)(P^iPr_3)_2\}_2$ ] (5)

A solution of 189 mg (0.19 mmol) of **4** in 15 ml of pentane was cooled at  $-30^\circ C$  and treated with 145 mg (0.38 mmol) of  $CH_3C\equiv CSnPh_3$ . The reaction mixture was slowly warmed to r.t. and stirred for 2.5 h. A change of color from violet to green occurred. The solution was filtered and the filtrate was brought to dryness in vacuo. The residue was dissolved in 3 ml of acetone and the solution was stored for 15 h at  $-65^\circ C$ . Green crystals precipitated which were separated from the mother liquor, washed twice with 2 ml of acetone ( $-20^\circ C$ ) each and dried; yield 169 mg (64%), m.p. (dec.)  $40^\circ C$ . Anal. Found: C, 59.26; H, 8.91. Calc. for  $C_{52}H_{96}P_4Rh_2$ : C, 59.42; H, 9.21%. IR (Nujol):  $\nu(C=C)$   $1618\text{ cm}^{-1}$ . UV-vis (hexane):  $\lambda_{max}$  456, 614 nm.  $^1H$ -NMR ( $C_6D_6$ , 400 MHz):  $\delta$  7.19 (br s, 4H,  $C_6H_4$ ), 2.75 (m, 12H,  $PCHCH_3$ ), 2.18 [t,  $J(P,H) = 2.0$  Hz, 6H,  $\equiv C-CH_3$ ], 1.51 [t,  $J(P,H) = 3.5$  Hz, 2H,  $Rh=C=CH$ ], 1.39 [dvt,  $N = 13.5$ ,  $J(H,H) = 7.0$  Hz, 72H,  $PCHCH_3$ ].  $^{13}C$ -NMR ( $C_6D_6$ , 100.6 MHz):  $\delta$  289.7 [dt,  $J(Rh,C) = 48.5$ ,  $J(P,C) = 16.2$  Hz,  $Rh=C$ ], 131.5 [d,  $J(Rh,C) = 10.1$  Hz,  $Rh-C\equiv C$ ], 125.8 (s,  $C_6H_4$ ), 121.1 (s, *ipso*-C of  $C_6H_4$ ), 115.9 [dt,  $J(Rh,C) = 11.1$ ,  $J(P,C) = 5.1$  Hz,  $Rh=C=CH$ ], 109.9 [dt,  $J(Rh,C) = 37.6$ ,  $J(P,C) = 18.3$  Hz,  $Rh-C\equiv C$ ], 25.7 (vt,  $N = 20.4$  Hz,  $PCHCH_3$ ), 20.7 (s,  $PCHCH_3$ ), 16.7 [d,  $J(Rh,C) = 3.0$  Hz,  $\equiv C-CH_3$ ].  $^{31}P$ -NMR ( $C_6D_6$ , 162.0 MHz):  $\delta$  47.3 [d,  $J(Rh,P) = 137.3$  Hz].

