

# Chemistry of Metal–Metal-Bonded Early–Late Heterobimetallals: Cooperative Reactions of Functional Groups at a Persistent Organometallic Zr–Rh Framework

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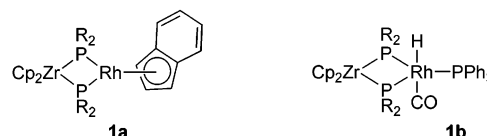
The reaction of  $(C_5H_4-PPh_2)_2Zr(CH_3)_2$  (**5a**) with  $HRh(CO)(PPh_3)_3$  (**6**) leads to methane evolution and the formation of the early–late heterobimetallic complex  $[(\mu-C_5H_4-PPh_2)_2-(H_3C-Zr-Rh(CO)PPh_3)]$  (**7a**), which was characterized by X-ray diffraction ( $d(Zr-Rh) = 2.863(1) \text{ \AA}$ ). The analogous dialkylphosphino-substituted complexes  $(C_5H_4-PR_2)_2Zr(CH_3)_2$  (**5b**, R = isopropyl; **5c**, R = cyclohexyl) react with the hydrido–rhodium reagent **6** to initially form the analogous bimetallic (Zr–Rh) complexes **7b,c**, respectively. However, these complexes are not stable at ambient temperature in toluene solution, due to an equilibration with the products  $[(\mu-C_5H_4-PR_2)_2(\mu-CH_3-Zr-Rh(PPh_3))]$  (**11**) and  $[(\mu-C_5H_4-PR_2)_2(H_3C-Zr-Rh(CO)_2)]$  (**10**). Treatment of the initially formed complexes **7b,c** with carbon monoxide rapidly leads to the formation of the  $H_3C(Zr-Rh)$ –dicarbonyl complexes **10b,c**. The product **10c** was characterized by X-ray crystal structure analysis. The systems **7b,c** are not stable in dichloromethane. They react readily with the solvent by abstraction of two chlorine atoms to yield the compounds  $[(\mu-C_5H_4-PR_2)_2(\mu-O=C(CH_3))(Cl-Zr-Rh-Cl)]$  (**12b,c**). Both products were characterized by X-ray diffraction. A cooperative action of the involved metals is assumed to account for the observed reactions at the intact heterobimetallic Zr–Rh framework.

## Introduction

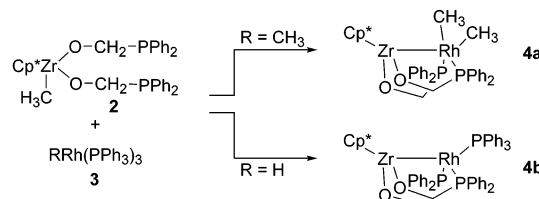
Early–late heterobimetallic (ELHB) complexes may offer unique pathways of transforming organic substrates, since they have the potential to open cooperative reaction channels in which both transition-metal centers may participate in the activation of reagents and/or stabilization of transition states or products.<sup>1</sup> In the past, ELHB complexes of a great structural variety were prepared and tested: e.g., as models for otherwise heterogeneously catalyzed reactions.<sup>2,3</sup> The group 4 metals have participated significantly in this development.<sup>4–10</sup> However, surprisingly few Zr/Rh complexes of this type have been described so far: among these, only very few examples that contained a Zr–Rh metal–metal bond.<sup>11–16</sup>

The two most important classes of heterobimetallic Zr/Rh systems used pendant donor ligands at the periphery of the group 4 metal component to coordinate to the late metal. These were either part of the  $\sigma$ -ligand system<sup>11–13</sup> (e.g. the examples in Chart 1 and Scheme

Chart 1



Scheme 1



1) or they were attached to, for example, the ubiquitous Cp ligands at zirconium (see Scheme 2).<sup>14–16</sup> The Zr...Rh separation in the typical examples of the type I complexes (**1a,b**)<sup>11</sup> shown in Chart 1 is  $>3 \text{ \AA}$ ; structural and electronic features make the presence of a metal–metal bond in these systems unlikely. In contrast, the reaction of  $Cp^*ZrMe(OCH_2PPh_2)_2$  (**2**) with  $RRh(PPh_3)_3$  (**3a**, R =

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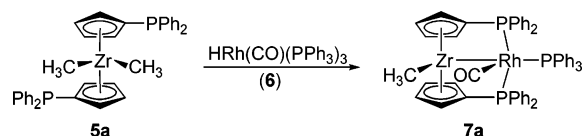
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Scheme 2



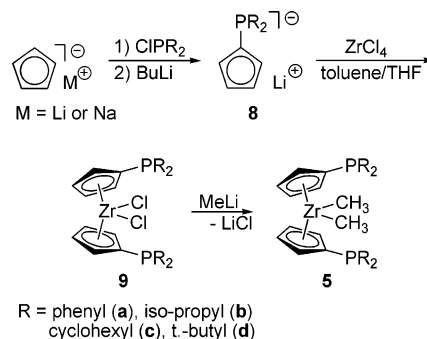
Me; **3b**, R = H) led to the metal–metal-bonded complexes **4a,b**, respectively, as shown by Wolczanski et al. (see Scheme 1).<sup>13</sup> Complex **4a** features a Zr–Rh bond length of 2.444(1) Å in the crystal state, which is far below the sum of the covalent radii (2.70 Å) or metal atom radii (2.94 Å) of these metals.

We had recently described the reaction of the complex (C<sub>5</sub>H<sub>4</sub>–PPh<sub>2</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (**5**) with HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (**6**) to yield the heterobimetallic product **7**.<sup>16</sup> Complex **7** was characterized spectroscopically. It was thought to contain a Zr–Rh metal–metal bond. Complex **7** is a very active (but not very selective) hydroformylation catalyst. We have now been able to characterize this very sensitive complex by X-ray diffraction, and we have prepared several related examples of this general structural type by using dialkylphosphino donor groups attached at the Cp ligands. These systems underwent some surprising reactions involving the  $\sigma$  ligands at both metal centers along the persistent Zr–Rh framework. These reactions and the structures of the resulting novel early–late heterobimetallic complexes will be described in this article.

## Results and Discussion

**Synthesis and Characterization of the (C<sub>5</sub>H<sub>4</sub>–PR<sub>2</sub>)<sub>2</sub>ZrX<sub>2</sub> Complexes.** We chose to prepare a series

Scheme 3



of phosphino-substituted cyclopentadienides using a method analogous to that described by Casey et al. for the preparation of the reagent **8a**.<sup>17</sup> Lithium or sodium cyclopentadienide was treated with the respective di-aryl- or dialkylchlorophosphine ClPR<sub>2</sub> (R = Ph, isopropyl, cyclohexyl, *tert*-butyl) in toluene. The in situ formed mixture of the R<sub>2</sub>P-substituted cyclopentadiene products were not isolated but directly deprotonated by subsequent treatment with *n*-butyllithium to give the corresponding [C<sub>5</sub>H<sub>4</sub>–PR<sub>2</sub>]<sup>–</sup>Li<sup>+</sup> reagents (**8a–d**). The diisopropyl- and cyclohexyl-substituted reagents were isolated in excellent yields (**8b**, 86%; **8c**, 99%); only the bulky di-*tert*-butylphosphino–CpLi analogue (**8d**) was obtained in rather poor yield (24%), even after several attempts (see Scheme 3).

Transmetalation of the reagents **8a–d** with zirconium tetrachloride was carried out similarly, as previously

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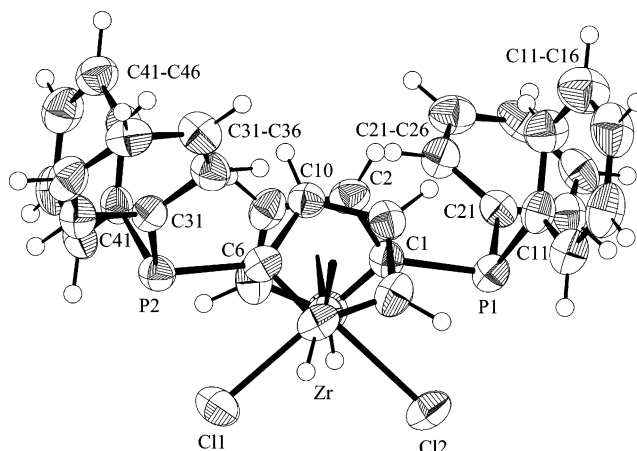
**Table 1.** Comparison of  $^{31}\text{P}$  NMR Chemical Shifts of the  $[\text{C}_5\text{H}_4\text{-PR}_2]_n\text{M}$  Compounds **8**, **9**, and **5**

| compd    | M               | n | R                                   |                                       |                                        |                                       |
|----------|-----------------|---|-------------------------------------|---------------------------------------|----------------------------------------|---------------------------------------|
|          |                 |   | $\text{C}_6\text{H}_5$ ( <b>a</b> ) | $i\text{-C}_3\text{H}_7$ ( <b>b</b> ) | $\text{C}_6\text{H}_{11}$ ( <b>c</b> ) | $t\text{-C}_4\text{H}_9$ ( <b>d</b> ) |
| <b>8</b> | Li              | 1 | -18.8                               | 3.1                                   | -11.8                                  | 25.3                                  |
| <b>9</b> | $\text{ZrCl}_2$ | 2 | -17.3                               | 5.1                                   | -3.0                                   | 34.4                                  |
| <b>5</b> | $\text{ZrMe}_2$ | 2 | -18.9                               | 2.3                                   | -6.1                                   | 31.7                                  |

described by Tikkanen et al. for the synthesis of **9a**.<sup>18,19</sup> The reaction in toluene solution that contained ca. 0.4% of THF cleanly gave the corresponding phosphino-substituted zirconocene dichloride complexes **9a–d** (isolated in yields around ca. 70%). Subsequent treatment with 2 molar equiv of methyllithium eventually converted them into the dimethylzirconocene complexes **5a–d** (see Scheme 3).

The compounds **5**, **8**, and **9a–d** were characterized spectroscopically (for a compilation of their typical  $^{31}\text{P}$  NMR shifts see Table 1). In solution they feature the typical  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of conformationally rapidly equilibrating, open bent-metallocene systems (e.g. **9b**;  $^1\text{H}$  NMR  $\delta$  6.68, 6.53 ( $\text{C}_5\text{H}_4$ ),  $\delta$  2.05 (sept), 1.15 (dd,  $^2J_{\text{PH}} = 13.7$  Hz,  $^3J_{\text{HH}} = 7.1$  Hz), and 0.99 (dd,  $^2J_{\text{PH}} = 12.7$  Hz,  $^3J_{\text{HH}} = 7.1$  Hz, isopropyl)). The corresponding diisopropylphosphino-substituted dimethylzirconocene complex (**5b**) also shows a pair of diastereotopic isopropyl  $\text{CH}_3$  NMR resonances ( $^{13}\text{C}$  NMR  $\delta$  20.2 (d,  $^2J_{\text{PC}} = 3.0$  Hz) and 20.1 (d,  $^2J_{\text{PC}} = 6.0$  Hz)) in addition to the  $\text{Zr-CH}_3$  signals at  $\delta$  -0.32 ( $^1\text{H}$ , s, 6H) and  $\delta$  32.2 ( $^{13}\text{C}$ , t,  $J_{\text{PC}} = 3.4$  Hz).

The zirconocene dichloride complexes **9a–d** and the dimethylzirconocenes **5b,c** were characterized by X-ray



**Figure 1.** View of the molecular structure of complex **9a**, showing the bis-lateral:anti metallocene conformation. Selected bond lengths (Å) and angles (deg):  $\text{Zr-Cl1} = 2.414(1)$ ,  $\text{Zr-Cl2} = 2.423(1)$ ,  $\text{P1-C1} = 1.839(4)$ ,  $\text{P1-C11} = 1.849(5)$ ,  $\text{P1-C21} = 1.839(5)$ ,  $\text{P2-C6} = 1.831(4)$ ,  $\text{P2-C31} = 1.834(4)$ ,  $\text{P2-C41} = 1.856(4)$ ;  $\text{Cl1-Zr-Cl2} = 96.10(5)$ ,  $\text{C1-P1-C11} = 100.5(2)$ ,  $\text{C1-P1-C21} = 100.4(2)$ ,  $\text{C11-P1-C21} = 101.7(2)$ ,  $\text{C6-P2-C31} = 99.8(2)$ ,  $\text{C6-P2-C41} = 100.5(2)$ ,  $\text{C31-P2-C41} = 101.7(2)$ .

diffraction. The structural features of complex **5a** had previously been described by us.<sup>16</sup> All these systems show the typical structural properties of open, non-bridged group 4 bent-metallocene frameworks. However, they seem to belong to two slightly different conformational metallocene types in the crystal.<sup>20</sup> The diphenylphosphino- $\text{C}_5\text{H}_4$  system **9a** features a very typical conformational arrangement that has both  $\text{C}(\text{Cp})\text{-P}$  vectors almost ideally pointing toward the opposite lateral sectors at the bent-metallocene framework (bis-lateral:anti orientation, see Figure 1). The bulky  $-\text{PPh}_2$  substituents thus are placed at a maximal distance from each other ( $d(\text{P1}\cdots\text{P2}) = 7.58$  Å; see Table 2). Both phenyl groups at the phosphorus atoms of complex **9a** are oriented toward the backside of the bent-metallocene wedge; their lone pairs are directed toward the front side. The related  $(\text{C}_5\text{H}_4\text{-PPh}_2)_2\text{Zr}(\text{CH}_3)_2$  complex **5a** shows a very similar conformational arrangement in the crystal.

All the (dialkylphosphino- $\text{Cp}$ ) $_2\text{ZrX}_2$  complexes investigated in the course of this study show a metallocene conformation that features the bulky  $-\text{PR}_2$  substituents oriented substantially closer to the narrow backside of the bent-metallocene wedge. A typical example is complex **9b** ( $\text{R} = \text{isopropyl}$ ). The conformational type (bis-lateral:gauche) shows a torsional angle between the  $\text{Cp}$  ligand vectors of only ca.  $-102.6^\circ$ , which brings the phosphorus atoms much closer together (5.26 Å) than in **9a** (see above). All the other (dialkylphosphino- $\text{C}_5\text{H}_4$ ) $_2\text{ZrX}_2$  complexes (**9c,d** and **5b,c**) show analogous structural features (Figure 2 and Table 2; for details see the Supporting Information).

