



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 681 (2003) 70–81

Journal  
of Organo  
metallic  
Chemistry[www.elsevier.com/locate/jorgchem](http://www.elsevier.com/locate/jorgchem)

# Preparation of cyclopentadienylrhodium(I) compounds with a dangling $\text{CH}_2\text{C}_5\text{H}_5$ unit and their use as starting materials for the synthesis of hetero-bimetallic Rh–Ti and Rh–Zr complexes

Bernd Stempfle, Olaf Gevert, Helmut Werner\*

*Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

Received 27 January 2003; received in revised form 16 May 2003; accepted 16 May 2003

Dedicated to Professor Bernd Krebs on the occasion of his 65th birthday

## Abstract

A series of cyclopentadienylrhodium(I) complexes of the general composition  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{L})(\text{L}')]$  ( $\text{L} = \text{L}' = \text{C}_2\text{H}_4$ ,  $\text{C}_8\text{H}_{14}$ ;  $\text{L} = \text{P}^i\text{Pr}_3$ ,  $\text{L}' = \text{C}_2\text{H}_4$ ,  $\text{CPh}_2$ ,  $\text{C}=\text{C}=\text{CPh}_2$ ;  $\text{L} = \text{Sb}^i\text{Pr}_3$ ,  $\text{L}' = \text{CPh}_2$ ) with a dangling  $\text{CH}_2\text{C}_5\text{H}_5$  unit at the  $\pi$ -bonded five-membered ring has been prepared from the corresponding rhodium(I) precursors and  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  in THF. The compound  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_5)\text{Rh}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)]$  has similarly been obtained and characterized by single-crystal X-ray diffraction analysis. Deprotonation of  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{L})_2]$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{L})(\text{L}')]$  with either  $n\text{-BuLi}$  or  $\text{NaN}(\text{SiMe}_3)_2$  affords the corresponding anions which react with  $[(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_3]$  ( $\text{M} = \text{Ti}, \text{Zr}$ ) to give hetero-bimetallic Rh–Ti and Rh–Zr complexes with the dianion  $[(\eta^5\text{-C}_5\text{H}_4)_2\text{CH}_2]^{2-}$  as the bridging ligand. Treatment of the dinuclear tetrachloro compound  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{RhCl}_2(\text{P}^i\text{Pr}_3)\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}]$ , obtained from the related alkyne complex  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}]$  and HCl, with methyl lithium leads to the formation of the tetramethyl derivative  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{CH}_3)_2(\text{P}^i\text{Pr}_3)\}\{\text{Ti}(\text{CH}_3)_2(\eta^5\text{-C}_5\text{H}_5)\}]$ . On a similar route, the hetero-bimetallic dimethyl compound  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{C}=\text{CPh}_2)(\text{CO})\}\{\text{Zr}(\text{CH}_3)_2(\eta^5\text{-C}_5\text{H}_5)\}]$  has been prepared.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Bis(cyclopentadienyl)methane; Hetero-bimetallic complexes; Rhodium; Titan; Zirkonium

## 1. Introduction

Following our research on compounds of the general composition  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{M}(\text{L})_2\}_2]$  with  $\text{M} = \text{Co}$  [1], Rh [2] and Ir [3], we became interested in learning whether complexes of this type with different metal centers can equally be prepared. After we succeeded with the preparation of compounds where one metal is rhodium and the second is cobalt or iridium [4], we showed that instead of the electron-rich Co or Ir in the oxidation +I and +III also the electron-poor Nb and Mo in the oxidation state +V and +VI with stabilizing

imido ligands can be connected to the anionic  $[\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)]$  unit [5]. In continuing these studies, we recently focussed our effort on the coordination of  $[\text{TiX}_2(\eta^5\text{-C}_5\text{H}_5)]$  and  $[\text{ZrX}_2(\eta^5\text{-C}_5\text{H}_5)]$  fragments to the dangling cyclopentadienyl group of the rhodium-containing anion since we anticipated that due to their potential cooperative behavior hetero-bimetallic Rh–Ti and Rh–Zr complexes could be interesting candidates as catalysts or catalyst precursors for olefin polymerization.

In this paper, we report the synthesis of a variety of mononuclear rhodium compounds of the type  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{L})_2]$  and  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{L})(\text{L}')]$  and illustrate that, after they have been converted to the corresponding anion, they are useful starting materials for the formation of hetero-bimetallic complexes with one  $d^8$ - or  $d^6$ - and one  $d^0$ -metal center.

\* Corresponding author. Tel.: +49-931-888-5270; fax: +49-931-888-4623.

E-mail address: [helmut.werner@mail.uni-wuerzburg.de](mailto:helmut.werner@mail.uni-wuerzburg.de) (H. Werner).

## 2. Results and discussion

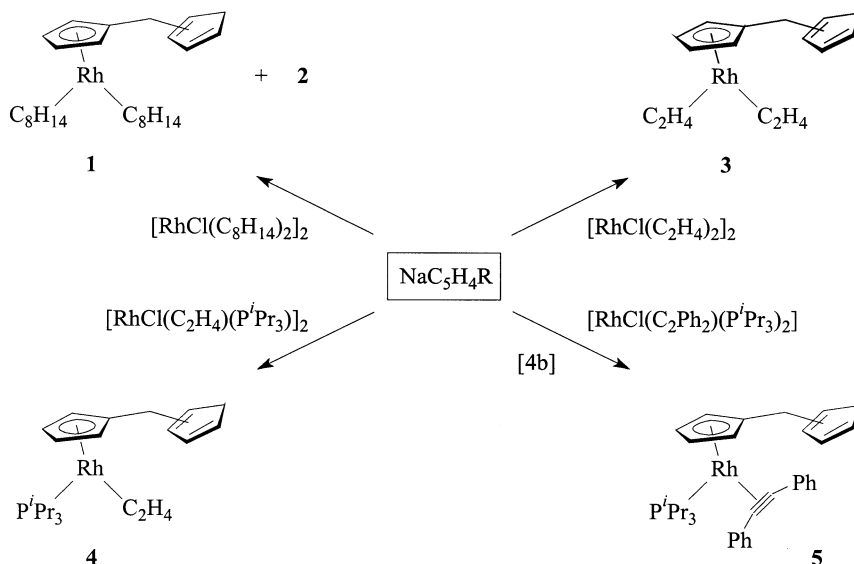
The sodium salt of the substituted cyclopentadienyl anion  $[\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5]^-$ , which has been prepared from  $\text{CH}_2(\text{C}_5\text{H}_5)_2$  and  $\text{NaNH}_2$  in THF [4a], reacts with the dimeric rhodium(I) precursors  $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ ,  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  and  $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{P}^i\text{Pr}_3)]_2$  to give the halfsandwich-type complexes **1**, **3** and **4** in 57–74% yield (Scheme 1). In the reaction with the bis(cyclooctene) derivative, the dinuclear compound **2** has been obtained as a by-product and separated from **1** by column chromatography. For the original preparation of **2**, the disodium salt  $[\text{CH}_2(\text{C}_5\text{H}_4)_2]\text{Na}_2$  was used as the substrate [4b]. Similar to **5** [4b], the related compounds **1**, **3** and **4** are isolated as yellow or orange oils that are moderately air-sensitive and readily soluble in all common organic solvents. They can be stored under argon at  $-78^\circ\text{C}$  for weeks but slowly decompose at room temperature or in solution. The  $^1\text{H-NMR}$  spectra of **1**, **3** and **4** display six signals for the olefinic protons of the dangling  $\text{C}_5\text{H}_5$  moiety between  $\delta$  5.9 and 6.6 ppm, indicating that two isomers in the approximate ratio of 1:1 are present. We assume that the uncoordinated  $\text{C}_5\text{H}_5$  ring is linked either at C(2) or C(3) to the  $[\text{CH}_2\text{C}_5\text{H}_4\text{Rh}(\text{L})_2]$  or  $[\text{CH}_2\text{C}_5\text{H}_4\text{Rh}(\text{L})(\text{L}')]_2$  fragment and thus a similar situation as that found for **5** exists [4b]. The assignment for the  $^{13}\text{C}$  resonances of the  $\text{C}_5\text{H}_4$  carbon atoms follows the rule proposed by Coville and coworkers [6] that C(1) (*ipso*-C) is less shielded than C(2) and C(5) and these are less so than C(3) and C(4). The chemical shift of the bridging  $\text{CH}_2$  carbon of the  $\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  ligand corresponds to that of  $\text{CH}_2\text{Ph}_2$ , which is in full agreement with the increment tables for disubstituted methane derivatives [7].

After we failed to crystallize compounds **1**, **3**, **4** and **5**, we prepared for comparison the related complex **6**

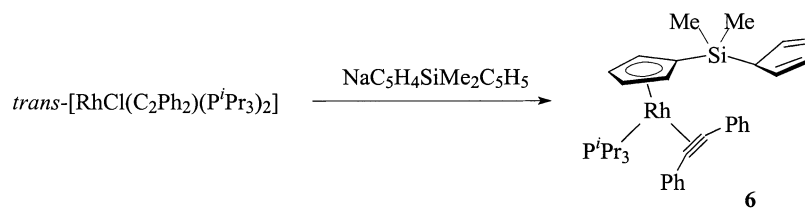
containing the  $\text{SiMe}_2\text{C}_5\text{H}_5$  group as a substituent at the  $\pi$ -bonded five-membered ring. The preparative procedure was similar to that used for **5** [4b] and gave the required product **6** as a yellow solid in 70% isolated yield (Scheme 2).

Single crystals of **6** could be grown from hexane and investigated by X-ray diffraction. The result of the structure analysis is shown in Fig. 1. The molecule has the expected piano-stool-type structure with bond angles  $\text{P-Rh-C}(1)$  and  $\text{P-Rh-C}(2)$  that deviate only slightly from  $90^\circ$ . Both the  $\text{Rh-C}(1)$  and  $\text{Rh-C}(2)$  bond lengths as well as the  $\text{C}(1)\text{-C}(2)\text{-C}(20)$  and  $\text{C}(2)\text{-C}(1)\text{-C}(10)$  bond angles are nearly identical (see Table 1). A remarkable feature is that the uncoordinated  $\text{C}_5\text{H}_5$  ring occupies a sterically rather unfavorable position since it lies relatively near to the phenyl group having C(20) as the *ipso*-carbon atom. We also note that the  $\text{SiMe}_2$  moiety is linked to the  $\text{sp}^3$ -hybridized carbon atom of the  $\text{C}_5\text{H}_5$  ring, analogous as suggested by Komatsu and Yamazaki [8] for the cobalt complex  $[\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_5]\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ .

Besides the  $[\text{Rh}(\text{olefin})_2]$ ,  $[\text{Rh}(\text{C}_2\text{H}_4)(\text{P}^i\text{Pr}_3)]$  and  $[\text{Rh}(\text{C}_2\text{Ph}_2)(\text{P}^i\text{Pr}_3)]$  fragments, related units containing a  $\text{Rh}=\text{CPh}_2$  or  $\text{Rh}=\text{C}=\text{C}=\text{CPh}_2$  group as a building block could also be coordinated to the  $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5]^-$  anion. The results of these studies are summarized in Scheme 3. The reactions of the corresponding rhodium(I) precursors with  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  were carried out in THF between  $-78^\circ\text{C}$  and room temperature and gave the products **7–9** as blue or violet oils in 64–77% yields. The metal–stibine bond of **9** is rather labile and thus upon passing a slow stream of CO through a solution of **9** in pentane, a quantitative conversion to the carbonyl(carbene) complex **10** takes place. The most typical spectroscopic features of the carbenerhodium(I) compounds **7**, **9** and



Scheme 1.



**10** are the two slightly separated signals for the  $^{13}\text{C}$  nuclei of the carbene carbon atom at  $\delta$  262.0 and 261.8 (for **7**), 258.2 and 258.0 (for **9**) and 285.7 and 284.9 (for **10**) ppm, the two sets being due to the presence of two isomers as already discussed for compounds **1**, **3** and **4**. The  $^{13}\text{C}$ -NMR spectrum of **8** also displays two resonances for the  $\alpha$ -carbon atom of the  $\text{Rh}=\text{C}=\text{C}=\text{CPh}_2$  chain at  $\delta$  232.7 and 229.8 ppm, whereas only a single resonance for the  $\beta$ -C and a single resonance for the  $\gamma$ -C carbon atom is observed. We note that the missing link between **7** and **8** with the composition  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{C}=\text{C}=\text{CPh})_2(\text{P}^i\text{Pr}_3)]$  has previously been prepared from the alkynyl(hydrido)rhodium(III) precursor  $[\text{RhH}(\text{C}\equiv\text{CPh})\text{Cl}(\text{py})(\text{P}^i\text{Pr}_3)_2]$  and  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  in 76% yield [4b]. The counterpart of **8** with an unsubstituted cyclopentadienyl ring is also known [9].

To use the mononuclear cyclopentadienylrhodium(I) compounds with the dangling  $\text{CH}_2\text{C}_5\text{H}_5$  unit as starting materials for the synthesis of hetero-bimetallic complexes, the corresponding anions had to be generated. This was done by treating the precursors **1**, **3**, **5** and **7**

with either  $n\text{BuLi}$  or  $\text{NaN}(\text{SiMe}_3)_2$  and reacting the in situ formed anions with  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  as the substrate. On this route, the Rh–Ti compounds **11**–**14** were obtained in 54–86% yield (Scheme 4). The composition of the red microcrystalline solids, which for a short period of time can be handled in air, has been confirmed both by elemental analysis and spectroscopic techniques. The  $^1\text{H}$ - as well as the  $^{13}\text{C}$ -NMR spectra of **11**–**14** display two sets of signals for each  $\text{C}_5\text{H}_4$  moiety with chemical shifts comparable to those of the homobimetallic compounds  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{L})(\text{L}')\}_2]$  [3] and  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}_2]$  [10], respectively. The resonance for the carbene carbon atom appears in the  $^{13}\text{C}$ -NMR spectrum of **14** at  $\delta$  261.1 ppm as a doublet of doublets, the chemical shift being nearly identical to that of the isomers of the precursor **7** ( $\delta$  262.0 and 261.8 ppm).

Upon treatment with HCl, compound **13** can be converted to the Rh(III)–Ti(IV) derivative **15** in nearly quantitative yield (Scheme 5). If we take our experience with the protonation of electron-rich cyclopentadienyl complexes of Group 9 into consideration [11], we

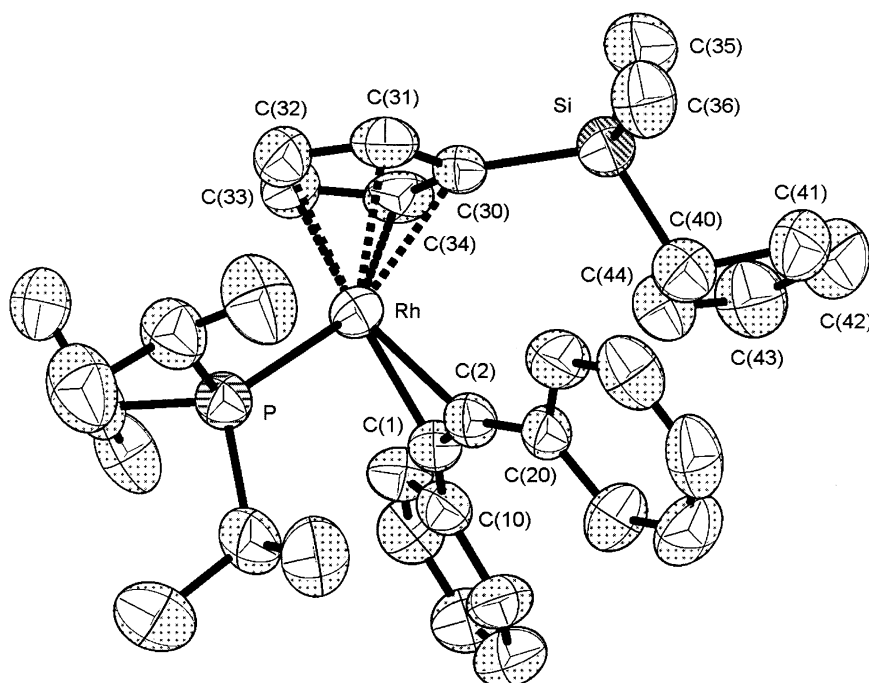


Fig. 1. Molecular structure of compound **6**; anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1  
Selected bond distances (Å) and bond angles (°) with estimated S.D. for compound **6**

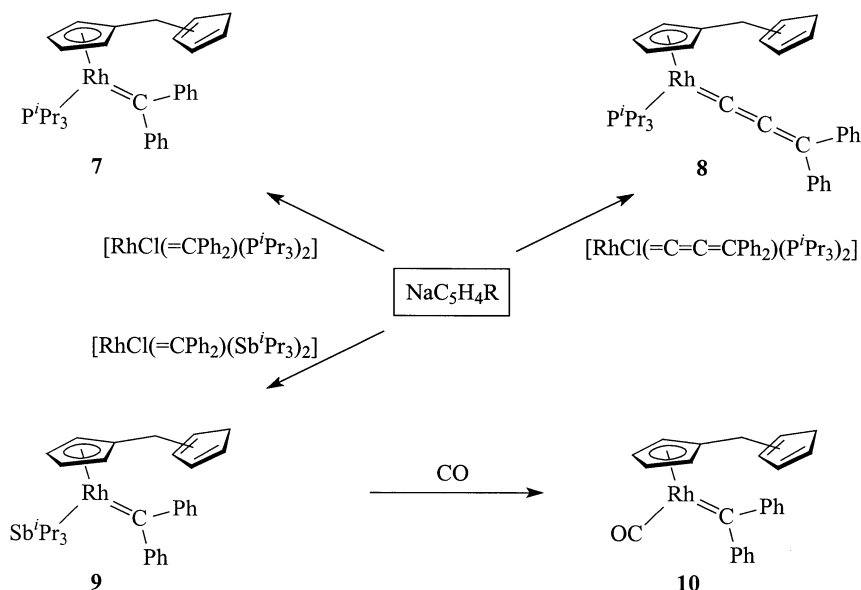
|                    |          |                   |         |             |         |
|--------------------|----------|-------------------|---------|-------------|---------|
| Bond distances (Å) |          |                   |         |             |         |
| Rh–P               | 2.242(3) | C(2)–C(20)        | 1.43(1) | C(40)–C(41) | 1.48(2) |
| Rh–C(1)            | 2.06(1)  | Si–C(30)          | 1.87(1) | C(41)–C(42) | 1.32(2) |
| Rh–C(2)            | 2.07(1)  | Si–C(35)          | 1.89(1) | C(42)–C(43) | 1.43(2) |
| C(1)–C(2)          | 1.27(1)  | Si–C(36)          | 1.86(1) | C(43)–C(44) | 1.33(2) |
| C(1)–C(10)         | 1.44(1)  | Si–C(40)          | 1.90(1) | C(44)–C(40) | 1.48(2) |
| Bond angles (°)    |          |                   |         |             |         |
| C(1)–Rh–P          | 93.5(3)  | Si–C(40)–C(41)    |         | 109.3(9)    |         |
| C(2)–Rh–P          | 93.6(3)  | Si–C(40)–C(44)    |         | 110.6(9)    |         |
| C(2)–C(1)–C(10)    | 150(1)   | C(40)–C(41)–C(42) |         | 110(1)      |         |
| C(1)–C(2)–C(20)    | 150(1)   | C(41)–C(40)–C(44) |         | 101(1)      |         |
| C(30)–Si–C(40)     | 112.1(5) | C(41)–C(42)–C(43) |         | 110(1)      |         |
| C(30)–Si–C(35)     | 108.9(5) | C(42)–C(43)–C(44) |         | 108(1)      |         |
| C(30)–Si–C(36)     | 108.7(5) | C(43)–C(44)–C(40) |         | 111(1)      |         |
| C(35)–Si–C(36)     | 110.5(6) |                   |         |             |         |

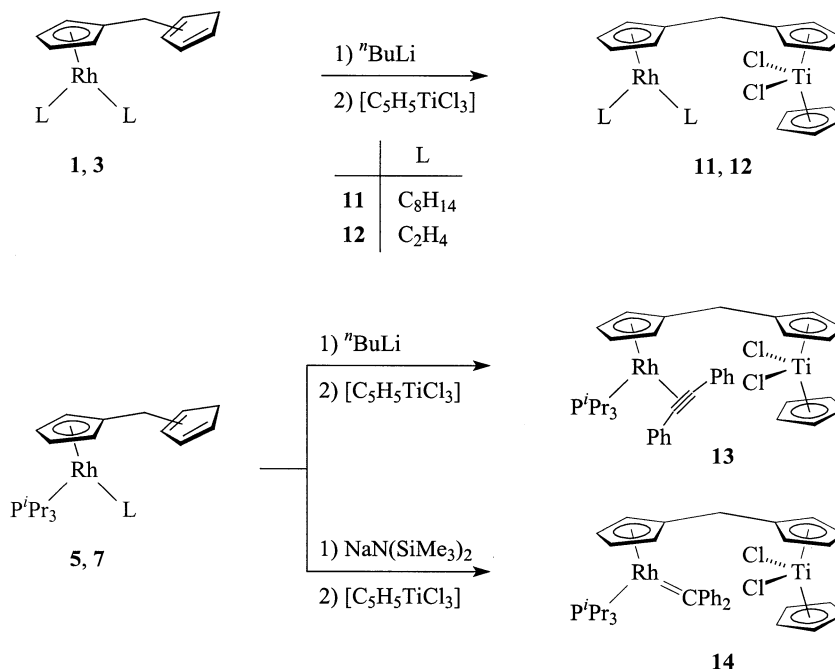
assume that in the initial step of the reaction an attack of HCl at the rhodium center takes place which is followed by a migratory insertion of the alkyne ligand into the generated Rh–H bond. The vinylrhodium intermediate would then react with a second molecule of HCl by cleavage of the Rh–CPh=CHPh bond and elimination of stilbene [12].