### 3.5. Preparation of *trans*-[ $\{\mu$ -1,4- $C_6H_4(CH=C=)$ ] $\}_2\{Rh(C\equiv CPh)(P^iPr_3)_2\}_2$ ] (6)

A solution of 152 mg (0.15 mmol) of **4** in 20 ml of pentane was cooled at  $-30^\circ C$  and treated with 136 mg (0.30 mmol) of  $PhC\equiv CSnPh_3$ . The reaction mixture was slowly warmed to r.t. and stirred for 3 h. A change of color from violet to green occurred. The solution was filtered and the filtrate was concentrated to ca. 2 ml in vacuo. After the solution was stored for 15 h at  $-78^\circ C$ , a green solid precipitated which were separated from the mother liquor, washed twice with 2 ml of pentane ( $-30^\circ C$ ) each and dried; yield 166 mg (94%), m.p. (dec.)  $54^\circ C$ . Anal. Found: C, 63.34; H, 8.91. Calc. for  $C_{62}H_{100}P_4Rh_2$ : C, 63.37; H, 8.58%. MS (FAB):  $m/z = 1074 [M^+]$ ,  $812 [M^+ - 2P^iPr_3 - 2PhC\equiv C]$ . IR (Nujol):  $\nu(C\equiv C)$   $2073$ ,  $\nu(C=C)$   $1632\text{ cm}^{-1}$ . UV-vis (hexane):  $\lambda_{max}$  450, 620 nm.  $^1H$ -NMR ( $C_6D_6$ , 400 MHz):  $\delta$  7.42 (m, 4H, *ortho*-H von  $C_6H_5$ ), 7.17 (s, 4H,  $C_6H_4$ ), 7.13 (m, 4H, *meta*-H von  $C_6H_5$ ), 6.93 (m, 2H, *para*-H von  $C_6H_5$ ), 2.74 (m, 12H,  $PCHCH_3$ ), 1.58 [t,  $J(P,H) = 3.5$  Hz, 2H,  $Rh=C=CH$ ], 1.36 [dvt,  $N = 13.8$ ,  $J(H,H) = 7.0$  Hz, 72H,  $PCHCH_3$ ].  $^{13}C$ -NMR ( $C_6D_6$ , 100.6 MHz):  $\delta$  313.0 [dt,  $J(Rh,C) = 49.3$ ,  $J(P,C) = 15.2$  Hz,  $Rh=C$ ], 135.9 [d,  $J(Rh,C) = 8.8$  Hz,  $Rh-C\equiv C$ ], 128.9, 127.1, 124.0 (all

s,  $C_6H_5$ ), 127.9 (s, *ipso*-C of  $C_6H_5$ ), 125.4 [dt,  $J(Rh,C) = 55.6$ ,  $J(P,C) = 17.7$  Hz,  $Rh-C\equiv C$ ], 124.7 (s,  $C_6H_4$ ), 119.8 (s, *ipso*-C of  $C_6H_4$ ), 114.5 [dt,  $J(Rh,C) = 17.7$ ,  $J(P,C) = 5.0$  Hz,  $Rh=C=C$ ], 24.5 (vt,  $N = 20.2$  Hz,  $PCHCH_3$ ), 19.4 (s,  $PCHCH_3$ ).  $^{31}P$ -NMR ( $C_6D_6$ , 162.0 MHz):  $\delta$  47.5 [d,  $J(Rh,P) = 135.6$  Hz].

### 3.6. Preparation of *trans*-[ $(\mu-C\equiv C-C\equiv C)\{Rh(=C=CH(C_5H_4)Fe(C_5H_5))(P^iPr_3)_2\}_2$ ] (7)

A solution of 130 mg (0.20 mmol) of **2** in 12 ml of pentane was cooled at  $-30^\circ C$  and treated with 74 mg (0.10 mmol) of  $Ph_3SnC\equiv C-C\equiv CSnPh_3$ . The reaction mixture was slowly warmed to r.t. and stirred for 1.5 h. A change of color from violet to green and the precipitation of a white solid occurred. The solution was filtered and the filtrate was brought to dryness in vacuo. The residue was dissolved in 3 ml of acetone and the solution stored for 15 h at  $-60^\circ C$ . A green solid precipitated which were separated from the mother liquor, washed three times with 2 ml of acetone ( $-20^\circ C$ ) each and dried; yield 66 mg (48%), m.p. (dec.)  $38^\circ C$ . Anal. Found: C, 58.15; H, 7.65. Calc. for  $C_{64}H_{104}P_4Fe_2Rh_2$ : C, 58.46; H, 7.97%. IR (Nujol):  $\nu(C=C)$   $1628\text{ cm}^{-1}$ . UV-vis (hexane):  $\lambda_{max} = 637, 421$  nm.  $^1H$ -NMR ( $C_6D_6$ , 400 MHz):  $\delta$  4.34 (s, 10H,  $C_5H_5$ ), 4.25, 4.20 (both m, 8H,  $C_5H_4$ ), 3.05 (m, 12H,  $PCHCH_3$ ), 1.65 [dvt,  $N = 13.5$ ,  $J(H,H) = 6.4$  Hz, 72H,  $PCHCH_3$ ], 1.18 (m, 2H,  $=CHC_5H_4$ ).  $^{13}C$ -NMR ( $C_6D_6$ , 100.6 MHz):  $\delta$  309.9 [dt,  $J(Rh,C) = 48.0$ ,  $J(P,C) = 16.4$  Hz,  $Rh=C$ ], 123.9 [dt,  $J(Rh,C) = 39.2$ ,  $J(P,C) = 21.5$  Hz,  $Rh-C\equiv C$ ], 108.6 [dt,  $J(Rh,C) = 11.4$ ,  $J(P,C) = 6.3$  Hz,  $Rh=C=CH$ ], 71.8 (s, *ipso*-C of  $C_5H_4$ ), 69.1 (s,  $C_5H_5$ ), 67.3, 66.1 (both s,  $C_5H_4$ ), 25.5 (vt,  $N = 22.8$  Hz,  $PCHCH_3$ ), 20.8 (s,  $PCHCH_3$ ); signal for the  $Rh-C\equiv C$  carbon atom could not be exactly located.  $^{31}P$ -NMR ( $C_6D_6$ , 162.0 MHz):  $\delta$  47.8 [d,  $J(Rh,P) = 137.4$  Hz].