**Zr–Rh Heterobimetallic Systems.** The reactive organometallic bis(diphenylphosphino- $\text{Cp}$ ) $\text{ZrMe}_2$  chelate

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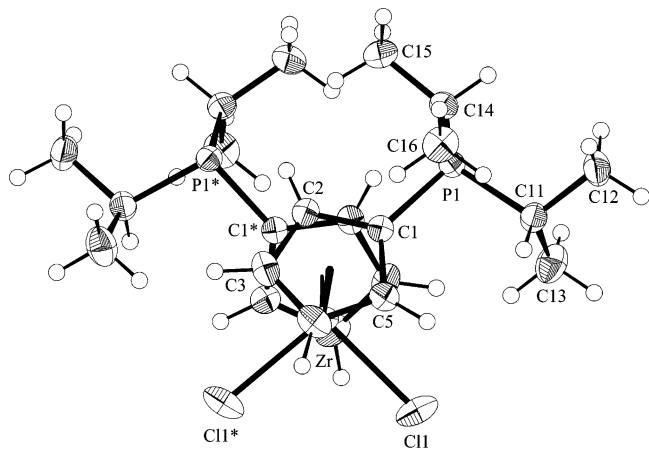
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Table 2. Selected Structural Parameters of the  $[\text{C}_5\text{H}_4\text{-PR}_2]_2\text{ZrX}_2$  Complexes **5** and **9**

| compd                       | <b>5a</b> <sup>16</sup> | <b>9a</b> | <b>5b</b>       | <b>9b</b> | <b>5c</b>       | <b>9c</b> | <b>9d</b> |
|-----------------------------|-------------------------|-----------|-----------------|-----------|-----------------|-----------|-----------|
| R                           | Ph                      | Ph        | i-Pr            | i-Pr      | Cy              | Cy        | t-Bu      |
| X                           | CH <sub>3</sub>         | Cl        | CH <sub>3</sub> | Cl        | CH <sub>3</sub> | Cl        | Cl        |
| X–Zr–X, deg                 | 92.9(2)                 | 96.10(5)  | 92.3(3)         | 95.34(3)  | 93.0(1)         | 94.20(3)  | 93.66(2)  |
| Cp–Zr–Cp, deg               | 130.2                   | 127.7     | 133.9           | 130.5     | 135.0           | 130.1     | 132.4     |
| $\theta$ , <sup>a</sup> deg |                         | –170.8    | 96.8            | –102.6    | –91.9           | –103.3    | 93.2      |
| P1⋯P2, Å                    | 7.59                    | 7.58      | 5.10            | 5.26      | 4.98            | 5.13      | 4.89      |

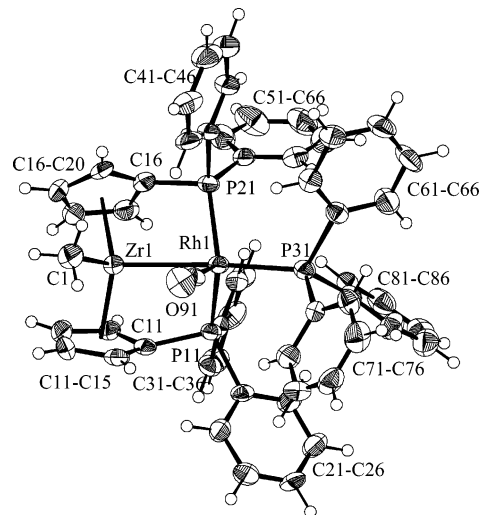
<sup>a</sup> Torsional angle between the substituent vectors, expressed as C(Cp)–Cp(centroid)–Cp(centroid)–C(Cp).



**Figure 2.** Molecular structure of complex **9b**. Selected bond lengths (Å) and angles (deg): Zr–C11 = 2.4439(6), P1–C1 = 1.834(2), P1–C11 = 1.859(2), P1–C14 = 1.868(2); C11–Zr–C11\* = 95.34(3), C1–P1–C11 = 101.89(8), C1–P1–C14 = 99.49(8), C11–P1–C14 = 102.79(9).

ligand<sup>21</sup> was treated with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  (**6**) as previously described by us<sup>16</sup> to yield the Zr–Rh-bonded heterobimetallic product **7a**. It was extremely difficult to separate the organometallic products from such reactions from the liberated triphenylphosphine. This was due to their similar solubilities, but in addition it turned out that the products **7** were rather unstable in the complete absence of  $\text{PPh}_3$ . The observed unusual chemical features of the corresponding  $-\text{P}(\text{isopropyl})_2$ - and  $-\text{P}(\text{cyclohexyl})_2$ -substituted products (**7b,c**; see below) may offer some explanation for this unexpected behavior. Complex **7a** can best be obtained free of  $\text{PPh}_3$  by Soxhlet extraction of the solid for 2 days with pentane under strictly anhydrous conditions. Complex **7a** had previously only been characterized spectroscopically. By slow evaporation of the solvent from a toluene solution, we were now able to obtain single crystals of **7a** that allowed an X-ray crystal structure analysis of this example of the novel Zr–Rh-bonded early–late heterobimetallic complex type.

In the crystal two independent molecules of complex **7a** were found (Figure 3). They are chemically equivalent. Values of the second molecule will be given in brackets. In **7a** the zirconium center is pseudotetrahedrally coordinated to a pair of  $\eta^5$ -bonded  $\text{C}_5\text{H}_4[\text{P}]$  ligands (the Zr–C(Cp) bond lengths are within a small range between 2.435(8) and 2.567(6) Å [2.461(6)–2.570(6) Å]), a  $\sigma$ -methyl group (Zr–C1 = 2.290(7) Å [2.278(6) Å]), and the rhodium center. The Zr–Rh distance amounts to 2.865(1) Å [2.860(1) Å]. This is between the values of the sum of the Zr/Rh covalent radii (2.70 Å) and the sum of the metal atom radii (2.91 Å), and this



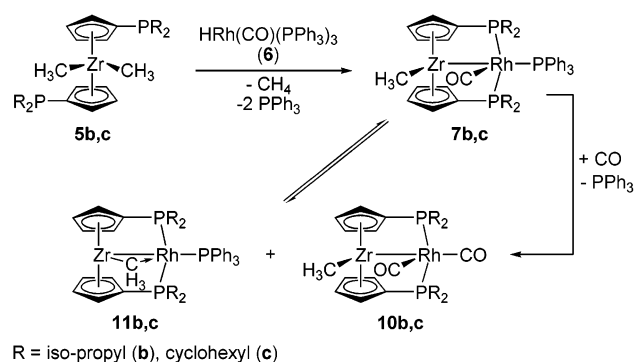
**Figure 3.** View of the molecular structure of the heterobimetallic Zr–Rh complex **7a**. Selected bond lengths (Å) and angle (deg) (values for the second molecule in brackets): Zr1–C1 = 2.290(7) [2.278(6)], Zr1–Rh1 = 2.865(1) [2.860(1)], Rh1–C91 = 1.877(7) [1.876(7)], Rh1–P11 = 2.306(2) [2.302(2)], Rh1–P21 = 2.319(2) [2.318(2)], Rh1–P31 = 2.386(2) [2.389(2)], C91–O91 = 1.146(7) [1.156(7)]; C1–Zr1–Rh1 = 107.1(2) [107.3(2)], Zr1–Rh1–P11 = 77.2(1) [76.7(1)], Zr1–Rh1–P21 = 79.0(1) [78.9(1)], Zr1–Rh1–P31 = 175.3(1) [173.4(1)], Zr1–Rh1–C91 = 80.9(2) [80.1(2)], P11–Rh1–P21 = 119.0(1) [119.8(1)], P11–Rh1–P31 = 102.2(1) [104.6(1)], P11–Rh1–C91 = 114.4(2) [111.3(2)], P21–Rh1–P31 = 105.3(1) [105.7(1)], P21–Rh1–C91 = 115.8(2) [117.4(2)], P31–Rh1–C91 = 95.3(2) [93.4(2)], Rh1–C91–O91 = 173.5(6) [175.9(6)]; C1–Zr1–Rh1–C91 = 15.6(3) [22.8(3)].

probably indicates the presence of a strong Zr–Rh metal–metal bond in these types of complexes. To our knowledge, the metal–metal distance in **7a** represents the second shortest Zr–Rh bonding interaction observed so far.

The Rh1–Zr1–CH<sub>3</sub> angle in **7a** amounts to the typical 107.1(2)° [107.3(2)°]. The Rh center in complex **7a** shows a distorted-trigonal-bipyramidal coordination geometry. In this arrangement the chelate (Cp)– $\text{PPh}_2$  donor ligands and the single CO group occupy the three equatorial positions (bond lengths Rh1–C91 = 1.877(7) Å [1.876(7) Å] and C91–O92 = 1.146(7) Å [1.156(7) Å] (angle Rh1–C91–O92 = 173.5(6)° [175.9(6)°]), Rh1–P11 = 2.306(2) Å [2.302(2) Å], and Rh1–P21 = 2.319(2) Å [2.318(2) Å]; bond angles P11–Rh1–P21 = 119.0(1)° [119.8(1)°], P11–Rh1–C91 = 114.4(2)° [111.3(2)°], and P21–Rh1–C91 = 115.8(2)° [117.4(2)°]). The axial positions are occupied by the remaining  $\text{PPh}_3$  ligand (Rh–P31 = 2.386(2) Å [2.389(2) Å]; this Rh–P bond is slightly longer than the adjacent ones) and the Zr center (angle Zr1–Rh1–P31 = 175.3(1)° [173.4(1)°]). All three angles between  $\text{Ph}_3\text{P}$  and the cis ligands are slightly larger

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Scheme 4



than the ideal  $90^\circ$  ( $\text{P31-Rh1-P11} = 102.2(1)^\circ$  [ $104.6(1)^\circ$ ],  $\text{P31-Rh1-P21} = 105.3(1)^\circ$  [ $105.7(1)^\circ$ ], and  $\text{P31-Rh1-C91} = 95.3(2)^\circ$  [ $93.4(2)^\circ$ ]). The three equatorial ligands are leaning slightly over to zirconium ( $\text{P11-Rh1-Zr1} = 77.2(1)^\circ$  [ $76.7(1)^\circ$ ] and  $\text{P21-Rh1-Zr1} = 79.0(1)^\circ$  [ $78.9(1)^\circ$ ]). This effect is not only observed inside the chelate framework but also includes the  $\text{C}\equiv\text{O}$  ligand, although here this structural effect is slightly less pronounced ( $\text{C91-Rh1-Zr1} = 80.9(2)^\circ$  [ $80.1(2)^\circ$ ]).

The bis(diisopropylphosphino-cyclopentadienyl)zirconium dimethyl reagent (**5b**) initially reacts in a similar way with the hydridecarbonylrhodium(I) complex **6**. We observed methane evolution<sup>22</sup> with formation of the heterobimetallic complex **7b** (see Scheme 4). Complex **7b** features two  $^{31}\text{P}$  NMR resonances in toluene- $d_8$  at 273 K in a 2:1 intensity ratio: the signal of the single remaining  $\text{PPh}_3$  ligand occurs at  $\delta$  47.8 as a doublet of triplets with coupling constants of  $^1J_{\text{RhP}} = 112.1$  Hz and  $^2J_{\text{PP}} = 34.4$  Hz, and the signal of the pair of symmetry-equivalent  $-\text{P}(\text{i-Pr})_2$  units is observed at  $\delta$  33.7 (dd,  $^1J_{\text{RhP}} = 154.5$  Hz,  $^2J_{\text{PP}} = 34.4$  Hz). The  $^1\text{H}$  NMR spectrum of **7b** shows four  $\text{C}_5\text{H}_4$  signals ( $\delta$  6.64, 6.10, 4.82, 4.17), and it features the resonances of the four diastereotopic isopropyl methyl groups ( $\delta$  1.23, 1.18, 1.10, 0.90). The  $^1\text{H}$  NMR signal of the  $\text{Zr-CH}_3$   $\sigma$ -ligand of **7b** appears at  $\delta$   $-0.46$  ( $^{13}\text{C}$   $\delta$  29.0), and the  $^{13}\text{C}$  NMR resonance was located at  $\delta$  194.5. Complex **7b** exhibits a  $\nu(\text{CO})$  IR band at  $1879\text{ cm}^{-1}$ .

Complex **7b** is not stable at room temperature for a prolonged time. At room temperature it reacts within days to give two new compounds (**10b** and **11b**). After 1 week ca. 20% of **7b** reacted to give these new compounds. Increasing the temperature to 373 K results in the rapid formation of an equilibrium mixture of ca. 7% of **7b** and 93% of the **10b/11b** mixture. Cooling shifts the equilibrium ratio back toward the starting material (**7b:10b/11b** = 19:81 (353 K), 40:60 (313 K), 65:35 (283 K)).

The product **10b** was obtained independently as a single product by bubbling CO gas through a toluene solution of **7b** at  $-30^\circ\text{C}$ . Complex **10b** contains two CO ligands at rhodium ( $\nu$  1959 and  $1913\text{ cm}^{-1}$ ;  $^{13}\text{C}$  NMR  $\delta$  213.3 and 191.5). It features a  $\sigma\text{-CH}_3$  ligand at zirconium ( $^1\text{H}$  NMR,  $\delta$   $-0.83$ ;  $^{13}\text{C}$  NMR,  $\delta$  28.9). The  $\text{H}_3\text{CZr-Rh}(\text{CO})_2$  subunit is held together by the typical rigid framework made up of the pair of  $\text{Cp-P}(\text{i-Pr})_2$  ligands located above and below the  $\sigma$  skeleton ( $^{31}\text{P}$  NMR,  $\delta$

54.6;  $^1\text{H}$  NMR,  $\delta$  6.23, 6.02, 4.80, 3.77 ( $\text{C}_5\text{H}_4$ ), 1.48, 1.40, 1.14, 1.00 (diastereotopic  $\text{CH}_3$  of the two pairs of isopropyl groups at P)).

The stoichiometric coproduct **11b** was formed from **7b** by dissociation of the carbon monoxide ligand. The complex also features the typical NMR signals of the rigid  $[\text{C}_5\text{H}_4\text{-P}(\text{i-Pr})_2]_2\text{Zr-Rh}$  framework ( $^1\text{H}$ ,  $\delta$  6.00, 5.91, 5.50, 4.75 ( $\text{C}_5\text{H}_4$ ), 1.41, 1.38, 1.13, 0.93 ( $\text{i-PrCH}_3$ )) characterized by the typical *cis/trans* differentiation of the pairs of  $\text{C}_5\text{H}_4$ - and isopropyl resonances. The  $^{31}\text{P}$  NMR signal of the remaining  $\text{PPh}_3$  ligand at Rh occurs at  $\delta$  33.4 (dt) with a  $^2J_{\text{PP}}$  coupling constant of 25.1 Hz that is typically observed at the intact heterobimetallic metal-metal-bonded Zr-Rh framework ( $^1J_{\text{RhP}} = 166.3$  Hz). The  $-\text{P}(\text{i-Pr})_2$   $^{31}\text{P}$  NMR resonance of complex **11b** occurs at  $\delta$  33.2 (243 K,  $d_8$ -toluene, dd,  $^1J_{\text{RhP}} = 195.9$  Hz,  $^2J_{\text{PP}} = 25.1$  Hz). The remaining methyl group at zirconium gives rise to  $^1\text{H}/^{13}\text{C}$  NMR signals at  $\delta$   $-0.26$  (d,  $^3J_{\text{PH}} = 3.8$  Hz)/ $\delta$  14.2 (at 243 K).