The chloro ligands of the hetero-bimetallic compound **15** can easily be substituted by methyl groups if the starting material is treated with an excess of methyl-lithium. Due to some unknown side reactions and the sensitivity of the product toward heat and light, the isolated yield of **16** was only 38%. The presence of two methyl units at rhodium and of two at titanium is confirmed by the <sup>1</sup>H-NMR spectrum of **16**, which shows for the Rh–CH<sub>3</sub> protons a doublet of doublets at  $\delta$  0.70 ppm and for the Ti–CH<sub>3</sub> protons a singlet at  $\delta$  0.01

ppm. The corresponding resonances for the <sup>13</sup>C nuclei appear in the <sup>13</sup>C-NMR spectrum at  $\delta$  –15.0 ppm (dd) and  $\delta$  45.8 ppm (s), respectively. Regarding the reactivity of **16**, we observed that the compound reacts photochemically with CO to presumably give the hetero-bimetallic dicarbonyl complex  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{CH}_3)_2(\text{P}^i\text{Pr}_3)\}\{\text{Ti}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}]$ . This molecule, however, is extremely air- and light-sensitive and thus we failed to characterize the compound by a correct elemental analysis.

The synthesis of the Rh–Zr complexes **17–19** (Scheme 6) proceeded analogous to that of the Rh–Ti counterparts. The yield of the hetero-bimetallic products, which are oily or low-melting substances, is good to excellent. Attempts to replace the chloro for hydrido ligands in **18** and **19**, using either NaBH<sub>4</sub> or LiAlH<sub>4</sub> as hydride source, remained unsuccessful. We note that a





Scheme 4.

relative of **17** with two CO instead of two ethene ligands and an indenyl instead of a cyclopentadienyl ring at rhodium is known and has been prepared stepwise from  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3(\text{dme})]$ ,  $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\text{Li}_2$  and  $[\text{RhCl}(\text{CO})_2]_2$  as starting materials [13].

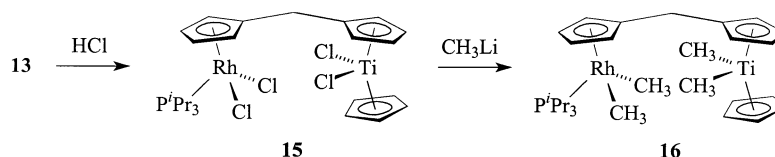
Similarly, as described for the preparation of **15**, the  $\text{Rh}(\text{C}_2\text{Ph}_2)$  unit of **18** could be converted to a  $\text{RhCl}_2$  moiety by treatment with HCl. The so-formed tetrachloro complex **20** was obtained as a red oil in 91% yield. While attempts to prepare the analogous carbonyl(dichloro)rhodium compound  $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{CO})\text{Cl}_2\}\{\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)\}]$  from **19** and HCl failed, the carbene(carbonyl) complex **19** afforded upon reaction with methylolithium the  $\text{Zr}(\text{CH}_3)_2$  derivative **21** in moderate yield (Scheme 7). Our hope that by careful warming or by low-temperature UV irradiation of **21** one of the methyl groups could be transformed from zirconium to rhodium, thereby generating an acyl or alkyl ligand at the electron-rich metal center and equally a metal–metal bond, was not fulfilled.

The results of some preliminary experiments regarding the catalytic potential of the apparently most suitable hetero-bimetallic complex **12** can be summarized as follows. With 0.058 mmol of **12** and an excess of MAO as co-catalyst (ratio **12**:MAO = 260),  $\text{C}_2\text{H}_4$  reacts

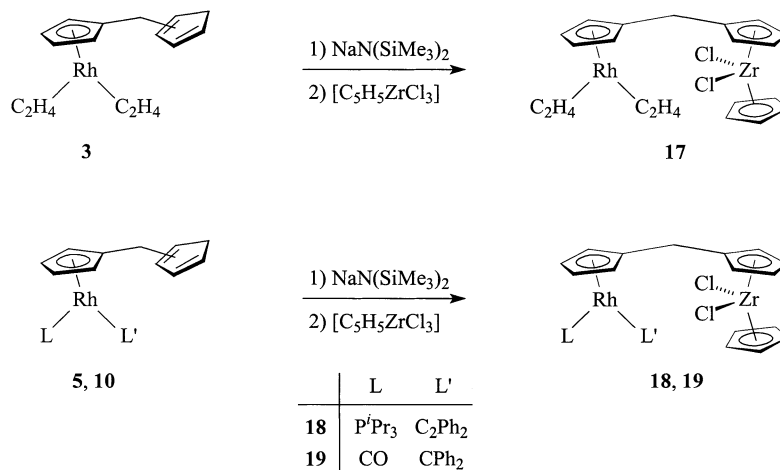
in toluene as solvent to give in 1 h 9.7 g of polyethylene (PE). The activity (g PE per g(**12**) h) at a pressure of 1 bar is 3490, which is comparable to that with  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$  and MAO as the catalytic system [14]. We are currently investigating, whether there is a difference in the tacticity of polypropylene if **12** or **17** and MAO instead of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{MCl}_2]$  (M = Ti, Zr) and MAO are used as catalysts for the polymerization of propylene, and we will report about the results of these studies in due course.

### 3. Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  [4a],  $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2$  [15],  $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$  [16],  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  [17],  $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{P}^i\text{Pr}_3)_2]$  [18], *trans*- $[\text{RhCl}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)_2]$  [12], *trans*- $[\text{RhCl}(\text{C}=\text{C}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2]$  (E = P, Sb) [19], *trans*- $[\text{RhCl}(\text{C}=\text{C}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2]$  [20],  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  [21] and  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3]$  [22] 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, and IR spectra on a Perkin–



Scheme 5.



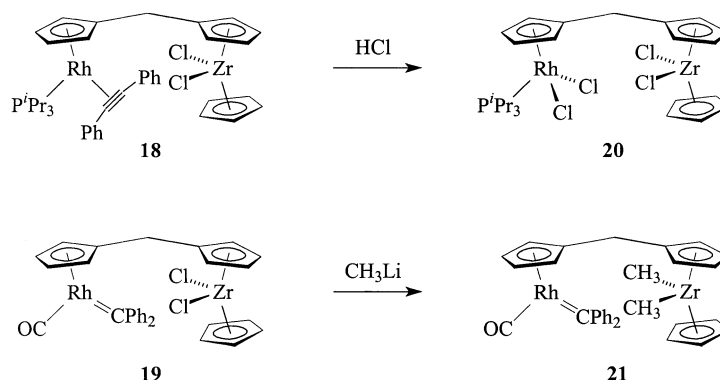
Scheme 6.

Elmer 1420 or an IFS 25 FT-IR infrared spectrometer. Melting points were determined by DTA. Abbreviations used: s, singlet; d, doublet; sept, septet; m, multiplet; br, broadened signal.

### 3.1. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{C}_8\text{H}_{14})_2]$ (**1**) and $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{C}_8\text{H}_{14})_2\}_2]$ (**2**)

A suspension of 109 mg (0.66 mmol) of  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  in 15 ml of THF was cooled to  $-78^\circ\text{C}$  and then treated under continuous stirring with a solution of 251 mg (0.35 mmol) of  $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$  in 10 ml of THF. After the reaction mixture was warmed to r.t., it was stirred for 2 h. The solvent was evaporated in vacuo, and the residue was extracted three times with 5 ml of hexane each. The combined extracts were concentrated to ca. 1 ml and the solution was chromatographed on  $\text{Al}_2\text{O}_3$  (neutral, activity grade III, length of column 10 cm). With hexane two fractions were eluted of which the first contained the mononuclear complex **1**. It was brought to dryness in vacuo, the residue was dissolved in 3 ml of hexane and the solution was again chromatographed on  $\text{Al}_2\text{O}_3$ . From the major fraction (the minor fraction contained small amounts of

**2**), the solvent was removed and the remaining yellow oil was dried in vacuo; yield 174 mg (57%). Anal. Found: C, 70.07; H, 8.71. Calc. for  $\text{C}_{27}\text{H}_{39}\text{Rh}$ : C, 69.52; H, 8.43%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  6.56, 6.40, 6.35, 6.24, 6.14, 5.99 (all m, 3H, olefinic protons of  $\text{C}_5\text{H}_5$ ), 4.92, 4.41 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.50, 3.43 (both m, 2H,  $\text{CH}_2$ ), 2.85 (m, 2H,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 2.30 (m, 4H, =CH of  $\text{C}_8\text{H}_{14}$ ), 1.58, 1.28 (both m, 24H,  $\text{CH}_2$  of  $\text{C}_8\text{H}_{14}$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50.3 MHz):  $\delta$  148.3, 146.3 (both s, carbon atom of  $\text{C}_5\text{H}_5$  connected with  $\text{CH}_2$ ), 135.5, 134.4, 133.1, 128.3, 127.6 (all s, =CH of  $\text{C}_5\text{H}_5$ ), 108.3, 107.4 (both s, *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 91.0, 90.1 (both d,  $J(\text{Rh},\text{C}) = 3.7$  Hz, C(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 88.2 (m, C(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 65.1, 64.2 (both m, =CH of  $\text{C}_8\text{H}_{14}$ ), 43.6, 41.9 (both s,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 33.4, 33.0, 27.0 (all s,  $\text{CH}_2$  of  $\text{C}_8\text{H}_{14}$ ), 27.1, 25.3 (both s,  $\text{CH}_2$ ) ppm. The solvent of the second fraction containing the dinuclear compound **2** was also evaporated in vacuo to give a light red oil; yield 61 mg (24%). Anal. Found: C, 65.75; H, 8.77. Calc. for  $\text{C}_{43}\text{H}_{66}\text{Rh}_2$ : C, 65.47; H, 8.43%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  4.93 (br s, 4H, H(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 4.42 (br s, 4H, H(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.46 (br s, 2H,  $\text{CH}_2$ ), 2.32 (m, 8H, =CH of  $\text{C}_8\text{H}_{14}$ ), 1.58, 1.30 (both m, 48H,  $\text{CH}_2$  of  $\text{C}_8\text{H}_{14}$ ) ppm.



Scheme 7.