### 3.7. Preparation of *trans*-[ $\{\mu-(Z,Z)-C(=CH[Fe])(C\equiv C)_2C(=CH[Fe])\}\{Rh(CO)(P^iPr_3)_2\}_2$ ] (8) ( $[Fe] = (C_5H_4)Fe(C_5H_5)$ )

A slow stream of CO was passed for 30 s through a solution of 239 mg (0.18 mmol) of **7** in 15 ml of pentane at r.t. A change of color from green to orange occurred. After the solution was stirred for 5 min, the solvents was evaporated in vacuo. The residue was recrystallized from toluene/pentane (1:5) to give orange crystals. These were separated from the mother liquor, washed twice with 2 ml of pentane each and dried in vacuo; yield 194 mg (78%), m.p. (dec.)  $96^\circ C$ . Anal. Found: C, 58.18; H, 7.32; Rh, 14.96. Calc. for  $C_{66}H_{104}P_4Rh_2Fe_2O_2$ : C, 57.81; H, 7.60; Rh, 15.02%. MS (FAB):  $m/z$  1370 [ $M^+$ ]. IR (Nujol):  $\nu(C\equiv C)$  2065,  $\nu(CO)$  1939  $\text{cm}^{-1}$ . UV-vis (hexane):  $\lambda_{max} = 347, 383, 448$  nm.  $^1H$ -NMR (toluene- $d_8$ , 200 MHz):  $\delta$  7.55 (br s, 2H,  $Rh=C=CH$ ), 4.84, 4.05

(both m, 4H each, C<sub>5</sub>H<sub>4</sub>), 4.09 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 2.40 (m, 12H, PCHCH<sub>3</sub>), 1.37 [dvt, *N* = 13.5, *J*(H,H) = 6.9 Hz, 36H, PCHCH<sub>3</sub>], 1.24 [dvt, *N* = 13.1, *J*(H,H) = 6.6 Hz, 36 H, PCHCH<sub>3</sub>]. <sup>31</sup>P-NMR (toluene-*d*<sub>8</sub>, 81.0 MHz): δ 43.0 [d, *J*(Rh,P) = 139.9 Hz].

### 3.8. Preparation of *trans*-[ {μ-(*Z,Z*)-C(C≡CPh)=CHC<sub>6</sub>H<sub>4</sub>CH=C(C≡CPh)} {Rh(CO)(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (9)