The observed small coupling with the  $\text{PPh}_3$  ligand at Rh causes us to believe that this methyl group is bridging between the early and the late metal inside the very rigid framework of complex **11b**.

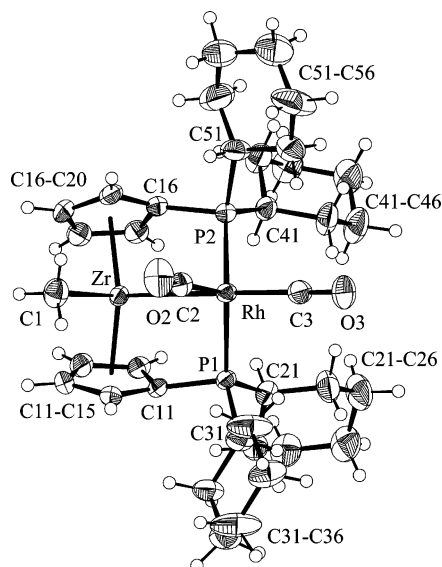
The  $[\text{C}_5\text{H}_4\text{-P}(\text{cyclohexyl})_2]_2\text{ZrMe}_2$  (**5c**) system reacts similarly with  $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$  (**6**). At  $-30^\circ\text{C}$  in toluene solution it rapidly forms the primary product **7c** with evolution of methane. Compound **7c** shows the typical NMR features of this dimetallic Zr-Rh complex type ( $^1\text{H}$ ,  $\delta$  6.86, 6.21, 4.71, 4.17 ( $\text{C}_5\text{H}_4$ ),  $-0.26$  ( $\text{Zr-CH}_3$ );  $^{31}\text{P}$ ,  $\delta$  51.0 (dt,  $^1J_{\text{RhP}} = 116.1$  Hz,  $^2J_{\text{PP}} = 32.6$  Hz,  $\text{PPh}_3$ ), 23.1 (dd,  $^1J_{\text{RhP}} = 152.8$  Hz,  $^2J_{\text{PP}} = 32.6$  Hz,  $-\text{PCy}_2$ );  $^{13}\text{C}$ ,  $\delta$  193.2 (CO), 29.1 ( $^1J_{\text{CH}} = 118.3$  Hz,  $\text{Zr-CH}_3$  at 243 K).

Again, complex **7c** is not very stable at room temperature. During ca. 12 h at ambient temperature it reacted further to give a mixture of the products **10c** and **11c**. In this case the dimetallic Zr-Rh dicarbonyl complex **10c** showed only a low solubility in toluene and precipitated from the solution as dark red crystals. Again, the Zr-Rh dicarbonyl **10c** could be prepared alternatively by treatment of **7c** with carbon monoxide. Formation of **10c** occurred instantaneously, and the product was isolated in close to quantitative yield. It features the typical NMR spectra of this type of complexes (**10c** in  $d_5$ -bromobenzene;  $^1\text{H}$ ,  $\delta$  6.44, 6.24, 5.15, 4.20 ( $\text{C}_5\text{H}_4$ ),  $-0.76$  ( $\text{Zr-CH}_3$ );  $^{13}\text{C}$ ,  $\delta$  28.9 ( $^1J_{\text{CH}} = 117.0$  Hz,  $\text{Zr-CH}_3$ )), and it was characterized by X-ray diffraction (see below).

Complex **11c** also features the typical NMR resonances of the rigid  $[(\text{C}_5\text{H}_4\text{-PR}_2)_2]\text{Zr-Rh}(\text{PPh}_3)$  framework ( $^{31}\text{P}$ ,  $\delta$  34.5 (dt,  $^1J_{\text{RhP}} = 164.4$  Hz,  $^2J_{\text{PP}} = 25.2$  Hz,  $\text{PPh}_3$ ), 26.3 (dd,  $^1J_{\text{RhP}} = 196.1$  Hz,  $^2J_{\text{PP}} = 25.2$  Hz);  $^1\text{H}$ ,  $\delta$  6.09, 5.94, 5.61, 4.84 ( $\text{C}_5\text{H}_4$ )). The  $^1\text{H}/^{13}\text{C}$  NMR resonances of the  $[\text{Zr}]\text{-CH}_3$   $\sigma$ -ligand of **11c** occur at  $\delta$   $-0.29$  (d,  $^3J_{\text{PH}} = 3.4$  Hz)/ $\delta$  14.4 ( $^1J_{\text{CH}} = 120.7$  Hz). Again, the observed coupling with the  $\text{PPh}_3$  phosphorus and the marked high-field shift of the  $^{13}\text{C}$  NMR resonance may indicate bridging of the methyl group across the Zr-Rh bond in complex **11c**.

Complex **10c** was characterized by X-ray diffraction (see Figure 4). Its general framework is very similar to that of complex **7a**. Complex **10c** features a strong Zr-Rh interaction ( $2.893(1)\text{ \AA}$ ) between the pseudo-trigonal bipyramidally coordinated Rh and the pseudotetrahedral Zr centers. The apical Rh-CO linkage ( $\text{Rh-C3} = 1.911(4)\text{ \AA}$ ,  $\text{C3-O3} = 1.147(5)\text{ \AA}$ , angle  $\text{Rh-C3-O3} =$

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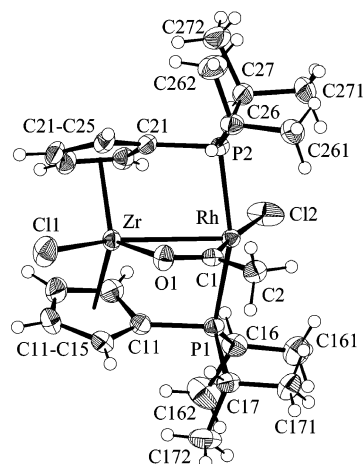


**Figure 4.** Projection of the molecular geometry of the heterobimetallic Zr–Rh complex **10c**. Selected bond lengths (Å) and angles (deg): Zr–C1 = 2.312(4), Zr–Rh = 2.893(1), Rh–C2 = 1.869(4), Rh–C3 = 1.911(4), Rh–P1 = 2.337(1), Rh–P2 = 2.328(1), C2–O2 = 1.155(5), C3–O3 = 1.147(5); C1–Zr–Rh = 108.1(1), Zr–Rh–P1 = 78.95(3), Zr–Rh–P2 = 78.37(3), Zr–Rh–C2 = 77.15(12), Zr–Rh–C3 = 175.05(13), P1–Rh–P2 = 123.97(4), P1–Rh–C2 = 114.60(13), P1–Rh–C3 = 98.36(13), P2–Rh–C2 = 109.09(13), P2–Rh–C3 = 99.98(13), C2–Rh–C3 = 107.8(2), Rh–C2–O2 = 170.8(4), Rh–C3–O3 = 179.3(4); C1–Zr–Rh–C2 = –4.4(2), C1–Zr–Rh–C3 = 171.7(2).

179.3(4)° is slightly longer than the equatorial Rh–CO bond (Rh–C2 = 1.869(4) Å). The Rh–P1 (2.337(1) Å) and Rh–P2 (2.328(1) Å) vectors are slightly leaning over to Zr (angles Zr–Rh–P1 = 78.95(3)°, Zr–Rh–P2 = 78.37(3)°, and Zr–Rh–C2 = 77.15(12)°) inside the distorted-trigonal-bipyramidal coordination geometry at Rh (angles P1–Rh–P2 = 123.97(4)°, P1–Rh–C2 = 114.60(13)°, P2–Rh–C2 = 109.09(13)°). The Zr–Rh–C3 angle between the Zr–Rh and the *trans*-Rh–CO vectors amounts to 175.05(13)°, and the angle between the *cis*-CO ligands at rhodium was found at 107.8(2)° (C2–Rh–C3). The methyl group at the adjacent zirconium center features a typical Zr–C(sp<sup>3</sup>)  $\sigma$ -bond distance (Zr–C1 = 2.312(4) Å, angle C1–Zr–Rh = 108.1(1)°), and the C<sub>5</sub>H<sub>4</sub>–[P] rings are rather uniformly  $\eta^5$ -coordinated to the early-metal center (Zr–C(Cp) ranging from 2.465(4) to 2.551(4) Å).

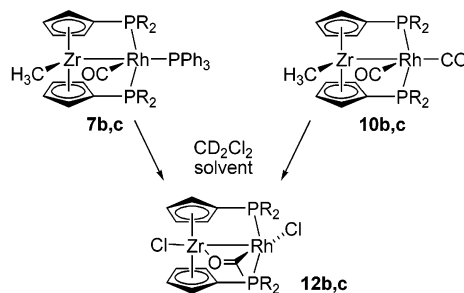
The complexes **7b,c** are not stable in chlorinated hydrocarbon solvents. When the reaction between, for example, **5b** with [HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>] (**6**) was carried out in dichloromethane or when the heterobimetallic product **7b** was dissolved in dichloromethane solvent at ambient temperature, a practically quantitative conversion to a single new product (**12b**) was observed. The same product (**12b**) was obtained when the heterobimetallic Zr–Rh dicarbonyl complex **10b** was kept in dichloromethane at room temperature for a prolonged time (16 h). The corresponding –P(cyclohexyl)<sub>2</sub>-substituted system (**12c**) was obtained by any of the three methods starting from **5c**, **7c**, or **10c** by analogous reactions with dichloromethane (see Scheme 5).

The complexes **12b,c** were both characterized by X-ray crystal structure analyses. The Zr–Rh distance



**Figure 5.** View of the molecular structure of the  $\mu$ -acetyl Zr–Rh complex **12b**. Selected bond lengths (Å) and angles (deg): Zr–C11 = 2.552(1), Zr–O1 = 2.216(2), Zr–Rh = 2.966(1), Rh–C12 = 2.436(1), Rh1–C1 = 1.916(2), Rh–P1 = 2.308(1), Rh–P2 = 2.322(1), O1–C1 = 1.271(3), C1–C2 = 1.511(3); C11–Zr–Rh = 138.92(2), O1–Zr–Rh = 63.99(4), C11–Zr1–O1 = 75.04(4), Zr–Rh–P1 = 81.72(2), Zr–Rh–P2 = 82.21(2), Zr–Rh–C1 = 67.13(6), Zr–Rh–C12 = 119.73(2), P1–Rh–P2 = 162.29(2), P1–Rh–C1 = 90.37(6), P1–Rh1–C12 = 91.64(2), P2–Rh–C1 = 90.22(6), P2–Rh–C12 = 89.89(2), C1–Rh–C12 = 173.07(6), Zr1–O1–C1 = 105.7(1), O1–C1–C2 = 114.6(2), O1–C1–Rh = 123.0(2), C2–C1–Rh = 122.4(2).

#### Scheme 5



R = iso-propyl (**b**), cyclohexyl (**c**)

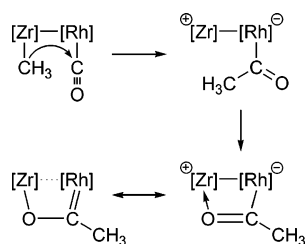
(2.966(1) Å) in complex **12b** (see Figure 5) is slightly larger than in the other Zr–Rh structures that were determined in this study, but this probably still represents a metal–metal-bonded interaction. The Zr–Rh bond in **12b** is bridged by a  $\mu$ (C,O)-acetyl ligand that was formed by an intramolecular CO insertion in a metal–carbon bond across the Zr–Rh linkage. Since such CO insertion reactions mechanistically are always migratory insertions,<sup>23</sup> our observation that the  $\mu$ -O=CMe ligand is oxygen-coordinated to zirconium and carbon-bonded to rhodium is not unexpected. The Zr–O bond length amounts to 2.216(2) Å.<sup>24</sup> The C=O bond length is 1.271(3) Å (C1–O1). The Rh–C1 bond<sup>25</sup> is rather short at 1.916(2) Å, which may indicate some Rh–C multiple-bond character<sup>26</sup> inside the planar  $\mu$ -acetyl (Zr–Rh) four-membered ring (see Scheme 6). The Zr–O1–C1 angle is found at 105.7(1)°, and the O1–C1–Rh angle amounts to 123.0(2)°.

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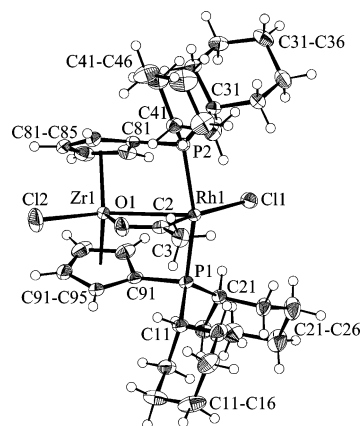
Scheme 6



In the  $\mu$ -acetyl(Zr–Rh) complex **12b** the rhodium center features a square-pyramidal coordination environment with the trans phosphines, a chloride (Cl2) and the acetyl carbon atom C1 being placed in the basal plane (Rh–P1 = 2.308(1) Å, Rh–P2 = 2.322(1) Å, Rh–Cl2 = 2.436(1) Å) and the zirconium atom in the apical position (see Figure 5). Consequently, the interligand angles at the base are all very close to ideal 90° (C1–Rh–P1 = 90.37(6)°, C1–Rh–P2 = 90.22(6)°, Cl2–Rh–P1 = 91.64(2)°, Cl2–Rh–P2 = 89.89(2)°), although all four ligands are leaning slightly over to zirconium (C1–Rh–Cl2 = 173.07(6)°, P1–Rh–P2 = 162.29(2)°). The Zr–O1 vector is bisecting the Rh–Zr–Cl angle inside the metallocene  $\sigma$ -ligand plane (Cl1–Zr–O1 = 75.04(4)°, Zr–Cl1 = 2.552(1) Å). The cyclopentadienyl ligands at the zirconium center are rather uniformly  $\eta^5$  coordinated, with the Zr–C(Cp) bond lengths ranging from 2.490(2) to 2.561(2) Å.