### 3.2. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2]$ (**3**)

A suspension of 179 mg (1.08 mmol) of  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  in 25 ml of THF was cooled to  $-78^\circ\text{C}$  and then treated under continuous stirring with a solution of 214 mg (0.55 mmol) of  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  in 10 ml of THF. After the reaction mixture was warmed to r.t., it was stirred for 3 h. The solvent was evaporated in vacuo and the residue was extracted three times with 5 ml of hexane each. The combined extracts were concentrated to ca. 1 ml and the solution was chromatographed on  $\text{Al}_2\text{O}_3$  (neutral, activity grade III, length of column 10 cm). With hexane, a bright yellow fraction was eluted from which after removal of the solvent a yellow oil was isolated; yield 241 mg (74%). Anal. Found: C, 59.73; H, 6.49. Calc. for  $\text{C}_{15}\text{H}_{19}\text{Rh}$ : C, 59.61; H, 6.34%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  6.52, 6.42, 6.33, 6.21, 6.14, 5.97 (all m, 3H, olefinic protons of  $\text{C}_5\text{H}_5$ ), 5.22 (m, 2H, H(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 5.01 (m, 2H, H(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 2.93, 2.90 (both s, 2H,  $\text{CH}_2$ ), 2.83 (m, 2H,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 2.65, 1.21 (both m, 8H,  $\text{C}_2\text{H}_4$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50.3 MHz):  $\delta$  147.8, 146.2 (s, carbon atom of  $\text{C}_5\text{H}_5$  connected with  $\text{CH}_2$ ), 133.4, 133.0, 132.4, 131.4, 128.4, 128.0 (all s, =CH of  $\text{C}_5\text{H}_5$ ), 110.7, 110.6 (both d,  $J(\text{Rh},\text{C}) = 3.0$  Hz, *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 88.6, 88.1 (both d,  $J(\text{Rh},\text{C}) = 3.8$  Hz, C(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 87.0 (m, C(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 43.3, 41.3 (both s,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 38.2 (m,  $\text{C}_2\text{H}_4$ ), 26.5, 25.6 (both s,  $\text{CH}_2$ ) ppm.

### 3.3. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)(\text{P}^i\text{Pr}_3)]$ (**4**)

This compound was prepared analogous as described for **3** from 164 mg (0.99 mmol) of  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  and 291 mg (0.45 mmol) of  $[\text{RhCl}(\text{C}_2\text{H}_4)(\text{P}^i\text{Pr}_3)]_2$ . After column chromatography and evaporation of the solvent, an orange oil was isolated; yield 133 mg (68%). Anal. Found: C, 60.49; H, 8.32. Calc. for  $\text{C}_{22}\text{H}_{36}\text{PRh}$ : C, 60.85; H, 8.36%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  6.42, 6.29, 6.21, 6.11, 6.00, 5.90 (all m, 3H, olefinic protons of  $\text{C}_5\text{H}_5$ ), 5.14, 5.08 (both m, 2H, H(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 5.00 (m, 2H, H(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.16, 3.11 (both m, 2H,  $\text{CH}_2$ ), 2.83, 2.78 (both m, 2H,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 2.33, 1.68 (both m, 2H each,  $\text{C}_2\text{H}_4$ ), 1.46 (m, 3H,  $\text{PCHCH}_3$ ), 1.00, 0.96 (both dd,  $J(\text{P},\text{H}) = 13.2$  Hz,  $J(\text{H},\text{H}) = 7.0$  Hz, 18H,  $\text{PCHCH}_3$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 50.3 MHz):  $\delta$  148.9, 146.5 (both s, carbon atoms of  $\text{C}_5\text{H}_5$  connected with  $\text{CH}_2$ ), 135.4, 133.3, 132.6, 130.9, 128.4, 127.5 (all s, =CH of  $\text{C}_5\text{H}_5$ ), 103.4, 102.7 (both dd,  $J(\text{Rh},\text{C}) = 8.0$  Hz,  $J(\text{P},\text{C}) = 3.0$  Hz, *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 86.4, 85.7 (both m, C(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 84.1 (m, C(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 43.4, 41.3 (both s,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 38.2 (d,  $J(\text{Rh},\text{C}) = 13.4$  Hz,  $\text{C}_2\text{H}_4$ ), 28.6 (br s,  $\text{CH}_2$ ), 25.0 (d,  $J(\text{P},\text{C}) = 19.5$  Hz,  $\text{PCHCH}_3$ ), 19.8 (s,  $\text{PCHCH}_3$ ) ppm.  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ ,

81.0 MHz):  $\delta$  71.8, 71.7 (both d,  $J(\text{Rh},\text{P}) = 200.5$  Hz) ppm.

### 3.4. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_5\text{H}_5)\text{Rh}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)]$ (**6**)

A suspension of 8 mg (0.20 mmol) of  $\text{NaNH}_2$  in 3 ml of THF was cooled to  $-78^\circ\text{C}$  and then treated under continuous stirring with a solution of 38 mg (0.20 mmol) of  $\text{Me}_2\text{Si}(\text{C}_5\text{H}_5)_2$  in 3 ml of THF. After the reaction mixture was warmed to r.t., it was irradiated in an ultrasound bath for 10 min. The milky suspension was again cooled to  $-78^\circ\text{C}$  and slowly evacuated to remove  $\text{NH}_3$ . While the low temperature was maintained, the suspension was treated with a solution of 115 mg (0.20 mmol) of *trans*- $[\text{RhCl}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)_2]$  in 5 ml of THF. The reaction mixture was warmed to r.t. and stirred for 3 h. The solvent was evaporated in vacuo and the residue was extracted three times with 5 ml of pentane each. The combined extracts were concentrated to ca. 2 ml in vacuo and the solution was chromatographed on  $\text{Al}_2\text{O}_3$  (neutral, activity grade III, length of column 10 cm). With hexane, first an off-white fraction was eluted which was withdrawn. Continuous elution with hexane gave a yellow fraction which was concentrated to ca. 1 ml in vacuo. After the solution was stored at  $-78^\circ\text{C}$ , yellow crystals precipitated which were separated from the mother liquor, washed with small quantities of pentane ( $-20^\circ\text{C}$ ) and dried; yield 88 mg (70%). Anal. Found: C, 67.32; H, 7.68. Calc. for  $\text{C}_{35}\text{H}_{46}\text{PRhSi}$ : C, 66.86; H, 7.38%. IR (hexane):  $\nu(\text{C}\equiv\text{C})$   $1830\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  8.05, 7.12 (both m, 10H,  $\text{C}_6\text{H}_5$ ), 6.32, 6.15 (both m, 4H, olefinic protons of  $\text{C}_5\text{H}_5$ ), 5.05, 4.95 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 2.85 (m, 1H,  $\text{SiCH}$  of  $\text{C}_5\text{H}_5$ ), 1.45 (m, 3H,  $\text{PCHCH}_3$ ), 1.07, 0.98 (both dd,  $J(\text{P},\text{H}) = 13.2$  Hz,  $J(\text{H},\text{H}) = 7.1$  Hz, 18H,  $\text{PCHCH}_3$ ), 0.30 (s, 6H,  $\text{SiCH}_3$ ) ppm.  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ , 81.0 MHz):  $\delta$  57.0 (d,  $J(\text{Rh},\text{P}) = 244.0$  Hz) ppm.

### 3.5. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(=\text{CPh}_2)(\text{P}^i\text{Pr}_3)]$ (**7**)

This compound was prepared analogous as described for **3** from 34 mg (0.21 mmol) of  $\text{NaC}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5$  and 127 mg (0.21 mmol) of *trans*- $[\text{RhCl}(=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2]$ . After column chromatography and evaporation of the solvent, a deep blue oil was isolated; yield 77 mg (65%). Anal. Found: C, 68.85; H, 7.22. Calc. for  $\text{C}_{33}\text{H}_{42}\text{PRh}$ : C, 69.21; H, 7.39%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  7.44 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.07 (m, 6H,  $\text{C}_6\text{H}_5$ ), 6.49, 6.41, 6.30, 6.22, 6.12, 5.97 (all m, 3H, olefinic protons of  $\text{C}_5\text{H}_5$ ), 5.02, 4.91 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 2.98 (br s, 2H,  $\text{CH}_2$ ), 2.91 (m, 2H,  $\text{CH}_2$  of  $\text{C}_5\text{H}_5$ ), 1.41 (m, 3H,  $\text{PCHCH}_3$ ), 1.01, 0.94 (both dd,  $J(\text{P},\text{H}) = 13.0$  Hz,  $J(\text{H},\text{H}) = 7.0$  Hz, 18H,  $\text{PCHCH}_3$ ) ppm.  $^{13}\text{C-NMR}$

(C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  262.0, 261.8 (both dd,  $J(\text{Rh},\text{C}) = 51.1$  Hz,  $J(\text{P},\text{C}) = 18.0$  Hz,  $\text{Rh}=\text{CPh}_2$ ), 150.6, 148.7 (both s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 147.2, 146.4 (both s, carbon atom of C<sub>5</sub>H<sub>5</sub> connected with CH<sub>2</sub>), 135.1, 135.0, 133.7, 131.9, 131.1, 130.1, 129.1, 128.1 (all s, C<sub>6</sub>H<sub>5</sub> and =CH of C<sub>5</sub>H<sub>5</sub>), 103.2, 101.1 (both dd,  $J(\text{Rh},\text{C}) = 5.7$  Hz,  $J(\text{P},\text{C}) = 2.7$  Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 85.9 (dd,  $J(\text{Rh},\text{C}) = J(\text{P},\text{C}) = 2.8$  Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 80.6 (m, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 43.3, 41.5 (both s, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>), 30.5, 30.2 (both s, CH<sub>2</sub>), 26.5 (d,  $J(\text{P},\text{C}) = 18.0$  Hz, PCHCH<sub>3</sub>), 20.4 (s, PCHCH<sub>3</sub>) ppm. <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 81.0 MHz):  $\delta$  58.1, 58.0 (both d,  $J(\text{Rh},\text{P}) = 242.8$  Hz) ppm.