A slow stream of CO was passed for 30 s through a solution of 128 mg (0.10 mmol) of **6** in 10 ml of pentane at r.t. A change of color from green to yellow occurred. After the solution was stirred for 5 min, it was concentrated to ca. 2 ml in vacuo. A yellow microcrystalline solid precipitated which was separated from the mother liquor, washed three times with 2 ml of pentane each and dried in vacuo; yield: 120 mg (97%), m.p. (dec.) 76 °C. Anal. Found: C, 62.17; H, 7.90; Rh, 17.10. Calc. for C<sub>64</sub>H<sub>100</sub>P<sub>4</sub>Rh<sub>2</sub>O<sub>2</sub>: C, 62.43; H, 8.19; Rh, 16.72%. IR (Nujol): ν(C≡C) 2148, ν(CO) 1944, ν(C=C) 1595 cm<sup>-1</sup>. UV-vis (hexane): λ<sub>max</sub> = 388, 416, 441 nm. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 8.08 [br d, *J*(Rh,H) = 2.4 Hz, 2H, Rh-C=CH], 7.56 (m, 4H, *ortho*-H of C<sub>6</sub>H<sub>5</sub>), 6.99 (m, 2H, *para*-H of C<sub>6</sub>H<sub>5</sub>), 2.40 (m, 12H, PCHCH<sub>3</sub>), 1.37 [dvt, *N* = 13.8, *J*(H,H) = 8.0 Hz, 36H, PCHCH<sub>3</sub>], 1.11 [dvt, *N* = 13.2, *J*(H,H) = 7.0 Hz, 36H, PCHCH<sub>3</sub>]; signals for *meta*-H of C<sub>6</sub>H<sub>5</sub> and those of C<sub>6</sub>H<sub>4</sub> were covered by the signal of the solvent. <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 162.0 MHz): δ 43.1 [d, *J*(Rh,P) = 139.0 Hz].

### 3.9. Preparation of [ {μ-1,1',4,4'-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>(C≡CH)<sub>2</sub>} {RhCl(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (11)

A solution of 233 mg (0.25 mmol) of **10** in 10 ml of ether was cooled at -30 °C and treated dropwise with a solution of 41 mg (0.25 mmol) of 1,1',4,4'-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>(C≡CH)<sub>2</sub> in 2 ml of acetone. A yellow solid precipitated, the formation of which was facilitated by addition of 10 ml of pentane (-20 °C). The solid was separated from the mother liquor, washed three times with 3 ml of ether (-20 °C) each and dried in vacuo; yield 279 mg (76%), m.p. (dec.) 67 °C. Anal. Found: C, 50.78; H, 8.38. Calc. for C<sub>46</sub>H<sub>92</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>: C, 51.26; H, 8.60%. IR (C<sub>6</sub>H<sub>6</sub>): ν(OH) 3585, ν(C≡C) 2096 cm<sup>-1</sup>. <sup>1</sup>H-NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.26 (br s, 4H, C<sub>6</sub>H<sub>4</sub>), 3.61 [d, *J*(Rh,H) = 2.6 Hz, 2H, C≡CH], 2.53 (m, 12H, PCHCH<sub>3</sub>), 1.41 [dvt, *N* = 13.8, *J*(H,H) = 7.3 Hz, 36H, PCHCH<sub>3</sub>], 1.30 [dvt, *N* = 12.8, *J*(H,H) = 6.6 Hz, 36H, PCHCH<sub>3</sub>], signal for the OH proton not observed. <sup>31</sup>P-NMR (81.0 MHz, C<sub>6</sub>D<sub>6</sub>): δ 32.4 [d, *J*(Rh,P) = 114.4 Hz].

### 3.10. Preparation of [ {μ-1,4-C<sub>6</sub>H<sub>4</sub>(C(Ph)(OH)C≡CH)<sub>2</sub>} {RhCl(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (12)