Complex **12c** shows an analogous structure in the crystal, only that two crystallographically independent molecules were observed (bonding parameters of the second molecule are listed in brackets). In **12c** the Zr–Rh bond length amounts to 2.980(1) Å [2.983(1) Å], and the Rh–carbon bond to the (Zr–Rh)  $\mu$ -acetyl ligand is 1.906(3) Å (Rh–C2; see Figure 6) [1.931(3) Å]. The acetyl C=O bond length in **12c** amounts to 1.253(3) Å [1.211(4) Å]. Again, the coordination geometry at Rh is square planar (Rh–P1 = 2.317(1) Å [2.313(1) Å], Rh–P2 = 2.325(1) Å [2.327(1) Å], Rh–Cl1 = 2.440(1) Å [2.434(1) Å]; angles C2–Rh–Cl1 = 168.06(10)° [166.91(9)°], P1–Rh–P2 = 160.45(3)° [160.44(3)°]). The Zr–O1 bond length in **12c** is 2.211(2) Å [2.213(2) Å], and the Cl2–Zr–O1  $\sigma$ -bond angle was found at 74.25(6)° [74.86(6)°] (Zr–Cl2 = 2.551(1) Å [2.553(1) Å]). In **12c** the Zr–C(Cp) bond lengths are also found in a rather small range between 2.479(3) and 2.542(3) Å [2.466(3)–2.546(3) Å].

In solution complex **12b** is characterized by a very typical  $^{13}\text{C}$  NMR  $\mu$ -acyl resonance at  $\delta$  290.3 (dt,  $^1J_{\text{RhC}} = 30.6$  Hz,  $^2J_{\text{PC}} = 8.1$  Hz; **12c**,  $\delta$  289.0,  $^1J_{\text{RhC}} = 23$  Hz).<sup>27,28</sup> The ligand framework of **12b** shows a  $^{31}\text{P}$  NMR resonance at  $\delta$  27.5 ( $^1J_{\text{RhP}} = 127.6$  Hz; **12c**,  $\delta$  19.7) and it features again the typical sets of four  $\text{C}_5\text{H}_4$   $^1\text{H}$  NMR multiplets ( $\delta$  6.49, 6.34, 6.00, 5.90) and the resonances of two pairs of diastereotopic isopropyl methyl groups ( $\delta$  1.53, 1.50, 1.35, 1.32). The  $\text{OC}(\text{CH}_3)$   $^1\text{H}/^{13}\text{C}$  NMR signals of complex **12b** were monitored at  $\delta$  2.47/40.4 ( $^1J_{\text{CH}} = 127.4$  Hz). The corresponding  $\text{COCH}_3$   $^1\text{H}$  NMR



**Figure 6.** Molecular structure of complex **12c**. Selected bond lengths (Å) and angles (deg) (values for the second molecule in brackets): Zr1–Cl2 = 2.551(1) [2.553(1)], Zr1–O1 = 2.211(2) [2.213(2)], Zr1–Rh1 = 2.980(1) [2.983(1)], Rh1–Cl1 = 2.440(1) [2.434(1)], Rh1–C2 = 1.906(3) [1.931(3)], Rh1–P1 = 2.317(1) [2.313(1)], Rh1–P2 = 2.325(1) [2.327(1)], O1–C2 = 1.253(3) [1.211(4)], C2–C3 = 1.512(4) [1.508(5)]; Cl2–Zr1–Rh1 = 137.96(2) [138.05(2)], O1–Zr1–Rh1 = 63.76(5) [63.48(6)], Cl2–Zr1–O1 = 74.25(6) [74.84(6)], Zr1–Rh1–P1 = 81.21(2) [81.35(2)], Zr1–Rh1–P2 = 81.40(2) [81.19(2)], Zr1–Rh1–C2 = 66.08(9) [65.28(9)], Zr1–Rh1–Cl1 = 125.79(2) [127.72(2)], P1–Rh1–P2 = 160.45(3) [160.44(3)], P1–Rh1–C2 = 90.81(8) [90.73(8)], P1–Rh1–Cl1 = 92.40(3) [92.98(3)], P2–Rh1–C2 = 90.25(8) [89.93(9)], P2–Rh1–Cl1 = 90.56(3) [90.76(3)], C2–Rh1–Cl1 = 168.06(10) [166.91(9)], Zr1–O1–C2 = 105.1(2) [105.6(2)], O1–C2–C3 = 114.7(3) [115.3(3)], O1–C2–Rh1 = 125.0(2) [125.3(2)], C3–C2–Rh1 = 120.4(2) [119.3(2)].

signal of complex **12c** was located at  $\delta$  2.45 (in  $d_2$ -dichloromethane at 298 K).

### Some Conclusions

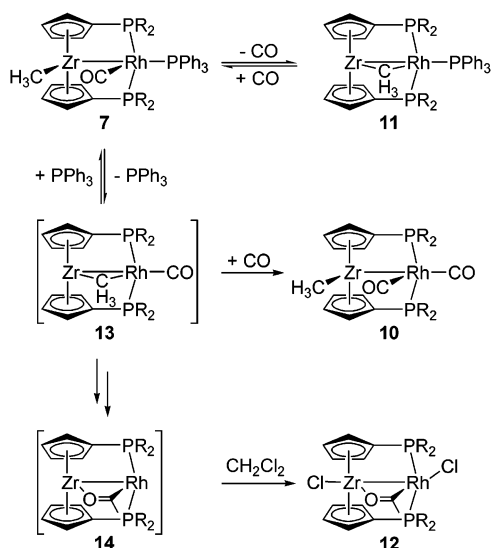
The metal–metal-bonded framework of the heterobimetallic complexes **7–12** behaves like an array of metal atoms that cooperatively determine the reactivity of their coordinated  $\sigma$  ligands by their special electronic features and at the same time influence the equilibrium of potential coupling or dissociation products. The observed reactions indicate that ligand dissociation from rhodium inside the heterodimetallic Zr–Rh complexes is easily achieved. It is probably much facilitated by a stabilization of Rh in the product by neighboring-group participation of the [Zr]–CH<sub>3</sub> ligand (potentially the rate of ligand dissociation is increased by anchimeric assistance by the H<sub>3</sub>C–[Zr] group). Principally, this process can lead to CO cleavage from rhodium to yield the stable product **11**, which is observed, or alternatively to PPh<sub>3</sub> liberation. The primary product (**13**) of the

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Scheme 7



competing phosphine cleavage pathway from **7** was not observed as a stable product in our reaction systems, but it is likely to occur. It is reasonable to assume that this reactive intermediate has picked up a CO molecule from the solution (or from **7**) with formation of the observed (Zr–Rh) dicarbonyl complex **10** (see Scheme 7).

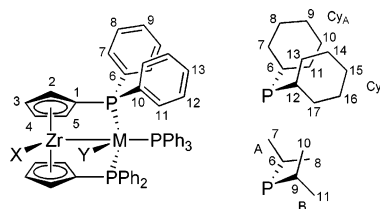
The formation of the  $\mu$ -acetyl (Zr–Rh) products (**12**) upon treatment of **7** with  $\text{CH}_2\text{Cl}_2$  is likely to also proceed via such a reactive intermediate. It is quite conceivable that migratory CO insertion is likely to occur at the stage of **13** to eventually lead to a reactive  $\mu$ -acetyl (Zr–Rh) species (**14**) that is able to pick up two chlorine atoms from the solvent to yield the stable complexes **12**. Although we were not yet able to identify the corresponding organic products, this pathway seems to be so highly effective that it completely overrides the otherwise predominant equilibration of **7** with the products **10** and **11**.

Our observations show that the reactions between fundamental small organic building blocks attached to the metal components of a ligand-stabilized (but not ligand-dominated) pair of early–late metals across the Zr–Rh metal–metal bond has a strong cooperative moment, similar as it may be at a variety of heterogeneous metal-induced reaction systems that involve combinations of metal components. In these easily available molecular models of such systems, we may be able to study fundamental reaction steps by very direct analytical techniques that might be of value for understanding more complex reaction cascades at mixed-metal compounds, and potentially we will see whether novel reaction pathways of organic intermediates can be induced if they are allowed to react at such metal–metal-bonded templates. The synthetic technique that we have used for the generation of the heterobimetallic complexes described and discussed in this article may make such systems readily available.

## Experimental Section

**General Considerations.** All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. Elemental

Chart 2



analyses were performed with a *Foss-Heraeus* CHN-O-Rapid instrument, and a *Nicolet 5DXC* FT-IR-spectrometer was used for IR spectra. NMR spectra were measured using a *Bruker* AC 200 P or a *Varian* Unity Plus 600 NMR spectrometer. Most assignments were based on a series of 2D NMR experiments. Numbering used for listing of the NMR data is depicted in Chart 2.

**X-ray Crystal Structure Analysis.** Data sets were collected with Enraf-Nonius CAD4 and Nonius KappaCCD diffractometers, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS<sup>29</sup> and COLLECT,<sup>30</sup> data reduction MolEN<sup>31</sup> and Denzo-SMN,<sup>32</sup> absorption correction for CCD data SORTAV,<sup>33</sup> structure solution SHELXS-97,<sup>34</sup> structure refinement SHELXL-97,<sup>35</sup> graphics DIAMOND<sup>36</sup> and SCHAKAL.<sup>37</sup>

**Preparation of Bis[ $\eta^5$ -(diphenylphosphino)cyclopentadienyl]dimethylzirconium (**5a**).** Methylolithium (19.7 mL, 31.6 mmol, 1.6 M in diethyl ether) was slowly added to a stirred solution of bis[ $\eta^5$ -(diphenylphosphino)cyclopentadienyl]-dichlorozirconium (**9a**; 9.45 g, 14.3 mmol) in toluene (100 mL) at  $-78^\circ\text{C}$ . Over 30 min the temperature was raised to  $0^\circ\text{C}$ , and stirring was continued for 2 h at room temperature. The resulting slurry was filtered over a bed of Celite, and the volume was reduced to 5 mL. After the addition of pentane (50 mL) the product was collected by filtration, washed three times with pentane, and dried in vacuo to yield 7.45 g (12.0 mmol, 84%) of compound **5a**.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 200.13 MHz):  $\delta$  7.32 (m, 20H,  $\text{C}_6\text{H}_5$ ), 6.12 (m, 4H,  $\text{C}_5\text{H}_4$ ), 5.98 (m, 4H,  $\text{C}_5\text{H}_4$ ),  $-0.41$  (s, 6H, Zr– $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 81.0 MHz):  $\delta$   $-18.9$  (s,  $\text{PPh}_2$ ).

**Preparation of Bis[ $\eta^5$ -(diisopropylphosphino)cyclopentadienyl]dimethylzirconium (**5b**).** Methylolithium (19.3 mL, 30.9 mmol, 1.6 M in diethyl ether) was slowly added to a stirred solution of bis[ $\eta^5$ -(diisopropylphosphino)cyclopentadienyl]-dichlorozirconium (**9b**; 7.16 g, 13.6 mmol) in toluene (100 mL) at  $-78^\circ\text{C}$ . Over 30 min the temperature was raised to  $0^\circ\text{C}$ , and stirring was continued for 2 h at room temperature. The resulting slurry was filtered over a bed of Celite, and the solvent was removed in vacuo. The residue was dissolved in pentane (3 mL) and stored at  $-30^\circ\text{C}$  for one night. Precooled perfluoromethylcyclohexane (30 mL) was added at  $-30^\circ\text{C}$ , and the microcrystalline product was collected by filtration, washed with perfluoromethylcyclohexane, and dried in vacuo to yield 5.88 g (12.2 mmol, 89%) of compound **5b**. Single crystals were obtained by cooling a concentrated solution in heptane to  $-20^\circ\text{C}$  for 2 days. Mp:  $218^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{24}\text{H}_{42}\text{P}_2\text{Zr}$  (483.8): C, 59.59; H, 8.75. Found: C, 59.21; H, 8.63.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 599.11 MHz):  $\delta$  6.30 (ps t, 4H, 3-H), 6.20 (m, 4H, 2-H), 1.95 (sept d,  $^3J_{\text{HH}} = 7.1$  Hz,  $^2J_{\text{PH}} = 1.4$  Hz, 4H, CH), 1.12 (dd,  $^3J_{\text{PH}} = 13.6$  Hz,  $^3J_{\text{HH}} = 7.1$  Hz, 12H,  $\text{CH}_3$ ), 0.92 (dd,  $^3J_{\text{PH}}$

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= 12.2 Hz,  $^3J_{\text{HH}} = 7.1$  Hz, 12H,  $\text{CH}_3$ ),  $-0.32$  (s, 6H,  $\text{Zr}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 150.6 MHz):  $\delta$  118.4 (d,  $^1J_{\text{PC}} = 24.6$  Hz, C-1), 115.5 (m, C-2), 114.1 (m, C-3), 32.2 (t,  $J_{\text{PC}} = 3.4$  Hz,  $\text{Zr}-\text{CH}_3$ ), 24.0 (d,  $^2J_{\text{PC}} = 12.8$  Hz, CH), 20.2 (d,  $^2J_{\text{PC}} = 3.0$  Hz,  $\text{CH}_3$ ), 20.1 (d,  $^2J_{\text{PC}} = 6.0$  Hz,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 81.02 MHz):  $\delta$  2.3 (s,  $P(\text{i-Pr})_2$ ).

**X-ray Crystal Structure Analysis for 5b:** formula  $\text{C}_{24}\text{H}_{42}\text{P}_2\text{Zr}$ ,  $M_r = 483.74$ , colorless crystal  $0.40 \times 0.25 \times 0.15$  mm,  $a = 8.680(2)$  Å,  $b = 11.311(1)$  Å,  $c = 14.041(2)$  Å,  $\alpha = 89.14(1)^\circ$ ,  $\beta = 87.76(1)^\circ$ ,  $\gamma = 67.47(1)^\circ$ ,  $V = 1272.4(4)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.263$  g cm<sup>-3</sup>,  $\mu = 5.65$  cm<sup>-1</sup>, no absorption correction ( $0.806 \leq T \leq 0.920$ ),  $Z = 2$ , triclinic, space group  $P\bar{1}$  (No. 2),  $\lambda = 0.71073$  Å,  $T = 223$  K,  $\omega/2\theta$  scans, 5518 reflections collected ( $+h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.62$  Å<sup>-1</sup>, 5162 independent ( $R_{\text{int}} = 0.021$ ) and 4309 observed reflections ( $I \geq 2\sigma(I)$ ), 254 refined parameters,  $R1 = 0.066$ ,  $wR2 = 0.215$ , maximum (minimum) residual electron density  $1.75$  ( $-1.97$ ) e Å<sup>-3</sup>, hydrogen atoms calculated and refined as riding atoms.