### 3.6. Preparation of [ $\{\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5\}\text{Rh}(\text{C}=\text{C}=\text{CPh}_2)(\text{P}^i\text{Pr}_3)_2$ ] (**8**)

A solution of 224 mg (0.34 mmol) of *trans*-[RhCl(=C=C=CPh<sub>2</sub>)(P<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>] in 25 ml THF was cooled to –78 °C and then treated under continuous stirring with a solution of 75 mg (0.45 mmol) of NaC<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>5</sub> in 15 ml of THF. After the reaction mixture was warmed to r.t., it was stirred for 3 h. The solvent was evaporated in vacuo and the residue was extracted three times with 10 ml of hexane each. To the combined extracts, 0.5 ml of CH<sub>3</sub>I was added and after stirring for 30 min, the solution was filtered. The filtrate was concentrated in vacuo to ca. 1 ml and the solution was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral, activity grade V, length of column 8 cm). With hexane, a violet fraction was eluted which was purified by a repeated chromatography. After evaporation of the solvent, a violet oil was obtained; yield 95 mg (64%). Anal. Found: C, 70.38; H, 6.99. Calc. for C<sub>35</sub>H<sub>42</sub>PRh: C, 70.46; H, 7.10%. IR (hexane):  $\nu(\text{C}=\text{C}=\text{C})$  1934 cm<sup>-1</sup>. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  7.92 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.19 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.49, 6.42, 6.27, 6.19, 6.08, 5.92 (all m, 3H, olefinic protons of C<sub>5</sub>H<sub>5</sub>), 5.17, 4.89 (both m, 4H, C<sub>5</sub>H<sub>4</sub>Rh), 3.10 (br s, 2H, CH<sub>2</sub>), 2.79, 2.75 (both s, 2H, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>), 2.13 (m, 3H, PCHCH<sub>3</sub>), 0.97 (dd,  $J(\text{P},\text{H}) = 13.2$  Hz,  $J(\text{H},\text{H}) = 7.1$  Hz, 18H, PCHCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  232.7, 229.8 (both dd,  $J(\text{Rh},\text{C}) = 68.3$  Hz,  $J(\text{P},\text{C}) = 28.0$  Hz, Rh=C), 202.6 (dd,  $J(\text{Rh},\text{C}) = 16.3$  Hz,  $J(\text{P},\text{C}) = 7.0$  Hz, Rh=C=C), 149.6, 148.9 (both s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 146.2, 146.0 (both s, carbon atom of C<sub>5</sub>H<sub>5</sub> connected with CH<sub>2</sub>), 135.0, 134.7, 133.0, 131.9, 130.8, 130.3, 128.1, 127.0 (all s, C<sub>6</sub>H<sub>5</sub> and =CH of C<sub>5</sub>H<sub>5</sub>), 120.9 (dd,  $J(\text{Rh},\text{C}) = 2.1$  Hz,  $J(\text{P},\text{C}) = 4.9$  Hz, Rh=C=C=C), 104.7, 103.7 (both dd,  $J(\text{Rh},\text{C}) = 4.8$  Hz,  $J(\text{P},\text{C}) = 2.8$  Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 84.9 (dd,  $J(\text{Rh},\text{C}) = J(\text{P},\text{C}) = 3.8$  Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 81.7 (m, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 43.2, 41.8 (both s, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>), 31.1, 30.9 (both s, CH<sub>2</sub>), 26.8 (d,  $J(\text{P},\text{C}) = 22.1$  Hz, PCHCH<sub>3</sub>), 19.8 (s, PCHCH<sub>3</sub>) ppm. <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 81.0 MHz):  $\delta$  69.0, 68.9 (both d,  $J(\text{Rh},\text{P}) = 199.2$  Hz) ppm.

### 3.7. Preparation of [ $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{C}=\text{CPh}_2)(\text{Sb}^i\text{Pr}_3)_2$ ] (**9**)

This compound was prepared analogous as described for **3** from 66 mg (0.40 mmol) of NaC<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>5</sub> and 320 mg (0.40 mmol) of *trans*-[RhCl(=CPh<sub>2</sub>)(Sb<sup>*i*</sup>Pr<sub>3</sub>)<sub>2</sub>]. After column chromatography and evaporation of the solvent, a deep blue oil was isolated; yield 206 mg (77%). Anal. Found: C, 59.93; H, 6.49. Calc. for C<sub>33</sub>H<sub>42</sub>RhSb: C, 59.75; H, 6.38%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  7.70 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.04 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.52, 6.40, 5.34, 6.26, 6.10, 5.92 (all m, 3H, olefinic protons of C<sub>5</sub>H<sub>5</sub>), 5.14, 4.98 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.02 (br s, 2H, CH<sub>2</sub>), 2.91 (m, 2H, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>), 1.33 (sept, 3H,  $J(\text{H},\text{H}) = 6.9$  Hz, SbCHCH<sub>3</sub>), 1.08 (d, 18H,  $J(\text{H},\text{H}) = 7.0$  Hz, SbCHCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  258.2, 258.0 (both d,  $J(\text{Rh},\text{C}) = 46.9$  Hz, Rh=CPh<sub>2</sub>), 166.6, 160.0 (both s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 148.1, 147.4 (both s, carbon atom of C<sub>5</sub>H<sub>5</sub> connected with CH<sub>2</sub>), 135.1, 135.0, 133.7, 131.9, 131.1, 130.1, 129.1, 128.1 (all s, C<sub>6</sub>H<sub>5</sub> and =CH of C<sub>5</sub>H<sub>5</sub>), 102.5, 101.6 (both d,  $J(\text{Rh},\text{C}) = 5.7$  Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 84.4, 84.3 (both d,  $J(\text{Rh},\text{C}) = 3.8$  Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 80.7 (d,  $J(\text{Rh},\text{C}) = 2.2$  Hz, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 43.4, 41.3 (both s, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>), 31.6, 30.9 (both s, CH<sub>2</sub>), 22.0 (s, SbCHCH<sub>3</sub>), 18.4 (d,  $J(\text{Rh},\text{C}) = 3.1$  Hz, SbCHCH<sub>3</sub>) ppm.

### 3.8. Preparation of [ $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_5)\text{Rh}(\text{C}=\text{CPh}_2)(\text{CO})$ ] (**10**)

A slow stream of CO was passed through a solution of 206 mg (0.31 mmol) of **9** in 20 ml of pentane. After the gas flow was stopped, the solution was stirred for 1 h at r.t., which led to a change of color from blue to deep red. The solvent was evaporated in vacuo, the residue was dissolved in 2 ml of hexane and the solution was chromatographed on Al<sub>2</sub>O<sub>3</sub> (neutral, activity grade III, length of column 10 cm). With hexane, a red fraction was eluted from which a red oil was isolated; yield 130 mg (95%). Anal. Found: C, 68.10; H, 4.83. Calc. for C<sub>25</sub>H<sub>21</sub>ORh: C, 68.19; H, 4.81%. IR (hexane):  $\nu(\text{CO})$  1980 cm<sup>-1</sup>. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  7.43 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 6.99 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.51, 6.46, 6.33, 6.25, 6.07, 5.88 (all m, 3H, olefinic protons of C<sub>5</sub>H<sub>5</sub>), 5.22, 4.90 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.15, 3.04 (both s, 2H, CH<sub>2</sub>), 2.76, 2.69 (both s, 2H, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  285.7, 284.9 (both d,  $J(\text{Rh},\text{C}) = 47.8$  Hz, Rh=CPh<sub>2</sub>), 192.9, 192.4 (both d,  $J(\text{Rh},\text{C}) = 100.4$  Hz, CO), 165.0, 161.3 (both s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 146.5, 145.0 (both s, carbon atom of C<sub>5</sub>H<sub>5</sub> connected with CH<sub>2</sub>), 134.8, 133.7, 131.9, 130.8, 128.8, 127.1, 126.8, 125.3 (all s, C<sub>6</sub>H<sub>5</sub> and =CH of C<sub>5</sub>H<sub>5</sub>), 105.4, 104.3 (both d,  $J(\text{Rh},\text{C}) = 4.8$  Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 90.2, 90.1 (both d,  $J(\text{Rh},\text{C}) = 3.5$  Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 88.7 (d,  $J(\text{Rh},\text{C}) = 3.0$  Hz, C(3,4) of



C<sub>5</sub>H<sub>4</sub>Rh), 43.5, 41.3 (both s, CH<sub>2</sub> of C<sub>5</sub>H<sub>5</sub>), 30.9 (br s, CH<sub>2</sub>) ppm.

### 3.9. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{C}_8\text{H}_{14})_2\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (11)

A solution of 176 mg (0.38 mmol) of **1** in 15 ml of hexane was cooled to  $-78^\circ\text{C}$  and then treated with 0.20 ml (0.40 mmol) of a 2.0-M solution of *n*-butyllithium in hexane. After the reaction mixture was warmed to r.t., it was stirred for 20 min. The solvent was removed in vacuo, the residue was washed twice with 5 ml of hexane each and then dissolved in 15 ml of THF. The solution containing the lithium salt of the anion of **1** was cooled to  $-78^\circ\text{C}$  and added dropwise to a solution of 86 mg (0.39 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  in 15 ml of THF. The reaction was warmed slowly (ca. 2 h) to r.t. and stirred for 2 h. The solvent was evaporated in vacuo and the residue was extracted three times with 10 ml of toluene each. The combined extracts were concentrated to ca. 2 ml in vacuo and the solution layered with 15 ml of pentane. After storing the mixture at  $-78^\circ\text{C}$ , red crystals precipitated which were filtered, washed twice with 5 ml of pentane each and dried; yield 133 mg (54%). Anal. Found: C, 59.59; H, 6.60. Calc. for C<sub>32</sub>H<sub>43</sub>Cl<sub>2</sub>RhTi: C, 59.18; H, 6.67%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  6.58 (s, 5H, C<sub>5</sub>H<sub>5</sub>Ti), 6.43, 6.31 (both vt,  $N=2.1$  Hz, 2H each, C<sub>5</sub>H<sub>4</sub>Ti), 4.95 (m, 4H, H(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 4.45 (m, 4H, H(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 3.03 (br s, 2H, CH<sub>2</sub>), 2.31 (m, 4H, =CH of C<sub>8</sub>H<sub>14</sub>), 1.60, 1.29 (both m, 24H, CH<sub>2</sub> of C<sub>8</sub>H<sub>14</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz):  $\delta$  136.8 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Ti), 121.9 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Ti), 119.8 (s, C<sub>5</sub>H<sub>5</sub>Ti), 117.9 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Ti), 108.0 (d,  $J(\text{Rh,C})=3.2$  Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 90.1 (d,  $J(\text{Rh,C})=3.8$  Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 88.2 (d,  $J(\text{Rh,C})=3.4$  Hz, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 64.7 (m, =CH of C<sub>8</sub>H<sub>14</sub>), 33.4, 32.1, 31.2, 27.1 (all s,  $\mu\text{-CH}_2$  and CH<sub>2</sub> of C<sub>8</sub>H<sub>14</sub>).