A solution of 248 mg (0.27 mmol) of **10** in 8 ml of ether was cooled at -20 °C and treated dropwise with a solution of 91 mg (0.27 mmol) of 1,4-C<sub>6</sub>H<sub>4</sub>[C(Ph)(OH)C≡CH]<sub>2</sub> in 4 ml of acetone. A yellow solid precipitated, the formation of which was facilitated by addition of 10 ml of pentane (-20 °C). The solid was separated from the mother liquor, washed three times with 3 ml of ether (-20 °C) each and dried in vacuo; yield 258 mg (76%), m.p. (dec.) 85 °C. IR (C<sub>6</sub>H<sub>6</sub>): ν(OH) 3587, ν(C≡C) 2105 cm<sup>-1</sup>. <sup>1</sup>H-NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.79 (m, 4H, *ortho*-H of C<sub>6</sub>H<sub>5</sub>), 7.71 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 7.07 (m, 4H, *meta*-H of C<sub>6</sub>H<sub>5</sub>), 6.93 (m, 2H, *para*-H of C<sub>6</sub>H<sub>5</sub>), 3.83 [d, *J*(Rh,H) = 2.5 Hz, 2H, C≡CH], 2.01 (m, 12H, PCHCH<sub>3</sub>), 1.13 [dvt, *N* = 14.8, *J*(H,H) = 7.4 Hz, 36H, PCHCH<sub>3</sub>], 1.05 [dvt, *N* = 14.4, *J*(H,H) = 7.0 Hz, 36H, PCHCH<sub>3</sub>], signal for the OH proton not observed. <sup>31</sup>P-NMR (81.0 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 33.0 [d, *J*(Rh,P) = 113.8 Hz].

### 3.11. Preparation of [ {μ-1,1',4,4'-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>(CH=C=) } {RhCl(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (13)

A solution of 114 mg (0.12 mmol) of **10** in 8 ml of ether was treated dropwise with a solution of 19 mg (0.12 mmol) of 1,1',4,4'-C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>(C≡CH)<sub>2</sub> in 2 ml of acetone at r.t. A change of color from red to yellow occurred. After 5 min, 1 ml of triethylamine was added and the reaction mixture stirred for 12 h at r.t. The solvent was evaporated in vacuo, and the residue was recrystallized from acetone at 0 °C. A blue microcrystalline solid precipitated which was separated from the mother liquor, washed twice with 3 ml of ether (-20 °C) each and dried; yield 101 mg (78%), m.p. (dec.) 76 °C. Anal. Found: C, 51.34; H, 8.99. Calc. for C<sub>46</sub>H<sub>92</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>: C, 51.26; H, 8.60%. IR (C<sub>6</sub>H<sub>6</sub>): ν(OH) 3580, ν(C=C) 1715 cm<sup>-1</sup>. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 5.64 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 2.78 (m, 12H, PCHCH<sub>3</sub>), 1.50 (s, 2H, OH), 1.31 [dvt, *N* = 13.6, *J*(H,H) = 6.8 Hz, 72H, PCHCH<sub>3</sub>], 0.13 [t, *J*(P,H) = 3.2 Hz, 2H, =C=CH]. <sup>13</sup>C-NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 287.5 [dt, *J*(Rh,C) = 61.4, *J*(P,C) = 16.1 Hz, Rh=C=C], 132.3 (s, C<sub>6</sub>H<sub>4</sub>), 114.1 [dt, *J*(Rh,C) = 16.1, *J*(P,C) = 6.0 Hz, Rh=C=C], 58.4 (s, *i*-C of C<sub>6</sub>H<sub>4</sub>), 23.9 (vt, *N* = 20.0 Hz, PCHCH<sub>3</sub>), 20.6 (s, PCHCH<sub>3</sub>). <sup>31</sup>P-NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 40.9 [d, *J*(Rh,P) = 133.8 Hz].

### 3.12. Preparation of [ {μ-1,4-C<sub>6</sub>H<sub>4</sub>(C(Ph)(OH)CH=C=) } {RhCl(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (14)

This compound was prepared analogously as described for **13**, from 143 mg (0.15 mmol) of **10**, 51 mg (0.15 mmol) of 1,4-C<sub>6</sub>H<sub>4</sub>[C(Ph)(OH)C≡CH]<sub>2</sub> and 3 ml of triethylamine. The product was recrystallized from