**Preparation of Bis[ $\eta^5$ -(dicyclohexylphosphino)cyclopentadienyl]dimethylzirconium (5c).** Methylolithium (13.0 mL, 20.8 mmol, 1.6 M in diethyl ether) was slowly added to a stirred solution of bis[ $\eta^5$ -(dicyclohexylphosphino)cyclopentadienyl]dichlorozirconium (**9c**; 6.46 g, 9.4 mmol) in toluene (100 mL) at  $-78^\circ\text{C}$ . Over 30 min the temperature was raised to  $0^\circ\text{C}$ , and stirring was continued for 1 h at  $0^\circ\text{C}$ . The resulting slurry was filtered over a bed of Celite, and the solvent was removed in vacuo. After the addition of pentane (20 mL) the product was collected by filtration, washed with three small portions of pentane, and dried in vacuo to yield 5.00 g (7.8 mmol, 82%) of compound **5c**. Single crystals were obtained by cooling a concentrated solution in toluene to  $-30^\circ\text{C}$  for 1 day. Mp:  $237^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{36}\text{H}_{58}\text{P}_2\text{Zr}$  (644.0): C, 67.14; H, 9.08. Found: C, 66.78; H, 8.69.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400.14 MHz):  $\delta$  6.28 (ps t, 4H, 3-H), 6.18 (ps t, 4H, 2-H), 1.89–1.56 (m, 24H,  $\text{C}_6\text{H}_{11}$ ), 1.36–1.21 (m, 16H,  $\text{C}_6\text{H}_{11}$ ), 0.95 (m, 4H,  $\text{C}_6\text{H}_{11}$ ),  $-0.34$  (s, 6H,  $\text{Zr}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100.63 MHz):  $\delta$  118.6 (d,  $^1J_{\text{PC}} = 23.3$  Hz, C-1), 115.9 (m, C-2), 114.1 (m, C-3), 34.2 (d,  $J_{\text{PC}} = 12.9$  Hz,  $\text{C}_6\text{H}_{11}$ ), 31.8 (t,  $^3J_{\text{PC}} = 3.6$  Hz,  $\text{Zr}-\text{CH}_3$ ), 31.1 (d,  $J_{\text{PC}} = 12.9$  Hz,  $\text{C}_6\text{H}_{11}$ ), 30.7 (d,  $J_{\text{PC}} = 12.9$  Hz,  $\text{C}_6\text{H}_{11}$ ), 27.9 (d,  $J_{\text{PC}} = 10.1$  Hz,  $\text{C}_6\text{H}_{11}$ ), 27.7 (d,  $J_{\text{PC}} = 9.1$  Hz,  $\text{C}_6\text{H}_{11}$ ), 26.9 (s,  $\text{C}_6\text{H}_{11}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 80.02 MHz):  $\delta$   $-6.1$  (s,  $\text{PCy}_2$ ).

**X-ray Crystal Structure Analysis for 5c:** formula  $\text{C}_{36}\text{H}_{58}\text{P}_2\text{Zr}$ ,  $M_r = 643.98$ , colorless crystal  $0.35 \times 0.35 \times 0.30$  mm,  $a = 10.269(1)$  Å,  $b = 14.541(1)$  Å,  $c = 23.755(1)$  Å,  $\beta = 99.39(1)^\circ$ ,  $V = 3499.6(4)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.222$  g cm<sup>-3</sup>,  $\mu = 4.87$  cm<sup>-1</sup>, empirical absorption correction ( $0.865 \leq T \leq 0.823$ ),  $Z = 4$ , monoclinic, space group  $C2/c$  (No. 15),  $\lambda = 0.71073$  Å,  $T = 198$  K,  $\omega$  and  $\varphi$  scans, 15 483 reflections collected ( $\pm h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.68$  Å<sup>-1</sup>, 4292 independent ( $R_{\text{int}} = 0.028$ ) and 3723 observed reflections ( $I \geq 2\sigma(I)$ ), 178 refined parameters,  $R1 = 0.031$ ,  $wR2 = 0.072$ , maximum (minimum) residual electron density  $0.32$  ( $-0.46$ ) e Å<sup>-3</sup>, hydrogen atoms calculated and refined as riding atoms.

**Preparation of Bis[ $\eta^5$ -(di-tert-butylphosphino)cyclopentadienyl]dimethylzirconium (5d).** Methylolithium (4.5 mL, 7.26 mmol, 1.6 M in diethyl ether) was slowly added to a stirring solution of bis[ $\eta^5$ -(di-tert-butylphosphino)cyclopentadienyl]dichlorozirconium (**9d**; 1.88 g, 3.2 mmol) in toluene (50 mL) at  $-78^\circ\text{C}$ . Over 30 min the temperature was raised to  $0^\circ\text{C}$  and stirring was continued for 1 h at  $0^\circ\text{C}$ . The resulting slurry was filtered over a bed of Celite, and the solvent was removed in vacuo. After the residue was dissolved in pentane (5 mL), perfluoromethylcyclohexane (20 mL) was added and the product was collected by filtration, washed with perfluoromethylcyclohexane, and dried in vacuo to yield 1.37 g (2.54 mmol, 78%) of compound **5d**. Mp:  $96^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{50}\text{P}_2\text{Zr}$  (539.9): C, 62.29; H, 9.34. Found: C, 62.54; H, 8.89.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 599.11 MHz):  $\delta$  6.39 (m, 4H,  $\text{C}_5\text{H}_4$ ), 6.36 (m, 4H,  $\text{C}_5\text{H}_4$ ), 1.14 (d,  $^3J_{\text{PH}} = 11.2$  Hz, 36H,  $\text{C}(\text{CH}_3)_3$ ),  $-0.27$  (s, 6H,  $\text{Zr}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 150.6 MHz):  $\delta$  120.4

(d,  $^1J_{\text{PC}} = 35.1$  Hz, C-1), 117.5 (m, C-2), 114.6 (m, C-3), (m, 33.4 (d,  $^1J_{\text{PC}} = 22.1$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 33.1 (s,  $\text{Zr}-\text{CH}_3$ ), 30.9 (d,  $^2J_{\text{PC}} = 13.7$  Hz,  $\text{C}(\text{CH}_3)_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 81.02 MHz):  $\delta$  31.7 (s,  $P(\text{tBu})_2$ ).

**Reaction of (Cp-PPh<sub>2</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (5a) with HRh(CO)-(PPh<sub>3</sub>)<sub>3</sub> (6). Formation of 7a.** Precooled dichloromethane (1 mL) was added to a mixture of **5a** (62 mg, 0.10 mmol) and **6** (92 mg, 0.10 mmol) at room temperature. The color changed to dark red, and gas evolution occurred. After 30 min the solvent was removed in vacuo and the solid was extracted with pentane for 2 days to yield 35 mg (0.04 mmol, 40%) of compound **7a** as a brown powder. Single crystals were obtained by slow evaporation of the solvent of a solution in toluene.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 200.13 MHz):  $\delta$  7.43–7.02, 6.85 (2 m, 35H,  $\text{C}_6\text{H}_5$ ), 6.62 (s, 2H,  $\text{C}_5\text{H}_4$ ), 6.40 (m, 2H,  $\text{C}_5\text{H}_4$ ), 5.31 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.11 (s, 2H,  $\text{C}_5\text{H}_4$ ),  $-0.82$  (s, 3H,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 81.02 MHz):  $\delta$  45.5 (dt,  $^1J_{\text{RHP}} = 110.3$  Hz,  $^2J_{\text{PP}} = 36.5$  Hz,  $\text{PPh}_3$ ), 26.1 (dd,  $^1J_{\text{RHP}} = 161.3$  Hz,  $^2J_{\text{PP}} = 36.5$  Hz,  $\text{PPh}_2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\bar{\nu}(\text{CO})$  1977 cm<sup>-1</sup>.

**X-ray Crystal Structure Analysis for 7a:** formula  $\text{C}_{54}\text{H}_{46}\text{OP}_3\text{RhZr}$ ,  $M_r = 997.95$ , red crystal  $0.15 \times 0.10 \times 0.05$  mm,  $a = 24.970(1)$  Å,  $b = 12.621(1)$  Å,  $c = 28.554(1)$  Å,  $V = 8998.7(9)$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.473$  g cm<sup>-3</sup>,  $\mu = 7.44$  cm<sup>-1</sup>, empirical absorption correction ( $0.897 \leq T \leq 0.964$ ),  $Z = 8$ , orthorhombic, space group  $Pca2_1$  (No. 29),  $\lambda = 0.71073$  Å,  $T = 198$  K,  $\omega$  and  $\varphi$  scans, 61 070 reflections collected ( $\pm h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.62$  Å<sup>-1</sup>, 17 442 independent ( $R_{\text{int}} = 0.086$ ) and 12 617 observed reflections ( $I \geq 2\sigma(I)$ ), 1083 refined parameters,  $R1 = 0.051$ ,  $wR2 = 0.082$ , maximum (minimum) residual electron density  $0.53$  ( $-0.42$ ) e Å<sup>-3</sup>, hydrogen atoms calculated and refined as riding atoms, two almost identical molecules in the asymmetric unit, crystal seems to be a racemic twin.

**Reaction of (Cp-P(i-Pr))<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (5b) with HRh(CO)-(PPh<sub>3</sub>)<sub>3</sub> (6). Formation of 7b, 10b, and 11b.** Precooled *ds*-toluene (1 mL) was added to a mixture of **5b** (22 mg, 45.4  $\mu\text{mol}$ ) and **6** (42 mg, 45.4  $\mu\text{mol}$ ) at room temperature. The color changed to brownish dark red, and gas evolution occurred. After 5 min the solvent of the crude mixture was removed and the residue washed with pentane (0.5 mL) and dried in vacuo to yield 11 mg of a brown powder. If the crude mixture was stored at room temperature for a few weeks or heated to elevated temperatures, disproportionation of **7b** to **10b** and **11b** can be observed via NMR experiment.

Data for **7b** are as follows. Anal. Calcd for  $\text{C}_{42}\text{H}_{54}\text{OP}_3\text{RhZr} \cdot 0.6\text{C}_{18}\text{H}_{15}\text{P}$  (1019.3): C, 62.21; H, 6.23. Found: C, 62.37; H, 5.88.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 599.11 MHz, 298 K):  $\delta$  7.35 (br s, 18H,  $\text{C}_6\text{H}_5$ ), 6.99 (m, 27H,  $\text{C}_6\text{H}_5$ ), 6.64 (br, 2H, 2-H), 6.10 (m, 2H, 3-H), 4.86 (m, 2H, 4-H), 4.22 (br, 2H, 5-H), 2.37 (sept.,  $J = 7.2$  Hz, 2H, 9-H), 1.65 (sept.,  $J = 7.0$  Hz, 2H, 6-H), 1.21 (ps q, 6H, 10-H), 1.18 (ps q, 6H, 11-H), 1.09 (ps q, 6H, 7-H), 0.93 (ps q, 6H, 8-H),  $-0.49$  (m, 3H,  $\text{Zr}-\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 150.7 MHz, 298 K):  $\delta$  194.7 (CO, resonance acquired from the  $^1\text{H}-^{13}\text{C}$  ghmhc experiment), 134.2 (d,  $J = 17.8$  Hz,  $\text{C}_6\text{H}_5$ ), 128.5 (br s,  $\text{C}_6\text{H}_5$ ), 115.9 (s, C-3), 114.3 (t,  $J = 4.5$  Hz, C-2), 107.3 (m, C-4), 106.2 (ps t, C-1), 100.6 (m, C-5), 30.5, 30.4 (C-6, C-9), 28.9 ( $\text{Zr}-\text{CH}_3$ ), 22.0 (C-7), 21.6 (C-10), 20.1 (t,  $J = 3.2$  Hz, C-8), 19.7 (C-11) (some  $^{13}\text{C}_{\text{arom}}$  resonances are not listed due to the complexity of the  $^{13}\text{C}$  NMR spectra).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 242.53 MHz, 298 K):  $\delta$  47.2 (br s,  $\text{PPh}_3$ ), 33.9 (d,  $^1J_{\text{RHP}} = 154.3$  Hz,  $P(\text{i-Pr})_2$ ). IR (toluene):  $\bar{\nu}(\text{CO})$  1879 cm<sup>-1</sup>.

Data for **11b** are as follows.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 599.11 MHz, 298 K):  $\delta$  6.00 (m, 2H, 2-H), 5.91 (m, 2H, 3-H), 5.50 (m, 2H, 5-H), 4.75 (m, 2H, 4-H), 2.44 (m, 2H, 6-H), 2.02 (m, 2H, 9-H), 1.41 (m, 6H, 7-H), 1.38 (m, 6H, 8-H), 1.13 (m, 6H, 10-H), 0.93 (m, 6H, 11-H),  $-0.35$  (d,  $^3J_{\text{PH}} = 3.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 150.6 MHz, 298 K):  $\delta$  116.5 (m, C-1), 114.4 (m, C-2), 112.6 (m, C-3), 109.1 (m, C-4), 103.1 (m, C-5), 32.1 (m, C-6), 30.4 (m, C-9), 23.1 (m, C-7), 21.7 (m, C-8), 20.6 (m, C-10), 19.7 (m, C-11), 14.2 (m,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 81.02 MHz, 298 K):  $\delta$  33.6 (d,  $^1J_{\text{RHP}} = 188.4$  Hz,  $P(\text{i-Pr})_2$ ).

**Reaction of (Cp-PCy<sub>2</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> (5c) with HRh(CO)-(PPh<sub>3</sub>)<sub>3</sub> (6) in Toluene. Formation of 7c, 10c, and 11c.** Precooled (−30 °C) *d*<sub>8</sub>-toluene was added to a stirred mixture of 5c (64 mg, 0.1 mmol) and 6 (92 mg, 0.1 mmol) at room temperature. After one night complex 10c occurs as a dark red crystalline material. The supernatant solution contains the compounds 10c, 7c, and 11c in a ratio of 1:11:16 and triphenylphosphine. The solid was collected by filtration, washed twice with toluene (0.5 mL each), and dried in vacuo to yield 25 mg (28 μmol, 56%) of compound 10c.