### 3.10. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{C}_2\text{H}_4)_2\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (12)

A solution of 149 mg (0.49 mmol) of **3** in 15 ml of hexane was cooled to  $-78^\circ\text{C}$  and then treated with 0.20 ml (0.50 mmol) of a 2.5-M solution of *n*-butyllithium in hexane. After the reaction mixture was warmed to r.t., it was stirred for 1 h. The solvent was removed in vacuo, the residue was washed twice with 5 ml of hexane each and then dissolved in 15 ml of THF. The solution containing the lithium salt of the anion of **3** was cooled to  $-78^\circ\text{C}$  and added dropwise to a solution of 110 mg (0.50 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  in 10 ml of THF. The reaction was warmed slowly (ca. 2 h) to r.t. and stirred for 3 h. The solvent was evaporated in vacuo and the residue was extracted three times with 10 ml of toluene each. The combined extracts were concentrated to ca. 2

ml in vacuo and the solution layered with 15 ml of pentane. After storing the mixture at  $-78^\circ\text{C}$ , red crystals precipitated which were filtered, washed twice with 5 ml of pentane each and dried; yield 159 mg (66%). Anal. Found: C, 49.91; H, 4.86; Rh, 20.87; Ti, 9.33. Calc. for C<sub>20</sub>H<sub>23</sub>Cl<sub>2</sub>RhTi: C, 49.52; H, 4.78; Rh, 21.21; Ti, 9.87%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  6.55 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.42, 6.39 (both vt,  $N=2.1$  Hz, 2H each, C<sub>5</sub>H<sub>4</sub>Ti), 5.27, 4.99 (both m, 4H, C<sub>5</sub>H<sub>4</sub>Rh), 3.82 (s, 2H, CH<sub>2</sub>), 2.72, 1.25 (both br s, C<sub>2</sub>H<sub>4</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50.3 MHz):  $\delta$  136.4 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Ti), 122.9 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Ti), 117.1 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Ti), 119.9 (s, C<sub>5</sub>H<sub>5</sub>Ti), 111.2 (m, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 89.0 (d,  $J(\text{Rh,C})=3.0$  Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 87.0 (d,  $J(\text{Rh,C})=3.6$  Hz, C(3,4) of C<sub>5</sub>H<sub>4</sub>Ti), 39.2 (m, C<sub>2</sub>H<sub>4</sub>), 29.9 (s, CH<sub>2</sub>) ppm.

### 3.11. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (13)

This compound was prepared analogous as described for **11** from 224 mg (0.38 mmol) of  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4\text{Li})\text{Rh}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)]$  (prepared from **5** and an equimolar amount of *n*-butyllithium) and 83 mg (0.38 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  in 30 ml of THF. After recrystallization from toluene/hexane, a light red solid was isolated; yield 251 mg (86%). Anal. Found: C, 60.08; H, 5.99; Rh, 13.11. Calc. for C<sub>39</sub>H<sub>46</sub>Cl<sub>2</sub>PRhTi: C, 61.04; H, 6.04; Rh, 13.41%. IR (toluene):  $\nu(\text{C}\equiv\text{C})$  1832 cm<sup>-1</sup>. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  8.10, 7.08 (both m, 10H, C<sub>6</sub>H<sub>5</sub>), 6.54 (s, 5H, C<sub>5</sub>H<sub>5</sub>Ti), 6.48, 6.36 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Ti), 5.52, 5.25 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.38 (s, 2H, CH<sub>2</sub>), 1.61 (m, 3H, PCHCH<sub>3</sub>), 0.90 (dd,  $J(\text{P,H})=12.9$  Hz,  $J(\text{H,H})=7.1$  Hz, 18H, PCHCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  136.7 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Ti), 133.7 (s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 132.0, 128.2, 126.0 (all s, C<sub>6</sub>H<sub>5</sub>), 121.9 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Ti), 117.3 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Ti), 119.9 (s, C<sub>5</sub>H<sub>5</sub>Ti), 104.6 (dd,  $J(\text{Rh,C})=12.0$  Hz,  $J(\text{P,C})=3.6$  Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 96.1, 95.9 (both dd,  $J(\text{Rh,C})=18.3$  Hz,  $J(\text{P,C})=4.9$  Hz, C $\equiv$ C), 87.9 (m, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 82.9 (m, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 30.2 (s, CH<sub>2</sub>), 26.1 (d,  $J(\text{P,C})=21.6$  Hz, PCHCH<sub>3</sub>), 19.9 (s, PCHCH<sub>3</sub>) ppm. <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 81.0 MHz):  $\delta$  73.1 (d,  $J(\text{Rh,P})=200.5$  Hz) ppm.

### 3.12. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(=\text{CPh}_2)(\text{P}^i\text{Pr}_3)\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (14)

A solution of 158 mg (0.28 mmol) of **7** in 20 ml ether was cooled to  $-78^\circ\text{C}$  and then treated with a solution of 51 mg (0.28 mmol) of NaN(SiMe<sub>3</sub>)<sub>2</sub> in 10 ml of ether. After the reaction mixture was slowly warmed to r.t., it was stirred for 30 min. The solvent was removed in vacuo, the residue was washed twice with 5 ml of pentane each and then dissolved in 15 ml of THF. The

solution containing the sodium salt of anion of **6** was cooled to  $-78\text{ }^{\circ}\text{C}$  and added dropwise to a solution of 62 mg (0.28 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3]$  in 15 ml of THF. The reaction was warmed slowly (ca. 4 h) to r.t. and stirred for 6 h. The solvent was evaporated in vacuo and the residue was extracted three times with 10 ml of toluene each. The combined extracts were concentrated to ca. 2 ml in vacuo and the solution layered with 10 ml of pentane. After storing the mixture at  $-78\text{ }^{\circ}\text{C}$ , dark red crystals precipitated which were filtered, washed twice with 5 ml of pentane each and dried; yield 132 mg (63%). Anal. Found: C, 60.09; H, 6.21. Calc. for  $\text{C}_{38}\text{H}_{46}\text{Cl}_2\text{PRhTi}$ : C, 60.44; H, 6.09%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  7.43 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.04 (m, 6H,  $\text{C}_6\text{H}_5$ ), 6.49 (s, 5H,  $\text{C}_5\text{H}_5\text{Ti}$ ), 6.42, 6.18 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Ti}$ ), 5.12, 4.94 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.74 (s, 2H,  $\text{CH}_2$ ), 1.40 (m, 3H,  $\text{PCHCH}_3$ ), 0.99 (dd,  $J(\text{P,H}) = 13.0\text{ Hz}$ ,  $J(\text{H,H}) = 7.0\text{ Hz}$ , 18H,  $\text{PCHCH}_3$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 100.6 MHz):  $\delta$  261.1 (dd,  $J(\text{Rh,C}) = 51.4\text{ Hz}$ ,  $J(\text{P,C}) = 18.0\text{ Hz}$ ,  $\text{Rh}=\text{CPh}_2$ ), 150.6, 148.7 (both s, *ipso*-C of  $\text{C}_6\text{H}_5$ ), 136.5 (s, *ipso*-C of  $\text{C}_5\text{H}_4\text{Ti}$ ), 131.4, 131.0, 130.2, 129.0, 128.1, 126.3 (all s,  $\text{C}_6\text{H}_5$ ), 122.3 (s, C(2,5) of  $\text{C}_5\text{H}_4\text{Ti}$ ), 117.9 (s, C(3,4) of  $\text{C}_5\text{H}_4\text{Ti}$ ), 119.9 (s,  $\text{C}_5\text{H}_5\text{Ti}$ ), 102.9 (dd,  $J(\text{Rh,C}) = 5.8\text{ Hz}$ ,  $J(\text{P,C}) = 2.7\text{ Hz}$ , *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 85.9 (dd,  $J(\text{Rh,C}) = J(\text{P,C}) = 2.8\text{ Hz}$ , C(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 80.6 (m, C(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 30.8 (s,  $\text{CH}_2$ ), 26.5 (d,  $J(\text{P,C}) = 18.0\text{ Hz}$ ,  $\text{PCHCH}_3$ ), 20.4 (s,  $\text{PCHCH}_3$ ) ppm.  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ , 81.0 MHz):  $\delta$  58.0 (d,  $J(\text{Rh,P}) = 242.8\text{ Hz}$ ) ppm.

### 3.13. Preparation of $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{RhCl}_2(\text{P}^i\text{Pr}_3)\}\{\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_5)\}]$ (**15**)

A slow stream of dry HCl was passed at  $-78\text{ }^{\circ}\text{C}$  for 10 s through a solution of 167 mg (0.22 mmol) of **13** in 20 ml THF. The solution was then slowly warmed to room temperature and stirred for 30 min. The solvent was evaporated in vacuo and the residue extracted three times with 5 ml of  $\text{CHCl}_3$  each. The combined extracts were concentrated to ca. 2 ml in vacuo and the solution was layered with 6 ml of pentane. After the mixture was stored at  $-78\text{ }^{\circ}\text{C}$  for 24 h, a dark red solid precipitated which was washed twice with small amounts of pentane and dried; yield 129 mg (89%). Anal. Found: C, 45.17; H, 5.55; Rh, 15.29; Ti, 7.01. Calc. for  $\text{C}_{25}\text{H}_{36}\text{Cl}_4\text{PRhTi}$ : C, 45.48; H, 5.50; Rh, 15.59; Ti, 7.20%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  6.55 (s, 5H,  $\text{C}_5\text{H}_5\text{Ti}$ ), 6.41, 6.28 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Ti}$ ), 5.58, 5.36 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.79 (br s, 2H,  $\text{CH}_2$ ), 2.88 (m, 3H,  $\text{PCHCH}_3$ ), 1.25 (dd,  $J(\text{P,H}) = 13.8\text{ Hz}$ ,  $J(\text{H,H}) = 7.2\text{ Hz}$ , 18H,  $\text{PCHCH}_3$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 100.6 MHz):  $\delta$  137.0 (s, *ipso*-C von  $\text{C}_5\text{H}_4\text{Ti}$ ), 122.6 (s, C(2,5) of  $\text{C}_5\text{H}_4\text{Ti}$ ), 118.2 (s, C(3,4) of  $\text{C}_5\text{H}_4\text{Ti}$ ), 121.2 (s,  $\text{C}_5\text{H}_5\text{Ti}$ ), 90.3 (dd,  $J(\text{Rh,C}) = 12.2\text{ Hz}$ ,  $J(\text{P,C}) = 3.8\text{ Hz}$ , *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 86.0 (br s,  $\text{C}_5\text{H}_4\text{Rh}$ ), 82.5 (dd,  $J(\text{Rh,C}) = J(\text{P,C}) = 3.8\text{ Hz}$ ,  $\text{C}_5\text{H}_4\text{Rh}$ ), 32.7 (br s,  $\text{CH}_2$ ),

24.5 (d,  $J(\text{P,C}) = 22.4\text{ Hz}$ ,  $\text{PCHCH}_3$ ), 20.6 (s,  $\text{PCHCH}_3$ ) ppm.  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ , 162.0 MHz):  $\delta$  57.9 (d,  $J(\text{Rh,P}) = 133.0\text{ Hz}$ ) ppm.