CHCl<sub>3</sub>–ether (2:5) at 5 °C. A dark blue microcrystalline solid was obtained; yield 155 mg (82%), m.p. (dec.) 132 °C. Anal. Found: C, 57.12; H, 7.98. Calc. for C<sub>60</sub>H<sub>102</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>: C, 57.37; H, 8.19%. IR (C<sub>6</sub>H<sub>6</sub>):  $\nu(\text{OH})$  3568,  $\nu(\text{C}=\text{C})$  1644 cm<sup>-1</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (m, 4H, *ortho*-H of C<sub>6</sub>H<sub>5</sub>), 7.34 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 7.22 (m, 6H, *meta*- and *para*-H of C<sub>6</sub>H<sub>5</sub>), 2.65 (m, 12H, PCHCH<sub>3</sub>), 2.60 (s, 2H, OH), 1.18 [dvt,  $N = 14.0$ ,  $J(\text{H,H}) = 7.2$  Hz, 72H, PCHCH<sub>3</sub>], 1.00 [t,  $J(\text{P,H}) = 3.2$  Hz, 2H, Rh=C=CH]. <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  285.3 [dt,  $J(\text{Rh,C}) = 61.4$ ,  $J(\text{P,C}) = 16.1$  Hz, Rh=C=C], 148.4, 147.1 (both s, *ipso*-C of C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>), 128.3, 127.9, 125.1, 124.7 (all s, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>), 117.2 [dt,  $J(\text{Rh,C}) = 15.1$ ,  $J(\text{P,C}) = 5.0$  Hz, Rh=C=C], 67.1 (s, Rh=C=C–C), 23.2 (vt,  $N = 19.9$  Hz, PCHCH<sub>3</sub>), 19.9 (s, PCHCH<sub>3</sub>). <sup>31</sup>P-NMR (162.0 MHz, CDCl<sub>3</sub>):  $\delta$  41.2 [d,  $J(\text{Rh,P}) = 132.5$  Hz].

### 3.13. Preparation of [ $\mu$ -1,4-C<sub>6</sub>H<sub>4</sub>(CPh=C=C=)<sub>2</sub>]{RhCl(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (15)

A solution of 286 mg (0.23 mmol) of **14** in 5 ml of CHCl<sub>3</sub> was brought up on a column filled with Al<sub>2</sub>O<sub>3</sub> (acidic, activity grade I, length of column 5 cm). A change of color from blue to red–violet occurred. The elution of the generated compound was carried out first with CHCl<sub>3</sub> and then with ether. The combined fractions were brought to dryness in vacuo. The residue was dissolved in 3 ml of CHCl<sub>3</sub> and the solution was layered with 5 ml of ether. After the mixture was stored for 15 h at 8 °C, red–violet crystals were formed which were separated from the mother liquor, washed twice with 1 ml of acetone (0 °C) each and dried; yield 221 mg (80%), m.p. (dec.) 143 °C. Anal. Found: C, 58.73; H, 7.89. Calc. for C<sub>60</sub>H<sub>98</sub>Cl<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>: C, 59.07; H, 8.10%. IR (C<sub>6</sub>H<sub>6</sub>):  $\nu(\text{C}=\text{C}=\text{C})$  1858 cm<sup>-1</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.67 (m, 6H, *ortho*- and *para*-H of C<sub>6</sub>H<sub>5</sub>), 7.55 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 7.08 (m, 4H, *meta*-H of C<sub>6</sub>H<sub>5</sub>), 2.80 (m, 12H, PCHCH<sub>3</sub>), 1.26 [dvt,  $N = 13.2$ ,  $J(\text{H,H}) = 7.2$  Hz, 72H, PCHCH<sub>3</sub>]. <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  250.7 [dt,  $J(\text{Rh,C}) = 15.1$ ,  $J(\text{P,C}) = 6.0$  Hz, Rh=C=C=C], 221.7 [dt,  $J(\text{Rh,C}) = 67.4$ ,  $J(\text{P,C}) = 17.1$  Hz, Rh=C=C=C], 153.3, 151.1 (both s, *ipso*-C of C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>), 143.8 (s, Rh=C=C=C), 129.1, 127.2, 125.7, 122.7 (all s, C<sub>6</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>), 23.8 (vt,  $N = 19.4$  Hz, PCHCH<sub>3</sub>), 20.1 (s, PCHCH<sub>3</sub>). <sup>31</sup>P-NMR (162.0 MHz, CDCl<sub>3</sub>):  $\delta$  36.9 [d,  $J(\text{Rh,P}) = 130.6$  Hz].

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