**Carbonyl[bis(η<sup>5</sup>-(dicyclohexylphosphino)cyclopentadienyl)methylzirconium-κ<sup>2</sup>P,P'](triphenylphosphine)-rhodium (Rh–Zr) (7c).** <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 599.11 MHz, 298 K): δ 6.81 (s, 2H, 2-H), 6.20 (s, 2H, 3-H), 4.91 (m, 2H, 4-H), 4.32 (m, 2H, 5-H), 2.52 (m, 4H, 6-H + Cy<sub>B</sub>), 2.13 (m, 2H, Cy<sub>A</sub>), 2.03 (m, 2H, Cy<sub>B</sub>), 1.69 (m, 4H, Cy<sub>A</sub> + Cy<sub>B</sub>), 1.59 (m, 2H, Cy<sub>A</sub>), 1.56 (m, 2H, Cy<sub>B</sub>), 1.53 (m, 4H, Cy<sub>A</sub>), 1.47 (m, 2H, Cy<sub>B</sub>), 1.41 (m, 2H, Cy<sub>B</sub>), 1.32 (m, 2H, Cy<sub>A</sub>), 1.25 (m, 4H, Cy<sub>B</sub>), 1.11 (m, 2H, Cy<sub>A</sub>), 1.10 (m, 2H, 6-H), 1.07 (m, 2H, Cy<sub>A</sub>), 1.05 (m, 2H, Cy<sub>B</sub>), 1.04 (m, 2H, Cy<sub>A</sub>), 1.00 (m, 2H, Cy<sub>A</sub>), 0.94 (m, 2H, Cy<sub>B</sub>), −0.42 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 150.6 MHz, 298 K): δ 116.6 (s, C-3), 114.2 (m, C-2), 107.2 (m, C-1), 106.7 (m, C-4), 100.4 (m, C-5), 44.2 (m, C-6), 43.4 (m, C-7), 32.9 (s, Cy<sub>A</sub>), 30.9 (m, Cy<sub>B</sub>), 30.5 (m, Cy<sub>B</sub>), 30.1 (m, Cy<sub>A</sub>), 29.2 (m, Cy<sub>A</sub>), 29.1 (m, Cy<sub>A</sub>), 29.0 (s, CH<sub>3</sub>), 28.7 (m, Cy<sub>B</sub>), 27.8 (m, Cy<sub>B</sub>), 27.1 (m, Cy<sub>A</sub>), 26.8 (m, Cy<sub>B</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 242.53 MHz, 298 K): δ 49.9 (very broad, PPh<sub>3</sub>), 23.0 (d, <sup>1</sup>J<sub>RhP</sub> = 152.7 Hz, PCy<sub>2</sub>).

**Bis(carbonyl)[bis(η<sup>5</sup>-(dicyclohexylphosphino)cyclopentadienyl)methylzirconium-κ<sup>2</sup>P,P']rhodium (Rh–Zr) (10c).** Anal. Calcd for C<sub>37</sub>H<sub>55</sub>O<sub>2</sub>P<sub>2</sub>RhZr (787.9): C, 56.40; H, 7.04. Found: C, 56.76; H, 6.75. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 599.11 MHz, 298 K): δ 6.37 (br m, 2H, 2-H), 6.07 (br m, 2H, 3-H), 4.83 (br m, 2H, 4-H), 3.95 (br m, 2H, 5-H), 2.59 (br m, 2H, Cy), 2.34 (m, 2H, Cy), 2.20–1.03 (m, 40H, Cy), −0.76 (br s, 3H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 81.02 MHz): δ 46.8 (d, <sup>1</sup>J<sub>RhP</sub> = 149.4 Hz, PCy<sub>2</sub>). IR (KBr): ν(CO) 1930, 1862 cm<sup>−1</sup>.

**[Bis(η<sup>5</sup>-(dicyclohexylphosphino)cyclopentadienyl)zirconium-κ<sup>2</sup>P,P'](μ-methyl)(triphenylphosphine)rhodium (Rh–Zr) (11c).** <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 599.11 MHz, 298 K): δ 7.45 (m, 6H, *o*-C<sub>6</sub>H<sub>5</sub>), 7.04 (m, 6H, *m*-C<sub>6</sub>H<sub>5</sub>), 6.96 (m, 3H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.09 (m, 2H, 2-H), 5.94 (m, 2H, 3-H), 5.61 (m, 2H, 5-H), 4.84 (m, 2H, 4-H), 2.37 (m, 2H, Cy, resonances are acquired from the <sup>1</sup>H–<sup>1</sup>H TOCSY and the two-dimensional <sup>1</sup>H–<sup>13</sup>C correlation experiments), 2.25 (m, 4H, Cy<sub>A</sub> + Cy<sub>B</sub>), 2.14 (m, 2H, 6-H), 1.96 (m, 2H, 7-H), 1.85 (m, 2H, Cy<sub>A</sub>), 1.80 (m, 2H, Cy<sub>B</sub>), 1.77 (m, 2H, Cy<sub>A</sub>), 1.72 (m, 2H, Cy<sub>A</sub>), 1.62 (m, 2H, Cy<sub>A</sub>), 1.61 (m, 2H, Cy<sub>B</sub>), 1.56 (m, 2H, Cy<sub>A</sub>), 1.51 (m, 2H, Cy<sub>B</sub>), 1.39 (m, 6H, Cy<sub>A</sub> + Cy<sub>B</sub>), 1.25 (m, 2H, Cy<sub>A</sub>), 1.23 (m, 2H, Cy<sub>B</sub>), 1.22 (m, 2H, Cy<sub>A</sub>), 1.00 (m, 2H, Cy<sub>B</sub>), 0.98 (m, 2H, Cy<sub>B</sub>), 0.65 (m, 2H, Cy<sub>B</sub>), −0.29 (d, <sup>3</sup>J<sub>PH</sub> = 3.4 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 150.6 MHz, 298 K): δ 140.3 (m, *i*-C<sub>6</sub>H<sub>5</sub>), 133.7 (d, <sup>1</sup>J<sub>PC</sub> = 15.3 Hz, *o*-C<sub>6</sub>H<sub>5</sub>), 128.2 (m, *m*-C<sub>6</sub>H<sub>5</sub>), 125.4 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 115.4 (m, C-1), 114.7 (m, C-2), 112.5 (m, C-3), 108.9 (m, C-4), 103.2 (m, C-5), 44.6 (m, C-6), 41.9 (m, C-7), 34.0 (m, Cy<sub>A</sub>), 31.6 (m, Cy<sub>A</sub>), 31.2 (m, Cy<sub>B</sub>), 29.7 (m, Cy<sub>B</sub>), 29.2 (m, Cy<sub>A</sub>), 28.7 (m, Cy<sub>A</sub> + Cy<sub>B</sub>), 27.8 (m, Cy<sub>B</sub>), 27.0 (m, Cy<sub>A</sub> + Cy<sub>B</sub>), 14.4 (s, <sup>1</sup>J<sub>CH</sub> = 120.7 Hz, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 242.53 MHz, 298 K): δ 34.5 (dt, <sup>1</sup>J<sub>RhP</sub> = 164.4 Hz, <sup>2</sup>J<sub>PP</sub> = 25.2 Hz, PPh<sub>3</sub>), 26.3 (dd, <sup>1</sup>J<sub>RhP</sub> = 196.1 Hz, <sup>2</sup>J<sub>PP</sub> = 25.2 Hz, PCy<sub>2</sub>).

**Phosphino-Substituted Cyclopentadienides 8. General Procedure.** Chlorophosphine (10 mmol) with the desired substituents was slowly added to a solution of lithium cyclopentadienide (8a–c; 10 mmol) or sodium cyclopentadienide (8d; 10 mmol) in THF (10 mL) at −78 °C. The solution was warmed to room temperature overnight, and the solvent was removed in vacuo. Toluene (10 mL) was added, and the slurry was filtered over a bed of Celite. *n*-Butyllithium (10 mmol, 1.6 M in hexane) was then added to the filtrate at −78 °C. The solution was warmed to room temperature overnight, and the solvent was removed in vacuo. The residue was stirred with

pentane, and the product was collected by filtration, washed three times with pentane, and dried in vacuo.

**Preparation of Lithium (Diphenylphosphino)cyclopentadienide (8a).** Following the general procedure freshly distilled chlorodiphenylphosphine (31.71 mL, 38.18 g, 0.18 mol) was reacted with lithium cyclopentadienide (12.73 g, 0.18 mol) and subsequently with *n*-butyllithium (110.3 mL, 0.18 mol, 1.6 M in hexane) to yield 36.38 g (0.14 mol, 80%) of compound 8a. <sup>1</sup>H NMR (*d*<sub>8</sub>-THF, 200.13 MHz): δ 7.35–7.20 (m, 4H, *o*-C<sub>6</sub>H<sub>5</sub>), 7.20–7.00 (m, 6H, *m*-C<sub>6</sub>H<sub>5</sub> and *p*-C<sub>6</sub>H<sub>5</sub>), 6.00–5.93 (m, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 81.02 MHz): δ −18.8 (s, PPh<sub>2</sub>).

**Preparation of Lithium (Diisopropylphosphino)cyclopentadienide (8b).** Following the general procedure chlorodiisopropylphosphine (21.65 g, 0.14 mol) was reacted with lithium cyclopentadienide (9.81 g, 0.14 mol) and subsequently with *n*-butyllithium (9.81 g, 0.14 mol, 1.6 M in hexane) to yield 21.94 g (0.12 mmol, 86%) of compound 8b. Mp: 81 °C. Anal. Calcd for C<sub>11</sub>H<sub>18</sub>PLi (188.2): C, 70.21; H, 9.64. Found: C, 69.46; H, 9.57. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200.13 MHz): δ 5.74 (ps s, 4H, C<sub>5</sub>H<sub>4</sub>), 1.87 (sept d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>2</sup>J<sub>PH</sub> = 2.7 Hz, 2H, CH), 1.12 (dd, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, <sup>3</sup>J<sub>PH</sub> = 1.0 Hz, 6H, CH<sub>3</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 50.32 MHz): 111.7 (d, <sup>2</sup>J<sub>PC</sub> = 9.1 Hz, C-2), 109.7 (d, <sup>1</sup>J<sub>PC</sub> = 7.4 Hz, C-1), 106.6 (d, <sup>3</sup>J<sub>PC</sub> = 5.8 Hz, C-3), 23.6 (d, <sup>1</sup>J<sub>PC</sub> = 9.1 Hz, CH), 20.6 (d, <sup>2</sup>J<sub>PC</sub> = 28.2 Hz, CH<sub>3</sub>), 20.4 (d, <sup>2</sup>J<sub>PC</sub> = 30.7 Hz, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 81.02 MHz): δ 0.1 (s, P(*i*Pr)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 81.02 MHz): δ 3.1 (s, P(*i*Pr)<sub>2</sub>).

**Preparation of Lithium (Dicyclohexylphosphino)cyclopentadienide (8c).** Following the general procedure chlorodicyclohexylphosphine (10.43 mL, 10.99 g, 47.0 mmol) was reacted with lithium cyclopentadienide (3.39 g, 47.0 mmol) and subsequently with *n*-butyllithium (29.4 mL, 47.0 mmol, 1.6 M in hexane) to yield 12.43 g (46.3 mmol, 99%) of compound 8c. Mp: 213 °C. Anal. Calcd for C<sub>17</sub>H<sub>26</sub>LiP (268.3): C, 76.10; H, 9.77. Found: C, 75.85; H, 10.28. <sup>1</sup>H NMR (*d*<sub>8</sub>-THF, 200.13 MHz): δ 5.90 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5.84 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 1.69, 1.36–1.01 (2 m, 22H, C<sub>6</sub>H<sub>11</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 50.32 MHz): δ 107.4 (d, <sup>2</sup>J<sub>PC</sub> = 17.8 Hz, C-2), 100.8 (d, <sup>3</sup>J<sub>PC</sub> = 7.5 Hz, C-3), 99.7 (d, <sup>1</sup>J<sub>PC</sub> = 5.1 Hz, C-1), 30.0 (d, <sup>1</sup>J<sub>PC</sub> = 12.7 Hz, C<sub>6</sub>H<sub>11</sub>), 26.7 (d, <sup>1</sup>J<sub>PC</sub> = 17.8 Hz, C<sub>6</sub>H<sub>11</sub>), 25.5 (d, <sup>1</sup>J<sub>PC</sub> = 10.2 Hz, C<sub>6</sub>H<sub>11</sub>), 23.6 (d, <sup>1</sup>J<sub>PC</sub> = 15.2 Hz, C<sub>6</sub>H<sub>11</sub>), 23.5 (s, C<sub>6</sub>H<sub>11</sub>), 22.8 (s, C<sub>6</sub>H<sub>11</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 81.02 MHz): δ −11.8 (s, PCy<sub>2</sub>).

**Preparation of Lithium (Di-*tert*-butylphosphino)cyclopentadienide (8d).** Following the general procedure chlorodi-*tert*-butylphosphine (5.49 g, 29.2 mmol) was reacted with sodium cyclopentadienide (2.57 g, 29.2 mmol) and subsequently with *n*-butyllithium (18.3 mL, 29.2 mmol, 1.6 M in hexane) to yield 1.49 g (6.9 mmol, 24%) of compound 8d. Mp: 224 °C. Anal. Calcd for C<sub>13</sub>H<sub>22</sub>LiP (216.2): C, 72.21; H, 10.26. Found: C, 71.89; H, 10.14. <sup>1</sup>H NMR (*d*<sub>8</sub>-THF, 200.13 MHz): δ 6.03 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5.84 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 1.12 (d, <sup>3</sup>J<sub>PH</sub> = 10.6 Hz, 18H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 50.32 MHz): δ 114.6 (d, <sup>1</sup>J<sub>PC</sub> = 21.5 Hz, C<sub>5</sub>H<sub>4</sub>), 106.7 (d, <sup>1</sup>J<sub>PC</sub> = 9.9 Hz, C-1), 105.4 (d, <sup>1</sup>J<sub>PC</sub> = 8.2 Hz, C<sub>5</sub>H<sub>4</sub>), 32.6 (d, <sup>1</sup>J<sub>PC</sub> = 21.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 31.5 (d, <sup>2</sup>J<sub>PC</sub> = 14.9 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 81.02 MHz): δ 25.3 (s, P(*t*Bu)<sub>2</sub>).

**Phosphino-Substituted Zirconocene Dichlorides 9. General Procedure.** A Schlenk flask was charged with phosphino-substituted cyclopentadienide (10 mmol) and zirconium tetrachloride (5 mmol). After the addition of precooled toluene (50 mL) and THF (0.2 mL) at −78 °C, the solution was warmed to room temperature overnight. The resulting slurry was filtered over a bed of Celite, and the volume of the filtrate was reduced to 5 mL. Subsequent addition of pentane leads to the formation of a slightly yellow precipitate, which was collected by filtration, washed three times with pentane, and dried in vacuo.

**Preparation of Bis[η<sup>5</sup>-(diphenylphosphino)cyclopentadienyl]dichlorozirconium (9a).** Following the general procedure lithium (diphenylphosphino)cyclopentadienide (8a;

13.00 g, 50.7 mmol) was reacted with zirconium tetrachloride (5.91 g, 25.4 mmol) to yield 11.54 g (19.3 mmol, 76%) of compound **9a**. Single crystals were obtained by cooling a concentrated solution in toluene to  $-30\text{ }^{\circ}\text{C}$  for 1 day.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 599.11 MHz):  $\delta$  7.33 (m, 20H,  $\text{C}_6\text{H}_5$ ), 6.39, (m, 4H, 2-H), 6.35 (m, 5H, 3-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50.32 MHz):  $\delta$  136.8 (d,  $^1J_{\text{PC}} = 12\text{ Hz}$ ,  $i\text{-C}_6\text{H}_5$ ), 133.9 (d,  $^2J_{\text{PC}} = 20\text{ Hz}$ ,  $o\text{-C}_6\text{H}_5$ ), 129.3 (s,  $p\text{-C}_6\text{H}_5$ ), 128.5 (d,  $^3J_{\text{PC}} = 7\text{ Hz}$ ,  $m\text{-C}_6\text{H}_5$ ), 125.1 (d,  $^1J_{\text{PC}} = 17\text{ Hz}$ , C-1), 122.1 (d,  $^2J_{\text{PC}} = 10\text{ Hz}$ , C-2), 118.2 (s, C-3).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 242.53 MHz, 298 K):  $\delta$   $-17.3$  (s,  $\text{PPh}_2$ ).