### 3.14. Preparation of $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{CH}_3)_2(\text{P}^i\text{Pr}_3)\}\{\text{Ti}(\text{CH}_3)_2(\eta^5\text{-C}_5\text{H}_5)\}]$ (**16**)

A solution of 284 mg (0.43 mmol) of **15** in 20 ml THF was cooled to  $-78\text{ }^{\circ}\text{C}$  and then treated with 0.95 ml (1.75 mmol) of a 1.85-M solution of methyllithium in hexane. The reaction mixture was slowly warmed to  $0\text{ }^{\circ}\text{C}$ , stirred for 3 h and then warmed to r.t. A small amount of water (ca. 0.2 ml) was added to remove the excess of  $\text{CH}_3\text{Li}$ . The solvent was evaporated in vacuo and the residue was extracted three times with 10 ml of hexane each. The combined extracts were concentrated to ca. 2 ml in vacuo and the solution stored at  $-78\text{ }^{\circ}\text{C}$  for 24 h. Orange crystals precipitated which were filtered, washed twice with 2 ml of pentane each ( $0\text{ }^{\circ}\text{C}$ ) and dried; yield 94 mg (38%). Anal. Found: C, 59.73; H, 8.22. Calc. for  $\text{C}_{29}\text{H}_{48}\text{PRhTi}$ : C, 60.25; H, 8.30%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  5.74 (s, 5H,  $\text{C}_5\text{H}_5\text{Ti}$ ), 5.68, 5.59 (both m, 4H,  $\text{C}_5\text{H}_4\text{Ti}$ ), 5.14, 4.93 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.32 (br s, 2H,  $\text{CH}_2$ ), 1.99 (m, 3H,  $\text{PCHCH}_3$ ), 1.02 (dd,  $J(\text{P,H}) = 13.0\text{ Hz}$ ,  $J(\text{H,H}) = 7.0\text{ Hz}$ , 18H,  $\text{PCHCH}_3$ ), 0.70 (dd,  $J(\text{Rh,H}) = 2.6\text{ Hz}$ ,  $J(\text{P,H}) = 3.5\text{ Hz}$ , 6H,  $\text{RhCH}_3$ ), 0.01 (s, 6H,  $\text{TiCH}_3$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 100.6 MHz):  $\delta$  134.2 (s, *ipso*-C of  $\text{C}_5\text{H}_4\text{Ti}$ ), 122.8 (s, C(2,5) of  $\text{C}_5\text{H}_4\text{Ti}$ ), 118.8 (s,  $\text{C}_5\text{H}_5\text{Ti}$ ), 114.7 (s, C(3,4) of  $\text{C}_5\text{H}_4\text{Ti}$ ), 108.1 (d,  $J(\text{Rh,C}) = 3.8\text{ Hz}$ , *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 89.7 (d,  $J(\text{Rh,C}) = 3.4\text{ Hz}$ ,  $\text{C}_5\text{H}_4\text{Rh}$ ), 88.5 (m,  $\text{C}_5\text{H}_4\text{Rh}$ ), 45.8 (s,  $\text{TiCH}_3$ ), 29.0 (s,  $\text{CH}_2$ ), 25.3 (d,  $J(\text{P,C}) = 20.0\text{ Hz}$ ,  $\text{PCHCH}_3$ ), 20.0 (s,  $\text{PCHCH}_3$ ),  $-15.0$  (dd,  $J(\text{Rh,C}) = 29.8\text{ Hz}$ ,  $J(\text{P,C}) = 13.6\text{ Hz}$ ,  $\text{RhCH}_3$ ) ppm.  $^{31}\text{P-NMR}$  ( $\text{C}_6\text{D}_6$ , 162.0 MHz):  $\delta$  62.7 (d,  $J(\text{Rh,P}) = 169.8\text{ Hz}$ ) ppm.

### 3.15. Preparation of $[\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{C}_2\text{H}_4)_2\}\{\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)\}]$ (**17**)

A solution of 180 mg (0.60 mmol) of **3** in 15 ml of ether was cooled to  $-78\text{ }^{\circ}\text{C}$  and then treated with a solution of 109 mg (0.60 mmol) of  $\text{NaN}(\text{SiMe}_3)_2$  in 10 ml of ether. After the reaction mixture was warmed to r.t., it was stirred for 30 min. The solvent was removed in vacuo, the residue was washed twice with 5 ml of pentane each and then dissolved in 15 ml of THF. The solution containing the sodium salt of anion of **3** was cooled to  $-78\text{ }^{\circ}\text{C}$  and added dropwise to a solution of 160 mg (0.60 mmol) of  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3]$  in 10 ml of THF. The reaction was warmed slowly (ca. 3 h) to r.t., stirred for 8 h and then worked up as described for **12**. An orange microcrystalline solid was isolated; yield 231 mg (73%). Anal. Found: C, 46.29; H, 4.22. Calc. for  $\text{C}_{21}\text{H}_{23}\text{Cl}_2\text{RhZr}$ : C, 46.67; H, 4.29%.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,

400 MHz):  $\delta$  6.41 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.31, 6.20 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Zr), 5.22, 5.03 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.72 (s, 2H, CH<sub>2</sub>), 2.61, 1.30 (both m, 4H each, C<sub>2</sub>H<sub>4</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz):  $\delta$  132.2 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Zr), 117.9 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Zr), 116.2 (s, C<sub>5</sub>H<sub>5</sub>Zr), 113.8 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Zr), 111.2 (d, *J*(Rh,C) = 2.6 Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 88.9 (d, *J*(Rh,C) = 3.2 Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 86.2 (d, *J*(Rh,C) = 3.6 Hz, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 38.2 (m, C<sub>2</sub>H<sub>4</sub>), 31.0 (s, CH<sub>2</sub>).

### 3.16. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{PhC}\equiv\text{CPh})(\text{P}^i\text{Pr}_3)\}\{\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (**18**)

A solution of 365 mg (0.62 mmol) of **5** in 15 ml of ether was cooled to  $-78^\circ\text{C}$  and then treated with a solution of 114 mg (0.62 mmol) of NaN(SiMe<sub>3</sub>)<sub>2</sub> in 10 ml of ether. After the reaction mixture was warmed to r.t., it was stirred for 30 min. The solvent was removed in vacuo, the residue was washed twice with 5 ml of pentane each and then dissolved in 15 ml of THF. The solution containing the sodium salt of anion of **5** was cooled to  $-78^\circ\text{C}$  and added dropwise to a solution of 165 mg (0.62 mmol) of [ $\eta^5\text{-C}_5\text{H}_5\text{ZrCl}_3$ ] in 15 ml of THF. The reaction was warmed slowly (ca. 3 h) to r.t. and then stirred for 8 h. The solvent was evaporated in vacuo and the residue extracted three times with 10 ml of CH<sub>2</sub>Cl<sub>2</sub> each. The combined extracts were concentrated to ca. 1 ml in vacuo and the solution was layered with 15 ml of pentane. After cooling to  $-78^\circ\text{C}$ , a brownish-yellow solid precipitated which upon warming to r.t. became an oil; yield 327 mg (65%). Anal. Found: C, 57.49; H, 5.66. Calc. for C<sub>39</sub>H<sub>46</sub>Cl<sub>2</sub>PRhZr: C, 57.76; H, 5.72%. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{C}\equiv\text{C})$  1826 cm<sup>-1</sup>. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  8.20 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.19 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.50 (s, 5H, C<sub>5</sub>H<sub>5</sub>Zr), 6.34, 6.20 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Zr), 5.42, 5.21 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.78 (s, 2H, CH<sub>2</sub>), 1.60 (m, 3H, PCHCH<sub>3</sub>), 0.90 (dd, *J*(P,H) = 12.9 Hz, *J*(H,H) = 7.2 Hz, 18H, PCHCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  133.7 (s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 132.8 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Zr), 131.5, 128.1, 125.5 (all s, C<sub>6</sub>H<sub>5</sub>), 117.9 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Zr), 116.6 (s, C<sub>5</sub>H<sub>5</sub>Zr), 113.8 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Zr), 105.2 (dd, *J*(Rh,C) = 11.7 Hz, *J*(P,C) = 2.4 Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 96.2, 96.0 (both dd, *J*(Rh,C) = 17.5 Hz, *J*(P,C) = 5.3 Hz, C $\equiv$ C), 87.7 (dd, *J*(Rh,C) = *J*(P,C) = 2.6 Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 82.6 (d, *J*(Rh,C) = 4.0 Hz, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 31.0 (s, CH<sub>2</sub>), 26.1 (d, *J*(P,C) = 21.0 Hz, PCHCH<sub>3</sub>), 19.9 (s, PCHCH<sub>3</sub>) ppm. <sup>31</sup>P-NMR (C<sub>6</sub>D<sub>6</sub>, 81.0 MHz):  $\delta$  71.6 (d, *J*(Rh,P) = 200.2 Hz) ppm.

### 3.17. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{CPh}_2)(\text{CO})\}\{\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (**19**)

This compound was prepared analogous as described for **17** from 115 mg (0.26 mmol) of **10**, 55 mg (0.30

mmol) of NaN(SiMe<sub>3</sub>)<sub>2</sub> and 81 mg (0.31 mmol) of [ $\eta^5\text{-C}_5\text{H}_5\text{ZrCl}_3$ ]. After extraction of the crude product with pentane (three times with 20 ml each), a yellow oil was obtained; yield 140 mg (81%). Anal. Found: C, 53.88; H, 3.79. Calc. for C<sub>30</sub>H<sub>25</sub>Cl<sub>2</sub>ORhZr: C, 54.06; H, 3.78%. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  1971 cm<sup>-1</sup>. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  7.41 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.02 (m, 6H, C<sub>6</sub>H<sub>5</sub>), 6.49 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.41, 6.23 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Zr), 5.22, 4.90 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.89 (s, 2H, CH<sub>2</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz):  $\delta$  284.9 (d, *J*(Rh,C) = 48.6 Hz, Rh=CPh<sub>2</sub>), 192.2 (d, *J*(Rh,C) = 100.8 Hz, CO), 165.1, 160.4 (both s, *ipso*-C of C<sub>6</sub>H<sub>5</sub>), 134.0 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Zr), 128.8, 128.3, 127.7, 127.0, 126.6, 125.4 (all s, C<sub>6</sub>H<sub>5</sub>), 117.3 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Zr), 115.4 (s, C<sub>5</sub>H<sub>5</sub>), 113.2 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Zr), 104.7 (d, *J*(Rh,C) = 4.8 Hz, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 90.0 (d, *J*(Rh,C) = 3.6 Hz, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 88.7 (d, *J*(Rh,C) = 3.0 Hz, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 32.0 (s, CH<sub>2</sub>) ppm.

### 3.18. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{RhCl}_2(\text{P}^i\text{Pr}_3)\}\{\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (**20**)

A slow stream of dry HCl was passed for 30 s through a solution of 260 mg (0.32 mmol) of **18** in 20 ml of CHCl<sub>3</sub>. The solution was stirred for 1 h at r.t., and then the solvent was evaporated in vacuo. The residue was dissolved in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> and the extract was filtered. The filtrate was brought to dryness in vacuo and the remaining red oil washed three times with 10 ml of pentane each; yield 205 mg (91%). Anal. Found: C, 42.89; H, 4.99. Calc. for C<sub>26</sub>H<sub>36</sub>Cl<sub>4</sub>PRhZr: C, 43.65; H, 5.07%. <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  6.48 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.33, 6.20 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Zr), 5.62, 5.41 (both m, 2H each, C<sub>5</sub>H<sub>4</sub>Rh), 3.92 (br s, 2H, CH<sub>2</sub>), 2.85 (m, 3H, PCHCH<sub>3</sub>), 1.35 (dd, *J*(P,H) = 14.0 Hz, *J*(H,H) = 7.2 Hz, 18H, PCHCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz):  $\delta$  133.7 (s, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Zr), 116.9 (s, C(2,5) of C<sub>5</sub>H<sub>4</sub>Zr), 116.0 (s, C<sub>5</sub>H<sub>5</sub>), 113.2 (s, C(3,4) of C<sub>5</sub>H<sub>4</sub>Zr), 104.7 (m, *ipso*-C of C<sub>5</sub>H<sub>4</sub>Rh), 86.8 (m, C(2,5) of C<sub>5</sub>H<sub>4</sub>Rh), 80.8 (m, C(3,4) of C<sub>5</sub>H<sub>4</sub>Rh), 32.1 (s, CH<sub>2</sub>), 25.6 (d, *J*(P,C) = 20.9 Hz, PCHCH<sub>3</sub>), 20.2 (s, PCHCH<sub>3</sub>) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>, 162.0 MHz):  $\delta$  58.5 (d, *J*(Rh,P) = 134.7 Hz) ppm.

### 3.19. Preparation of [ $\{\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2\}\{\text{Rh}(\text{CPh}_2)(\text{CO})\}\{\text{Zr}(\text{CH}_3)_2(\eta^5\text{-C}_5\text{H}_5)\}$ ] (**21**)

A solution of 180 mg (0.27 mmol) of **19** in 15 ml THF was cooled to  $-78^\circ\text{C}$  and then treated with 0.20 ml (0.30 mmol) of a 1.5-M solution of methyllithium in hexane. The reaction mixture was slowly warmed to  $0^\circ\text{C}$ , stirred for 3 h and then warmed to r.t. A small amount of water (ca. 0.1 ml) was added to remove the excess of CH<sub>3</sub>Li. The solvent was evaporated in vacuo and the residue was extracted three times with 15 ml of

hexane each. The combined extracts were concentrated to ca. 2 ml in vacuo and the solution stored at  $-78\text{ }^{\circ}\text{C}$  for 3 days. Deep red crystals precipitated which upon warming to r.t. became an oil; yield 76 mg (49%). Anal. Found: C, 60.88; H, 4.57. Calc. for  $\text{C}_{32}\text{H}_{31}\text{ORhZr}$ : C, 61.44; H, 4.96%. IR (hexane):  $\nu(\text{CO})$   $1964\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  7.44 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.07 (m, 6H,  $\text{C}_6\text{H}_5$ ), 6.52 (s, 5H,  $\text{C}_5\text{H}_5$ ), 6.38, 6.18 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Zr}$ ), 5.09, 4.79 (both m, 2H each,  $\text{C}_5\text{H}_4\text{Rh}$ ), 3.67 (s, 2H,  $\text{CH}_2$ ),  $-0.29$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ , 100.6 MHz):  $\delta$  287.8 (d,  $J(\text{Rh},\text{C}) = 45.5$  Hz,  $\text{Rh}=\text{CPh}_2$ ), 189.8 (d,  $J(\text{Rh},\text{C}) = 98.8$  Hz, CO), 165.2, 160.5 (both s, *ipso*-C of  $\text{C}_6\text{H}_5$ ), 129.9 (s, *ipso*-C of  $\text{C}_5\text{H}_4\text{Zr}$ ), 128.9, 128.2, 127.6, 127.0, 126.4, 125.4 (all s,  $\text{C}_6\text{H}_5$ ), 116.4 (s, C(2,5) of  $\text{C}_5\text{H}_4\text{Zr}$ ), 114.2 (s,  $\text{C}_5\text{H}_5$ ), 113.1 (s, C(3,4) of  $\text{C}_5\text{H}_4\text{Zr}$ ), 105.0 (d,  $J(\text{Rh},\text{C}) = 4.9$  Hz, *ipso*-C of  $\text{C}_5\text{H}_4\text{Rh}$ ), 90.1 (d,  $J(\text{Rh},\text{C}) = 3.6$  Hz, C(2,5) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 88.7 (d,  $J(\text{Rh},\text{C}) = 3.0$  Hz, C(3,4) of  $\text{C}_5\text{H}_4\text{Rh}$ ), 32.2 (s,  $\text{ZrCH}_3$ ), 31.4 (s,  $\text{CH}_2$ ) ppm.

### 3.20. Crystal structure analysis of **6**

Crystals were obtained from hexane at  $-78\text{ }^{\circ}\text{C}$ . Crystal structure determination of **6**:  $\text{C}_{35}\text{H}_{46}\text{PRhSi}$ ,  $M_r = 628.69$ ; tetragonal, space group  $P4/n$  (No. 85),  $Z = 8$ ,  $a = b = 26.020(5)\text{ \AA}$ ,  $c = 10.125(5)\text{ \AA}$ ,  $V = 6855(4)\text{ \AA}^3$ ,  $D_{\text{calc}} = 1.218\text{ g cm}^{-3}$ ,  $\lambda = 0.71073\text{ \AA}$ ,  $T = 293(2)\text{ K}$ ,  $\mu(\text{Mo-K}\alpha) = 0.594\text{ mm}^{-1}$ . Crystal size  $0.10 \times 0.23 \times 0.23\text{ mm}^3$ ;  $2\theta_{\text{max}} = 50^{\circ}$ ; 5557 reflections were measured, 5320 of these were independent ( $R_{\text{int}} = 0.0664$ ) and employed in the structure refinement (352 parameters). The  $R$  values are  $R_1 = 0.0559$  and  $wR_2 = 0.1415$  [ $I > 2\sigma(I)$ ] and  $R_1 = 0.1961$  and  $wR_2 = 0.1932$  (all data); reflex/parameter ratio = 15.1; min./max. residual electron density:  $0.975/-352\text{ e \AA}^{-3}$ . Data were collected on a Enraf-Nonius CAD 4 diffractometer. A semi-empirical absorption correction was applied. The structure was solved by direct methods (SHELXS-86) [23] and refined against  $F^2$  by least-squares (SHELXL-93) [24]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H,  $0.95\text{ \AA}$ ) and used only in structure factor calculations.

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 201883 for compound **6**. Copies of this information may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. Moreover, we acknowledge support by Mrs. R. Schedl and Mr. C.P. Kneis (elemental analysis and DTA), and Mrs. M.L. Schäfer and Dr. W. Buchner (NMR spectra).

## References

- [1] (a) H. Werner, F. Lippert, T. Bohley, *J. Organomet. Chem.* 369 (1989) C27; (b) H. Werner, F. Lippert, T. Bohley, *Z. Anorg. Allg. Chem.* 620 (1994) 2053; (c) F. Lippert, Dissertation, Universität Würzburg, 1989.
- [2] (a) H. Werner, H.J. Scholz, R. Zolk, *Chem. Ber.* 118 (1985) 4531; (b) H. Werner, M. Treiber, A. Nessel, F. Lippert, P. Betz, C. Krüger, *Chem. Ber.* 125 (1992) 337; (c) M. Treiber, Dissertation, Universität Würzburg, 1989.
- [3] (a) A. Nessel, O. Nürnberg, J. Wolf, H. Werner, *Angew. Chem.* 103 (1991) 999; (b) A. Nessel, O. Nürnberg, J. Wolf, H. Werner, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1006; (c) H. Werner, J. Wolf, A. Nessel, A. Fries, B. Stempfle, O. Nürnberg, *Can. J. Chem.* 73 (1995) 1050.
- [4] (a) H. Werner, D. Schneider, M. Schulz, *Chem. Ber.* 125 (1992) 1017; (b) D. Schneider, H. Werner, *Organometallics* 12 (1993) 4420.
- [5] B. Stempfle, S. Schmidt, J. Sundermeyer, H. Werner, *Chem. Ber.* 128 (1995) 877.
- [6] L. Carlton, P. Johnston, N.J. Coville, *J. Organomet. Chem.* 339 (1988) 339.
- [7] E. Breitmaier, W. Voelter, *Carbon-13 NMR Spectroscopy*, VCH, Weinheim, 1987.
- [8] H. Komatsu, H. Yamazaki, *J. Organomet. Chem.* 634 (2001) 109.
- [9] H. Werner, R. Wiedemann, M. Laubender, B. Windmüller, P. Steinert, O. Gevert, J. Wolf, *J. Am. Chem. Soc.* 124 (2002) 6966.
- [10] B. Stempfle, H. Werner, *Gazz. Chim. Ital.* 125 (1995) 287.
- [11] (a) H. Werner, *Angew. Chem.* 95 (1983) 932; (b) H. Werner, *Angew. Chem. Int. Ed. Engl.* 22 (1983) 927.
- [12] H. Werner, J. Wolf, U. Schubert, K. Ackermann, *J. Organomet. Chem.* 317 (1986) 327.
- [13] G.M. Diamond, M.L.H. Green, N.A. Popham, A.N. Chernega, *J. Chem. Soc. Chem. Commun.* (1994) 727.
- [14] K.H. Reichert, *Transition metal-catalyzed polymerizations*, in: R.P. Quirk (Ed.), *Alkenes and Dienes*, Part B, Harwood Academic Publishers, New York, 1983.
- [15] E.W. Abel, M.O. Dunster, A. Waters, *J. Organomet. Chem.* 49 (1973) 287.
- [16] A. van der Ent, A.L. Onderdelinden, *Inorg. Synth.* 14 (1973) 92.
- [17] R. Cramer, *Inorg. Synth.* 15 (1974) 1501.
- [18] H. Werner, R. Feser, *J. Organomet. Chem.* 232 (1982) 351.
- [19] H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert, J. Wolf, *Chem. Eur. J.* 3 (1997) 1375.
- [20] H. Werner, T. Rappert, *Chem. Ber.* 126 (1993) 669.
- [21] R.D. Gorsich, *J. Am. Chem. Soc.* 82 (1958) 4211.
- [22] G. Erker, K. Berg, L. Treschanke, K. Engel, *Inorg. Chem.* 21 (1982) 1277.
- [23] G.M. Sheldrick, *Acta. Crystallogr. Sect. A* 46 (1990) 467.
- [24] G.M. Sheldrick, Program for crystal structure refinement, University of Göttingen, Göttingen, 1993.