**X-ray Crystal Structure Analysis for 9a:** formula  $\text{C}_{34}\text{H}_{28}\text{Cl}_2\text{P}_2\text{Zr}$ ,  $M_r = 660.62$ , yellow crystal  $0.20 \times 0.20 \times 0.10\text{ mm}$ ,  $a = 9.360(1)\text{ \AA}$ ,  $b = 12.047(1)\text{ \AA}$ ,  $c = 14.230(1)\text{ \AA}$ ,  $\alpha = 101.32(1)^\circ$ ,  $\beta = 97.43(1)^\circ$ ,  $\gamma = 103.58(1)^\circ$ ,  $V = 1503.3(2)\text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.459\text{ g cm}^{-3}$ ,  $\mu = 6.72\text{ cm}^{-1}$ , empirical absorption correction ( $0.877 \leq T \leq 0.936$ ),  $Z = 2$ , triclinic, space group  $P1$  (No. 2),  $\lambda = 0.710\text{ 73 \AA}$ ,  $T = 198\text{ K}$ ,  $\omega$  and  $\varphi$  scans, 17 932 reflections collected ( $\pm h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.60\text{ \AA}^{-1}$ , 5269 independent ( $R_{\text{int}} = 0.070$ ) and 3883 observed reflections ( $I \geq 2\sigma(I)$ ), 352 refined parameters,  $R1 = 0.054$ ,  $wR2 = 0.089$ , maximum (minimum) residual electron density  $0.29$  ( $-0.36$ )  $\text{e \AA}^{-3}$ , hydrogen atoms calculated and refined as riding atoms.

**Preparation of Bis( $\eta^5$ -(diisopropylphosphino)cyclopentadienide)dichlorozirconium (9b).** Following the general procedure lithium (diisopropylphosphino)cyclopentadienide (**8b**; 9.50 g, 50.5 mmol) was reacted with zirconium tetrachloride (5.88 g, 25.2 mmol) to yield 11.54 g (19.3 mmol, 76%) of compound **9b**. Single crystals were obtained by cooling a concentrated solution in toluene to  $-30\text{ }^{\circ}\text{C}$  for 1 day. Mp:  $118\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{P}_2\text{Zr}$  (524.6): C, 50.37; H, 6.92. Found: C, 49.50; H, 7.05.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 599.11 MHz):  $\delta$  6.68 (m, 4H, 2-H), 6.53 (m, 4H, 3-H), 2.05 (sept,  $^3J_{\text{HH}} = 7.1\text{ Hz}$ , 2H, CH), 1.15 (dd,  $^2J_{\text{PH}} = 13.7\text{ Hz}$ ,  $^3J_{\text{HH}} = 7.1\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 0.99 (dd,  $^3J_{\text{PH}} = 12.7\text{ Hz}$ ,  $^1J_{\text{HH}} = 7.1\text{ Hz}$ , 6H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100.63 MHz):  $\delta$  124.9 (d,  $^1J_{\text{PC}} = 30.6\text{ Hz}$ , C-1), 123.5 (m, C-2), 118.4 (m, C-3), 24.2 (d,  $^1J_{\text{PC}} = 12.9\text{ Hz}$ , CH), 20.4 (d,  $^2J_{\text{PC}} = 20.1\text{ Hz}$ ,  $\text{CH}_3$ ), 20.2 (d,  $^2J_{\text{PC}} = 23.1\text{ Hz}$ ,  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 242.53 MHz):  $\delta$  5.1 (s,  $\text{P}(i\text{-Pr})_2$ ).

**X-ray Crystal Structure Analysis for 9b:** formula  $\text{C}_{22}\text{H}_{36}\text{Cl}_2\text{P}_2\text{Zr}$ ,  $M_r = 524.57$ , colorless crystal  $0.35 \times 0.15 \times 0.10\text{ mm}$ ,  $a = 8.656(1)\text{ \AA}$ ,  $b = 20.384(1)\text{ \AA}$ ,  $c = 14.203(1)\text{ \AA}$ ,  $\beta = 93.21(1)^\circ$ ,  $V = 2502.1(4)\text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.393\text{ g cm}^{-3}$ ,  $\mu = 7.87\text{ cm}^{-1}$ , empirical absorption correction ( $0.770 \leq T \leq 0.926$ ),  $Z = 4$ , monoclinic, space group  $C2/c$  (No. 15),  $\lambda = 0.710\text{ 73 \AA}$ ,  $T = 198\text{ K}$ ,  $\omega$  and  $\varphi$  scans, 12 320 reflections collected ( $\pm h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.66\text{ \AA}^{-1}$ , 2981 independent ( $R_{\text{int}} = 0.045$ ) and 2538 observed reflections ( $I \geq 2\sigma(I)$ ), 127 refined parameters,  $R1 = 0.030$ ,  $wR2 = 0.062$ , maximum (minimum) residual electron density  $0.24$  ( $-0.54$ )  $\text{e \AA}^{-3}$ , hydrogen atoms calculated and refined as riding atoms.

**Preparation of Bis( $\eta^5$ -(dicyclohexylphosphino)cyclopentadienide)dichlorozirconium (9c).** Following the general procedure lithium (dicyclohexylphosphino)cyclopentadienide (**8c**; 8.00 g, 29.8 mmol) was reacted with zirconium tetrachloride (3.47 g, 14.9 mmol) to yield 8.05 g (11.8 mmol, 79%) of compound **9c**. Single crystals were obtained by slow evaporation of the solvent of a solution in heptane. Mp:  $173\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{34}\text{H}_{52}\text{Cl}_2\text{P}_2\text{Zr}$  (684.9): C, 59.63; H, 7.65. Found: C, 57.12; H, 7.36.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 599.11 MHz):  $\delta$  6.67 (m, 4H,  $\text{C}_5\text{H}_4$ ), 6.49 (m, 4H,  $\text{C}_5\text{H}_4$ ), 1.84 (m, 12H,  $\text{C}_6\text{H}_{11}$ ), 1.69 (m, 12H,  $\text{C}_6\text{H}_{11}$ ), 1.36–1.13 (m, 16H,  $\text{C}_6\text{H}_{11}$ ), 0.97 (m, 4H,  $\text{C}_6\text{H}_{11}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100.63 MHz):  $\delta$  124.4 (d,  $^1J_{\text{PC}} = 29.8\text{ Hz}$ , C-1), 124.1 (m,  $\text{C}_5\text{H}_4$ ), 118.4 (m,  $\text{C}_5\text{H}_4$ ), 34.1 (d,  $J_{\text{PC}} = 13.7\text{ Hz}$ ,  $\text{C}_6\text{H}_{11}$ ), 31.1 (d,  $J_{\text{PC}} = 12.1\text{ Hz}$ ,  $\text{C}_6\text{H}_{11}$ ), 30.7 (d,  $J_{\text{PC}} = 12.9\text{ Hz}$ ,  $\text{C}_6\text{H}_{11}$ ), 27.8 (d,  $J_{\text{PC}} = 10.5\text{ Hz}$ ,  $\text{C}_6\text{H}_{11}$ ), 27.6 (d,  $J_{\text{PC}} = 9.7\text{ Hz}$ ,  $\text{C}_6\text{H}_{11}$ ), 26.8 (d,  $J_{\text{PC}} = 1.6\text{ Hz}$ ,  $\text{C}_6\text{H}_{11}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 242.53 MHz):  $\delta$   $-3.0$  (s,  $\text{PCy}_2$ ).

**X-ray Crystal Structure Analysis for 9c:** formula  $\text{C}_{34}\text{H}_{52}\text{Cl}_2\text{P}_2\text{Zr}$ ,  $M_r = 684.82$ , light yellow crystal  $0.20 \times 0.15 \times 0.10\text{ mm}$ ,  $a = 14.049(1)\text{ \AA}$ ,  $b = 21.756(1)\text{ \AA}$ ,  $c = 11.484(1)\text{ \AA}$ ,  $\beta =$

$104.75(1)^\circ$ ,  $V = 3394.4(4)\text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.340\text{ g cm}^{-3}$ ,  $\mu = 5.97\text{ cm}^{-1}$ , empirical absorption correction ( $0.890 \leq T \leq 0.943$ ),  $Z = 4$ , monoclinic, space group  $P2_1/c$  (No. 14),  $\lambda = 0.710\text{ 73 \AA}$ ,  $T = 198\text{ K}$ ,  $\omega$  and  $\varphi$  scans, 20 971 reflections collected ( $\pm h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.65\text{ \AA}^{-1}$ , 7781 independent ( $R_{\text{int}} = 0.043$ ) and 5796 observed reflections ( $I \geq 2\sigma(I)$ ), 352 refined parameters,  $R1 = 0.047$ ,  $wR2 = 0.102$ , maximum (minimum) residual electron density  $1.71$  ( $-1.08$ )  $\text{e \AA}^{-3}$ , hydrogen atoms calculated and refined as riding atoms.

**Preparation of Bis( $\eta^5$ -(di-tert-butylphosphino)cyclopentadienide)dichlorozirconium (9d).** Following the general procedure lithium (di-tert-butylphosphino)cyclopentadienide (**8d**; 2.50 g, 11.6 mmol) was reacted with zirconium tetrachloride (1.35 g, 5.8 mmol) to yield 2.23 g (3.8 mmol, 66%) of compound **9d**. Single crystals were obtained by slow evaporation of the solvent of a solution in toluene. Mp:  $212\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{44}\text{P}_2\text{Cl}_2\text{Zr}$  (580.7): C, 53.78; H, 7.64. Found: C, 54.11; H, 7.63.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 200.13 MHz):  $\delta$  6.94 (m, 4H,  $\text{C}_5\text{H}_4$ ), 6.54 (m, 4H,  $\text{C}_5\text{H}_4$ ), 1.19 (d,  $^3J_{\text{PH}} = 11.5\text{ Hz}$ ,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 50.32 MHz): 125.9 (m,  $\text{C}_5\text{H}_4$ ), 118.3 (m,  $\text{C}_5\text{H}_4$ ), 33.8 (d,  $^1J_{\text{PC}} = 22.1\text{ Hz}$ ,  $\text{C}(\text{CH}_3)_3$ ), 30.8 (d,  $^2J_{\text{PC}} = 14.0\text{ Hz}$ ,  $\text{C}(\text{CH}_3)_3$ ), C-1 could not be detected.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 81.02 MHz):  $\delta$  34.4 (s,  $\text{P}(\text{t-Bu})_2$ ).

**X-ray Crystal Structure Analysis for 9d:** formula  $\text{C}_{26}\text{H}_{44}\text{Cl}_2\text{P}_2\text{Zr} \cdot 2\text{CH}_2\text{Cl}_2$ ,  $M_r = 750.52$ , light yellow crystal  $0.40 \times 0.30 \times 0.20\text{ mm}$ ,  $a = 24.693(1)\text{ \AA}$ ,  $b = 17.604(1)\text{ \AA}$ ,  $c = 8.137(1)\text{ \AA}$ ,  $\beta = 96.65(1)^\circ$ ,  $V = 3513.3(5)\text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.419\text{ g cm}^{-3}$ ,  $\mu = 8.78\text{ cm}^{-1}$ , empirical absorption correction ( $0.720 \leq T \leq 0.844$ ),  $Z = 4$ , monoclinic, space group  $C2/c$  (No. 15),  $\lambda = 0.710\text{ 73 \AA}$ ,  $T = 198\text{ K}$ ,  $\omega$  and  $\varphi$  scans, 13 483 reflections collected ( $\pm h, \pm k, \pm l$ ),  $(\sin \theta)/\lambda = 0.66\text{ \AA}^{-1}$ , 4172 independent ( $R_{\text{int}} = 0.032$ ) and 3775 observed reflections ( $I \geq 2\sigma(I)$ ), 174 refined parameters,  $R1 = 0.024$ ,  $wR2 = 0.061$ , maximum (minimum) residual electron density  $0.33$  ( $-0.43$ )  $\text{e \AA}^{-3}$ , hydrogen atoms calculated and refined as riding atoms.

**Preparation of Dicarbonyl[bis( $\eta^5$ -(diisopropylphosphino)cyclopentadienyl)methylzirconium- $\kappa^2\text{P,P'}$ ]rhodium (Rh–Zr) (10b).** Precooled ( $-30\text{ }^{\circ}\text{C}$ ) toluene was added to a stirred mixture of **5b** (22 mg, 45  $\mu\text{mol}$ ) and **6** (42 mg, 45  $\mu\text{mol}$ ) at room temperature. After 1 min CO was bubbled through the dark brownish solution until the color stayed dark red for 2 s. The volume was reduced in vacuo, and the solution was stored at  $-30\text{ }^{\circ}\text{C}$  for 2 days. Collection of the solid by filtration and drying in vacuo yielded 14 mg of compound **10b** as a microcrystalline solid. Anal. Calcd for  $\text{C}_{25}\text{H}_{39}\text{O}_2\text{P}_2\text{RhZr}$  (627.7): C, 47.84; H, 6.26. Found: C, 48.46; H, 5.71.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 599.11 MHz, 298 K):  $\delta$  6.23 (m, 2H, 2-H), 6.02 (m, 2H, 3-H), 4.80 (m, 2H, 4-H), 3.77 (m, 2H, 5-H), 2.39 (m, 2H, 9-H), 1.48 (m, 6H, 10-H), 1.40 (m, 8H, 6-H, 11-H), 1.14 (m, 6H, 7-H), 1.00 (m, 6H, 8-H),  $-0.83$  (m, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 150.6 MHz, 298 K):  $\delta$  213.3 (dt,  $^1J_{\text{RhC}} = 60.3\text{ Hz}$ ,  $^2J_{\text{PC}} = 14.8\text{ Hz}$ , CO), 191.5 (dt,  $^1J_{\text{RhC}} = 76.6\text{ Hz}$ ,  $^2J_{\text{PC}} = 10.9\text{ Hz}$ , CO), 115.5 (m, C-3), 114.8 (m, C-2), 108.3 (m, C-4), 101.2 (dd,  $J = 16.6\text{ Hz}$ ,  $J = 14.1\text{ Hz}$ , C-1), 100.4 (m, C-5), 30.3 (m, C-6), 30.1 (m, C-9), 28.9 (m,  $J_{\text{CH}} = 123\text{ Hz}$ ,  $\text{CH}_3$ ), 20.8 (m, C-7), 20.7 (m, C-11), 20.3 (m, C-10), 19.6 (m, C-8).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 242.53 MHz, 298 K):  $\delta$  54.6 (d,  $^1J_{\text{RhP}} = 150.6\text{ Hz}$ ,  $\text{P}(i\text{-Pr})_2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\bar{\nu}(\text{CO})$  1959, 1913  $\text{cm}^{-1}$ .

**Preparation of Dicarbonyl[bis( $\eta^5$ -(dicyclohexylphosphino)cyclopentadienyl)methylzirconium- $\kappa^2\text{P,P'}$ ]rhodium (Rh–Zr) (10c).** Precooled ( $-30\text{ }^{\circ}\text{C}$ ) toluene was added to a stirred mixture of **5c** (32 mg, 50  $\mu\text{mol}$ ) and **6** (46 mg, 50  $\mu\text{mol}$ ) at room temperature. The solution was stirred for 5 min at room temperature before CO was bubbled through it for 10 min. Immediately an orange precipitate appeared. The solid was collected by filtration, washed once with toluene (1 mL) and pentane (1 mL), and dried in vacuo to yield 31 mg of compound **10c**. Anal. Calcd for  $\text{C}_{37}\text{H}_{55}\text{O}_2\text{P}_2\text{RhZr}$  (787.9): C, 56.40; H, 7.04. Found: C, 56.76; H, 6.75.  $^1\text{H}$  NMR ( $d_5$ -bromobenzene, 599.11 MHz, 298 K):  $\delta$  6.44 (m, 2H, 2-H), 6.24 (m, 2H, 3-H), 5.15 (m, 2H, 4-H), 4.20 (m, 2H, 5-H), 2.62 (m,

2H, 17-H), 2.56 (m, 2H, 13-H), 2.26–2.18 (m, 4H, 8-H, 12-H), 1.98 (m, 2H, 7-H), 1.85 (m, 4H, 14-H, 16-H), 1.81–1.68 (m, 12H, 9-H, 11-H, 13-H, 15-H, 17-H), 1.63 (m, 2H, 10-H), 1.47 (m, 2H, 8-H), 1.35 (m, 4H, 14-H, 16-H), 1.28–1.21 (m, 6H, 6-H, 7-H, 15-H), 1.14 (m, 4H, 9-H, 10-H), –0.76 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>5</sub>-bromobenzene, 150.6 MHz, 298 K):  $\delta$  190.8 (CO, acquired from the <sup>1</sup>H–<sup>13</sup>C ghmbc experiment), 115.5 (m, C-3), 114.4 (m, C-2), 108.0 (m, C-4), 100.0 (m, C-5), 41.6 (m, C-12), 40.9 (m, C-6), 31.6 (s, C-11, C-17), 31.5 (s, C-8), 30.4 (m, C-13), 29.5 (m, C-7), 28.9 (s, <sup>1</sup>J<sub>CH</sub> = 117.0 Hz, CH<sub>3</sub>), 28.1 (m, C-9, C-14, C-16), 26.7 (s, C-15), 26.5 (s, C-10), n.o. (C-1). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>5</sub>-bromobenzene, 242.53 MHz, 298 K):  $\delta$  46.1 (d, *J*<sub>RhP</sub> = 149.1 Hz, PPh<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$ (CO) 1930, 1862 cm<sup>–1</sup>.

**X-ray Crystal Structure Analysis for 10c:** formula C<sub>44</sub>H<sub>63</sub>O<sub>2</sub>P<sub>2</sub>RhZr, *M*<sub>r</sub> = 880.01, red crystal 0.25 × 0.20 × 0.10 mm, *a* = 33.117(1) Å, *b* = 15.246(1) Å, *c* = 21.888(1) Å,  $\beta$  = 130.74(1)°, *V* = 8373.3(7) Å<sup>3</sup>,  $\rho_{\text{calcd}}$  = 1.396 g cm<sup>–3</sup>,  $\mu$  = 7.54 cm<sup>–1</sup>, empirical absorption correction (0.834 ≤ *T* ≤ 0.928), *Z* = 8, monoclinic, space group C2/c (No. 15),  $\lambda$  = 0.710 73 Å, *T* = 198 K,  $\omega$  and  $\varphi$  scans, 27 335 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), ( $\sin \theta$ )/ $\lambda$  = 0.66 Å<sup>–1</sup>, 9924 independent (*R*<sub>int</sub> = 0.058) and 6656 observed reflections (*I* ≥ 2σ(*I*)), 420 refined parameters, *R*1 = 0.050, *wR*2 = 0.104, maximum (minimum) residual electron density 1.20 (–0.66) e Å<sup>–3</sup>, hydrogen atoms calculated and refined as riding atoms.

**Formation of (μ-Acetyl-1κO:2κC)[bis(η<sup>5</sup>-(diisopropylphosphino)cyclopentadienyl)chlorozirconium-κ<sup>2</sup>P,P']-chlororhodium (Rh–Zr) (12b).** (a) **Reaction of 5b with 6.** Precooled (–30 °C) *d*<sub>2</sub>-dichloromethane (1 mL) was added to a stirred mixture of **5b** (22 mg, 45.4 μmol) and **6** (42 mg, 45.4 μmol). After 5 min at room temperature complete conversion to compound **12b** was observed by NMR spectroscopy. To remove part of the triphenylphosphine, the solvent was removed in vacuo. The crude product was washed once with pentane (0.5 mL) and dried in vacuo to yield 34 mg of an orange powder.

(b) **Reaction of 7b with CH<sub>2</sub>Cl<sub>2</sub>.** A solution of **7b** in toluene was prepared from **5b** (24 mg, 50.1 μmol) and **6** (46 mg, 50 μmol) as described above. Dichloromethane (3.2 μL, 50 μmol) was added to the crude mixture, and the color changed slowly to orange. After 1 h the orange solid was collected by filtration, washed with toluene (0.5 mL), and dried in vacuo to yield 42 mg of an orange solid (**12b**).

(c) **Reaction of 10b with CH<sub>2</sub>Cl<sub>2</sub>.** A solution of **10b** (32 mg, 50 μmol) in dichloromethane (2 mL) was stirred for 16 h at room temperature. Subsequently the solvent was removed in vacuo to yield 30 mg of compound **12b**. Anal. Calcd for C<sub>24</sub>H<sub>39</sub>Cl<sub>2</sub>OP<sub>2</sub>RhZr (670.5): C, 42.99; H, 5.86. Found: C, 42.92; H, 6.14. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 599.11 MHz, 298 K):  $\delta$  6.49 (m, 2H, 3-H), 6.34 (m, 2H, 4-H), 6.00 (m, 2H, 5-H), 5.90 (m, 2H, 2-H), 3.77 (m, 2H, 6-H), 2.47 (m, 3H, CH<sub>3</sub>), 1.82 (m, 2H, 9-H), 1.53 (m, 6H, 7-H), 1.50 (m, 6H, 10-H), 1.35 (m, 6H, 11-H), 1.32 (m, 6H, 8-H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 150.6 MHz, 298 K):  $\delta$  290.3 (dt, <sup>1</sup>J<sub>RhC</sub> = 30.6 Hz, <sup>2</sup>J<sub>PC</sub> = 8.1 Hz, CO), 126.8 (m, C-1), 120.6 (m, C-3), 113.6 (m, C-4), 111.1 (m, C-2), 105.9 (m, C-5), 40.4 (m, <sup>1</sup>J<sub>CH</sub> = 127.4 Hz, CH<sub>3</sub>), 27.5 (m, C-9), 25.3 (m, C-6), 21.5 (m, C-10), 19.9 (m, C-7 + C-8), 19.5 (m, C-11). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 242.53 MHz, 298 K):  $\delta$  27.5 (d, <sup>1</sup>J<sub>RhP</sub> = 127.6 Hz, P(*i*-Pr)<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$ (CO) 1434 cm<sup>–1</sup>.

**X-ray Crystal Structure Analysis for 12b:** formula C<sub>24</sub>H<sub>39</sub>Cl<sub>2</sub>OP<sub>2</sub>RhZr, *M*<sub>r</sub> = 670.52, orange crystal 0.15 × 0.15 × 0.05 mm, *a* = 9.290(1) Å, *b* = 11.545(1) Å, *c* = 14.362(2) Å,  $\alpha$  = 98.4(1)°,  $\beta$  = 97.70(1)°,  $\gamma$  = 112.41(1)°, *V* = 1380.2(2) Å<sup>3</sup>,  $\rho_{\text{calcd}}$  = 1.613 g cm<sup>–3</sup>,  $\mu$  = 13.00 cm<sup>–1</sup>, empirical absorption correction (0.829 ≤ *T* ≤ 0.938), *Z* = 2, triclinic, space group

*P*1̄ (No. 2),  $\lambda$  = 0.710 73 Å, *T* = 198 K,  $\omega$  and  $\varphi$  scans, 12 918 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), ( $\sin \theta$ )/ $\lambda$  = 0.66 Å<sup>–1</sup>, 6555 independent (*R*<sub>int</sub> = 0.035) and 5902 observed reflections (*I* ≥ 2σ(*I*)), 289 refined parameters, *R*1 = 0.027, *wR*2 = 0.065, maximum (minimum) residual electron density 0.57 (–0.62) e Å<sup>–3</sup>, hydrogen atoms calculated and refined as riding atoms.

**Formation of (μ-Acetyl-1κO:2κC)[bis(η<sup>5</sup>-(dicyclohexylphosphino)cyclopentadienyl)chlorozirconium-κ<sup>2</sup>P,P']-chlororhodium (Rh–Zr) (12c).** (a) **Reaction of 5c with 6.** Dichloromethane (1.5 mL) was added to a stirred mixture of **5c** (129 mg, 0.2 mmol) and **6** (184 mg, 0.2 mmol). Immediately the solution turned dark red and gas evolution occurred. After 5 min. the orange solid was collected by filtration, washed twice with precooled (–30 °C) dichloromethane and dried in vacuo to yield 129 mg of an orange powder.

(b) **Reaction of 7c with CH<sub>2</sub>Cl<sub>2</sub>.** A solution of **7c** in toluene was prepared from **5c** (32 mg, 50.0 μmol) and **6** (46 mg, 50 μmol) at –30 °C as described above. After 1 min dichloromethane (3.2 μL, 50 μmol) was added to the crude mixture and the color changed slowly to orange to form compound **12c**.

(c) **Reaction of 10b with CH<sub>2</sub>Cl<sub>2</sub>.** A solution of **10c** (8.0 mg, 9.1 μmol) in *d*<sub>2</sub>-dichloromethane (1 mL) was stirred for 1.5 h at room temperature. Subsequently the solvent was removed in vacuo to yield 7.5 mg of compound **12c**. Anal. Calcd for C<sub>36</sub>H<sub>55</sub>Cl<sub>2</sub>OP<sub>2</sub>RhZr·2CH<sub>2</sub>Cl<sub>2</sub> (1000.7): C, 45.61; H, 5.94. Found: C, 46.22; H, 6.89. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 599.11 MHz, 298 K):  $\delta$  6.47 (m, 2H, 3-H), 6.30 (br, 2H, 4-H), 5.91 (m, 2H, 5-H), 5.79 (m, 2H, 2-H), 3.54 (m, 2H, 6-H), 2.45 (s, 3H, CH<sub>3</sub>), 2.40 (m, 2H, Cy), 2.26 (m, 4H, Cy), 2.06 (m, 4H, Cy), 1.86–1.21 (m, 32H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 150.6 MHz, 298 K):  $\delta$  289.0 (dm, <sup>1</sup>J<sub>RhC</sub> = 23.3 Hz, CO), 125.6 (m, C-1), 121.1 (s, <sup>1</sup>J<sub>CH</sub> = 181 Hz, C-3), 113.2 (m, <sup>1</sup>J<sub>CH</sub> = 175 Hz, C-4), 110.7 (s, <sup>1</sup>J<sub>CH</sub> = 176 Hz, C-2), 105.3 (m, <sup>1</sup>J<sub>CH</sub> = 177 Hz, C-5), 39.0 (s, <sup>1</sup>J<sub>CH</sub> = 124 Hz, CH<sub>3</sub>), 37.8 (m, <sup>1</sup>J<sub>CH</sub> = 119 Hz, C-7), 35.0 (m, <sup>1</sup>J<sub>CH</sub> = 131 Hz, C-6), 31.8 (m, Cy<sub>B</sub>), 30.8 (s, Cy<sub>A</sub>), 30.7 (s, Cy<sub>B</sub>), 30.4 (s, Cy<sub>A</sub>), 28.6 (m, Cy<sub>A</sub>), 28.0 (m, Cy<sub>B</sub>), 27.9 (m, Cy<sub>A</sub> + Cy<sub>B</sub>), 27.0 (s, Cy<sub>A</sub>), 26.7 (s, Cy<sub>B</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 242.53 MHz, 298 K):  $\delta$  19.7 (d, <sup>1</sup>J<sub>RhP</sub> = 126.8 Hz, PCy<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$ (CO) 1434 cm<sup>–1</sup>.

**X-ray Crystal Structure Analysis for 12c:** formula C<sub>36</sub>H<sub>55</sub>Cl<sub>2</sub>OP<sub>2</sub>RhZr·C<sub>7</sub>H<sub>8</sub>, *M*<sub>r</sub> = 922.90, orange crystal 0.25 × 0.20 × 0.05 mm, *a* = 34.575(1) Å, *b* = 10.989(1) Å, *c* = 23.485(1) Å,  $\beta$  = 109.66(1)°, *V* = 8402.8(9) Å<sup>3</sup>,  $\rho_{\text{calcd}}$  = 1.459 g cm<sup>–3</sup>,  $\mu$  = 8.76 cm<sup>–1</sup>, empirical absorption correction (0.811 ≤ *T* ≤ 0.958), *Z* = 8, monoclinic, space group *P*2<sub>1</sub>/c (No. 14),  $\lambda$  = 0.710 73 Å, *T* = 198 K,  $\omega$  and  $\varphi$  scans, 47 132 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), ( $\sin \theta$ )/ $\lambda$  = 0.66 Å<sup>–1</sup>, 19 583 independent (*R*<sub>int</sub> = 0.051) and 14 192 observed reflections (*I* ≥ 2σ(*I*)), 905 refined parameters, *R*1 = 0.040, *wR*2 = 0.078, maximum (minimum) residual electron density 0.60 (–0.67) e Å<sup>–3</sup>, hydrogen atoms calculated and refined as riding atoms, two almost identical molecules in the asymmetric unit.

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**Supporting Information Available:** CIF files giving details of the X-ray crystal structure analysis (**5b,c**, **7a**, **9a–d**, **10c**, and **12b,c**) and text giving additional spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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